A VISCOMETRIC STUDY OF RHEOLOGICAL INTERACTION BETWEEN SELECTED COMMERCIAL DAIRY PROTEINS AND SELECTED GUMS IN AQUEOUS SOLUTION

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To my wife, Suwaranya, and
my daughter, Veeya,

ABSTRACT

Rheological interaction between solutions of four selected gum (locust bean gum (LB), sodium carboxymethycellulose (CMC), lambda-carrageenan (CR), xanthan gum (XN)) and solutions of four dairy proteins (sodium caseinate (SC), whey protein concentrate (WPC), coprecipitate (TMP), whey protein isolate (WPI)) were studied by steady shear viscometry using a Bohlin VOR Rheometer at 25 °C, natural pH and natural ionic strength. The rheological properties of mixed solutions were greatly influenced by presence of gum, gum concentration and gum type. Rheological synergism, with no obvious shear rate dependence, occurred between LB and SC, LB and WPC, LB and TMP, CMC and all dairy proteins, CR and WPC, CR and TMP, and XN and WPC. The degree of synergism, which was determined in a new way, was relatively much greater with TMP. The results are discussed in terms of Ca^{2+} bridging for TMP synergism and in terms of electrostatic and molecular space occupancy effects for SC, WPC and WPI synergism. No significant interaction occured between LB and WPI or between CR and SC or between CR and WPI or between XN and SC or between XN and TMP or between XN and WPI. Quantitative measures of synergism in mixed solutions prepared from 0.5% gum solution and 6.0% dairy protein solution were in close agreement with similar measures of synergism in mixed solutions prepared from 1.2% gum, 10.0% dairy protein and distilled water. Rheogical synergism was found to be unrelated to phase separation in the mixed solutions provided the phases remained intimately mixed. The relevance of this work to the use of the gum-dairy protein mixtures as rheologically-functional food ingredients is discussed.

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TABLE OF CONTENTS

	PAGE
ABSTRACT	i
ACKNOWLEDGEMENTS	ii
LIST OF TABLES	xiii
LIST OF FIGURES	xv
ABBREVIATIONS	xxxi
CHAPTER 1 INTRODUCTION	1
1.1 THE USE OF DAIRY PROTEINS AS RHEOLOGICALLY-FUNCTIONAL FOOD INGREDIENTS	1
1.1.1 Caseinates	2
1.1.2 Whey protein concentrate	2
1.1.3 Coprecipitate	3
1.2 THE USE OF GUMS AS RHEOLOGICALLY-FUNCTIONAL FOOD INGREDIENTS	4
1.2.1 Locust bean gum	4
1.2.2 Sodium carboxymethyl cellulose (CMC)	5
1.2.3 Carrageenans	5
1.2.4 Xanthan gum	5
1.3 THE USE OF GUM/DAIRY PROTEIN COMBINATIONS IN FOOD SYSTEMS	6
1.4 DISCUSSION AND PROJECT IDENTIFICATION	7

CHAPTER 2 LITERATURE REVIEW 8

2.1 INTRODUCTION 8

2.2 FUNDAMENTAL RHEOLOGY OF GUM SOLUTIONS 8

2.2.1 Intrinsic viscosity 8

2.2.2 Dilute solutions 11

2.2.3 Concentrated solutions 11

2.3 RHEOLOGICAL PROPERTIES OF CONCENTRATED GUM SOLUTIONS 11

2.3.1 Effect of concentration 12

2.3.2 Effect of pH 13

2.3.3 Effect of ionic strength 13

2.3.4 Effect of added sugar 13

2.4 GUM-GUM INTERACTIONS 13

2.5 FUNDAMENTAL RHEOLOGY OF PROTEIN SOLUTIONS 15

2.5.1 Intrinsic viscosity 15

2.5.2 Dilute solutions 17

2.5.3 Concentrated solutions 17

2.6 RHEOLOGICAL PROPERTIES OF CASEINATE SOLUTIONS 18

2.6.1 Effect of shear 18

2.6.2 Effect of concentration 18

2.6.3 Effect of pH 18

2.6.4 Effect of ionic strength 19

2.6.5 Effect of temperature and heat treatment 19

2.6.6 Effect of chemical agents 20

2.7 RHEOLOGICAL PROPERTIES OF WHEY PROTEIN CONCENTRATE (WPC) SOLUTIONS 21

2.7.1 Effect of shear 21

2.7.2 Effect of concentration 21

2.7.3 Effect of pH and ionic strength 21

2.7.4 Effect of temperature 22

2.8 RHEOLOGICAL PROPERTIES OF COPRECIPITATE SOLUTIONS 22

2.8.1 Effect of shear and calcium content 22

2.8.2 Effect of pH 23

2.8.3 Effect of temperature 23

2.9 GUM-PROTEIN INTERACTIONS 23

2.9.1 Homogeneous mixtures 23

2.9.2 Simple coacervation 24

2.9.3 Complex coacervation 26

2.10 GUM-MILK PROTEIN INTERACTIONS 27

2.10.1 Neutral gums 27

2.10.2 Anionic gums 28

2.10.2.1 Caseins 28

2.10.2.2 Whey proteins 29

2.11 GUM-DAIRY PROTEIN INTERACTIONS 30

2.12 VISCOMETRIC INVESTIGATIONS OF GUM-PROTEIN (INCLUDING GUM-DAIRY PROTEIN) MIXTURES 30

2.12.1 Milk proteins 31

2.12.2 Dairy proteins 32

2.12.3 Other proteins 34

2.13 DISCUSSION AND RECOMMENDATION 35

2.13.1 pH 36

2.13.2 Gum:protein ratios and concentrations 36

2.13.3 Salts 37

2.13.4 Heat 37

CHAPTER 3 PROJECT AIMS AND OVERALL PROJECT PLAN 39

3.1 PROJECT AIMS 39

3.2 OVERALL PROJECT PLAN 39

CHAPTER 4 MATERIALS AND METHODS 41

4.1 MATERIALS 41

4.1.1 Gums 41

4.1.2 Dairy Proteins 41

4.1.3 Other materials 41

4.2 PREPARATION OF SOLUTIONS 42

4.2.1 Preparation of gum solutions 42

4.2.2 Preparation of dairy protein solutions 42

4.2.3 Storage of pure protein and gum solutions (Aging trails) 42

4.2.4 Preparation of mixtures of gum solutions and dairy protein solutions 43

4.3 CENTRIFUGATION OF MIXED SOLUTIONS 43

4.4 MEASUREMENT OF SEDIMENT 43

4.5 RHEOLOGICAL MEASUREMENT 44

4.5.1 Experimental procedure for viscosity measurements 45

4.5.2 Recording of viscometric flow data 45

4.5.3 Model fitting for viscometric flow data 45

4.6 ANALYTICAL TESTS 47

4.6.1 Moisture determination of gum and dairy protein powders 47

4.6.2 Total solids in the supernatant 48

4.6.3 Protein determination 48

4.6.4 pH measurement 48

CHAPTER 5 RHEOLOGICAL CHARACTERISATION OF GUM AND DAIRY PROTEIN SOLUTIONS 50

5.1 INTRODUCTION 50

5.2 EXPERIMENTAL PLAN 50

5.3 PROCESSING AND PRESENTATION OF EXPERIMENTAL DATA 50

5.4 RESULTS 52

5.4.1 The flow properties of pure dairy protein and pure gum solutions 52

5.4.2 Effect of concentration on apparent viscosity of pure gum solutions 57

5.5 DISCUSSION 57

5.6 CONCLUSION 60

CHAPTER 6 RHEOLOGICAL SYNERGISM AND ANTAGONISM IN GUM-DAIRY PROTEIN MIXED SOLUTIONS 61

6.1 INTRODUCTION 61

6.2 EXPERIMENTAL PLAN 61

6.3 PROCESSING AND PRESENTATION OF EXPERIMENTAL DATA 62

6.4 RESULTS 89

6.4.1 The flow properties of mixed gum-protein solutions 89

6.4.2 Synergism and antagonism in mixed solutions 89

6.4.3 Sedimentation study 101

6.5 DISCUSSION 101

6.5.1 LB/dairy protein mixed solutions 101

6.5.2 CMC/dairy protein mixed solutions 103

6.5.3 CR/dairy protein mixed solutions 104

6.5.4 XN/dairy protein mixed solutions 104

6.6 CONCLUSION 105

CHAPTER 7 THE EFFECTS OF GUM : PROTEIN RATIO AND TOTAL POLYMER CONCENTRATION ON THE VISCOSITY OF GUM-DAIRY PROTEIN MIXED SOLUTIONS 107

7.1 INTRODUCTION 107

7.2 EXPERIMENTAL PLAN 107

7.3 PROCESSING AND PRESENTATION OF EXPERIMENTAL DATA 109

7.3.1 Viscosity 109

7.3.2 Power law constants 110

7.3.3 Z-ratios 110

7.3.4 Sedimentation results 114

7.4 RESULTS AND DISCUSSION 114

7.4.1 The effect of gum : protein ratio and total polymer concentration on the apparent viscosity of gum-dairy protein mixed solutions 114

7.4.2 The effect of gum : protein ratio and total polymer concentration on the rheological character of gum-dairy protein mixed solutions 123

7.4.3 Z-ratios 124

7.4.4 Sedimentation results 145

7.5 CONCLUSIONS 151

CHAPTER 8 FURTHER SEDIMENTATION EXPERIMENTS 152

8.1 INTRODUCTION 152

8.2 EXPERIMENTAL PLAN 152

8.3 PROCESSING AND PRESENTATION OF EXPERIMENTAL DATA 153

8.4 RESULTS AND DISCUSSION 156

8.4.1 Sedimentation results 156

8.4.2 Supernatant and sediment compositions 165

8.4.3 Rheology 165

8.5 CONCLUSION 168

CHAPTER 9 FINAL DISCUSSION AND CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK 170

REFERENCES 174

APPENDICES 190

APPENDIX 1: THE CONCENTRATIONS AND RATIOS OF DAIRY PROTEINS AND GUMS THAT HAVE BEEN USED IN FOODS. 190

APPENDIX 2: SPECIFICATIONS OF GUMS 191

APPENDIX 3: SPECIFICATION OF DAIRY PROTEINS 193

APPENDIX 4: PREPARATION OF GUM SOLUTIONS 195

APPENDIX 5: PREPARATION OF DAIRY PROTEIN SOLUTIONS 200

APPENDIX 6: STORAGE TIME STUDY 204

APPENDIX 7: MEASURED MOISTURE AND SOLIDS CONTENTS OF ALL GUM POWERS AND DAIRY PROTEIN POWDERS 205

APPENDIX 8: NATURAL pH VALUES OF 0.5% GUM SOLUTIONS AND 6.0% DAIRY PROTEIN SOLUTIONS 206

APPENDIX 9: X-RATIOS FOR MIXTURES OF 0.5% GUM AND 6.0% DAIRY PROTEIN SOLUTIONS 207

APPENDIX 10: X-RATIOS FOR MIXTURES OF 0.5% GUM SOLUTION AND WATER 211

APPENDIX 11: X'-RATIOS FOR MIXTURES OF 0.5% GUM AND 6.0% DAIRY PROTEIN SOLUTIONS 212

APPENDIX 12: Z-RATIOS FOR MIXTURES OF GUM-DAIRY PROTEIN SOLUTIONS 216

APPENDIX 13: MASS BALANCE AND COMPOSITION DATA FORMING THE BASIS OF TABLES 8.10 AND 8.11 217

LIST OF TABLES

PAGE

Table 5.1: The n and k values of 6.0% dairy protein and 0.5% gum solutions at 25 °C. 52

Table 6.1: Compositions of mixtures of 0.5% gum solution and 6.0% dairy protein solution. 62

Table 6.2: Sedimentation results (%) for gum-dairy protein mixed solutions. 102

Table 7.1: Compositions of the gum-dairy protein mixtures studied. 109

Table 7.2: n values for locust bean gum (LB) and dairy protein mixed solutions. 125

Table 7.3: n values for CMC and dairy protein mixed solutions. 126

Table 7.4: n values for lambda-carrageenan (CR) and dairy protein mixed solutions. 127

Table 7.5: n values for xanthan gum (XN) and dairy protein mixed solutions. 128

Table 7.6: k values for locust bean gum (LB) and dairy protein mixed solutions. 129

Table 7.7: k values for CMC and dairy protein mixed solutions. 130

Table 7.8: k values for lambda-carrageenan (CR) and dairy protein mixed solutions. 131

Table 7.9: k value for xanthan gum (XN) and dairy protein mixed solutions. 132

Table 7.10: Sedimentation results (%) for LB/dairy protein mixed solutions. 146

Table 7.11:	Sedimentation results (%) CMC/dairy protein mixed solutions	147
Table 7.12:	Sedimentation results (%) for CR/dairy protein mixed solutions.	148
Table 7.13:	Sedimentation results (%) of XN/dairy protein mixed solutions.	149
Table 8.1:	Compositions of mixtures designated Mixture 1.	152
Table 8.2:	Compositions of mixtures designated Mixture 2.	153
Table 8.3:	Sedimentation results (%) for batch 1.	157
Table 8.4:	Sedimentation results (%) for batch 2.1.	158
Table 8.5:	Sedimentation result (% w/w) for batch 2.2.	159
Table 8.6:	Sedimentation results (%) for Mixture 2.	160
Table 8.7:	Sedimentation results (%) and analytical results for batch 5	161
Table 8.8:	Sedimentation results (%) for Mixture 1 (Data from Tables 8.3 -8.5)	163
Table 8.9:	Sedimentation results (%) for Mixture 2 (Data from Table 8.6)	164
Table 8.10:	Sedimentation results, compositions, supernatant viscosities and X'-ratios for batch 5 mixed solutions. (Data ranked in descending order of the figure for the percentage of total gum in the mixed solution remaining in the supernatant after centrifugation)	166
Table 8.11:	Sedimentation results, compositions, supernatant viscosities and X'-ratios for batch 5 mixed solutions. (Data ranked in ascending order of sediment %).	167

LIST OF FIGURES

		PAGE
Fig. 2.1	Concentration dependence of 'zero shear' specific viscosity for random coil gum solutions (based on Morris (1983)).	10
Fig. 2.2	Generalised shear-thinning behaviour of concentrated gum solutions (based on Morris (1983)).	10
Fig. 2.3.	Schematic illustration of the phase-volume ratio method (based on Tolstoguzov (1990)). A % protein solution mixed with B % gum solution. C % and D % are protein % and gum % in mixture. E % and G % are the protein and gum concentrations in the protein rich phase. H % and F % are the protein and gum concentrations in the gum rich phase.	25
Fig. 4.1	Schematic diagram of Bohlin VOR Rheometer.	46
Fig. 4.2.	Schematic diagram of concentric cylinders, C25 system.	46
Fig. 5.1	Example (for 0.5% locust bean gum solution) of Bohlin plots of shear stress and apparent viscosity versus shear rate.	51
Fig. 5.2	Example of Bohlin printout of flow curve data (the data plotted in Fig 5.1).	51
Fig. 5.3a.	Flow properties of 0.5 % locust bean gum in distilled water at 25 °C	53
Fig. 5.3b.	Flow properties of 0.5 % CMC in distilled water at 25 °C	53
Fig. 5.3c.	Flow properties of 0.5 % lambda-carrageenan in distilled water at 25 °C	54
Fig. 5.3d.	Flow properties of 0.5 % xanthan gum in distilled water at 25	

°C 54

Fig. 5.4a. Flow properties of 6.0 % sodium caseinate in distilled water at 25 °C 55

Fig. 5.4b. Flow properties of 6.0 % WPC in distilled water at 25 °C 55

Fig. 5.4c. Flow properties of 6.0 % TMP in distilled water at 25 °C 56

Fig. 5.4d. Flow properties of 6.0 % WPI in distilled water at 25 °C 56

Fig. 5.5a. Apparent viscosity (mPa.s) versus concentration (%) for locust bean gum solutions. Power law constants (n and k values) for each concentration are also shown. 58

Fig. 5.5b. Apparent viscosity (mPa.s) versus concentration (%) for CMC solutions. Power law constants (n and k values) for each concentration are also shown. 58

Fig. 5.5c. Apparent viscosity (mPa.s) versus concentration (%) for lambda-carrageenan solutions. Power law constants (n and k values) for each concentration are also shown. 59

Fig. 5.5d. Apparent viscosity (mPa.s) versus concentration (%) for xanthan gum solutions. Power law constants (n and k values) for each concentration are also shown. 59

Fig. 6.1a. Apparent viscosity versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 63

Fig. 6.1b. Apparent viscosity versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k

are also shown. 63

Fig. 6.1c. Apparent viscosity versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 64

Fig. 6.1d. Apparent viscosity versus mixture composition for mixtures of 0.5 % LB and 6.0 % TMP solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 64

Fig. 6.1e. Apparent viscosity versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPI solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 65

Fig. 6.2a. Apparent viscosity versus mixture composition for mixtures of 0.5 % CMC and 6.0 % SC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 65

Fig. 6.2b. Apparent viscosity versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 66

Fig. 6.2c. Apparent viscosity versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 66

Fig. 6.2d. Apparent viscosity versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 67

Fig. 6.2e. Apparent viscosity versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPI solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 67

Fig. 6.3a. Apparent viscosity versus mixture composition for mixtures of 0.5 % CR and 6.0 % SC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 68

Fig. 6.3b. Apparent viscosity versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 68

Fig. 6.3c. Apparent viscosity versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 69

Fig. 6.3d. Apparent viscosity versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 69

Fig. 6.3e. Apparent viscosity versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPI solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 70

Fig. 6.4a. Apparent viscosity versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 70

Fig. 6.4b. Apparent viscosity versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 71

Fig. 6.4c. Apparent viscosity versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k also shown. 71

Fig. 6.4d. Apparent viscosity versus mixture composition for mixtures of 0.5 % XN and 6.0 % TMP solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 72

Fig. 6.4e. Apparent viscosity versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPI solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown. 72

Fig. 6.5. Schematic presentation of the possible rheological behaviour

patterns of gum-dairy protein mixed solutions. 74

Fig. 6.6. Schematic presentation of the possible rheological behaviour patterns of gum-dairy protein mixed solutions in terms of X-ratios. 74

Fig. 6.7a. X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown. 75

Fig. 6.7b. X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown. 75

Fig. 6.7c. X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown. 76

Fig. 6.7d. X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown. 76

Fig. 6.7e. X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown. 77

Fig. 6.8a. X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown. 77

Fig. 6.8b. X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown. 78

Fig. 6.8c. X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown. 78

Fig. 6.8d. X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown. 79

Fig. 6.8e. X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown. 79

Fig. 6.9a. X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown. 80

Fig. 6.9b. X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown. 80

Fig. 6.9c. X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown. 81

Fig. 6.9d. X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown. 81

Fig. 6.9e. X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown. 82

Fig. 6.10a. X-ratio versus mixture composition for mixtures of 0.5 % XN

and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown. 82

Fig. 6.10b. X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown. 83

Fig. 6.10c. X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown. 83

Fig. 6.10d. X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown. 84

Fig. 6.10e. X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown. 84

Fig. 6.11 Viscosity versus concentration for aqueous sucrose solutions at 25 °C, showing effect of non-linearity on predicted (expected) viscosity (Data from Norrish (1967)). 86

Fig. 6.12a. X-ratio versus mixture composition for mixtures of 0.5 % LB and water. 86

Fig. 6.12b. X-ratio versus composition for mixtures of 0.5 % CMC and water. 87

Fig. 6.12c. X-ratio versus mixture composition for mixtures of 0.5 % CR and water. 87

Fig. 6.12d. X-ratio versus mixture composition for mixtures of 0.5 % XN and water. 88

Fig. 6.13a. X'-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown. 91

Fig. 6.13b. X'-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown. 91

Fig. 6.13c. X'-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown. 92

Fig. 6.13d. X'-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown. 92

Fig. 6.13e. X'-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown. 93

Fig. 6.14a. X'-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown. 93

Fig. 6.14b. X'-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown. 94

Fig. 6.14c. X'-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown. 94

Fig. 6.14d. X'-ratio versus mixture composition for mixtures of 0.5 %

CMC and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown. 95

Fig. 6.14e. X'-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown. 95

Fig. 6.15a. X'-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown. 96

Fig. 6.15b. X'-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown. 96

Fig. 6.15c. X'-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown. 97

Fig. 6.15d. X'-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown. 97

Fig. 6.15e. X'-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown. 98

Fig. 6.16a. X'-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown. 98

Fig. 6.16b. X'-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions. Gum : protein ratios and total

concentrations are also shown. 99

Fig. 6.16c. X'-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown 99

Fig. 6.16d. X'-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown. 100

Fig. 6.16e. X'-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown. 100

Fig. 7.1. Compositions of the mixed gum-dairy protein solutions studied in Chapter 6. 108

Fig. 7.2a. Apparent viscosity versus gum : protein ratio and total polymer concentration for LB/SC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 115

Fig. 7.2b. Apparent viscosity versus gum : protein ratio and total polymer concentration for LB/WPC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 115

Fig. 7.2c. Apparent viscosity versus gum : protein ratio and total polymer concentration for LB/TMP mixtures. The x-axis is total polymer concentration (%), the y-axis is protein figure of the gum : protein ratio and the z-axis is apparent viscosity

(mPa.s). 116

Fig. 7.2d. Apparent viscosity versus gum : protein ratio and total polymer concentration for LB/WPI mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 116

Fig. 7.3a. Apparent viscosity versus gum : protein ratio and total polymer concentration for CMC/SC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 117

Fig. 7.3b. Apparent viscosity versus gum : protein ratio and total polymer concentration for CMC/WPC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 117

Fig. 7.3c. Apparent viscosity versus gum : protein ratio and total polymer concentration for CMC/TMP mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 118

Fig. 7.3d. Apparent viscosity versus gum : protein ratio and total polymer concentration for CMC/WPI mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 118

Fig. 7.4a. Apparent viscosity versus gum : protein ratio and total polymer concentration for CR/SC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 119

Fig. 7.4b. Apparent viscosity versus gum : protein ratio and total polymer concentration for CR/WPC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 119

Fig. 7.4c. Apparent viscosity versus gum : protein ratio and total polymer concentration for CR/TMP mixtures. The x-axis is the total polymer concentration (%), the y-axis is protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 120

Fig. 7.4d. Apparent viscosity versus gum : protein ratio and total polymer concentration for CR/WPI mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 120

Fig. 7.5a. Apparent viscosity versus gum : protein ratio and total polymer concentration for XN/SC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 121

Fig. 7.5b. Apparent viscosity versus gum : protein ratio and total polymer concentration for XN/WPC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of

the gum : protein ratio and z-axis is the apparent viscosity (mPa.s). 121

Fig. 7.5c. Apparent viscosity versus gum : protein ratio and total polymer concentration for XN/TMP mixtures. The x-axis is total polymer concentration (%), the y-axis is protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 122

Fig. 7.5d. Apparent viscosity versus gum : protein ratio and total polymer concentration for XN/WPI mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s). 122

Fig. 7.6a. n value versus gum concentration for LB/dairy protein mixed solutions. 133

Fig. 7.6b. n value versus gum concentration for CMC/dairy protein mixed solutions. 133

Fig. 7.6c. n value versus gum concentration for CR/dairy protein mixed solutions. 134

Fig. 7.6d. n value versus gum concentration for XN/dairy protein mixed solutions. 134

Fig. 7.7a. k value versus gum concentration for LB/dairy protein mixed solutions. 135

Fig. 7.7b. k value versus gum concentration for CMC/dairy protein mixed solutions. 135

Fig. 7.7c. k value versus gum concentration for CR/dairy protein mixed

	solutions.	136
Fig. 7.7d.	k value versus gum concentration for XN/dairy protein mixed solutions.	136
Fig. 7.8a.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions.	137
Fig. 7.8b.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPC solutions.	137
Fig. 7.8c.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % TMP solutions.	138
Fig. 7.8d.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPI solutions.	138
Fig. 7.9a.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % SC solutions.	139
Fig. 7.9b.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPC solutions.	139
Fig. 7.9c.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions.	140
Fig. 7.9d.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPI solutions.	140
Fig. 7.10a.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % SC solutions.	141
Fig. 7.10b.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPC solutions.	141
Fig. 7.10c.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions.	142

Fig. 7.10d.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPI solutions.	142
Fig. 7.11a.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions.	143
Fig. 7.11b.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPC solutions.	143
Fig. 7.11c.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % TMP solutions.	144
Fig. 7.11d.	Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPI solutions.	144
Fig. 8.1.	Sedimentation experiments carried out on Mixtures 1 and 2.	154
Fig. 8.2.	Sedimentation measurement and analyses carried out on batch 5 (Mixture 1).	154

ABBREVIATIONS

LB	=	Locust bean gum
CMC	=	Sodium Carboxymethylcellulose
CR	=	Lambda-carrageenan
XN	=	Xanthan gum
SC	=	Sodium caseinate
WPC	=	Whey protein concentrate
TMP	=	Total milk protein
WPI	=	Whey protein isolate
LB/SC	=	LB and SC mixed solutions
LB/WPC	=	LB and WPC mixed solutions
LB/TMP	=	LB and TMP mixed solutions
LB/WPI	=	LB and WPI mixed solutions
CMC/SC	=	CMC and SC mixed solutions
CMC/WPC	=	CMC and WPC mixed solutions
CMC/TMP	=	CMC and TMP mixed solutions
CMC/WPI	=	CMC and SC mixed solutions
CR/SC	=	CR and SC mixed solutions
CR/WPC	=	CR and WPC mixed solutions
CR/TMP	=	CR and TMP mixed solutions
CR/WPI	=	CR and WPI mixed solutions
XN/SC	=	XN and SC mixed solutions

XN/WPC	=	XN and WPC mixed solutions
XN/TMP	=	XN and TMP mixed solutions
XN/WPI	=	XN and WPI mixed solutions
N	=	No sediment was observed.
NG	=	Sediment was found but the solution appeared to be a gel-like mass.

CHAPTER 1

INTRODUCTION

The success of a food product often depends on the creation of a new texture or on increasing the shelf-life of the physical structure underlying an existing texture or on finding a new and possibly cheaper way of making a familiar product. The texture of many foods is defined and controlled by rheologically-functional food ingredients. They are those ingredients which can modify the rheological properties of food products by, for example, stabilisation, fat emulsification, viscosity increase, gelation, whipping, film formation and texturisation.

Proteins and gums are the major groups of rheologically- functional food ingredients (Hansen and Black, 1972; Tolstoguzov, 1986, 1990, 1991; Campbell and Pavlasek, 1987; Marrs, 1989). Addition of proteins and gums to foodstuffs can result in greater acceptability of the finished products with respect to appearance and eating qualities. Many protein products can be used in foods, but this work is concerned only with the use of dairy proteins.

1.1 THE USE OF DAIRY PROTEINS AS RHEOLOGICALLY-FUNCTIONAL FOOD INGREDIENTS

" Milk proteins " are defined here as the pure protein fractions that can be isolated from milk. These are alpha-s1-casein, α_{s2}-casein, β-casein, kappa-casein, gamma-casein, α-lactalbumin, β-lactoglobulin, proteose-peptones, immunoglobulins and bovine serum albumin. The main feature of the caseins is that they have an open dispersed structure. They also have an ability to interact with one another to form aggregates which in turn form micelles. The casein micelle is made up of mostly alpha- and beta-caseins. The whey proteins are known as globular proteins which means that their shape does not alter easily as the environment changes (Morr, 1979; Lim, 1980; Kinsella, 1984;).

" Dairy proteins " are defined here as commercial protein products made from milk. These are caseinates, whey protein concentrates and coprecipitates (Southward and Goldman, 1975; Evans, 1982; Southward and Walker, 1982; Southward, 1985; Kirkpatrick and Fenwick, 1987). The functional performance of these dairy proteins depends on their physical properties and their chemical structures (Morr, 1979, 1982, 1989; Kinsella, 1984).

1.1.1 Caseinates

Commercial caseinates are manufactured by adjusting rennet- or acid-coagulated casein to pH 6.7 with the appropriate amount of calcium or sodium hydroxide. Calcium caseinates, for example, are made from acid casein by adding calcium hydroxide to 1.5% at pH 6.5. The viscous suspension (20%) is then pasteurized and spray-dried (Kinsella, 1984; Southward,1985). In this discussion, emphasis is placed on sodium caseinate because it is more widely used as a food ingredient.

The rheologically-functional properties imparted to foods by sodium caseinate are fat emulsification, water-binding, stabilising and general improvement of consistency (Southward, 1985, 1986). Caseinates have been used as a water binding agent: for example, about 1-5% in a doughnut mix and about 5-10% in processed meat products (Southward and Walker, 1982). In yogurt and in cultured cream products, 2-3% sodium caseinate has been used as a stabilizer. It provides emulsification and improves body for coffee whiteners when it is incorporated at a level of 7-10% of the dry ingredients and for imitation milk at a level of 3.5% (Southward and Walker, 1982).

1.1.2 Whey protein concentrate

Whey protein concentrate (WPC) can be made by such processes as ultrafiltration, gel filtration, polyvalent ion precipitation, electrodialysis, and ion-exchange (de Wit et al, 1983; Harper, 1984; Kinsella, 1984). The functional properties of whey protein products vary with the processing procedures used (Morr et al, 1973).

Ultrafiltration WPC has been used to replace up to 100% of the milk solids-non-fat

(MSNF) of a standard ice-cream formulation (Morr, 1979). Polyphosphate-precipitated WPC is especially useful as an emulsifier. Ion exchange whey protein products have the highest protein content and have good aeration properties, for example high whipping. Electrodialysed whey protein products with low mineral contents are especially well suited for beverage applications (Harper,1984).

However, the major rheologically-functional property of whey protein is its gelling ability (Mangino, 1984; Kinsella, 1984; Zadow, 1986; de Wit, 1987; Kirkpatrick and Fenwick, 1987; de Wit et al, 1988). Even 10% WPC solution can form a firm gel when heated at 85 °C. WPCs can be added at 1-2% to improve the stability of the gel and reduce syneresis in yoghurt.

1.1.3 Coprecipitate

According to Southward (1985, 1986); Southward and Aird (1978), coprecipitate is a protein precipitate containing both the caseins and the whey proteins which is manufactured from skim milk under controlled conditions of heating (85-90 °C for 1-20 min), acidity level, and calcium level. The curd is subsequently washed and either dried to produce granular, insoluble coprecipitates, or dissolved in alkali to produce soluble coprecipitates. These "soluble" coprecipitates are not however completely soluble in alkali at pH 6.6-7.2. By application of a lower heat treatment to skim-milk under alkaline conditions it is possible to produce a coprecipitate which will dissolve completely in this pH range. This product is called "total milk protein"

The solubility characteristics of coprecipitates are controlled by the calcium level (Smith and Snow, 1968; Hayes et al, 1969). Low-calcium coprecipitates show good solubility above pH 5.2, increasing rapidly to 100% solubility at pH 6.4. High-calcium coprecipitates show poor solubility at all pHs (maximum 10% at pH 8.0).

Southward and Goldman (1978) suggested that co-precipitates can be added at a level of 1% by total weight of meat products for their water-binding capacity. Whipped toppings or simulated whipping creams are prepared using a blend of soluble coprecipitates as an ingredient. This functions as a stabilizer and bodying agent

1.2 THE USE OF GUMS AS RHEOLOGICALLY-FUNCTIONAL FOOD INGREDIENTS

Gums, also called hydrophillic colloids or polysaccharides or hydrocolloids, are one of the major groups of rheologically- functional food ingredients (Pederson, 1979; Glicksman, 1982; Igoe, 1982; Welsby et al.,1982; Aspinall, 1983; Morley, 1983; Walker, 1983; Pomeranz, 1975). Gums are used in a food formulation in order to impart a wide variety of characteristics to the finished product. In particular, they are employed to confer resistance to undesirable physical processes such as crystallization, gravitational sedimentation and mechanical disaggregation which might otherwise occur during distribution and storage.

Gums are either branched or linear. Some gums are naturally anionic, possessing acidic functional groups like carboxyl groups, sulphate groups, and phosphate groups. Other natural gums possess amino groups which are usually monoacetylated. Such gums may show cationic properties (Glicksman, 1980a; Whistler 1959, 1973). To visualize their behaviour more clearly, it is helpful to classify gums into 3 classes: a) those containing neutral groups (eg.locust bean gum) b) those containing carboxyl groups (eg. sodium carboxymethylcellulose (CMC) and xanthan gum) and c) those containing sulphate ester groups (eg. lambda-carrageenan). Gums falling into categories b) and (c) are anionic gums.

The discussion in this section concentrates on locust bean gum, CMC, lambda-carrageenan and xanthan gum since they were used in this study.

1.2.1 Locust bean gum

Seed gum from the locust bean is a polysaccharide containing galactose and mannose as the structural building blocks (Glicksman, 1986a; Seaman, 1980). It has been used at concentrations of 0.01 to 0.05% in combination with CMC to stabilize ice cream and sherbet (Guiseley et al., 1980). Rizzotti et al (1983) state that the mixture of sweetener and gum (locust bean gum or guar gum) can be used to optimise the viscosity of ice cream.

1.2.2 Sodium carboxymethylcellulose (CMC)

According to Batdorf (1957), Greminger and Krumel (1980) and Glicksman (1986b), CMC is a salt of carboxylic acid. Solutions of CMC have a pH value of about 7.5. The addition of 0.15-0.4% CMC to ice-cream gives a product with pleasing texture, body, and melting characteristics. Pomeranz (1975) stated that CMC can be used to prevent precipitation of soy and milk proteins at pH values close to the protein isoelectric point (IEP) in foods such as sour milk drinks. It is used as a stabilizer in dietetic foods.

1.2.3 Carrageenans

Carrageenans are the most important red seaweed polysaccharides used by the food industry. The physical properties of carrageenans depend on their molecular weight and their sulphate content (Guieseley et al, 1980; Glicksman, 1983). They contain three fractions - lambda-carrageenan, iota-carrageenan, and kappa-carrageenan - which differ in sulphate ester 3,6-anhydrogalactose content. Commercial carrageenans are usually blends of lambda-, iota- and kappa-carrageenans, sometimes with one type predominating.

In the dairy industry, carrageenans are predominantly used by themselves or blended with locust bean gum, pectin, alginate, or starch. The use of carrageenan (0.15-0.25 %) blended with starch (1.5-4.5 %) can improve the texture in UHT milk desserts. The addition of carrageenan (0.01-0.02%) provides stability in frozen desserts (Igoe, 1982). In cocoa milk drink, 0.025-0.035% carrageenan is used to keep the cocoa in suspension and give the drink a rich mouthfeel (Guiseley et al., 1980).

1.2.4 Xanthan gum

Until recently, xanthan gum has been the only microbial gum permitted for use in foods (Cottrell et al., 1980; Glicksman, 1980b). It can be used in a range of dry-mix product, such as milk shakes, bakery fillings, sauces, beverages, and desserts. In pastries or doughnuts, 0.2% xanthan gum inhibits syneresis and prevents the filling

from being absorbed by the pastry (Pettitt, 1979). Low-solid tomato sauce requires xanthan gum at 0.05% to provide complete stability (Igoe, 1982). Dressings containing 0.25-0.3% xanthan gum are shelf stable for many months. In order to provide body to artificial juice drinks 0.025% to 0.17% xanthan gum is added. A carbonated liquid yoghurt prepared from a dry mix may be stabilized with about 1.3% xanthan gum. An advantage in stability is reported for a chocolate flavoured liquid confection containing 0.05 to 0.75% xanthan gum (Pettitt, 1979).

1.3 THE USE OF GUM/DAIRY PROTEIN COMBINATIONS IN FOOD SYSTEMS

Dairy proteins and gums are widely used together as rheologically -functional food ingredients. Examples are given in Appendix 1. It has been found that combinations of proteins and gums in solution usually can improve the functional properties of food systems, for example by stabilizing emulsions and providing a gelling function (Marrs,1989).

The use of anionic gums makes it possible to increase the stability of protein-containing emulsions (Tolstoguzov and Braudo, 1985; Tokaev et al., 1987). Tokaev et al.(1987) reported that with the use of caseinate-pectate systems at pH 5.5 compared with caseinate alone, emulsions of corn oil in water have a greater stability to creaming. In pasteurized cream or ultra-high temperature treated (UHT) cream, the combination of 0.015% carrageenan and 0.25% whey protein with high melting milk fat fractions can be used to improve storage stability and whipping properties (Harper et al., 1980). The combination of 5.0% whey proteins and 0.8% CMC acts as an emulsifier in the formulation of imitation cheese (Harper, 1984).

Tolstoguzov et al.(1986) indicated that combinations of proteins and polysaccharides can improve gelling ability in food systems. A mixture of gelling agents (gelatin and agarose) forms gels at a far lower concentration than do solutions of the individual polymers. For imitation frozen desserts including ice cream, sherbets and specialty products, for example milk shake bases, the combination of protein and gum can act both as a stabiliser and a gelling agent . Examples include the combination of 0.1%

xanthan and 0.35% sodium caseinate in a stabilized frozen thick shake and the combination of 10% dairy protein blend (dry whey protein and caseinate) and 0.1% CMC in the formulation of strawberry- flavoured shakes (Harper, 1984). A frozen dessert formulation contained 3.0% of total milk protein and 0.3% gum (guar: CMC: carrageenan in the ratio of 60:30:10).

1.4 DISCUSSION AND PROJECT IDENTIFICATION

These mixtures of dairy proteins and gums in food systems have usually been developed by empirical methods. There are no fully-established scientific reasons why they give the specific rheological properties they do to foods. It is of concern that the process of food product development is often based very much on practical and some scientific experience rather than on fundamental understanding. This is due to the complex interactions of food ingredients in food systems. Fundamental physico-chemical and rheological studies on these food components have normally been conducted on dilute and semi-dilute solutions of pure substances, whereas most solutions in food products are more concentrated and the ingredients involved are commercial rather than pure substances. These facts, coupled with the complexity of food systems, led to a need to use model systems in the investigation of rheological interactions between selected dairy proteins and selected gums at food use concentrations. It was hoped that interpretation of the behaviour of model systems would be aided by the known behaviour of dilute solutions of pure substances, and that an understanding of the model systems would in turn help in fundamentally understanding real food systems. This is vital for future systematic food product development.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The rheology of gum and protein solutions is reviewed. Emphasis is placed on the rheological properties of both types of polymer solution at the level of concentrated solutions. The effects of environmental conditions such as pH, temperature and ionic strength on the rheological behaviour of these two polymers is also discussed. Interactions between gums and proteins is widely reviewed in this chapter but emphasis is given to the viscometric investigation of gum-protein mixtures. Finally, an experimental study for further research on the rheological properties of gum-protein interactions is formulated and recommended.

2.2 FUNDAMENTAL RHEOLOGY OF GUM SOLUTIONS

In order to understand the rheological properties of gum solutions, it is logical to deal firstly with intrinsic viscosity, then the viscosity of dilute solutions, and finally the viscosity of concentrated solutions.

2.2.1 Intrinsic viscosity

Launay et al., (1986) state that when a gum is dissolved at a concentration **c** (w/v) in a solvent, the solution zero shear viscosity is increased from that of the solvent η_s to a value η and, at a given temperature, the following parameters can be defined:

relative viscosity	η_r	=	η/η_s	(2.1)
specific viscosity	η_{sp}	=	$(\eta - \eta_s)/\eta_s$	(2.2)
reduced viscosity	η_{red}	=	$(\eta - \eta_s)/c\eta_s$	(2.3)
intrinsic viscosity	$[\eta]$	=	$\lim_{c->0}\eta_{red}$	(2.4)

The relative and specific viscosities are dimensionless. The reduced viscosity and intrinsic viscosity have units of concentration^{-1}, for example dl/g if c is expressed as g/dl.

The intrinsic viscosity [η] is a characteristic property of an isolated gum molecule in a given solvent. It can be a central parameter for interpreting flow properties by measuring the hydrodynamic volume occupied by the gum (Launay et al.,1986). The work of Mitchell (1979) shows that increasing the hydrodynamic volume of gum molecules increases the intrinsic viscosity of the gum solution. Gums with high [η] will have high viscosities because the level of intermolecular interaction will be high. Elfak et al.(1977) reported that guar gum solution has a higher [η] than that of locust bean gum. This may be due to guar gum having a more extended configuration than locust bean gum which can contribute to the greater hydrodynamic volume.

Morris (1983) stated that the [η] can be related to the radius of gyration (R_g) of the polymer coil and the molecular weight (M):

[η]	$\propto$	R_g^3/M	(2.5)
Number of coils per unit volume = n	$\propto$	c/M	(2.6)
Total volume of all coils	$\propto$	nR_g^3	(2.7)
	$\propto$	cR_g^3/M	(2.8)
	$\propto$	$[\eta]c$	(2.9)

The product c [η] therefore gives a measure of the extent of space-occupancy by the polymer. Fig 2.1 generalizes concentration-dependence of the zero shear specific viscosity for "random coil" gums in aqueous solutions. It shows that the onset of entanglement (c^* transition) for both neutral and anionic polysaccharides occurs when $c[\eta] = 4$. This corresponds to a zero shear specific viscosity of about 10 and, because water (viscosity about 1.0 mPa.s) is the solvent, to a zero shear viscosity, η_0 , of about 10 mPa.s. However, Morris et al., (1981, reviewed by Launay et al, 1986) found that the only exceptions to this generalized behaviour are guar gum and locust bean gum, where c^* occurs at a somewhat lower degree of coil overlap ($c[\eta] = 2.5$). This may be due to additional interchain associations (hyperentanglements) between polymer chains in solutions of these gums.

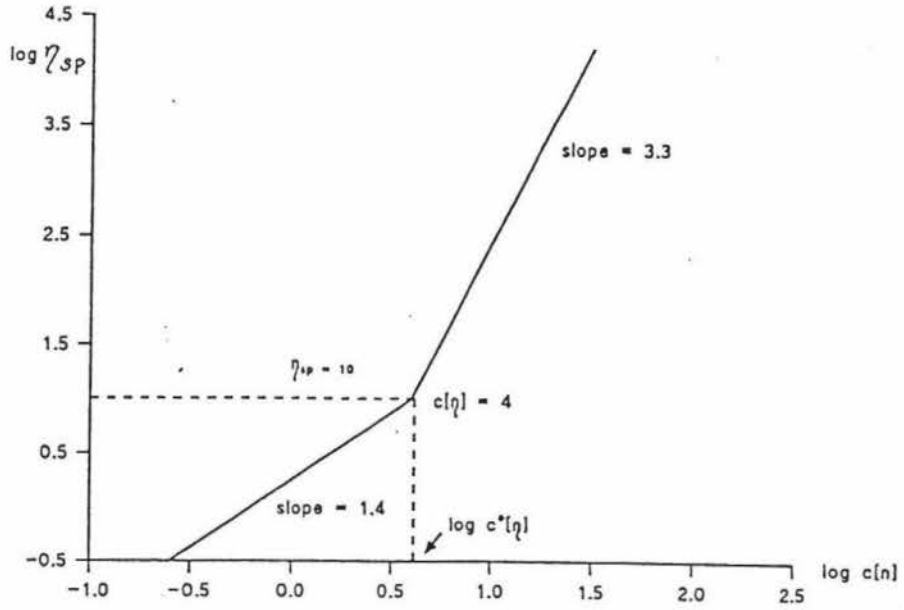


Fig. 2.1. Concentration dependence of 'zero shear' specific viscosity for random coil gum solutions (based on Morris (1983)).

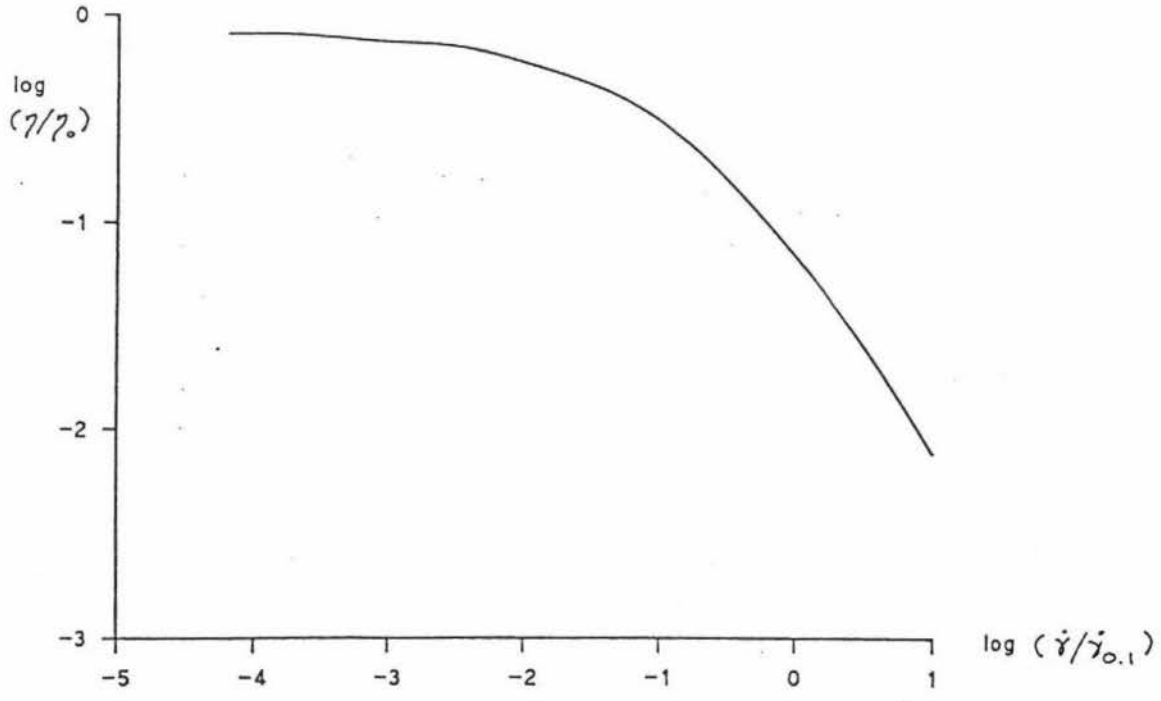


Fig. 2.2 Generalised shear-thinning behaviour of concentrated gum solutions (based on Morris (1983)).

2.2.2 Dilute solutions

In dilute solutions, below the onset of entanglement ($c < c^*$, where $c^* = 4/[\eta]$), viscosity shows only a slight dependence on the flow rate, this dependence being due to individual coils being stretched out by the flow and offering less resistance to movement. Thus dilute solutions show Newtonian behaviour.

2.2.3 Concentrated solutions

Concentrated gum solutions (i.e. solutions of concentration greater than c*) exhibit non-Newtonian behaviour (shear thinning) and may show viscoelastic properties (Morris, 1983). At very low shear rates there is sufficient time for new entanglements to form between different chain-partners. The viscosity remains constant at a fixed maximum value (the 'zero shear' viscosity,η_0). The different entangled'random coil' gum solutions can differ widely in their 'zero shear' viscosity. At higher shear-rates, the rate of re-entanglement falls behind the rate of disruption of existing entanglements. The extent of entanglement-coupling decreases progressively with increasing shear-rate and viscosity falls. However, the form of shear thinning behaviour can be described by the same general curve (Morris et al, 1981; reviewed by Morris,1983). According to this approach, the shear thinning behaviour of any gum solution can be defined by two parameters, the viscosity at zero shear rate (η_0), and the shear rate $\gamma_{0.1}$, defined as the shear rate required to reduce the viscosity to one tenth of η_0. By expressing measured viscosities relative to η_0, and applied shear rates relative to $\gamma_{0.1}$, experimental results for all random-coil gums can be made to fall on the same master curve (Figure 2.2).

2.3 RHEOLOGICAL PROPERTIES OF CONCENTRATED GUM SOLUTIONS

Most gums in food systems have been used in the concentration range from 0.05% to 5.0%. They give a high viscosity and exhibit pseudoplastic flow (i.e. their viscosity decreases with increasing shear rate)(Balmaceda et al, 1973; Krumel and Sarkar, 1975; Glicksman, 1982). Szczesniak (1985) stated that most gum solutions obey the

power law: $\tau = k\dot{\gamma}^n$ (2.10)

where τ is shear stress (Pa), $\dot{\gamma}$ is shear rate (s^{-1}), k is the consistency index ($Pa.s^{-1}$) and n is the flow behaviour index (dimensionless). For a Newtonian solution, viscosity is independent of shear rate, k = n and n=1. The lower the value of n, the greater the shear-thinning effect. The power law constants vary not only with the type of gum but also with its concentration. Krumel & Sarkar (1975) showed that the consistency index (k) increases and the n value decreases with increasing gum concentration.

Apparent viscosity is shear rate dependent for non-Newtonian liquids and is defined by the following equation:

$$\eta_{app} = \tau/\dot{\gamma} \quad (2.11)$$

where η_{app} = apparent viscosity (Pa.s)
τ = shear stress (Pa)
$\dot{\gamma}$ = shear rate (s^{-1})

In addition, the viscosity of gum solutions can also be influenced by previous shear history, temperature, the presence of salts, and the presence of other food ingredients. The dependence of viscosity on these factors varies for different gums. These factors are now discussed in more detail for some gums used in this study.

2.3.1 Effect of concentration

Locust bean gum, CMC and xanthan gum solutions exhibit pseudoplastic and slight time-dependent (thixotropic) behaviour (Seaman,1980). The viscosity increases nearly exponentially with concentration. Time-dependency also increases with increasing concentration (Szczesniak, 1985). Krumel and Sarkar (1975) found that for CMC solutions, pseudoplastic behaviour and thixotropic behaviour become more pronounced with increasing molecular weight. Xanthan gum solutions show a high degree of pseudoplasticity. Solutions of xanthan gum at 1% or higher concentrations appear almost gel-like at rest, indicating the presence of a yield stress.

2.3.2 Effect of pH

The pH range 3-11 has little effect on the viscosity of locust bean gum solutions. Solutions of CMC and carrageenan maintain their normal viscosity over a wide pH range. The viscosity of xanthan gum solution is unchanged over the pH range 1-13 (Glicksman, 1982).

2.3.3 Effect of ionic strength

Guiseley et al. (1980) found that increasing the ionic strength results in a decrease in viscosity in locust bean gum, CMC and carrageenan solutions. The effect of salts on the viscosity of xanthan gum solutions depends on the salt concentration. There is a slight decrease in viscosity at low salt concentration (below 0.15% NaCl) and an increase at higher salt concentrations.

2.3.4. Effect of added sugar

The rheological behaviour of gum solutions can be influenced by the presence of sugar which may result in restricted hydration of the gum (Elfak et al.,1977, 1979a, 1979b, 1980; Morley,1983). Elfak et al.(1977) reported that the viscosity of dilute solutions of neutral gums (guar gum and locust bean gum) containing sugar showed no evidence of interactions between the sugar and the gum molecules. In this respect there was a close similarity to the behaviour of anionic gums (CMC and kappa-carrageenan) (Elfak et al, 1978). Addition of sugar to concentrated solutions of guar gum, locust bean gum and CMC has no effect on the non-Newtonian behaviour of the gum solutions (Elfak et al., 1979a, 1979b). However, Elfak et al.,(1979b) found that the behaviour of kappa-carrageenan shows a marked difference at high concentrations of added glucose and sucrose which increase the non-Newtonian behaviour of solutions .

2.4 GUM-GUM INTERACTIONS

When two gums are blended together in a mixed solution, the interaction between the

gums can be referred to as synergism if the result is an increase in the mixture's viscosity over what would be expected and antagonism if the opposite occurs. Use has been made of the synergistic interactions between different gums in solution in recent years. A well-known example is the interaction of non-ionic gums (e.g. guar gum and locust bean gum) with xanthan gum. Clark et al.(1987) found that when xanthan gum is combined with guar gum, a synergistic increase in viscosity occurs. The viscoelastic properties of xanthan gum:guar gum blends show that the interaction has its maximum synergism at blend ratios of roughly 3:2. Addition of either sodium ions (at levels >0.003 M) or calcium ions (at level >0.0005 M) diminishes the interaction significantly. When xanthan gum is combined with locust bean gum, a thermoreversible and highly cohesive gel is obtained. Gel formation results from the build up of a complex network in which polymer molecules form highly ordered intermolecular associated regions known as junction zones. In view of this, it may be postulated that upon combining xanthan gum and locust bean gum solutions the gum molecules are rearranged from a more random coil conformation to a more orderly conformation containing the junction zones. At the same time stereochemical factors specific to the two colloids allow the formation of a complex network, resulting in gelation. The strength of the xanthan-locust bean gum gel depends upon the ratio of the two gums (Arnaud et al, 1989). Maximum gel strength is obtained with a xanthan gum:locust bean gum ratio of 1:1 indicating that there is about an equal number of junction sites available on each polymer molecule. The pH also has a significant effect on the gel strength. Maximum gel strengths are obtained in the pH range 6-8, and a rapid decline in gel strength is noted at both the alkaline and acid end of the pH spectrum.

Cottrell et al (1980) indicated that xanthan gum can also be used to modify the rheological behaviour of sodium alginate solutions. A combination of the two gums produces flow properties intermediate between the two materials.

Kaletunc-Gencer and Peleg (1986) have reported that in a mixture of carrageenan and guar gum, at a total concentration 1% w/w and pH 7, the synergism is significant when the guar gum proportion is above 50% and the effect is more pronounced at low shear rates (100 s^{-1}). Another case of synergism between gums is evident in the

behaviour of CMC and locust bean gum at a total concentration 0.5% w/w and pH 6.7. The effect increases dramatically with the mixture's overall concentration. A clear case of antagonism is evident from the rheological behaviour of alginate and CMC mixtures, the effect being stronger at low shear rates (50-100 s^{-1}).

A more recent example involves the interaction of carrageenan and starches. Descamps et al.(1986) found that a mixed iota-carrageenan/starch solution can provide a substantial increase in viscosity as compared with starch alone. Limited increases in viscosity were observed between lambda-carrageenan and starch. Kappa-carrageenan did not yield additional viscosity, but created a gel when the fraction of kappa-carrageenan in the carrageenan-starch mixture was greater than 0.3.

2.5 FUNDAMENTAL RHEOLOGY OF PROTEIN SOLUTIONS

The rheology of protein solutions can be viewed simply as resulting from the contribution of the geometry and the interactions of the molecules. It is more predominantly dependent on the association or disassociation of protein molecules under the influence of intermolecular interactions. In order to understand the rheological properties of protein solutions, it is logical to deal firstly with intrinsic viscosity, then the viscosity of dilute solutions, and finally the viscosity of concentrated solutions.

2.5.1 Intrinsic viscosity

In dilute solutions or in the absence of interactions, the viscosity of protein solutions is governed by the shape and size of the molecules. The following parameters can be defined:

$$\eta = \eta_s(1 + \beta\phi) \quad (2.12)$$

$$(\eta - \eta_s) / \eta_s = \eta_{sp} = \beta\phi \quad (2.13)$$

$$\phi = c(v_2 + \delta_1 v_1) \quad (2.14)$$

$$\eta_{sp} = \beta c(v_2 + \delta_1 v_1) \quad (2.15)$$

$$\eta_{red} = \eta_{sp} / c = \beta(v_2 + \delta_1 v_1) \quad (2.16)$$

$$[\eta] = \lim_{c \to 0} \eta_{red} = \beta(v_2 + \delta_1 v_1) \quad (2.17)$$

where

η = the zero shear viscosity of solution (mPas)

η_s = the viscosity of solvent (mPas)

ϕ = the volume fraction of solute (protein)

β = the shape factor (ß= 2.5 for spherical non-charged particles)

c = the weight concentration of protein (g/dl)

v_1 = the specific volume of associated solvent (dl/g)

v_2 = the specific volume of protein (dl/g)

δ_1 = the weight of solvent associated per unit weight of protein (g water/g protein)

$[\eta]$ = the intrinsic viscosity (dl/g)

Equation (2.17) indicates that the intrinsic viscosity is a measure of the hydrodynamic volume of the protein molecule, which in turn depends on the shape (conformation), size (molecular weight) and degree of hydration of the molecule (Rha and Pradipasena, 1986). The degree of hydration is related to the number of ionizable and hydrophillic groups in the molecule (Lee and Rha, 1979).

Rha and Pradipasena (1986) stated that proteins can be divided into two groups, globular proteins and fibrous proteins. Globular proteins have compact molecules and only have a small effect on the viscosity of water except at high concentrations (Rha, 1977). This is because their mobility is not hindered and the dynamics of the systems are not greatly disturbed. Most globular proteins in their native state have intrinsic viscosities of approximately 0.025-0.06 dl/g.

Fibrous protein molecules can generally be modelled by elongated ellipsoids or rods or, in some cases, flexible coils. The intrinsic viscosity of fibrous protein solutions may be an order of magnitude higher than that of globular protein solutions (i.e. greater than 0.10 dl/g).

The large difference in the intrinsic viscosity between globular and fibrous protein solutions illustrates the importance of the molecular shape on the flow behaviour of

the solution. However, Lee and Rha (1979) suggested that the intrinsic viscosity of a protein solution also depends on the treatment the protein has received such as sterilization, pumping, mixing, and alkali or acid treatments.

2.5.2 Dilute solutions

In dilute solutions, the protein molecules do not interact with each other. Pradipasena and Rha (1977a, 1977b), for example, reported that the apparent viscosity of 3-5% ß-lactoglobulin solutions remains constant and shows no time effect over the shear rate range of 6850-17000 s^{-1} (i.e the solutions are Newtonian). This dilute region can extend up to 10% ß-lactoglobulin and the concentrated region, where molecular interactions do occur, corresponds to levels above 10% ß-lactoglobulin.

2.5.3 Concentrated solutions

In concentrated solutions, the protein molecules come into contact. The viscosity of concentrated solutions reflects intermolecular interactions resulting from attractions between adjacent molecules which may lead to aggregation in the protein dispersion (Rha and Pradipasena, 1986). These solutions, therefore, exhibit non-Newtonian behaviour and may show viscoelastic properties (Rha and Pradipasena, 1986; Kinsella, 1984.).

As mentioned in the work of Pradipasena and Rha (1977a, 1977b), the concentrated region corresponds to levels above 10% for ß- lactoglobulin and the apparent viscosity of 10-40% ß- lactoglobulin solutions decreases as the shear rate increases. A rheopectic hysteresis effect was observed for 10 -30% ß-lactoglobulin solutions (i.e. the apparent viscosity increased with shearing time at a constant shear rate) whereas thixotropy was observed for 40% solutions (i.e. the apparent viscosity decreased with shearing time at a constant shear rate).

Since the work reported here involved the study of the rheological properties of dairy protein solutions, the next three sections of this review cover the rheogical properties of dilute and concentrated dairy protein solutions.

2.6 RHEOLOGICAL PROPERTIES OF CASEINATE SOLUTIONS

Caseinate solutions are prepared by either dissolving caseinate powder (i.e sodium caseinate, calcium caseinate) in water or casein in alkaline solution. For example, sodium caseinate solutions are prepared by soaking lactic casein in NaOH. The rheological properties of caseinate solutions are mainly influenced by shear rate, concentration, pH, ionic strength, temperature and heat treatment and the presence of various chemical agents.

2.6.1 Effect of shear

The viscosity of caseinate is dependent on shear rate. Two types of 15% caseinate solution, sodium caseinate and rennet casein dissolved in sodium tripolyphosphate solution, were observed by Towler (1974). It was found that 15% casein solutions exhibited Newtonian behaviour at low shear rates (eg. 1-100 s^{-1}) while a more pseudoplastic behaviour was exhibited at higher shear rates (>200 s^{-1}).

2.6.2 Effect of concentration

The work of Towler (1974) and Hermansson (1975) has shown that dispersions of sodium caseinate are almost Newtonian and show low viscosity at concentrations below 12%. At concentrations between 12% and 20%, they show slightly pseudoplastic behaviour. The degree of psuedoplasticity increases as the concentration of caseinate is increased . These flow characteristics indicate that increase in viscosity with concentration may be due to increasing intermolecular interaction.

2.6.3 Effect of pH

Hayes and Muller (1961) found that hydrochloric, lactic or sulphuric acid caseins dispersed with NaOH give a minimum viscosity when they are precipitated at pH 4.2-4.6. Precipitation below pH 4.2 gives higher viscosity, and very high viscosities are obtained when precipitation is carried out at pH 4.8-5.1. Casein solutions in borax and sodium hydroxide have a minimum viscosity at about pH 7.0 and a maximum at

pH 9.5 Ammonium hydroxide solutions of casein show little change in viscosity with pH between 6.5-8.5.

Hayes and Muller (1961) also found that with addition of varying amounts of calcium (as $CaCl_2$) to acid casein (dispersed in NaOH), above pH 7.0, the viscosity increases with increase in calcium concentration up to about 8 mg/g. It decreases sharply at pH values below 6.0. These low pH solutions have a white opaque appearance and show numerous small aggregates. 20% calcium caseinate (1.5% calcium) can form a gel at pH 5.4 and 63 °C, but the gel does not form at pH values above 6.0 and at temperatures up to 100 °C.

2.6.4 Effect of ionic strength

Hermansson (1975) reported that the viscosity of sodium caseinate in 0.2 M NaCl was higher than that in distilled water. The effect of salt can be interpreted in terms of either a hydration effect or a change in repulsive interaction between salt and protein. Hayes and Muller (1961) found that 20% calcium caseinate solutions (with 1% added calcium and at pH 5.4) show a gel formation when the solutions are heated up to 57 °C. The increasing calcium content increases the gelation temperature. It appears that about 0.8% calcium is the minimum necessary to induce gelation on heating

2.6.5 Effect of temperature and heat treatment

Rheological properties of caseinate are generally strongly temperature-dependent. Towler (1974) showed that an increasing temperature, in the temperature range 25-60 °C, caused a decrease in the viscosity of sodium caseinate solutions (7.5-15.0% w/w) and rennet casein solutions (7.5-15.0 w/w).

Korolczuk (1982) studied the behaviour of casein in neutral and acidic solutions in the temperature range 25-80 °C. Neutral caseinate solution was prepared by dissolving casein in 1 N NaOH solution and then spray drying it, while an acidified casein was prepared by dissolving sodium caseinate solution in water and then adding a cation exchange resin to decrease the pH of the solution to about 2.5. The resin was

separated by filtration and the protein solution was spray dried. Both the sodium caseinate and the acidic casein powder were dissolved again in water. The viscosity of the acidic casein solutions was found to be higher than that for sodium caseinate solution in the concentration range 2-17 %w/w and within the temperature range 25-60 °C. For temperatures over 60 °C, the viscosity of the acidic casein solutions rose during heating whereas the viscosity of the sodium caseinate solutions decreased. At the higher temperatures, the formation of intermolecular aggregates in acidic casein solution occurred due to the lower electrostatic repulsion forces and higher hydrophobic interaction. These caused the increase in the viscosity and gel formation of acidic casein. Roeper and Winter (1982) carried out an investigation of the viscosity of 15-51% sodium caseinate solutions at temperatures between 25-90 °C. It was found that the increase in viscosity with concentration can be regarded as a straight-line relationship on a log/linear scale at concentrations below 22 %. Consequently, the viscosity of more concentrated solution was not as high as expected.

2.6.6 Effect of chemical agents

Towler et al. (1984) found that the viscosity of 15% lactic casein (dissolved in sodium tripolyphosphate) can be reduced by the addition of ammonium mercaptoacetate (0.2-1.0% w/w of casein) or 2-mercaptoethanol (0.2-0.5% w/w casein). Both reagents are known to cause reduction of disulphide bonds within the caseins. The reduction of disulphide bonds allows free movement of the kappa-casein monomers and consequently a lower viscosity for the whole system. 15% w/w lactic casein solutions (in sodium tripolyphosphate) with and without viscosity-reducing agents exhibit thixotropy when subjected to sufficiently high shear rate.

In contrast, Korolczuk (1984) found that sodium caseinate can be polymerized using formaldehyde and glutaraldehyde as cross- linking agents. This leads to higher viscosity and increased hydration of the protein. For example, 10% untreated sodium caseinate had a viscosity of 200 cP whereas cross-linked sodium caseinate had a viscosity of 4000-7000 cP.

2.7 RHEOLOGICAL PROPERTIES OF WHEY PROTEIN CONCENTRATE (WPC) SOLUTIONS

The rheological properties of WPC solutions are also influenced by shear rate, concentration, pH, ionic strength, temperature and heat treatment.

2.7.1 Effect of shear

Hermansson (1975) reported that dispersions of WPC at a concentration of 20% show time-independent shear thinning. Qingnong (1990) found that WPC solutions exhibit apparent thixotropic behaviour at concentrations ≥ 30% at 25 °C, in which shear stress decreased with a shearing time at the beginning then reached a constant value after shearing for a short time.

2.7.2 Effect of concentration

The apparent viscosity of WPC increases with increasing protein concentration. Hermansson (1975) indicated that Newtonian flow was observed in the range of 4-12 % TS, pseudoplastic in the range of 14-16 % TS, and yield stress appeared at 18% and 20% TS. Qingnong (1990) conducted an investigation of the flow properties of three commercial WPCs at concentrations of 5-40%. He found that the flow of WPC solutions show Newtonian behaviour up to a concentration of 15 %, are slightly shear thinning at 20 and 25 %, and exhibit time dependent or thixotropic behaviour at concentrations of 30% and above.

2.7.3 Effect of pH and ionic strength

Increasing ionic strength or increasing pH has little effect on WPC solutions. Hermansson (1975) observed that the apparent viscosity of 12% WPC increased slightly with increasing pH from 6 to 10. Kinsella (1984) found that at pH 7-9 there was little change in viscosity until 70 °C when an abrupt increase in viscosity occurred. In the presence of 0.2 M NaCl the temperature transition as reflected in that the increase in viscosity was depressed to an increasing extent. Thus, at pH 9 the

transition occurred sharply at 65 °C in the presence of 0.2 NaCl, whereas in water it occurs at about 70 °C

2.7.4 Effect of temperature

Rheological properties of WPC are strongly temperature dependent. Qingnong (1990) conducted an investigation of three commercially available WPCs at temperatures of 5-90 °C. A high apparent viscosity was observed at 5 °C, decreasing as temperature increased until a minimum viscosity was attained at about 55-60 °C. Viscosity then increased rapidly with further increase in temperature above 60 C due to gel formation. He also found that 20 -30% WPC solutions exhibit time dependent shear thinning at 40-50 °C and time dependent thickening at 60 -70 °C.

2.8 RHEOLOGICAL PROPERTIES OF COPRECIPITATE SOLUTIONS

Southward and Goldman (1975) indicated that differences in rheological behaviour between different coprecipitates are due to the influence of protein-protein linkages formed during the heating of the milk in the manufacturing of the co-precipitates and the rheological behaviour of the solutions can be influenced by shear, calcium content, pH and temperature.

2.8.1 Effect of shear and calcium content

Southward and Goldman (1978) found that the apparent viscosity of coprecipitate solutions decreases with increasing shear rate indicating pseudoplastic behaviour. The viscosity patterns of low-calcium (0.02%) coprecipitate are similar to but slightly higher than those for caseinate. Southward and Goldman (1978) also indicated that the viscosity of low-calcium coprecipitate is lowest while that of medium-calcium coprecipitates is of intermediate value and high-calcium coprecipitate has the highest value. This indicates that the calcium content of coprecipitates is the major factor in increasing the viscosity of these proteins.

2.8.2 Effect of pH

Hayes et al.(1969) reported that low-calcium coprecipitate (0.5% calcium) tends to increase slightly in viscosity as the pH rises over the pH range 6.2-9.5. This may be due to more complete hydration of the protein. The medium-calcium coprecipitate (1% calcium) showed an even more marked viscosity increase above pH 7.0 than did low calcium when compared with sodium caseinate at high pH. Hayes et al. (1969) found that high calcium (3% calcium) coprecipitate shows much greater departure from Newtonian behaviour and can form gels above pH 9.

2.8.3 Effect of temperature

Hayes et al.(1969) indicated that the calcium content of a coprecipitate influences the temperature-viscosity relationship, especially at pHs above 7.0. This is due to the large range of viscosities encountered at high calcium levels. However, Hayes et al.(1968) showed that the straight line relationship no longer holds at calcium levels above 0.5% in the pH range 5.4-7.0. Hayes et al. (1969) showed that at pH 7.0, the viscosity of medium calcium coprecipitates (1% calcium) decreased logarithmically as the temperature increased between 30 and 70 °C. At higher temperatures, over the calcium range of 0.5-3.0% and the pH range 5.4-6.2, no evidence of gel formation was found. At higher temperatures there was a tendency for precipitation to occur.

2.9 GUM-PROTEIN INTERACTIONS

According to Tolstoguzov (1986), when a protein solution and a gum solution are mixed together, one of three things will happen. These are (a) the formation of an homogeneous mixture, (b) simple coacervation or the formation of a liquid-liquid two phase system and (c) complex coacervation or the formation of an insoluble complex.

2.9.1 Homogeneous mixtures

Homogeneous solutions are obtained when solutions of non-ionic gums (eg. guar and

locust bean gums) and proteins are mixed provided total mixture concentrations are below the levels at which thermodynamic incompatibility occurs. This indicates that no interaction occurs between gum and protein. Such solutions are also obtained when the two macromolecular components exist together as a soluble complex or when they are mixed under conditions of pH or ionic strength that prevent complex coacervation (Tolstoguzov, 1986).

2.9.2 Simple coacervation

Simple coacervation means separation of the gum-protein mixture into two liquid phases in which the two macromolecular components are mainly in different phases. This phenomenon depends upon certain pH values, ionic strengths and total concentrations (Antonov et al.,1979;1980; Suchkov et al., 1981: Tolstoguzov, 1986).

Fig 2.3 shows a schematic phase diagram for a gum-protein system. The binodal curve separates the regions of one- and two-phase states of the system. The region lying under the binodal curve corresponds to one-phase (homogeneous) mixtures of polymers, while the region lying above the curve represents compositions which will result in two-phase systems. Under the binodal curve, the mixed solution is thermodynamically stable whereas above the curve thermodynamic incompatibility exists.

Fig 2.3 also shows the critical point, the rectilinear diameter, a secant, and a tie-line. At a critical point, co-existing phases with equal volume or mass and with equal composition are formed. The tie-line connects the points representing the compositions of the two co-existing phases. The curve passing though the centres of the tie lines is the rectilinear diameter. It represents the compositions of mixtures separating into phases with equal mass. The critical point can be defined as the intercept of the binodal and the rectilinear diameter.

Generally, phase diagrams for gum-protein mixtures are asymmetric (i.e. the binodal curve lies nearer one axis than the other), for example phase diagrams of water-skimmed milk proteins-gum systems (W-SMP-G systems)(Zhuravskaya et al., 1986a, 1986b). Thus the establishment of phase equilibria in W-SMP-G systems

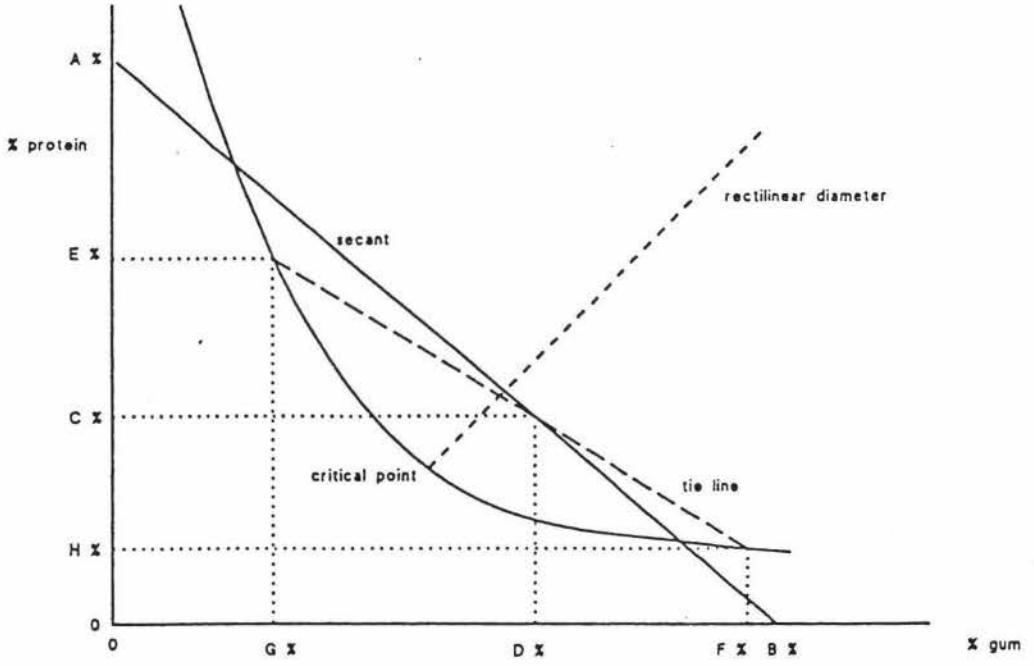


Fig. 2.3. Schematic illustration of the phase-volume ratio method (based on Tolstoguzov (1990)). A % protein solution mixed with B % gum solution. C % and D % are protein % and gum % in mixture. E % and G % are the protein and gum concentrations in the protein rich phase. H % and F % are the protein and gum concentrations in the gum rich phase.

involves the concentration of the skimmed milk proteins and dilution of the gum solution, so that the diluted gum and the concentrated protein phase are always in equilibrium. The process of protein concentration is effected by a transfer of the water from the protein solution to the gum solution and the formation of a two phase system. The principle of concentration in this way has been termed " membraneless osmosis" (Antonov et al., 1982; Tolstoguzov, 1988a, 1988b).

Antonov et al.(1979) indicate that systems containing linear gums undergo phase separation at lower total concentrations of macromolecular components than those containing branched gums such as gum arabic which have limited chain flexibility.

2.9.3 Complex coacervation

Complex coacervation results in both the macromolecular components moving into the same single concentrated phase. This phenomenon can be due to the formation of an insoluble electrostatic protein-anionic gum complex at pH levels below the protein's IEP or by calcium bridges forming between the gum and protein molecules at neutral pH. This system has been investigated by many researchers (Cluskey et al, 1969; Hansen and Crauer, 1971; Griberg and Tolstoguzov, 1972; Ganz, 1974; Antonov et al.,1977; Imeson et al.,1977, 1978; Zadow and Hill, 1978; Elfak et al., 1979c; ; Glahn, 1982; Gurov et al., 1974a,1974b, 1979,1988a, 1988b; Hansen, 1982 Manning et al, 1983 and Tolstoguzov, 1986,1988a, 1988b). Mixtures of proteins and anionic gums show some unusual properties. One of the most interesting of these is the non-equilibrium nature of the complexes (Gurov et al, 1974a). Non-equilibrium complexes have been studied in complexes of high molecular weight polymers, e.g. dextran sulfate (DS) with bovine serum albumin (BSA). It has been established that the nature of the BSA interaction with DS depends on the pH. When the macromolecular solutions are mixed under conditions of intense complexing (at pH values below the protein IEP), mixing complexes (M- complexes) are obtained, which will hardly dissolve in water. On the other hand, when the macromolecular solutions are mixed at a pH value around 9 (i.e. when complexing is inhibited) and if the resulting mixture is slowly acid-titrated to a lower pH, thereby gradually increasing the interaction, titration complexes (T-complexes) are obtained, which dissolve in

water fairly well.

Similar results can be obtained by varying the ionic strength of the mixture. At a low ionic strength and a pH value below the protein IEP, insoluble M-complexes are produced. At higher ionic strengths (but at the same low pH value), complex formation is inhibited, but subsequent dialysis against an acid solution at the same pH value produces a soluble complex similar to a T-complex. Thus at the same protein:gum ratio and the same pH complexes of widely different solubilities can be formed. Both M- and T-complexes are very stable. Aqueous solutions of T-complexes and suspensions of M-complexes can be stored for long periods of time without showing any tendency to precipitate (T-complexes) or dissolve (M-complexes)(Tolstoguzov, 1986).

2.10 GUM-MILK PROTEIN INTERACTIONS

Interaction between gums and milk proteins has been widely studied. It has been reported that such interaction is strongly dependent on the pH,ionic strength and anionic gum and milk protein types.

2.10.1 Neutral gums

No interaction between milk proteins and neutral gums (locust bean gum or guar gum) has been found (Grindrop and Nickerson, 1967; Hansen, 1968; Ganz, 1974; Elfak et al., 1979c). For example, Hansen (1968) found that guar gum and locust bean gum were unable to stabilise α_{s1}-casein against precipitation by calcium ions.

Phase separation of water (W)- 6.0% sodium caseinate (C)- 6.0% neutral gum (NG) systems at pH 6.5, 25 °C, ionic strength 0.15 mol NaCl/l and total concentration 9.0% was studied by Antonov et al (1977). Dextrans of different molecular weights, amylopectin and ficoll were used as neutral gums. It was found that similar conditions under which the stability of W-C-NG systems was disturbed, resulted in self-association of sodium caseinate molecules and their separation. An increase in pH value, an decrease in the ionic strength and temperature can maintain the stability of the systems. Antonov et al. (1980) also conducted an investigation of liquid two-phase

water-protein- neutral gum systems for other types of protein. These were albumins, globulins, glutelins (of which casein is an example) and prolamines. At total concentrations of polymers above 4% and a certain ionic strength, all these systems consist of two phases, each of the phases predominantly containing a protein or a gum.

2.10.2 Anionic gums

The interaction between anionic gums and milk proteins, namely caseins and whey protein, are discussed as followed.

2.10.2.1 Caseins

One of the most important industrial applications of kappa-, lambda- and iota-carrageeanans, is their use as thickeners and stabilizers of milk products. It appears that their mode of action is not simply through modification of solution rheology, because there is evidence that they bind to casein micelles (Hood and Allen, 1977). Carrageenan was found to interact with the casein fraction both at the pH of normal milk (pH 6.7) and at the isoelectric point of casein (pH 4.6) (Lin, 1977). Hansen (1968) found that when carrageenan was dissolved in skimmilk dialyzed free of soluble milk salts, it was shown that 60% of the carrageenan remained in the supernatant after ultracentrifugation, while 40% sedimented with some protein. Apparently, calcium ions are important in this reaction, since upon addition of calcium chloride to these systems all the soluble carrageenan sedimented with the casein.

Grindrop and Nickerson (1967), Hansen (1968), Payens (1972) and Skura and Nakai (1980) concluded that the kappa-casein was the only milk casein component that specifically interacted with kappa-carrageenan in a calcium free system. This may be due to electrostatic interactions, via specific positively charged regions of the kappa-casein molecule (Snoeren et al.,1975). Snoeren et al (1975) and Skura and Nakai (1981) also suggested that the lack of reactivity of the other caseins (α_{s1}- and β-casein) towards carrageenan is due to differences in the primary structure of these proteins. However, Hansen (1968) demonstrated that kappa-carrageenan could stabilize the calcium sensitive alpha-s1-casein fraction of milk against precipitation by calcium

ion (0.01 M) at pH 6.6. The stabilizing ability of kappa-carrageenan decreases with increasing ionic strength. One possible mechanism of interaction of negatively charged carrageenan with caseins and casein micelles, which are also negatively charged, is by the calcium ion acting as a cross-linking agent between α- and β-caseins and carrageenans.

Further study by Dalgleish and Morris (1988) on complexes of casein micelles with lambda, iota and kappa-carrageenans (concentrations of up to 0.2 mg/ml) have been made in solutions containing milk diluted 100-fold. The results are consistent with binding of carrageenan to casein micelles until the surfaces of micelles are saturated, after which some further aggregation of complexes could occur. Conformationally -ordered (helical) iota-carrageenan and conformationally- disordered (random coil) lambda-carrageenan both showed similar aggregation behaviour. Kappa-carrageenan, by contrast, gave no evidence of micellar aggregation when present as a random coil, but on conversion to the helical form (by addition of K^+) it caused precipitation of casein micelles.

2.10.2.2 Whey proteins

Hidalgo and Hansen (1969) found carrageenan interacts with β-lactoglobulin at pH 4.0 or below. When the pH of the solution was raised to 5 or above, no interaction was observed. Hansen et al.(1971) and Hansen and Crauer (1971) also found that the maximum interaction of β-lactoglobulin and CMC to form insoluble complexes occurs at pH 4.0 when the ionic strength is less than 0.1 M NaCl. At higher ionic strengths, the complex was shown to dissociate and dissolve. The maximum efficiency of precipitation increased with the degree of substitution (DOS) of CMC (Hill and Zadow, 1974). After formation of the CMC-whey protein complex, the CMC can be separated from the protein by precipitation as its calcium salt (Hill and Zadow 1978).

Hansen and Crauer (1971) stated that complex formation between whey protein and anionic gums (CMC, carrageenan and cellulose sulfate) can be brought about by adjusting the pH to 3.2. This complex was solubilized by adding alkali to pH 7.0. By controlling pH, gum concentration and ionic strength, more than 85% of the protein

from acid whey could be removed in a single-pass process.

2.11 GUM-DAIRY PROTEIN INTERACTIONS

Elfak et al. (1979c) and Towler (1975) found that sodium caseinate can interact electrostatically with anionic gums (kappa-carrageenan, CMC) at pH 5.3-5.9. The rheological properties of sodium caseinate-gum combinations have been investigated by many researchers such as Schmidt and Padua (1982), Lawn et al. (1989), Renner et al (1989), Lelievre and Husbands (1989) and Gencer (1989). Interactions with calcium caseinate were also observed by Gencer (1989). For WPC and gum interactions, some work was conducted by Schmidt and Padua (1982), Schmidt and Smith, (1988) and Nakamura (1988). Nakamura (1988) also carried out an investigation of the interaction of WPC and gum (kappa-carrageenan or xanthan gum) in a model ham formulation. These investigations are discussed in more detail in Section 2.12.

For mixtures of coprecipitate and gum, Southward and Goldman (1978) observed the stability of soluble high calcium co-precipitate solutions in the presence of anionic and non-ionic gums at various pH values and at several different concentrations of sugar and salt. Equal parts of gum solution and soluble high-calcium coprecipitate were mixed to produce a solution containing 0.25% gum and 2.5% protein. It was found that some anionic gums, such as low-methoxyl pectin, gum acacia, and propylene glycol alginate, caused precipitation of the protein. In the presence of 2% salt, only xanthan gum prevented precipitation of the protein.

2.12 VISCOMETRIC INVESTIGATIONS OF GUM-PROTEIN (INCLUDING GUM-DAIRY PROTEIN) MIXTURES

The rheological behaviour of interactions between a protein and a gum is very much dependent on the natures of the protein and the gum and environmental conditions such as pH, ionic strength and heat treatment. The gum:protein ratio in the mixtures is also a major factor affecting rheological behaviour.

2.12.1 Milk proteins

Gurov and Tolstoguzov (1988) stated that bovine serum albumin (BSA) can form complexes with dextran sulphate (DS) at pH 5.6. It was found that the intrinsic viscosity of complexes grows linearly with increasing DS weight fraction in the complex. Studies by Takada and Nelson (1983) show that BSA can interact electrostatically with pectin at a pH below the protein isolectric point, giving a maximum viscosity at pH 4.2. The viscosity decreased rapidly below pH 4.0

Castelain et al. (1986, 1988) shows that BSA-CMC and BSA- hydroxymethyl cellulose mixtures exhibited shear thinning behaviour caused by simple coacervation (in 0.1 M NaCl solution and at pH 7). The exclusion process of both systems can establish additional structure and increase apparent viscosity at low shear rate.

The viscosity of mixtures of BSA and anionic gums in the presence of low levels of calcium was reported by Hughes et al. (1980). 1% BSA was incorporated into gum solution (either 1% sodium alginate or 1% sodium pectate) together with sufficient calcium to cause incipient gelation in the absence of the protein. BSA inhibited the formation of an alginate gel, the effect increasing with increasing pH. This may be due to BSA molecules binding calcium thus making them unavailable for gel formation or interacting with the alginate and inhibiting the formation of the calcium alginate crosslinking reaction. In contrast, BSA caused gel formation in the presence of pectate below pH 6.0. This may be due to an electrostatic interaction between the protein and pectate molecule where a protein molecule can act as a bridge between two gum molecules.

Ozawa et al.(1984) found that 0.5% β-casein decreased the viscosity of 1.0% kappa-carrageenan solutions in the absence of calcium. Ozawa et al. (1984, 1985) also found that the addition of 0.008 M calcium ion to a mixed solution of β-casein and kappa-carrageenan can produce a rapid increase in viscosity. This may be due to the fact that β-casein promotes the calcium-induced gelation of kappa-carrageenan

In food products, many anionic gum types (eg. propylene glycol alginate, CMC and

pectin) can stabilize the casein particles in sour drink systems (Glahn, 1982) and in cultured milk beverages (Towler ,1984) at pHs below the protein isoelectric point. When milk is acidified at pH 4.6 and subsequently stirred or homogenized, a suspension of casein particles is formed . The size of the particles depends on the conditions of acidification. The stabilization can be seen as a binding of the gum to the casein particles which are positively charged at pH values below their IEP. The charge will gradually decrease as the negatively charged gum binds to the particles. The decrease in the positive charge on the particles will reduce the repulsion between them and increase their tendency to adhere to each other giving rise to the increased viscosity at low gum concentrations. With increasing gum concentrations the particles obtain a negative charge, the repulsion between the particles increases, decreasing the adherence between them, which gives rise to the observed fall in viscosity. The minimum gum concentration for complete stability depends on the size of the casein particles and the total surface area. If the casein particles are very small, a relatively high gum concentration is required indicating that the total surface has to be covered with gum. The increase in suspension stability suggested by the decrease in viscosity, indicates that the particles are kept in suspension by mutual repulsion.

2.12.2 Dairy proteins

Elfak et al. (1979c) indicated that addition of casein (10-40 g/l) at pH 5.3-5.9 has no effect on the viscosity of neutral gum solutions such as guar and locust bean gum. It does affect, because of an electrostatic interaction, the rheology of solutions of polyanionic gums such as kappa-carrageenan and CMC. In the kappa-carrageenan and casein system, Elfak et al. (1979c) found that the viscosity of the mixed solution reached a maximum at a gum:protein ratio of 1:4 at pH values 5.3-5.9. A large increase of viscosity in a mixture containing 0.01 kg/l carrageenan and 0.025 kg/l of sodium caseinate at pH values about 6.2 was found following a freeze-thaw cycle by Towler (1975). As pH was increased to 6.95, the viscosity of the mixture decreased linearly. This may be due to the net negative charge of caseinate increasing, so leaving less positive groups available for interaction.

Lawn et al. (1989) investigated the effect of 0.1-0.5% w/w gum on the viscosity of

10 % sodium caseinate solution (Alanate 180) after mixing at 80 °C for 30 min and 2 hr then cooling overnight. It was found that kappa-carrageenan and propylene glycol aginate (PGA) caused viscosity synergism. The degree of synergism was more pronounced after overnight cooling for kappa-carrageenan and after 30 minutes mixing for PGA. Antagonism was observed when xanthan gum was added.

Lelievre and Husbands (1989) found that the addition of sodium caseinate to starch pastes can cause the swollen starch particles in pastes to increase in volume. This increased the viscosity of starch pastes synergistically.

The flow behaviour of 1:1 mixtures of carrageenan-guar and CMC-locust bean gum in the presence of dairy protein (sodium caseinate or calcium caseinate) were observed by Gencer (1989). It was found that the addition of 1.0 or 10.0% sodium caseinate completely eliminated the gel matrix present in the mixture carrageenan-guar gum (0.5% total weight). Calcium caseinate had a drastic effect on the yield stress at low concentrations but not at the high concentration of 10%.

For the CMC-locust bean gum mixture, sodium caseinate had no effect on the rheological properties of the gum mixture. Calcium caseinate had some antagonistic activity but the reason for this is not very clear.

Schmidt and Padua (1982) added kappa-carrageenan at a level of 0.10, 0.15 and 0.20% to 7% sodium caseinate and 7 % WPC dispersions. Then, the kappa-carrageenan and dairy protein mixtures were heated at 80 °C for 1 hr followed by cooling to 25 °C. The addition of carrageenan lowered the solubility of WPC but had no effect on sodium caseinate. All heated carrageenan/protein systems exhibited pseudoplastic (shear thinning) flow behaviour. The highest viscosity and consistency index (k) values were observed for WPC. The k values for all carrageenan/protein mixtures increased with increased levels of carrageenan.

Nakamura (1988) conducted an investigation of the interaction between 10% WPC and 0.15-0.35 % gum (kappa-carrageenan or xanthan gum) in an aqueous mixed solution. Interactions were observed in aqueous systems and in a model ham formulation under

heat treatment in the range 75-90 °C for 30-60 min. It was found for both systems that both gums can prevent syneresis of WPC, but xanthan gum decreased the gel strength of WPC whereas kappa-carrageenan had the opposite effect. It was also found that the combination of 3.0% WPC and 0.15% gum decreased syneresis in a model ham formulation.

Schmidt and Smith (1988) found that the viscosity of 11 %(w/v) whey protein concentrate (WPC) solution is significantly increased by the addition of xanthan gum at the concentrations 0.05%-0.30%.

2.12.3 Other proteins

The effect of the gum : protein ratio on the reaction between soy protein and CMC at pH 4.5 was observed by Ganz (1973, 1974). At a total concentration of 1.0%, soy protein was not solubilized at a gum:protein ratio of 9:1, but was at a gum:protein ratio of 7:3. At a total concentration of 0.05%, mixed soy protein and CMC (ratio 1:1) gave little increase in viscosity over the viscosity of CMC by itself. Ganz (1973, 1974) also found that in mixtures of soy protein and CMC (gum:protein ratio 1:1) at pH 4.5, the protein is still solubilized and is protected from the effects of heat. Even in the presence of salts, the solubilizing effect of CMC upon the soy protein is not lost even when the solutions are heated. Although carrageenan solubilizes soy protein at its IEP, it does not protect the protein from the effects of heat

Adding 1% myoglobin into gum solutions with sufficient calcium to cause gelation in the pure gum solution, Hughes et al. (1980) found that myoglobin inhibited the formation of an alginate gel, the effect being greatest at a pH of about 6.3. In contrast, the addition of myoglobin caused gel formation in the presence of pectate below pH 6.0.

Similar behaviour was found when comparing 1.0% alginate solution with a 1.0% alginate solution containing 1.0% myoglobin (both systems containing 0.006 M calcium chloride). At pH 6.3, the viscosity of a 1% alginate solution is far greater than that of an alginate- myoglobin system. This may be due to decrease in the interaction

of protein with gum. At pH 6.0, the effect was also less pronounced since the myoglobin starts to precipitate (Summerlin,1978- reviewed by Ledward, 1979).

2.13 DISCUSSION AND RECOMMENDATION

Most gums in food systems show a high viscosity at low concentrations whereas dairy proteins require very high concentrations (possibly up to ten times as high) to reach the same viscosity at a given shear rate. The full hydration of gums and dairy proteins depends very much on the environmental conditions such as pH, ionic strength, temperature and time. Each dairy protein and gum type has its own character on dissolving in water. Therefore, in order to construct a model system for these major food ingredients, the appropriate method of mixed solution preparation is by making up the pure gum and dairy protein solutions individually and then mixing them. To explore the interaction between gums and dairy proteins, viscometric and viscoelastic measurements can be carried out on the mixture. Morris (1983) has pointed out that 'it is regrettably common for results [of studies of polymer interactions] to be reported showing that the addition of a small amount of polymer to a solution of another causes a large increase in viscosity, with the conclusion that the two materials are interacting specifically. It is obvious from [Fig. 2.1], however, that if the combined concentration of the two polymers exceeds c^*, (particularly if both components in isolation would be in the 'dilute' solution regime), a disproportionate enhancement of viscosity is to be expected from space-occupancy considerations alone'.

There are many types of gums used in food systems. Two main groups of gums were selected for this study. The non-ionic gum was locust bean gum and the anionic gums were CMC, carrageenan and xanthan gum. CMC and xanthan gums are anionic gums containing carboxyl groups while carrageenans are anionic gums containing sulphate groups. The rheological properties of these gum solutions have been investigated by many researchers such as Morris (1983), Glicksman (1982), Krumel and Sarkar (1975) and Elfak et al. (1978, 1979a, 1979b). The selected dairy proteins are important products of the New Zealand dairy industry. They were sodium caseinate, whey protein concentrate (WPC) and coprecipitate (TMP- total milk protein). Whey protein isolate (WPI), manufactured in the USA, was another dairy protein used in this study.

No published papers on the comparison of the rheological behaviours of WPC, sodium caseinate, coprecipitate and WPI was found. It was also found that there is little published information on the rheology of gum-dairy protein mixtures. What information there is discussed in terms of the effects of the environmental conditions.

2.13.1 pH

According to Tolstoguzov (1986), if gum solution and protein solution are mixed together at a pH value below the protein IEP, insoluble complexes (M-complexes) can be obtained. These M-complexes would be hard to investigate as modern rheometers still cannot measure sample solutions with large particles. However, if the gum solution and protein solution are mixed together at a pH above the protein IEP and the mixture is slowly acid-titrated down, soluble complexes or T-complexes can be obtained. The T-complexes, therefore, can be observed by rheometer. Study of the effect of pH on dairy protein and gum mixtures was only found in sodium caseinate and carrageenan systems within the pH value range of 6.20-6.95 (Towler, 1975).

2.13.2 Gum:protein ratios and concentrations

The gum:protein ratio and concentration have a great influence on the rheology of a mixed gum and protein solution (Glanhn, 1982; Towler , 1984; Ganz, 1973, 1974; Gorov and Tolstoguzov, 1988) Most studies on the effect of the gum:protein ratio deal with gum and casein in sour milk drinks at pH values below the protein IEP (Glahn, 1982; Towler, 1984). Only Schmidt and Smith (1988), who conducted an investigation of mixtures of xanthan gum and of guar gum with a high concentration of WPC, studied the effects of gum : protein ratio.

On consideration of the typical usage levels of gums and dairy proteins in foods (see Appendix 1) it was decided in this study to work initially with 0.5% w/w gum and 6.0% w/w protein solutions. No published studies on mixed gum and dairy protein solutions at these concentration levels have been found.

2.13.3 Salts

NaCl and $CaCl_2$ are the salts that are normally used in food systems. In gum/protein mixed solutions, NaCl can cause simple coacervation (Tosltoguzov, 1986), while $CaCl_2$ can induce gel formation in the mixtures (Hughes et al.,1980; Ozawa et al.,1985). It appears that there is no published research on gum and dairy protein mixtures containing NaCl or $CaCl_2$.

2.13.4 Heat

It has been found that some anionic gums (eg. CMC) can protect protein from heat denaturation (Ganz, 1973, 1974). Under the heading of heat treatment (one of the major unit operations for food processing) no reported work was found on gum and dairy protein mixtures.

This literature review suggested that the interactions between gums and dairy proteins at food use concentration levels in a model system can be a new research area for future systematic food product development. In order to relate the experimental work to the manufacturer's point of view, rheological investigations of gum and dairy protein mixtures should be conducted at natural pH and ionic strength. This is because the pH of most non-acidic food products is about neutral and because homogeneous mixed solutions or suspensions can be obtained which are appropriate for rheological measurement. Homogeneous solutions can be obtained with soluble complexes by titrating from higher pH values (above protein IEP) to lower pH values down to about the protein IEP in the case of anionic gum-protein mixtures. However, in food processing practice, this method could add complexity and cost to food production.

The influence of the gum:protein ratio has been emphasized in this research. The effect of salt may be considered as a result of the chemical structure of the dairy proteins themselves: sodium caseinate contains the sodium ion and coprecipitate (TMP) contains the calcium ion. The study of the effect of temperature or heating conditions is the most difficult task due to gel formation and protein denaturation in the mixtures. In this basic study, emphasis was placed on the properties at room

temperature.

It was hoped that this model system would exhibit interesting rheological properties and provide a better understanding of the interactions between these two major food ingredients.

CHAPTER 3

PROJECT AIMS AND OVERALL PROJECT PLAN

3.1 PROJECT AIMS

* To determine the possibility of monitoring and understanding the interactions between selected gums and selected dairy proteins through rheological measurements.
* To determine the effects of gum type and dairy protein type on the interactions
* To determine the effects of the ratio of gum to dairy protein and of the total polymer concentration on the interactions.
* To explore the reasons for interactions causing rheological synergism and antagonism.

3.2 OVERALL PROJECT PLAN

Firstly, the rheological properties of solutions of pure gums and dairy proteins were determined. Then the interactions between gums and dairy proteins were studied through measurement of the flow behaviours of mixed solutions. The extent of synergism or antagonism was determined with varying gum:protein ratios and total concentrations. Finally, for better understanding of the interactions causing synergism and antagonism, sedimentation studies were carried out.

Experimental work was carried out according to the following plan:

3.2.1 Measurement of the flow behaviour of 0.5 % gum solutions over the shear rate range 58 - 1470 s^{-1}.

3.2.2 Measurement of the effect of concentration on the apparent viscosity of pure gum solutions. Gum concentration was in the range 0.05% to 1.5% w/w and the shear rate range was 58 - 1470 s^{-1}.

3.2.3 Measurement of the flow behaviour of 6.0% (w/w) dairy protein solutions over the shear rate range 58 - 1470 s^{-1}.

3.2.4 Measurement of the effects of the gum:protein ratio and total polymer concentration on the extent of rheological synergism or antagonism . This was made on mixtures of 0.5% gum solution and 6.0% dairy protein solution in the shear rate range 58 - 1470 s^{-1}.

3.2.5 Measurement of the effects of gum:protein ratio and total concentration on the apparent viscosity of mixed solutions. The gum:protein ratios were 1:36, 1:16, 1:8 and 1:4 while the total polymer concentrations were 2.0%, 2.5%, 3.5% and 4.0% w/w. Mixed solutions were prepared by mixing together 1.2% gum solutions, 10% dairy protein solutions, and distilled water (where necessary).

3.2.6 Measurement of the effects of gum:protein ratio and total polymer concentration on the formation of insoluble material separable by centrifugal sedimentation. Measurements were carried out on the mixtures studied in 3.2.4 and 3.2.5.

CHAPTER 4

MATERIALS AND METHODS

4.1 MATERIALS

4.1.1 Gums

The gums selected for this experimental work were locust bean gum, lambda-carrageenan, sodium carboxymethycellulose (CMC) and xanthan gum. These gums were obtained commercially in the form of dry powders from Davis Gelatine (N.Z.) Limited, Christchurch, New Zealand. The specification of each product is given in Appendix 2.

4.1.2 Dairy Proteins

The dairy proteins for this work were suggested by the New Zealand Dairy Research Institute (NZDRI), Palmerston North, New Zealand. They were sodium caseinate (Alanate 180), coprecipitate (total milk protein)(TMP 1100), whey protein concentrate (WPC) (Alacen 132) and whey protein isolate (WPI)(Bipro). All dairy proteins were supplied by NZDRI in the form of dry powders. The specification of each product is given in Appendix 3.

4.1.3 Other materials

Other materials (sodium azide, sodium chloride, sodium hydroxide, citric acid) were used in the form of standard laboratory reagents.

4.2 PREPARATION OF SOLUTIONS

4.2.1 Preparation of gum solutions

Gum solutions were prepared on a dry weight basis at the concentration levels of 0.25, 0.5 and 1.2 % (w/w). Solution preparation involved essentially adding the gum powder to hot water with high speed mixing, entrained air being removed subsequently by centrifugation. Details of preparation procedures for the four gums used are given in Appendix 4.

4.2.2 Preparation of dairy protein solutions

Dairy protein solutions were also prepared on a dry weight basis. The concentration levels were 1.5, 3.0, 6.0 and 10.0% (w/w). Details of preparation procedures for the four dairy proteins used are given in Appendix 5.

4.2.3 Storage of pure protein and gum solutions (Aging trails)

Trials were conducted to investigate the influence of time on the rheological properties of prepared solutions. Solutions of the four types of gum (locust bean gum, lambda-carrageenan, CMC and xanthan gum) were prepared as described in 4.2.1 at the concentration level of 0.25% w/w. A 3.0% (w/w) solution of sodium caseinate was used to represent the dairy protein solutions. It was prepared by the method as described in 4.2.2. All solutions were kept at room temperature for 7 days. Rheological measurements were preformed on the solutions on days 3, 5 and 7. The results are tabulated in Appendix 6. These show that no significant changes in rheological properties occurred over a 7 day storge period.

The power law (equation 2.10) was used to fit flow curves (see Section 4.4.3). For each solution, one-way analyses of variance were performed in order to determine whether or not significant changes occurred in the values of the power law constants n and k over the 7 day storage period. The results are presented in Appendix 6. These show that no significant changes in either of these factors occurred for any of the solutions. This indicates that sodium azide was an effective preservative.

4.2.4 Preparation of mixtures of gum solutions and dairy protein solutions

Mixtures were prepared by combining either gum solutions and dairy protein solutions or gum solutions, dairy protein solutions and distilled water together in predetermined proportions.

The mixed solutions were prepared at room temperature to a total weight of 150 g. No adjustments were made to the pH or to the ionic strength of any of the mixed solutions. The solutions were homogenised with a Silverson mixer (model Laboratory, Machaines Ltd., England) at high speed for 4 minutes. After mixing for 4 minutes, the air bubbles in the mixtures were removed either by placing them in a vacuum chamber at an absolute pressure of less than 1 kPa and room temperature for 6- 8 hours or by centrifuging them (Sorvall SS-3 centrifuge, Du Pont Instruments) (see Section 4.3).

4.3 CENTRIFUGATION OF MIXED SOLUTIONS

To deaerate solutions and to determine sediment volume, a Sorvall SS-3 centrifuge (Du Pont Instruments, USA) was used. The HB-4 rotor was used for this work. It accepts four 50 ml titanium buckets which can be used with 50 ml plastic centrifuge tubes. Two speeds of centrifugation were used: 5000 rpm for 3-4 minutes (for deaeration) and 20,000 rpm for 12 minutes for recovery of sediment (see Section 4.4)

4.4 MEASUREMENT OF SEDIMENT

In order to be able to measure the weight of the sediment in samples after centrifugation, the centrifuge tubes were calibrated with distilled water as follows. A known weight of water (eg 0.5 g) was placed into a centrifuge tube. Then, the level (mm) of water in the tube was measured. This procedure was repeated with different weights of water (eg. 1.0, 3.0, 5.0, 7.0, 9.0, 10.0, 15.0 and 20.0 g).

Measurements were carried out as follows. 37 g of sample were weighed into a

centrifuge tube. Centrifugation was carried out at 20,000 rpm for 12 minutes. The appearance and level of visible insoluble matter at the bottom of the tube were, respectively, observed and measured, and weight of sediment calculated. The weight of sediment was expressed as a percentage of the weight of solution in the centrifuge tube. It was assumed that all sediments had the same density as water.

4.5 RHEOLOGICAL MEASUREMENT

A Bohlin VOR Rheometer (Bohlin Reologi AB, Sweden) was used to determine the flow behaviour of all solutions. Fig. 4.1 shows a schematic diagram of the rheometer. The principle of operation is that a controlled shear strain or strain rate is applied to the sample and the resulting shear stress is measured. The basic operational modes of the Bohlin VOR Rheometer are the viscometry mode, the oscillation mode and the stress relaxation mode. In this study, the viscometry mode only was used.

To measure flow curves, the sample was placed in the gap between a fixed inner cylinder (the bob) and a rotating outer cylinder (the cup)(5). A steady rotational speed is used in the viscometry mode. It is obtained by using a DC motor drive (1) and gear boxes (2) with clutch (3) disengaged. The motor drive electronics have a brake function ensuring rapid velocity decrease or stopping. Torque measurement involves the use of a torque bar (9) and a linear voltage displacement transducer (LVDT)(8). The choice of torque bar determines deflection as measured by the LVDT, which sends a torque signal to the software. Sample temperature is controlled by a temperature control unit which circulates water through a jacket surrounding the cup. The unit senses temperature by means of a thermocouple situated inside the jacket.

This instrument is fully computer controlled by means of a PC. The keyboard gives complete control of the experiment from a menu system. Permanent records are made in printed format, in graphical form and on hard disc. The Bohlin VOR Rheometer can cover 6 orders of magnitude of shear rate from 10^{-3} to 10^{3} s^{-1}, and can measure shear stress values from 10^{-3} Pa to 10^{5} Pa. The accessible range of viscosities is 10^{-4} to 10^{8} Pas.

The Bohlin VOR Rheometer software is of two types: rheometer operational software and analytical software. The basic set of operational software consists of programs for viscometry mode testing as well as for two small amplitude viscoelastic tests: oscillation and shear stress relaxation. The analytical software is headed by the data handling software by which it is possible to manipulate data stored on disc and to perform model fitting.

4.5.1 Experimental procedure for viscosity measurements

All flow curves were measured at 25 C. The measuring system used was the C25 concentric cylinders system. The dimensions of this system are shown in Fig 4.2. The sample was placed in the cup, care being taken to avoid the inclusion of air bubbles. The bob was then lowered into position. A torsion bar of 4.26 or 42.9 g.cm was used depending on the viscosity of the solution. Measurements were made in steady shear over the range 58-1470 s^{-1}. To erase time-dependency, the solution was first presheared at maximum shear rate (1470 s^{-1}.) for 60-90 sec.

4.5.2 Recording of viscometric flow data

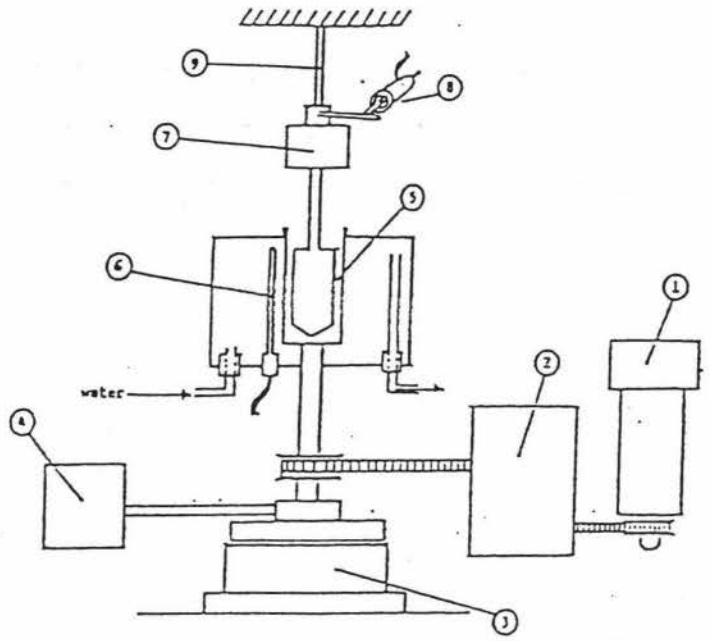
Measured data was recorded automatically in tabular and graphical forms by means of a printer and a plotter. The UP (increasing shear rate) and DOWN (decreasing shear rate) curves were plotted as viscosity (Pa.s) or apparent viscosity (Pa.s) (see equation 2.11) and shear stress (Pa) against shear rate (s^{-1})

4.5.3 Model fitting for viscometric flow data

The software allows models of different types to be used to fit rheometer data. Models available are the power Law, Casson, Bingham, and Cross equations. In this work, the power law equation was found to fit all flow data well. The equation is:

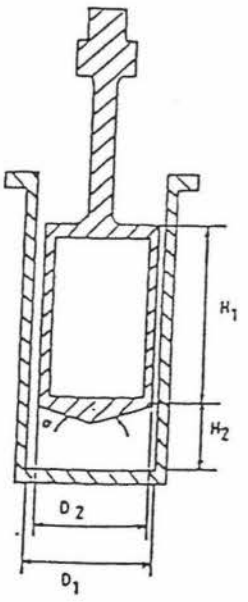
$$\tau = k\dot{\gamma}^{n} \qquad (4.1)$$

where τ is shear stress (Pa), $\dot{\gamma}$ is shear rate (s^{-1}), k is the consistency index ($Pa.s^{-n}$)



1 - DC motor with tacho
2 - Gear boxes
3 - Clutch
4 - Position servo actuator
5 - Sample cell
6 - Temperature sensor
7 - Air bearing
8 - LVDT torque
9 - Torque bar

Fig. 4.1. Schematic diagram of Bohlin VOR Rheometer.



CONCENTRIC CYLINDERS, C25

measure		C25
D_1	cup diameter (mm)	27.5
D_2	bob diameter (mm)	25
H_1	bob height (mm)	37.5
H_2	depth (mm)	12.4
α	cone angle (°)	150

Fig. 4.2. Schematic diagram of concentric cylinders, C25 system.

and n is the flow behaviour index (dimensionless). In this model, shear rate is the independent variable and shear stress the dependent variable. For all samples, both UP and DOWN data were used in the determination of both k and n.

4.6 ANALYTICAL TESTS

4.6.1 Moisture determination of gum and dairy protein powders

To prepare solutions on a dry weight basis, the moisture contents of the gum and dairy protein powders had to be measured. The moisture determination procedure, which was carried out in duplicate for all samples, was as follows.

About 3-5 g of sample were weighed into a tared aluminium moisture dish. The dish, with its cover beneath it, was placed in an hot air oven (Contherm, Cataloque 240, Contherm Scientific Company, New Zealand) for 6 hours at 100 ± 2 C. The dish was removed from the oven, covered with its lid, and allowed to cool in a desiccator for 30 min before being weighed.

Calculations:

$$\%\text{moisture} = \frac{\text{loss in weight (g)}}{\text{weight of sample (g)}} * 100$$

$$\%\text{solids} = 100 - \%\text{moisture}$$

Example calculation:

Weight of CMC before drying		4.1235 g
Weight of CMC after drying		3.8324 g
loss in weight		0.2911 g
% moisture = (0.2911/4.1235)*100	=	7.06 %
%solids = 100 - 7.06%	=	92.94 %

The measured moisture contents of all gum powders and dairy protein powders are given in Appendix 7.

4.6.2 Total solids in the supernatant

The total solids contents of the supernatants and sediments of centrifuged samples were measured using the moisture measurement procedure described in Section 4.6.1 - but with an oven residence time of 8 instead of 6 hours.
Calculations:

$$\%\text{moisture} = \frac{\text{loss in weight (g)}}{\text{weight of sample (g)}} * 100$$

$$\%\text{solid} = 100 - \%\text{moisture}$$

Example calculation:

Weight of supernatant sample from a centrifuged CMC/TMP mixture (gum solution : protein solution ratio 75:25, total polymer concentration 1.875%)

before drying		3.9477 g		
weight after drying		0.0867 g		
loss in weight		3.8610 g		
% moisture	=	(3.8610/3.9477)*100	=	97.80 %
%solids	=	100 - 97.80%	=	2.196 %

4.6.3 Protein determination

Nitrogen contents of samples were determined by the Kjeldahl procedure using the Kjeltec 1026 system (Model 1026, Tecator, Sweden). Protein contents were calculated from:

$$\%\text{ protein (w/w)} = \%\text{ N (w/w)} * 6.38$$

4.6.4 pH measurement

All pH measurements were made at room temperature with a pH meter (PHM 61 Laboratory pH meter, Radiometer A/S Copenhagen, Denmark), the meter's electrode being immersed in the solution. Readings were recorded when they become constant

(after 1-2 minutes).

The natural pH values of 0.5% solutions of the gums studied and of 6.0% solutions of the dairy proteins studied are given in Appendix 8.

CHAPTER 5

RHEOLOGICAL CHARACTERISATION OF GUM AND DAIRY PROTEIN SOLUTIONS

5.1 INTRODUCTION

In order to monitor and understand the interactions between selected gums and dairy proteins through rheological measurement, it was logical to firstly characterise the rheology of the selected pure gum and pure dairy protein solutions. The effect of concentration on the apparent viscosities of the gum solutions was also determined.

5.2 EXPERIMENTAL PLAN

The flow curves at 25 °C of pure 0.5% (w/w) gum solutions and pure 6.0% (w/w) dairy protein solutions were obtained over the shear rate range 116 s^{-1} to 1470 s^{-1}. Then, the effect of concentration (0.05% to 1.5% w/w) on the apparent viscosities of pure gum solutions was determined.

5.3 PROCESSING AND PRESENTATION OF EXPERIMENTAL DATA

For each flow curve, viscometric data were obtained from the Bohlin Rheometer in the form of plots of shear stress and apparent viscosity versus shear rate and in the from of a table containing the same data. An example of the plots is given in Fig. 5.1 and of the table in Fig. 5.2.

Flow curves, in the from of apparent viscosity versus shear rate (on arithmetic co-ordinates), are shown for the four gum solutions in Figs. 5.3a to 5.3d and for the four protein solutions in Figs. 5.4a to 5.4d.

Values of the power law constants n and k are tabulated for all gum and protein solutions in Table 5.1. In every case, the power law fitted the experimental data with a correlation coefficient greater than 0.99.

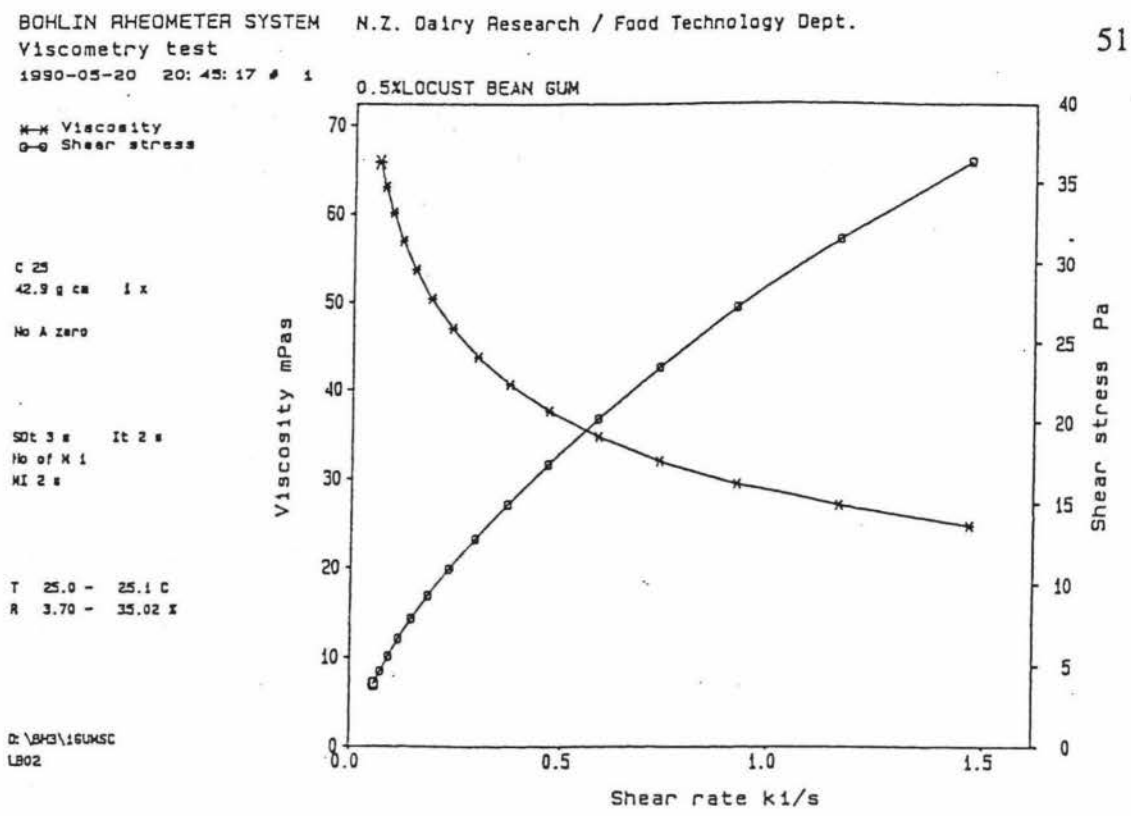


Fig. 5.1 Example (for 0.5% locust bean gum solution) of Bohlin plots of shear stress and apparent viscosity versus shear rate.

N.Z. Dairy Research / Food Technology Dept.

BOHLIN RHEOMETER SYSTEM
Viscometry test
1990-05-20 20:45:17

0.5%LOCUST BEAN GUM
1
Measuring system: C 25
Torque element: 42.9 g cm
No autozero.
Strain delay time: 3 s

Sensitivity: 1 x
Integration time: 2 s

Temperature: Manual
No of measurements: 1

Measurement interval: 2 s

D:\BH3\1GUMSC
File name: LB02

Time s	Temp xC.	Shear rate no	1/s	Shear stress Pa	Viscosity Pas	Range %
4.0	25.0	46	5.830E+1	3.837E+0	6.579E-2	3.7
9.6	25.0	47	7.005E+1	4.622E+0	6.598E-2	4.5
14.6	25.0	48	9.232E+1	5.554E+0	6.016E-2	5.4
19.2	25.0	49	1.163E+2	6.628E+0	5.700E-2	6.4
23.6	25.1	50	1.467E+2	7.869E+0	5.364E-2	7.6
27.6	25.1	51	1.846E+2	9.298E+0	5.038E-2	9.0
31.4	25.1	52	2.322E+2	1.091E+1	4.697E-2	10.5
35.2	25.0	53	2.923E+2	1.277E+1	4.368E-2	12.3
38.7	25.0	54	3.682E+2	1.491E+1	4.049E-2	14.4
42.2	25.0	55	4.634E+2	1.736E+1	3.747E-2	16.8
45.6	25.0	56	5.830E+2	2.019E+1	3.461E-2	19.5
48.9	25.0	57	7.343E+2	2.345E+1	3.194E-2	22.6
52.2	25.0	58	9.246E+2	2.719E+1	2.941E-2	26.2
55.4	25.0	59	1.164E+3	3.144E+1	2.701E-2	30.4
58.7	25.0	60	1.465E+3	3.628E+1	2.476E-2	35.0
61.9	25.0	59	1.164E+3	3.144E+1	2.701E-2	30.3
65.1	25.0	58	9.246E+2	2.719E+1	2.940E-2	26.2
68.5	25.0	57	7.343E+2	2.345E+1	3.194E-2	22.6
71.9	25.0	56	5.830E+2	2.019E+1	3.462E-2	19.5
75.4	25.0	55	4.634E+2	1.737E+1	3.749E-2	16.8
79.0	25.0	54	3.682E+2	1.492E+1	4.052E-2	14.4
82.7	25.0	53	2.923E+2	1.273E+1	4.370E-2	12.3
86.5	25.0	52	2.322E+2	1.092E+1	4.701E-2	10.5
90.5	25.0	51	1.846E+2	9.299E+0	5.036E-2	9.0
94.7	25.0	50	1.467E+2	7.869E+0	5.363E-2	7.6
99.3	25.0	49	1.163E+2	6.627E+0	5.699E-2	6.4
104.4	25.0	48	9.232E+1	5.550E+0	6.012E-2	5.4
109.8	25.0	47	7.335E+1	4.624E+0	6.303E-2	4.5
115.8	25.1	46	5.830E+1	3.844E+0	6.590E-2	3.7

Fig. 5.2 Example of Bohlin printout of flow curve data (the data plotted in Fig 5.1).

Plots of apparent viscosity versus concentration, with shear rate as parameter, are shown for the four gums in Figs. 5.5a to 5.5d. Given in each figure is the variation with concentration of the power law constants n and k.

5.4 RESULTS

5.4.1 The flow properties of pure dairy protein and pure gum solutions

Newtonian flow was observed in SC, WPC and WPI solutions at 6.0% w/w concentration (Figs. 5.4a,b, and d) with n values very close to 1 (Table 5.1). The viscosities of these solutions were independent of shear rate. Slight pseudoplastic behaviour was found in TMP at low shear rate but viscosity remained constant at higher shear rates (Figure 5.4c). TMP solutions had lower n-values than any other dairy protein solution (Table 5.1). The viscosities of the dairy protein solutions (6% w/w) were in the order: TMP> SC> WPC> WPI.

Table 5.1: The n and k values of 6.0% dairy protein and 0.5% gum solutions at 25 °C.

Sample	n value	k value (Pas^n)
6.0% SC solution	1.03	5.45
6.0% WPC solution	0.98	2.36
6.0% TMP solution	0.97	9.19
6.0% WPI solution	1.01	1.75
0.5% LB solution	0.69	241
0.5% CMC solution	0.59	589
0.5% CR solution	0.74	142
0.5% XN solution	0.25	2652

The viscosities of the dairy protein solutions were far lower than the viscosities of the gum solutions. Figs. 5.3a to 5.3d show clearly that 0.5% w/w pure LB, CMC, CR and XN solutions all exhibited pseudoplastic behaviour as there was a decrease in apparent viscosity with increasing rate of shear. The pure XN solution had the highest degree of pseudoplasticity.

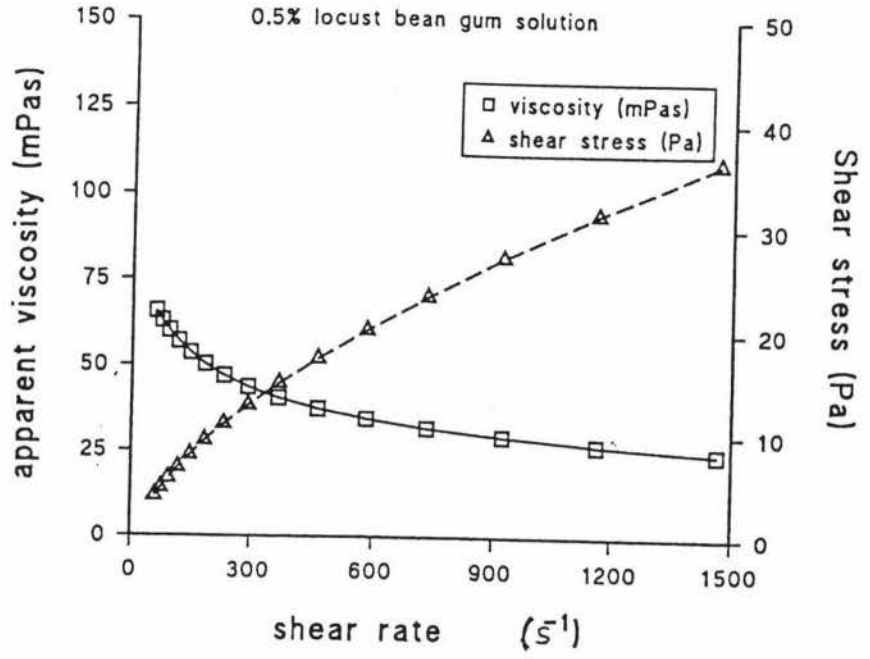


Fig. 5.3a. Flow properties of 0.5 % locust bean gum in distilled water at 25 °C

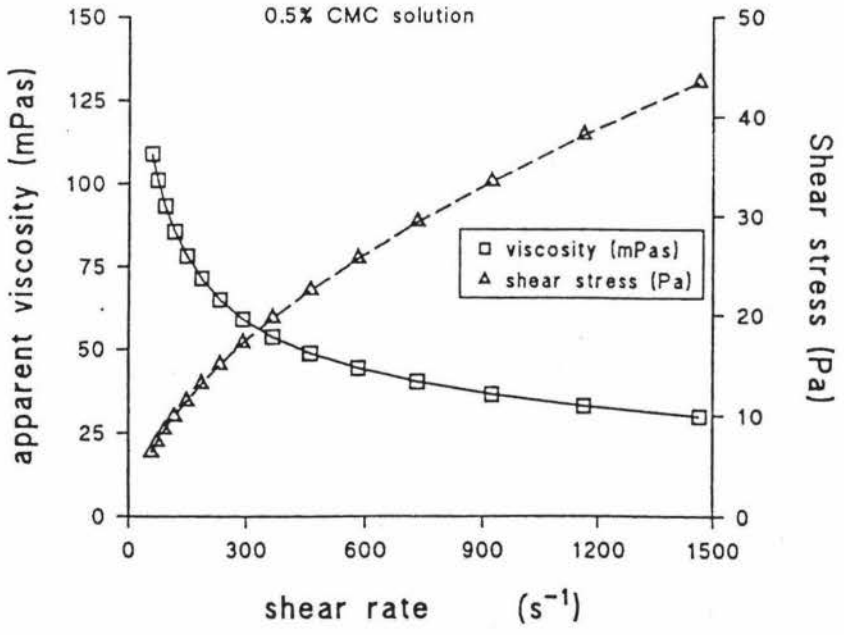


Fig. 5.3b. Flow properties of 0.5 % CMC in distilled water at 25 °C

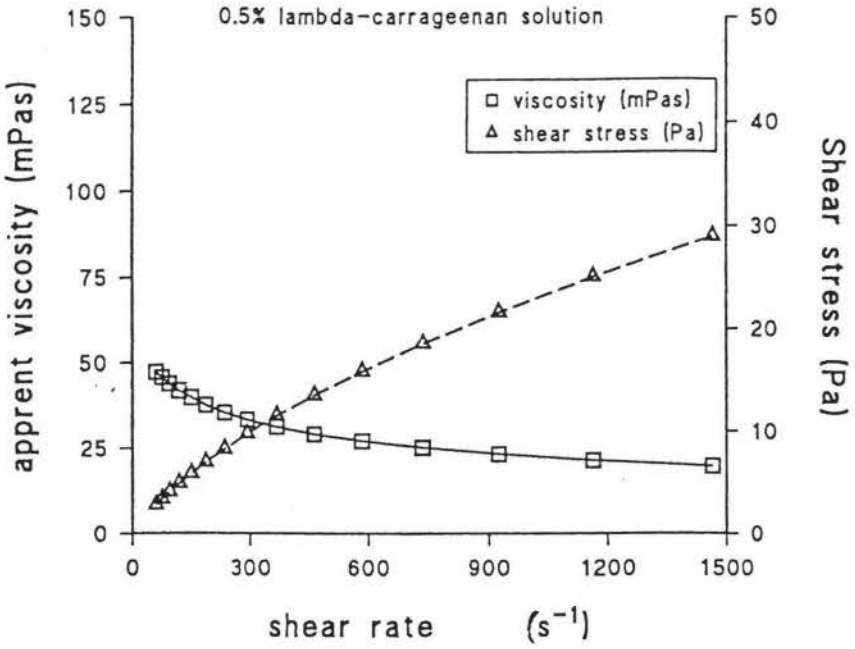


Fig. 5.3c. Flow properties of 0.5 % lambda-carrageenan in distilled water at 25 °C

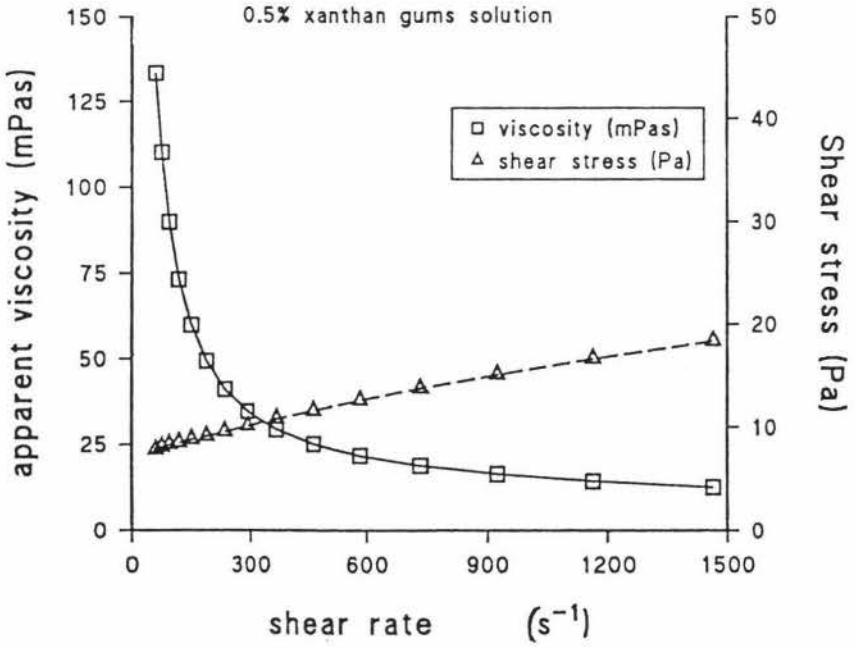


Fig. 5.3d. Flow properties of 0.5 % xanthan gum in distilled water at 25 °C

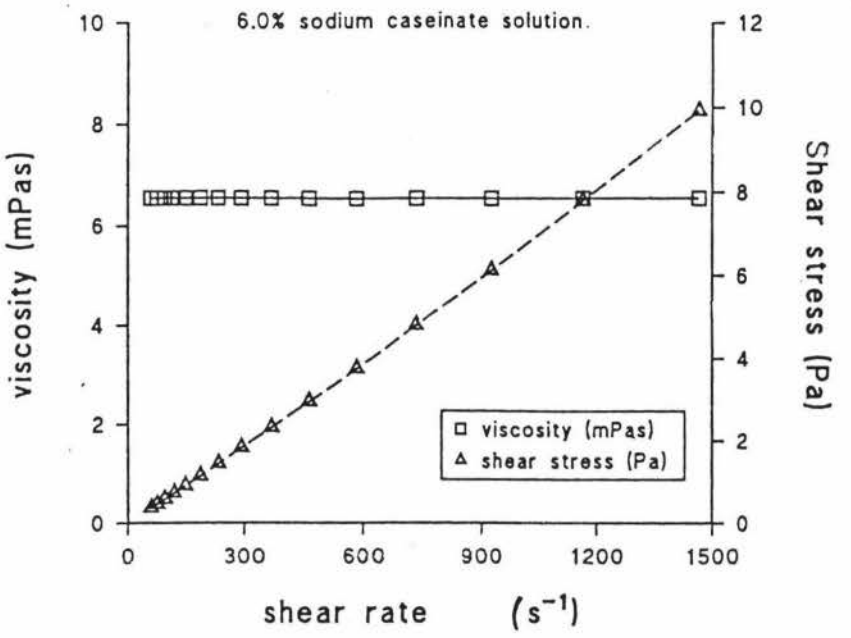


Fig. 5.4a. Flow properties of 6.0 % sodium caseinate in distilled water at 25 °C

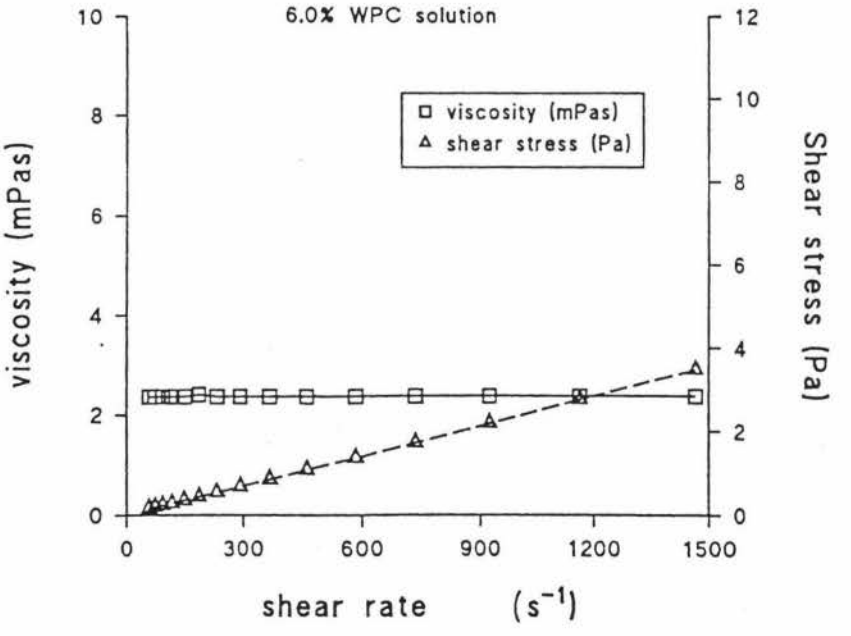


Fig. 5.4b. Flow properties of 6.0 % WPC in distilled water at 25 °C

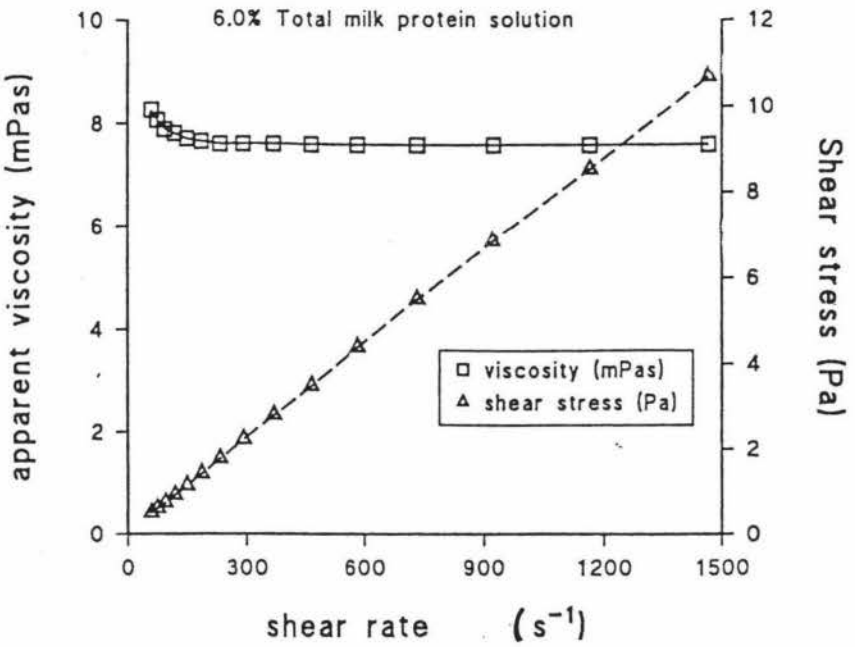


Fig. 5.4c. Flow properties of 6.0 % TMP in distilled water at 25 °C

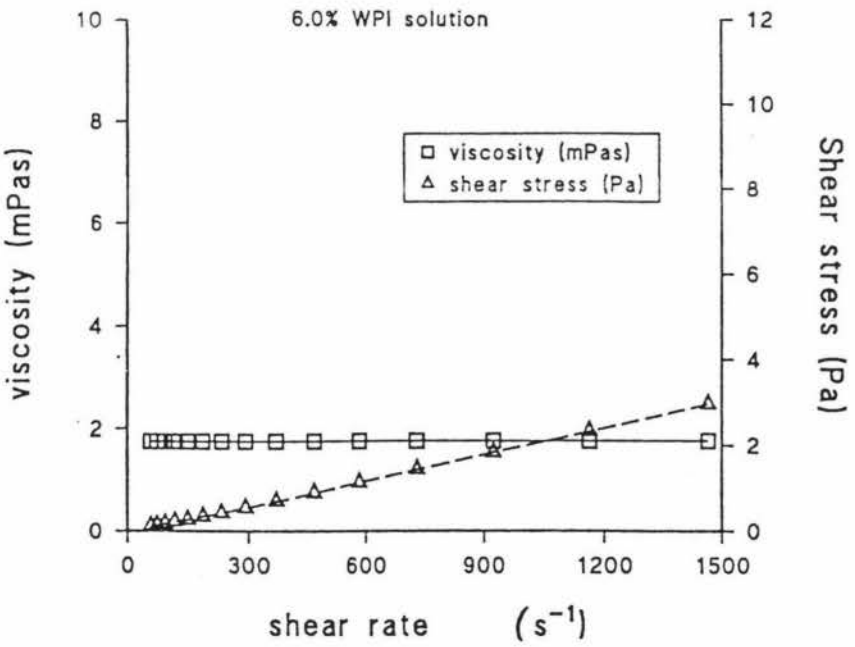


Fig. 5.4d. Flow properties of 6.0 % WPI in distilled water at 25 °C

The values of the power law constants for the gum solutions in Table 5.1 show that as the consistency index (k) increased, the n value decreased. The n values of the gum solutions (0.5% w/w) followed the order: CR > LB > CMC > XN. Thus the carrageenan solution was the least pseudoplastic and the xanthan gum solution the most pseudoplastic. The k values of the solutions cannot be compared because the units of k depend upon the value of n.

5.4.2 Effect of concentration on apparent viscosity of pure gum solutions

The plots in Figs. 5.5a to 5.5d show that for all four gums apparent viscosity increased with concentration at a given shear rate but decreased with shear rate at a given concentration. Thus solutions were pseudoplastic at all concentrations. For each gum, the n value decreased with increasing concentration while the k value increased.

At a given shear rate, the apparent viscosity increased approximately exponentially with concentration for LB, CMC and CR, but increased in a nearly linear manner for XN.

5.5 DISCUSSION

The difference in viscosity between SC, WPC, TMP and WPI solutions may depend on the degree of swelling or hydration of the protein molecules. The lower viscosities in WPC and WPI solutions (i.e. globular proteins of low molecular weight) may be due to their low swelling ability (Hermansson, 1972). In contrast, pure SC and TMP solutions have high initial swelling ability (Southward and Goldman, 1978). A higher degree of swelling is likely to lead to increase in the effective volume or hydrodynamic volume, thus decreasing the distance between protein molecules and increasing the viscosity (Lee and Rha, 1979). It was found that the viscosity of coprecipitate (TMP) was higher than that of SC. Southward and Goldman (1978) also observed that coprecipitates had higher viscosities than SC. They indicated that the calcium content of coprecipitates was the major factor in increasing the viscosity of this protein.

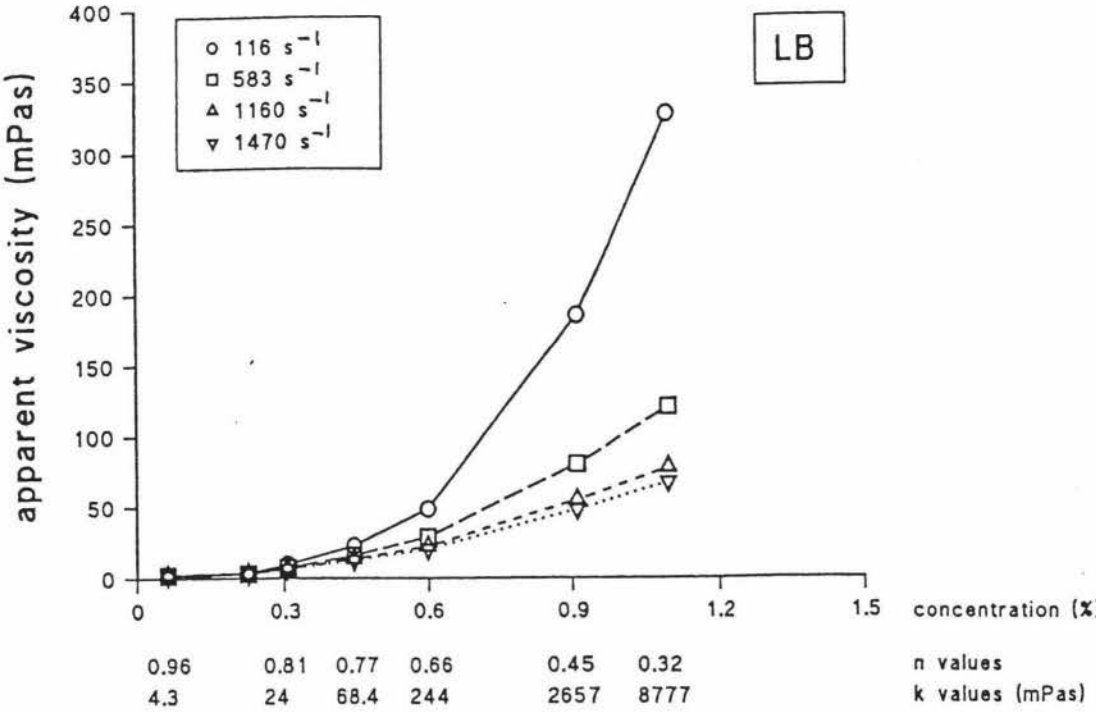


Fig. 5.5a. Apparent viscosity (mPa.s) versus concentration (%) for locust bean gum solutions. Power law constants (n and k values) for each concentration are also shown.

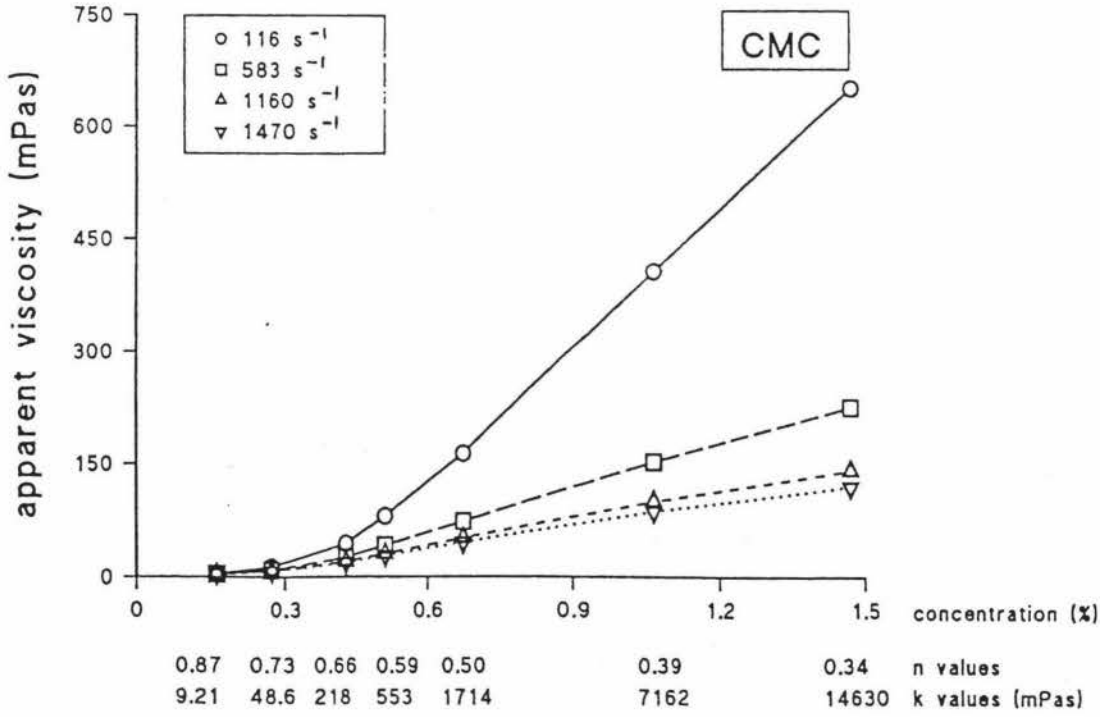


Fig. 5.5b. Apparent viscosity (mPa.s) versus concentration (%) for CMC solutions. Power law constants (n and k values) for each concentration are also shown.

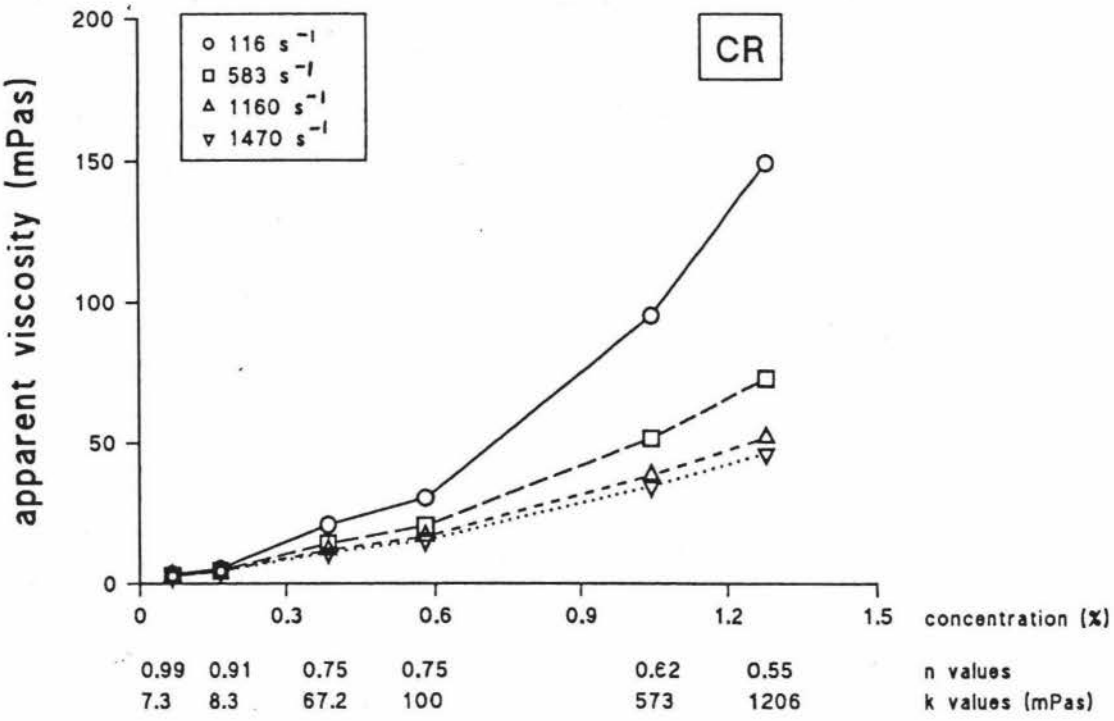


Fig. 5.5c. Apparent viscosity (mPa.s) versus concentration (%) for lambda-carrageenan solutions. Power law constants (n and k values) for each concentration are also shown.

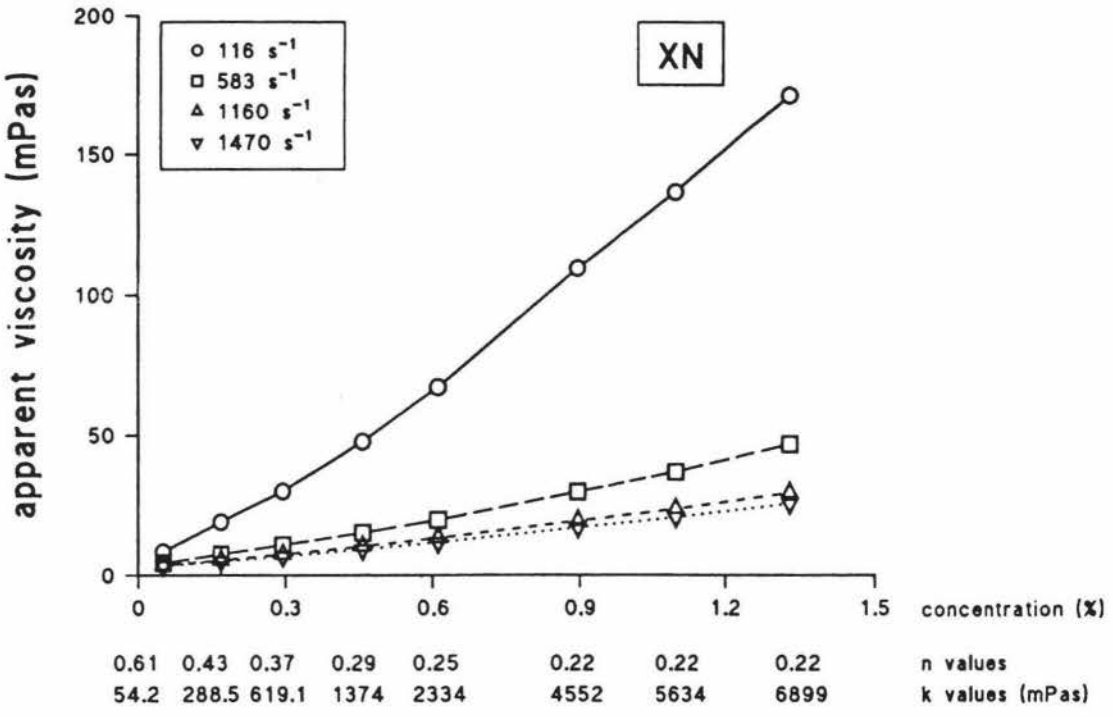


Fig. 5.5d. Apparent viscosity (mPa.s) versus concentration (%) for xanthan gum solutions. Power law constants (n and k values) for each concentration are also shown.

All gum solutions (LB, CMC, CR and XN) were non-Newtonian. They had relatively high apparent viscosities and exhibited pseudoplasticity or shear thinning. This behaviour is typical of gums and is caused by their hydrophillic nature and their long random-coil molecules. These characteristics cause both high viscosity and pseudoplasticity; thus, both viscosity and the degree of departure from Newtonian behaviour (lower n) increase with increasing concentration.

5.6 CONCLUSION

The pure 6.0% SC, WPC and WPI solutions were Newtonian. Slight pseudoplastic behaviour was found in 6.0% TMP solution. The pure 0.5% LB, CMC, CR, and XN solutions were pseudoplastic. The highest degree of pseudoplasticity was observed in 0.5% XN solution. An increase in gum concentration in the gum solutions resulted in a decrease in n value and an increase in k value, corresponding to increased pseudoplasticity and increased viscosity.

CHAPTER 6

RHEOLOGICAL SYNERGISM AND ANTAGONISM IN GUM-DAIRY PROTEIN MIXED SOLUTIONS

6.1 INTRODUCTION

When solutions of two polymers are mixed together, the viscosity of the mixed solution can be predicted from the viscosities of the pure polymer solutions and the proportions of each solution in the mixture provided there is no interaction between the polymers. Sometimes the viscosity may be greater or less than the predicted viscosity and the polymer solutions are then said to interact. Morris (1984) and Kaletunc-Gencer and Peleg (1986) stated that interaction between two polymers can be termed "synergism" if the measured viscosity of the mixture is higher than that predicted, and "antagonism" if lower.

Gum and dairy protein interactions were studied here by preparing solutions of the two kinds of polymer and mixing them in various proportions. The apparent viscosities of the mixed solutions were determined at different shear rates, so that the effects of shear rate on any interactions could be determined. Measured and predicted apparent viscosities were then compared as described below in Section 6.3.

6.2 EXPERIMENTAL PLAN

The polymer solutions were mixed at the following gum solution : protein solution ratios: 0.25/0.75, 0.50/0.50, 0.75/0.25 by weight. This gave the total concentrations and gum:protein ratios shown in Table 6.1. Each gum was mixed with each protein at these concentrations and ratios, giving in total 16 gum:protein combinations. The mixtures were prepared as described in Section 4.2.4. The rheological properties of the samples were observed within 4 hours after deareation.

Table 6.1: Compositions of mixtures of 0.5% gum solution and 6.0% dairy protein solution.

Gum solution:protein solution ratio	Gum:protein ratio	Mixed solutions %gum	%protein	Total conc.(%)
0:100	0:1	0.000	6.000	6.000
25:75	1:36	0.125	4.500	4.625
50:50	1:12	0.250	3.000	3.250
75:25	1:4	0.375	1.500	1.875
100:0	1:0	0.500	0.000	0.500

The Bohlin Rheometer was used to measure the viscosities as described in Section 4.5. In this study, viscosities were measured at the following shear rates: 116, 583, 1160, 1470 s^{-1}. The same batches of mixed solutions were kept for another 12 hours for sedimentation studies. The degree of sedimentation of each sample was obtained as a weight percentage according to the method described in Sections 4.3 and 4.4.

6.3 PROCESSING AND PRESENTATION OF EXPERIMENTAL DATA

For each gum-protein combination, measured apparent viscosities of the pure gum solution, the pure protein solution and the gum solution-protein solution mixtures are presented in Figs. 6.1 to 6.4 as plots of apparent viscosity versus mixture composition and mixture rheology, with shear rate as parameter.

For each gum-protein combination, the expected viscosities (at a given shear rate) of the different solution mixtures were calculated from:

$$b = wG + (1-w)P \qquad (6.1)$$

where

b = expected apparent viscosity of mixed solution (mPas)

w = weight fraction of gum solution

G = apparent viscosity of the 0.5% gum solution (mPa.s)

P = apparent viscosity of the 6.0% dairy protein solution (mPa.s)

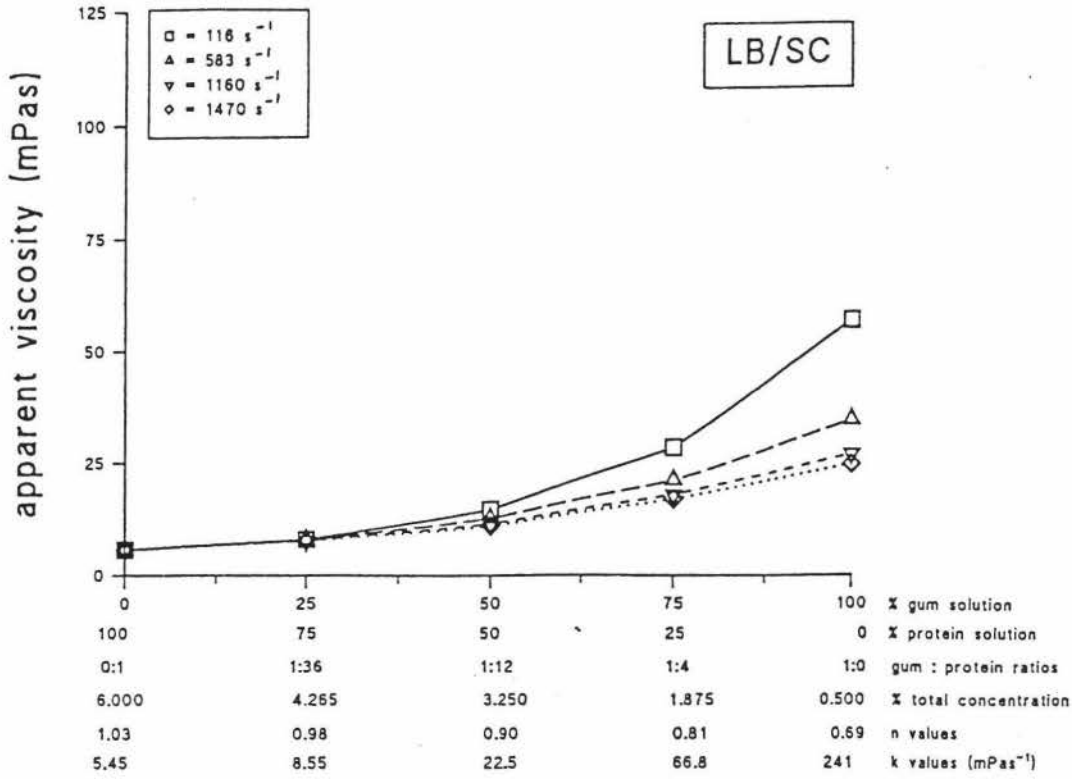


Fig. 6.1a. Apparent viscosity versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

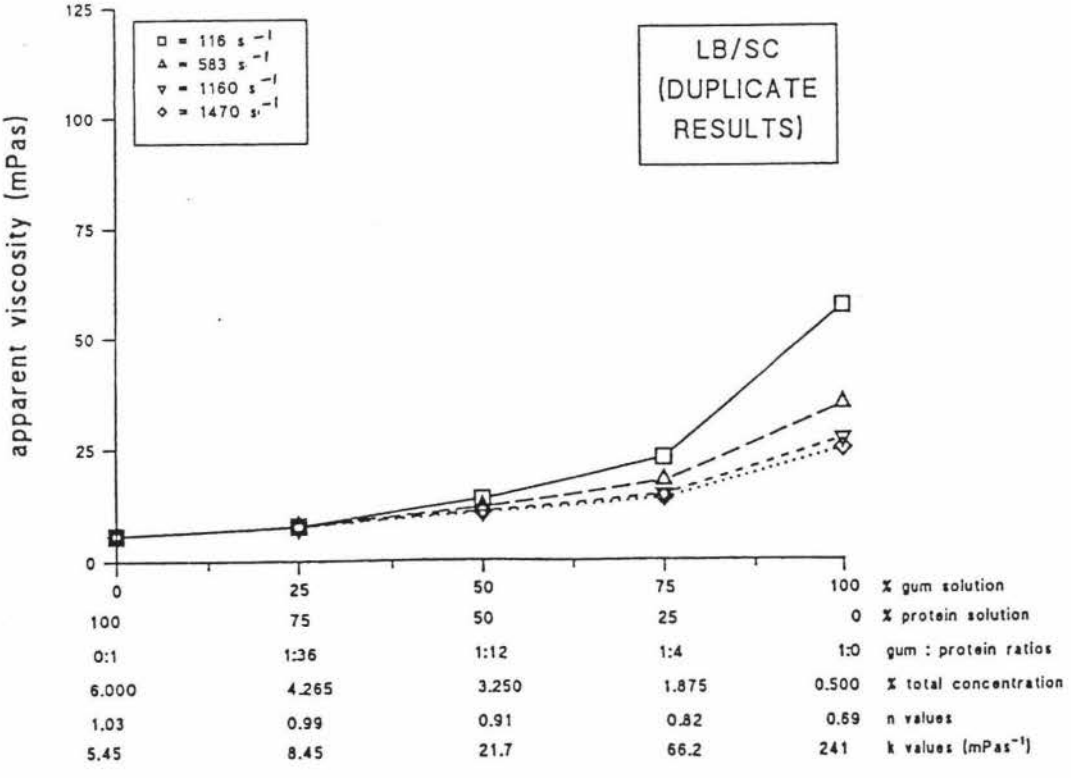


Fig. 6.1b. Apparent viscosity versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

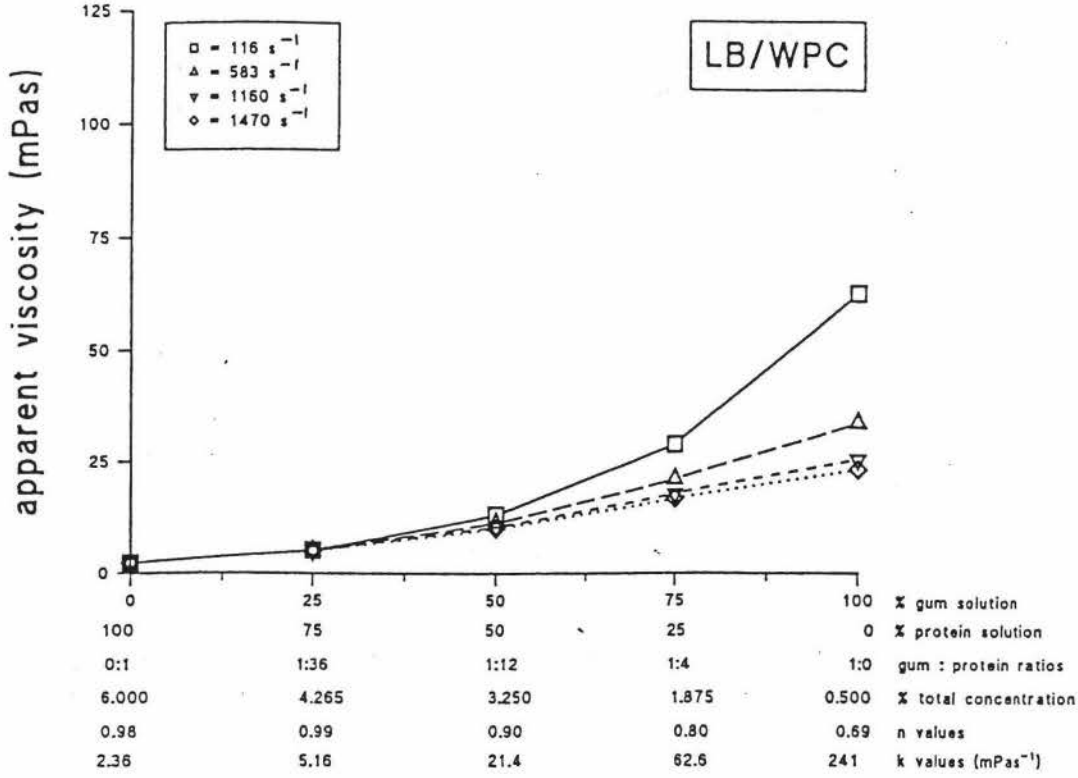


Fig. 6.1c. Apparent viscosity versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

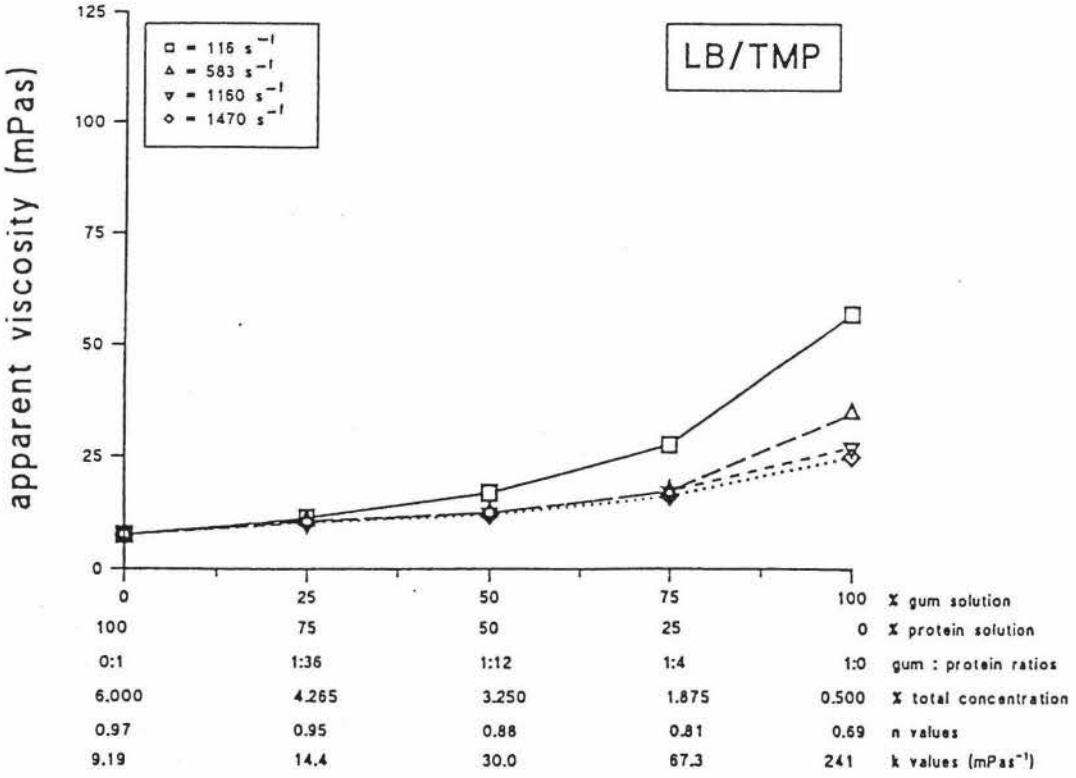


Fig. 6.1d. Apparent viscosity versus mixture composition for mixtures of 0.5 % LB and 6.0 % TMP solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

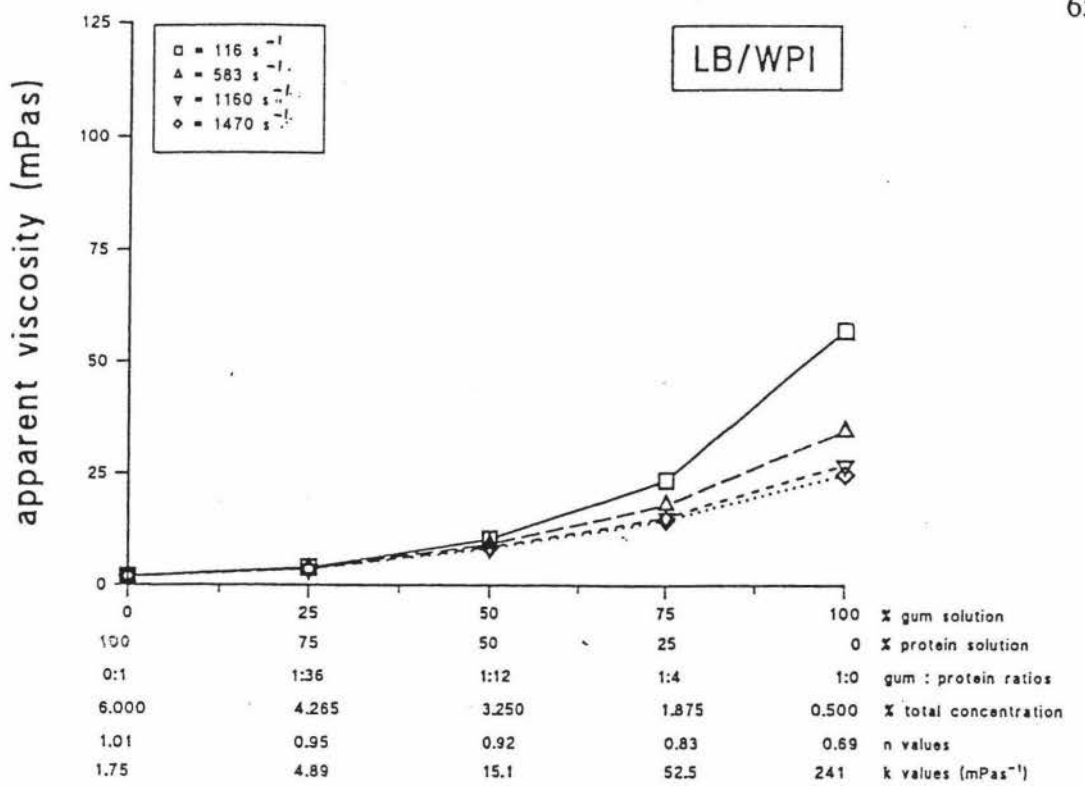


Fig. 6.1e. Apparent viscosity versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPI solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

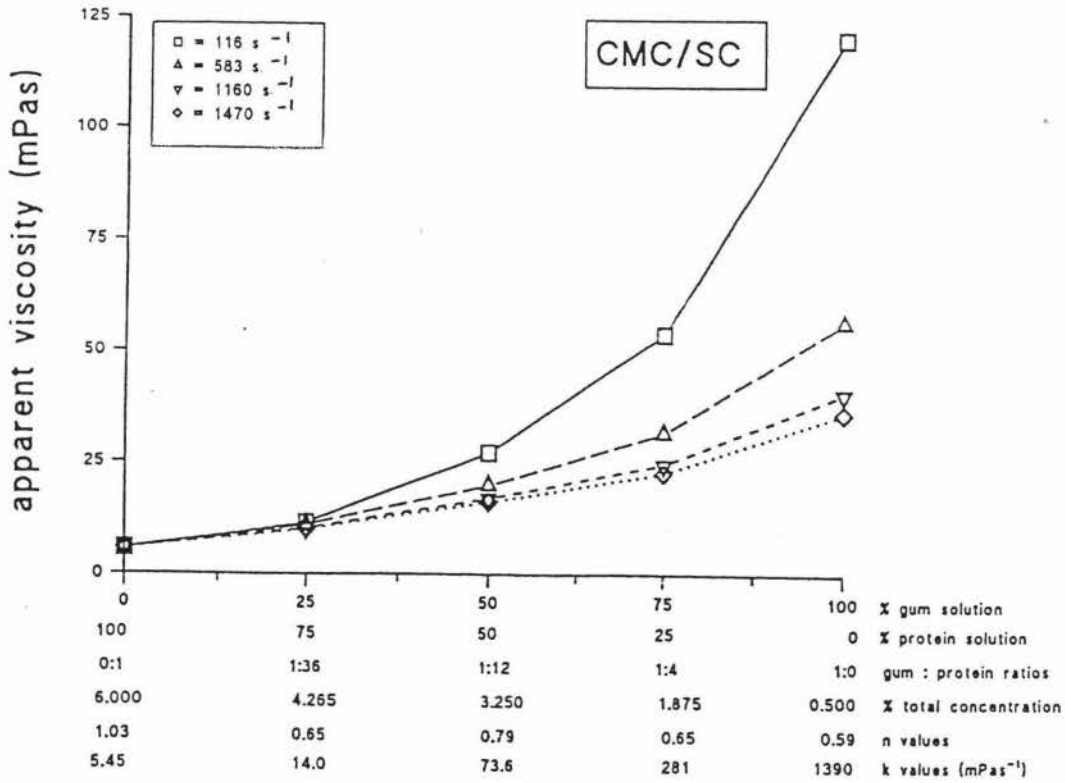


Fig. 6.2a. Apparent viscosity versus mixture composition for mixtures of 0.5 % CMC and 6.0 % SC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

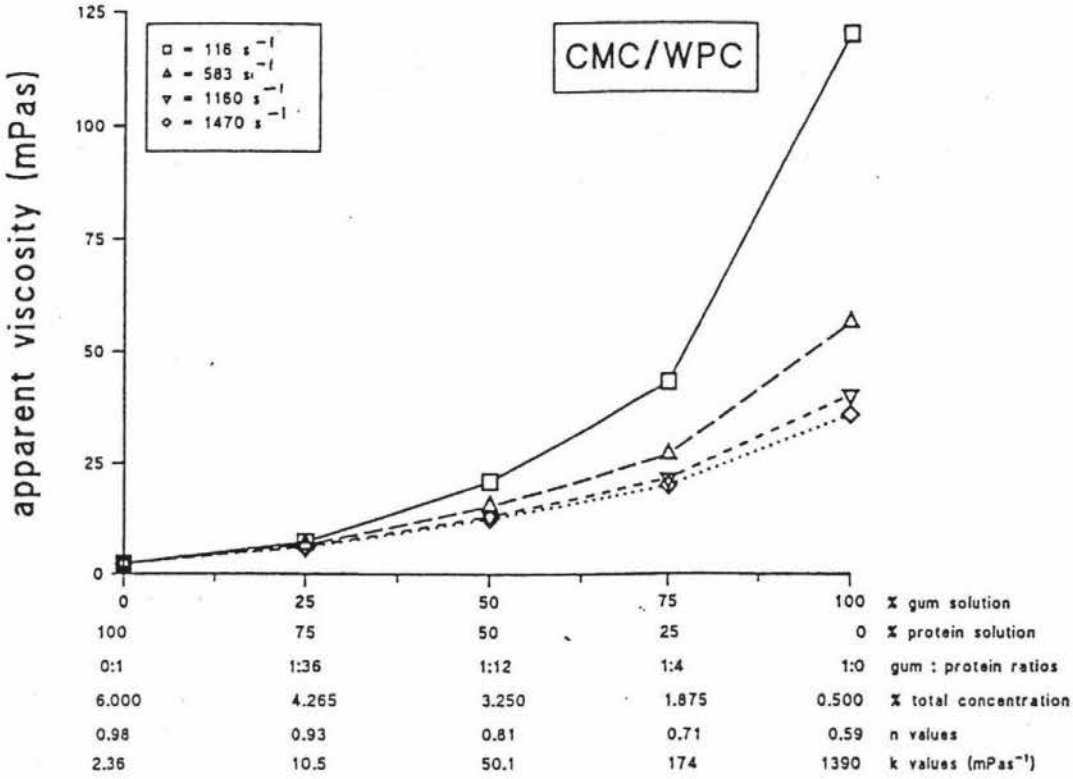


Fig. 6.2b. Apparent viscosity versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

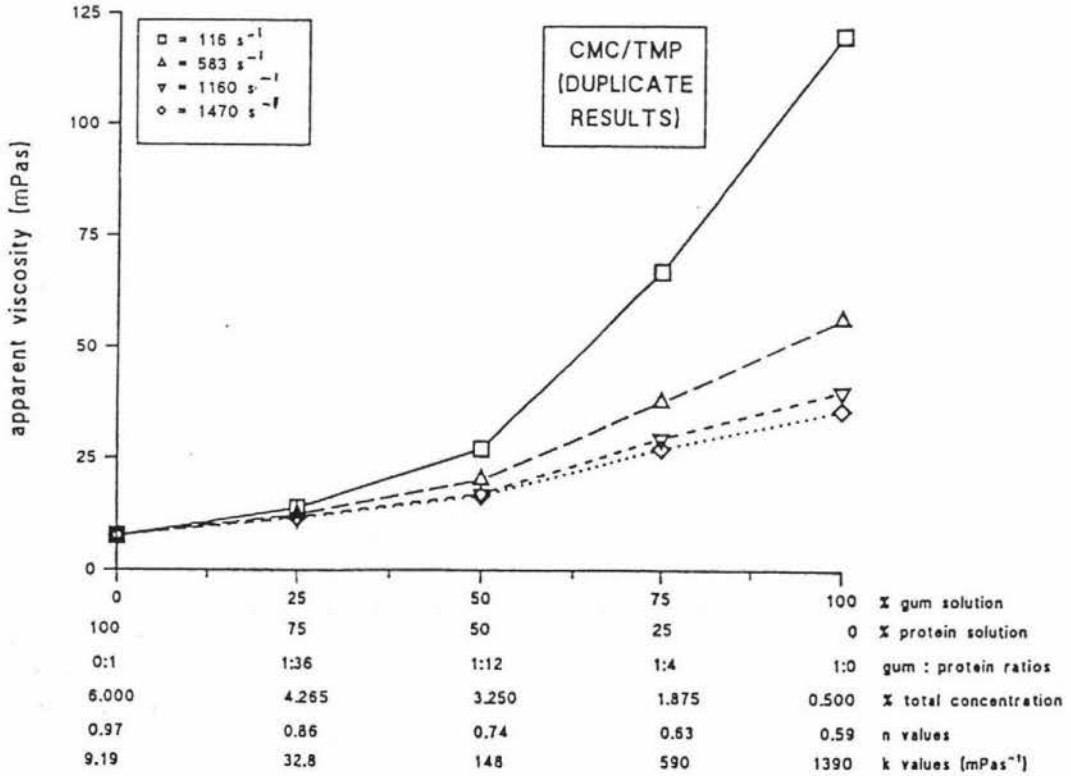


Fig. 6.2c. Apparent viscosity versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

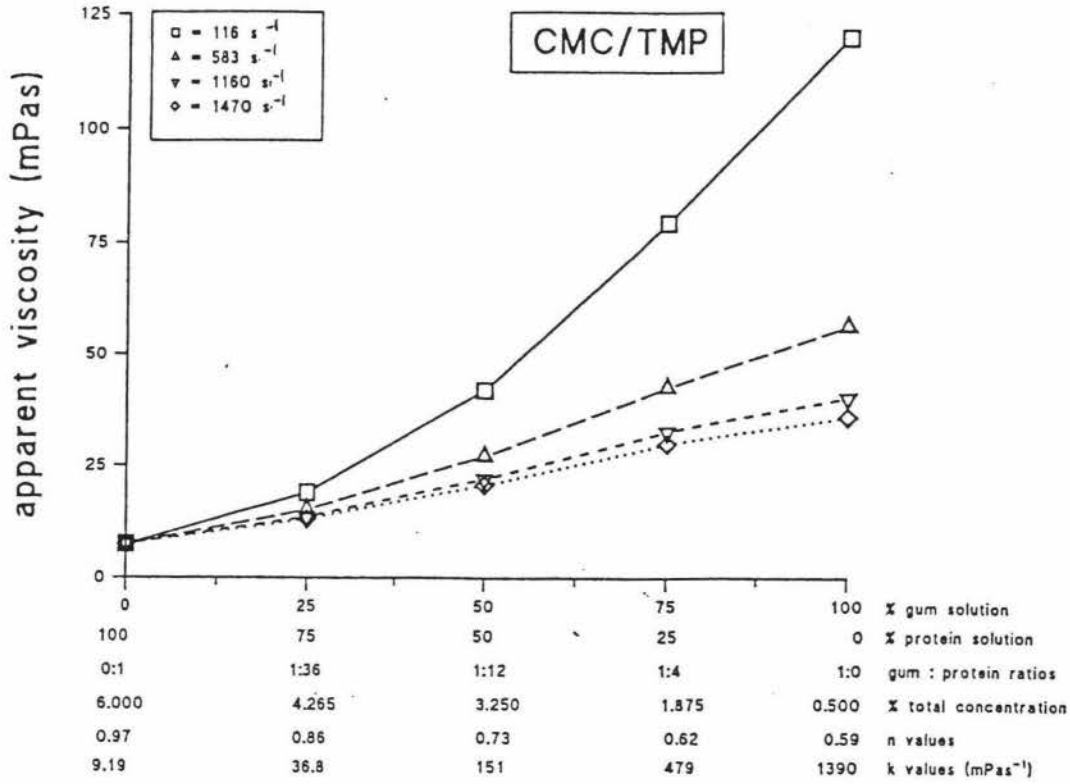


Fig. 6.2d. Apparent viscosity versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

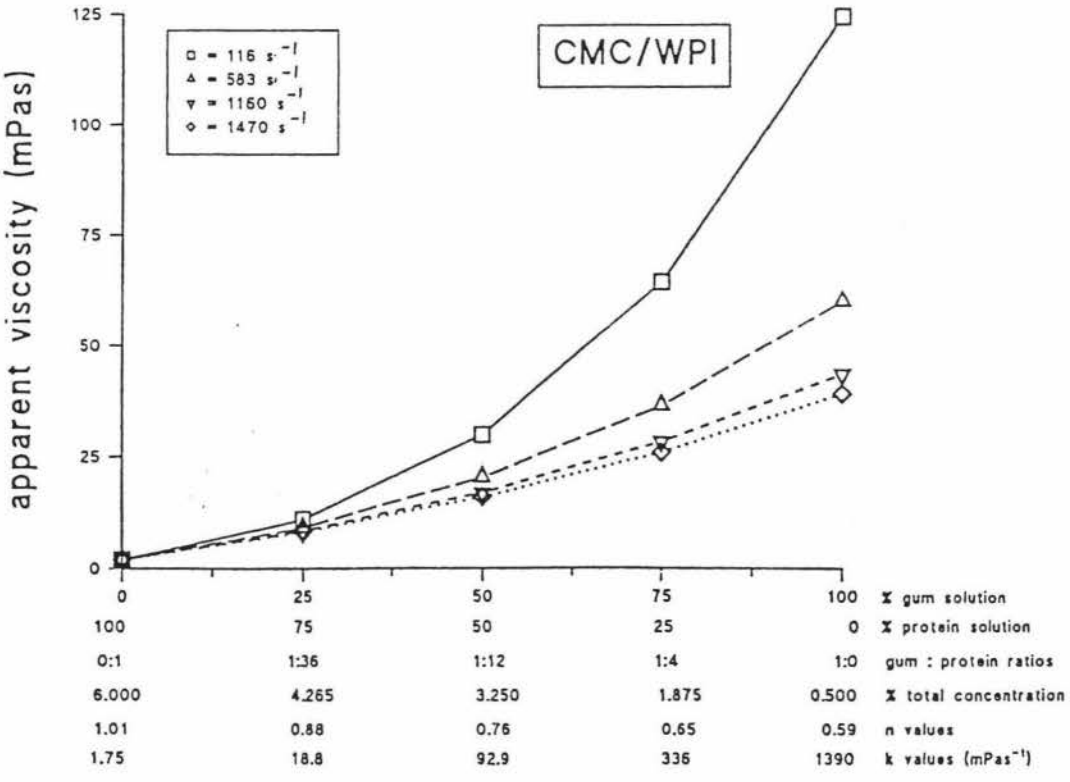


Fig. 6.2e. Apparent viscosity versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPI solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

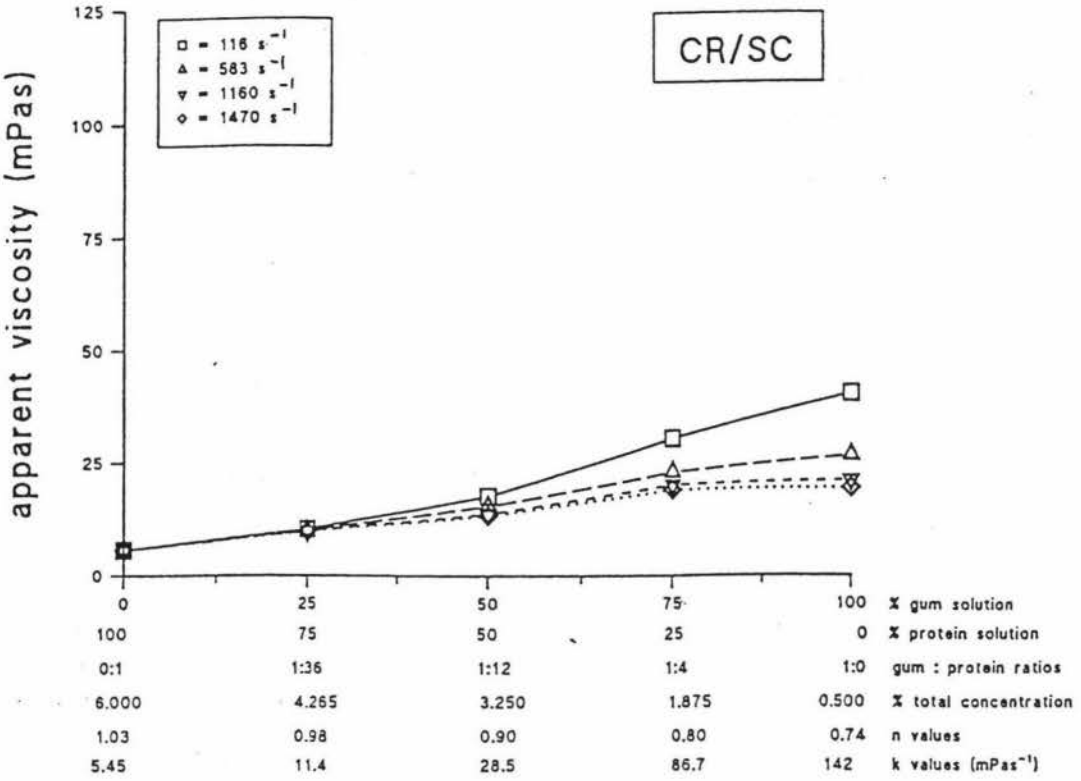


Fig. 6.3a. Apparent viscosity versus mixture composition for mixtures of 0.5 % CR and 6.0 % SC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

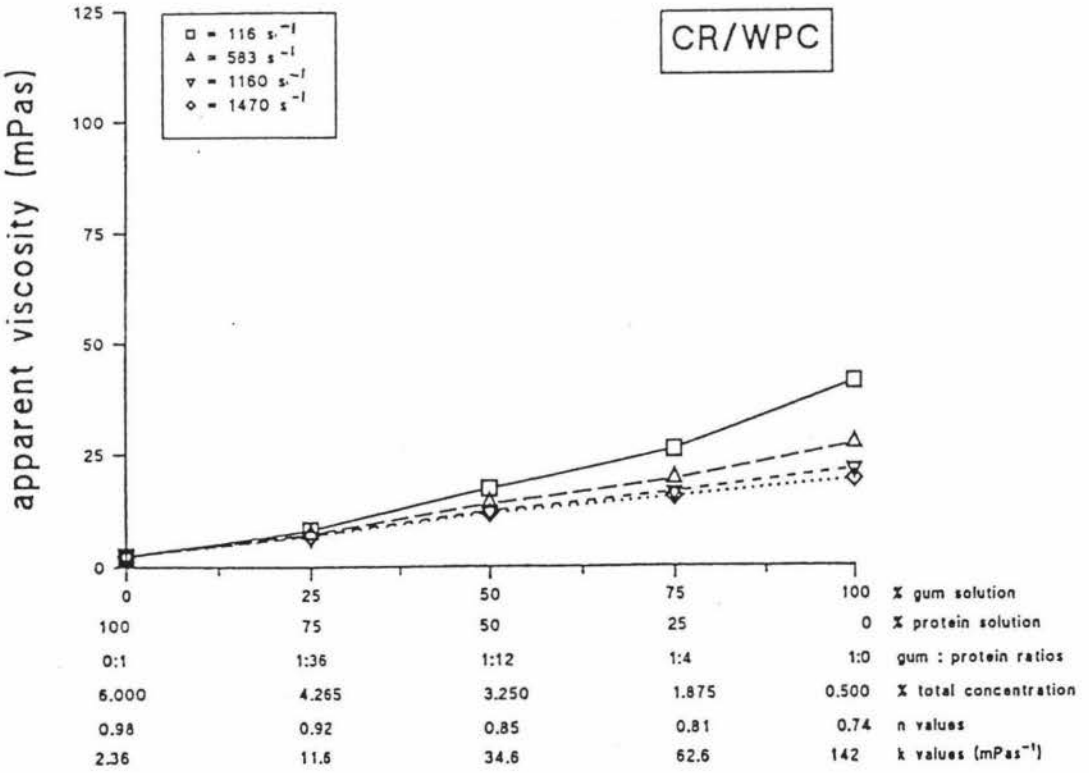


Fig. 6.3b. Apparent viscosity versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

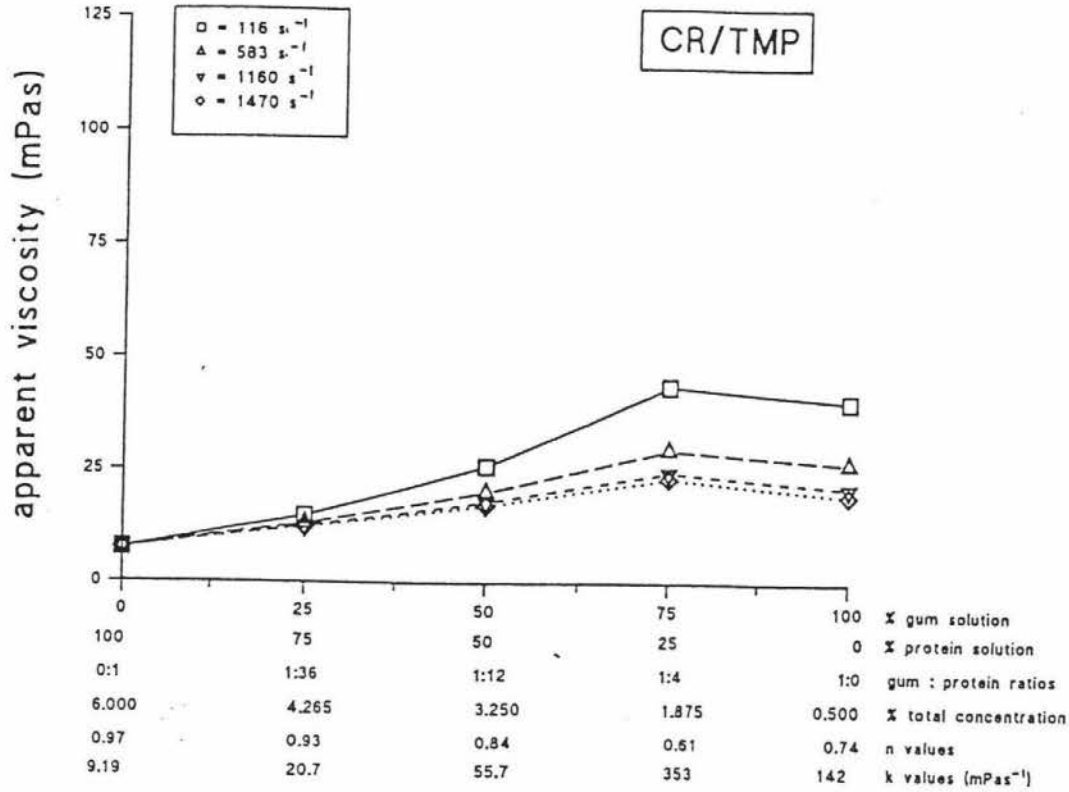


Fig. 6.3c. Apparent viscosity versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

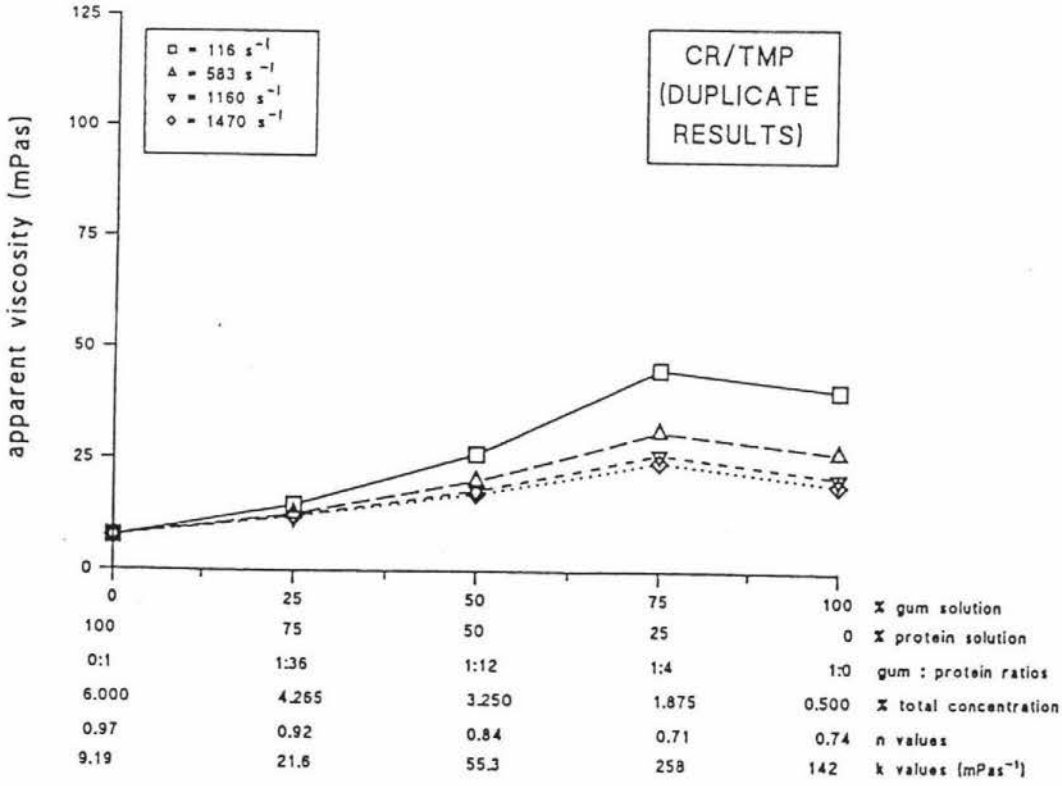


Fig. 6.3d. Apparent viscosity versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

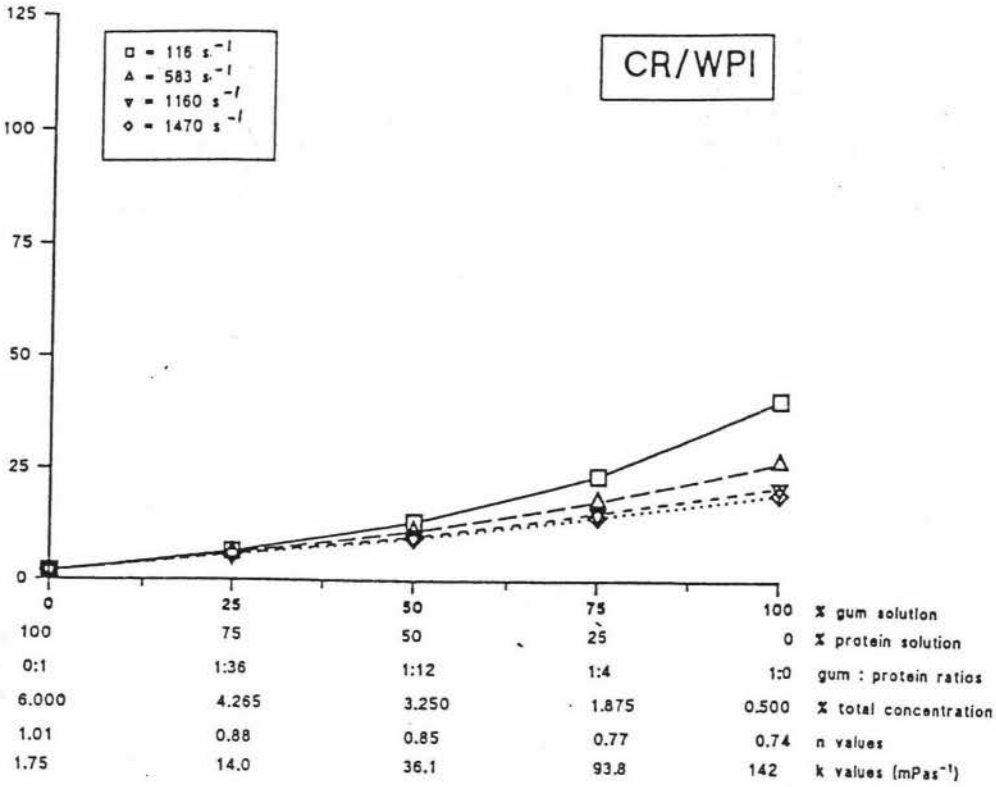


Fig. 6.3e. Apparent viscosity versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPI solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

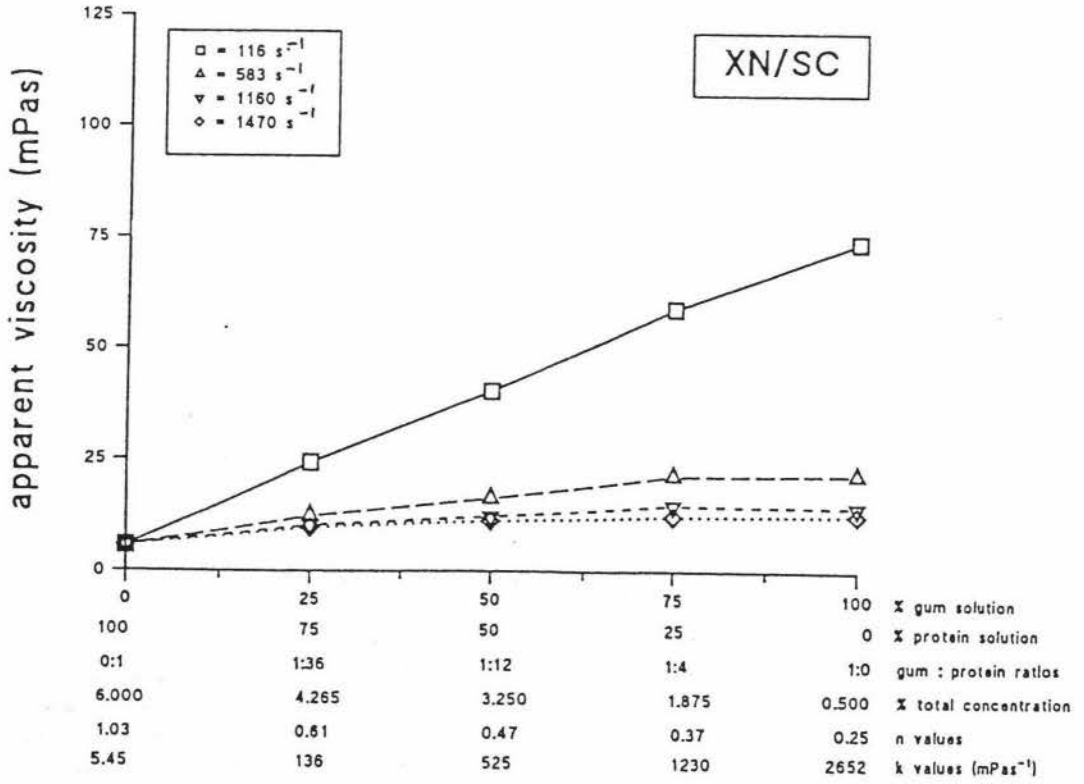


Fig. 6.4a. Apparent viscosity versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

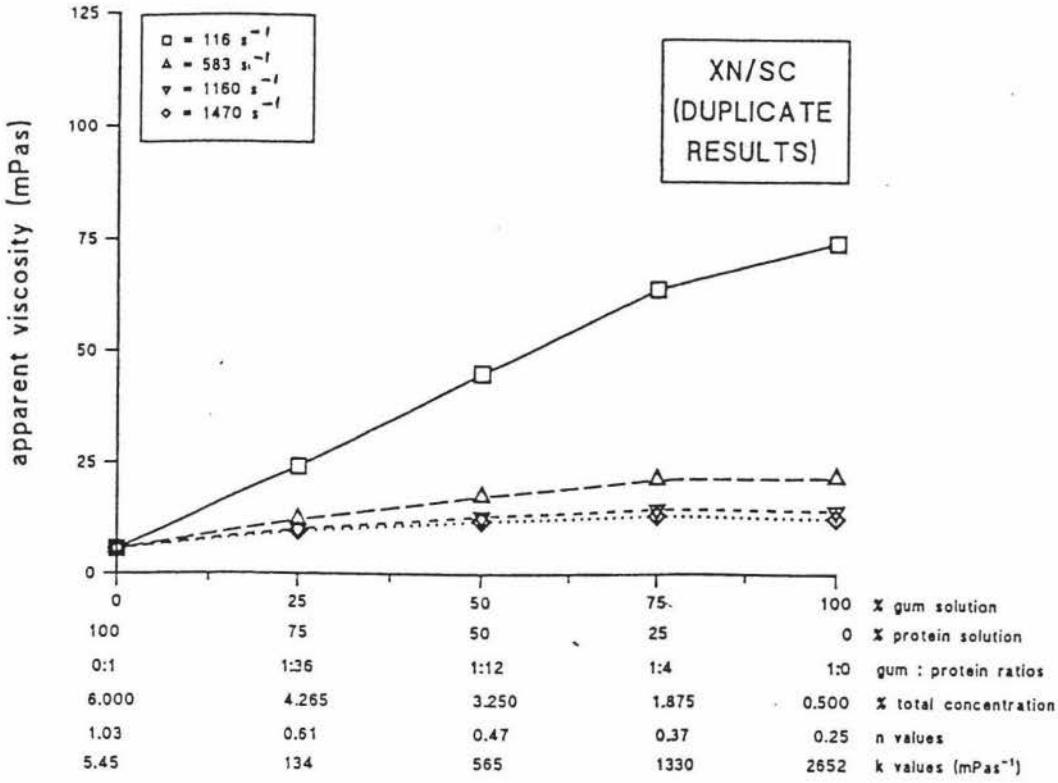


Fig. 6.4b. Apparent viscosity versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

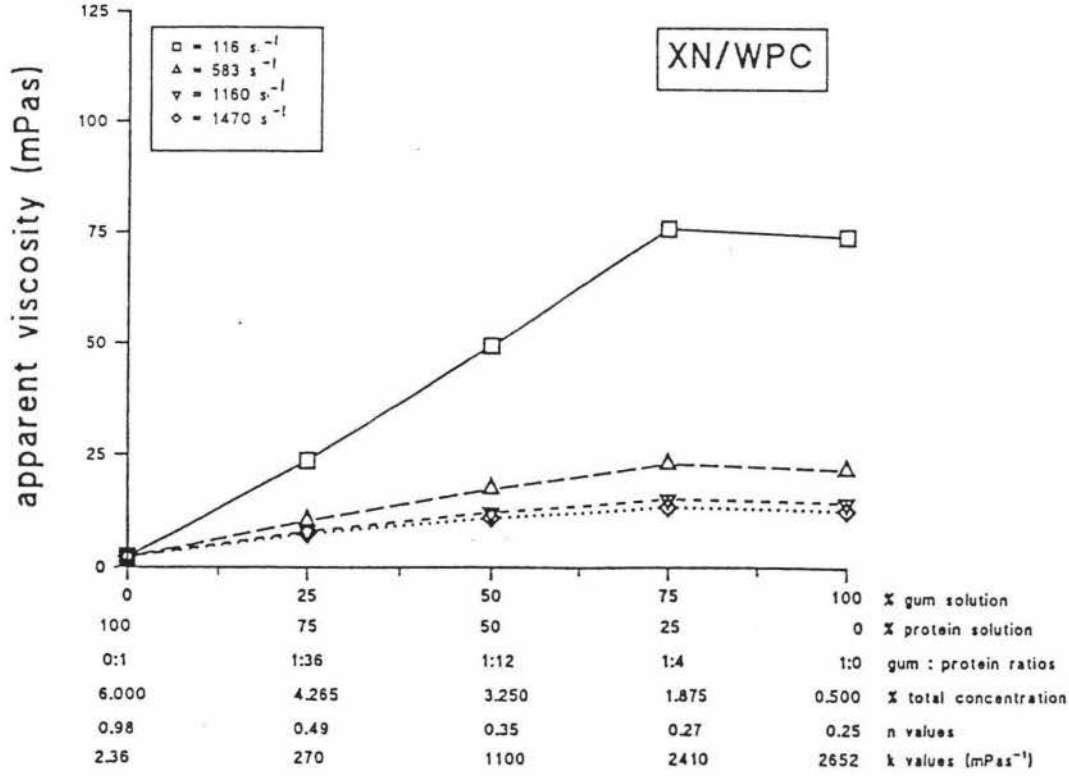


Fig. 6.4c. Apparent viscosity versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPC solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k also shown.

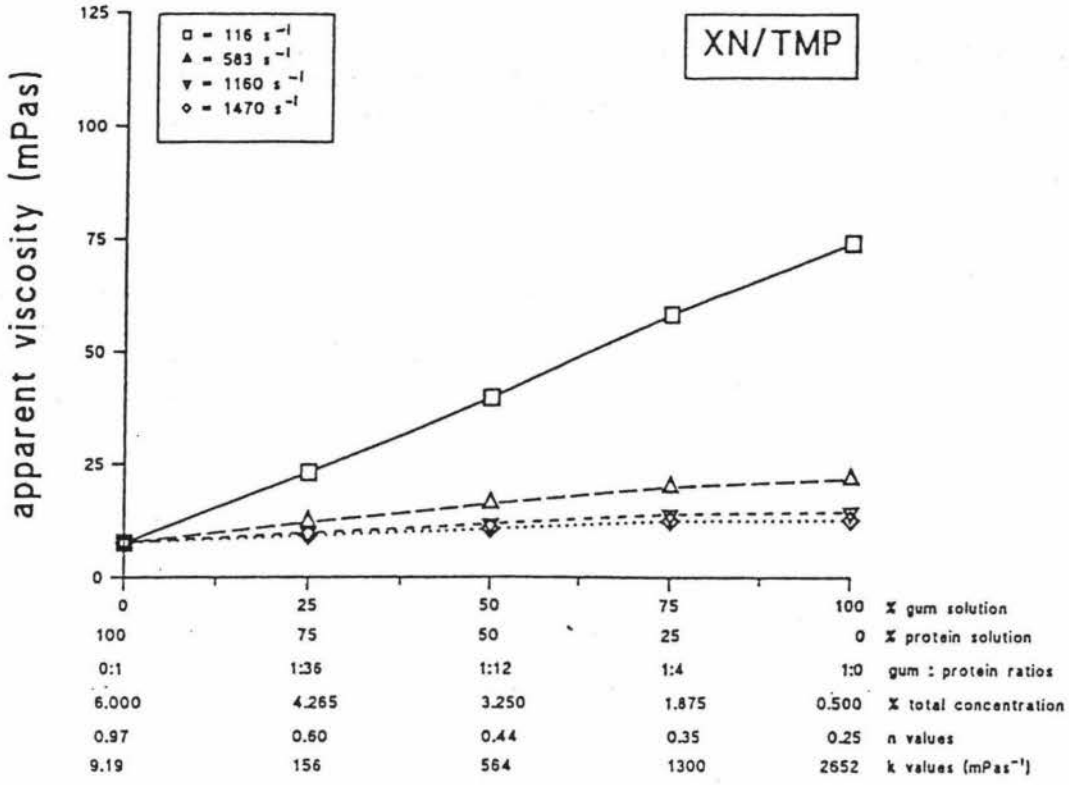


Fig. 6.4d. Apparent viscosity versus mixture composition for mixtures of 0.5 % XN and 6.0 % TMP solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

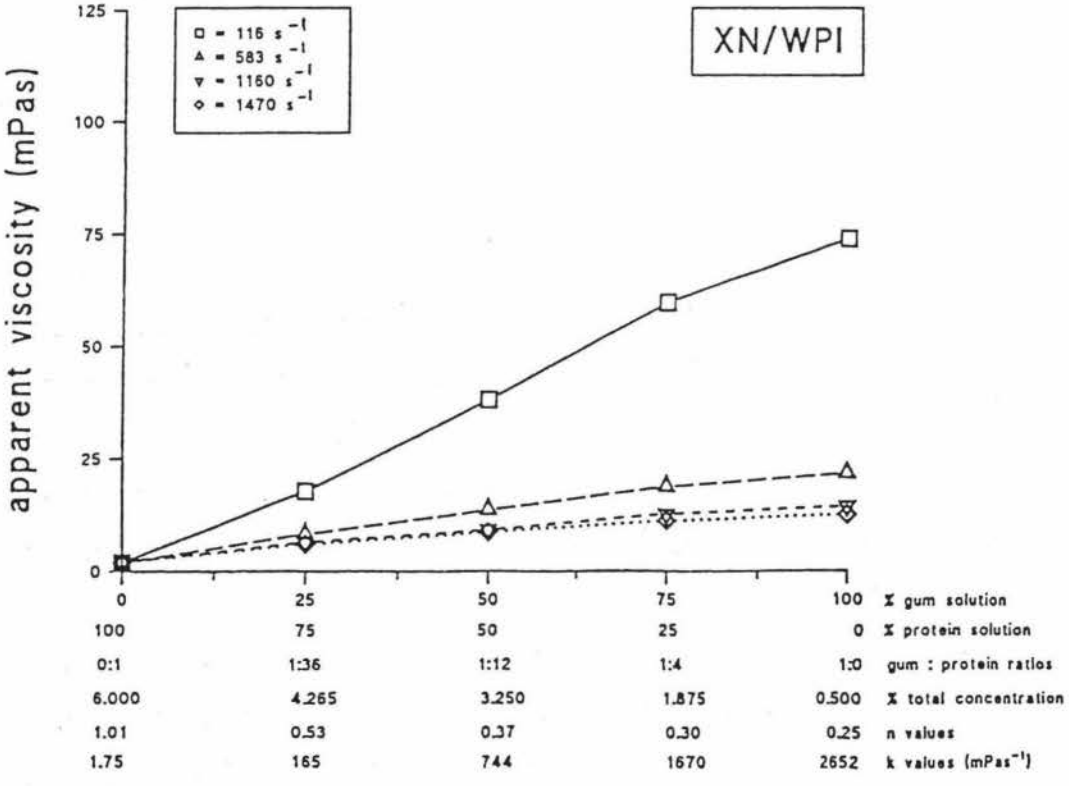


Fig. 6.4e. Apparent viscosity versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPI solutions. Gum : protein ratios, total concentrations, and values of the power law constants n and k are also shown.

This equation assumes no interaction. It is displayed graphically in Fig 6.5. Fig 6.5 also demonstrates how measured viscosity might vary with mixture composition if synergism or antagonism occurs.

In order to display and quantify any synergism or antagonism in a neater and more readily-comprehensible way than that shown in Fig 6.5, viscometric data is displayed here in the form used by Kaletunc-Gencer and Peleg (1986). This is shown in Fig 6.6, where

$$\text{X-ratio} = a/b \qquad (6.2)$$

where a = measured viscosity (mPa.s).

According to Kaletunc-Gencer and Peleg (1986) an X-ratio greater than 1.0 indicates apparent synergism while an X-ratio smaller than 1.0 indicates apparent antagonism. An X-ratio of 1.0 indicates no interaction.

X-ratio plots for all the gum-dairy protein combinations studied are shown in Figs 6.7 to 6.10. X-ratios themselves are tabulated in Appendix 9, Tables A9.1 to A9.4. Duplicate results for LB/SC, CMC/TMP, CR/TMP and XN/SC are included in these figures and tables.

The words "synergism" and "antagonism" are qualified above by the word "apparent". This is because equation (6.1) not only assumes no rheological interaction, it also assumes that the viscosities of each of the individual polymer solutions varies in a directly proportional way with polymer concentration. This important point has not been made by Kaletunc-Gencer and Peleg (1986) or by Morris (1983) -another worker who advocates the detection of synergism/antagonism by the method described above.

The effect of a relationship between viscosity and concentration that is not one of direct proportionality can be demonstrated by considering what happens if a 20% sucrose solution (viscosity = 1.695 mPa.s) is mixed with a 40% sucrose solution (viscosity = 5.164 mPa.s) at 25 °C in the ratio 50:50 to make a 30% solution. (Sucrose solutions are considered here because comprehensive accurate viscosity data are

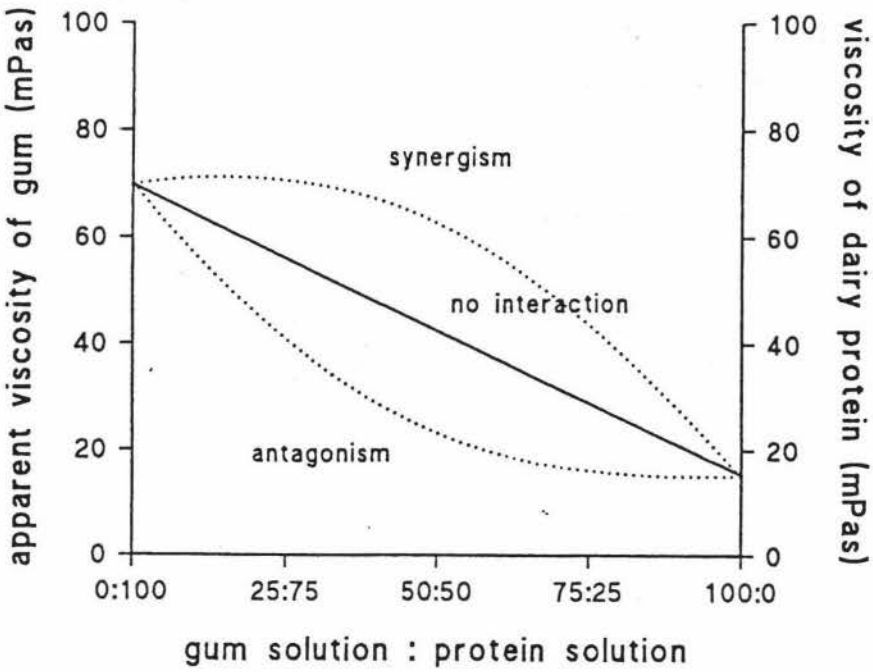


Fig. 6.5. Schematic presentation of the possible rheological behaviour patterns of gum-dairy protein mixed solutions.

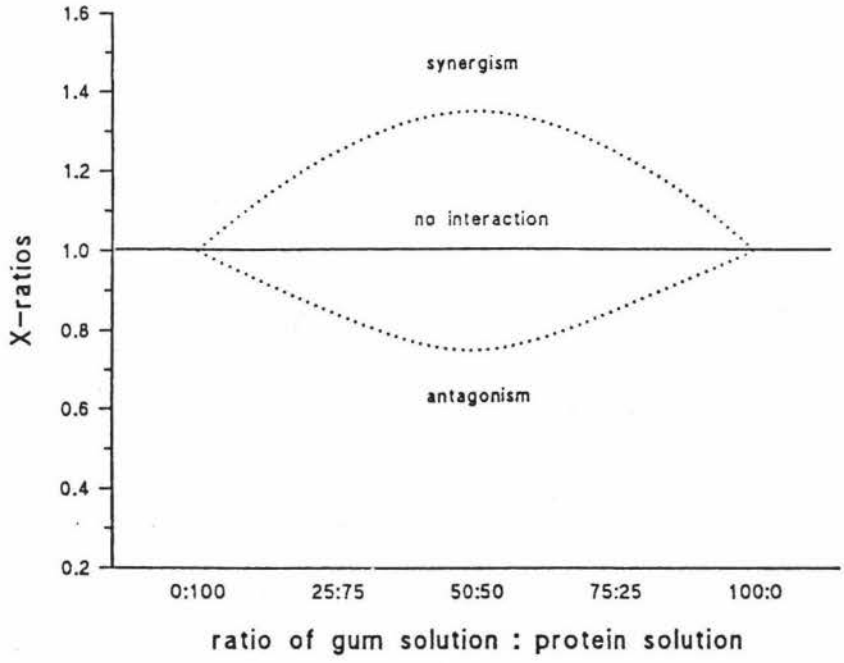


Fig. 6.6. Schematic presentation of the possible rheological behaviour patterns of gum-dairy protein mixed solutions in terms of X-ratios.

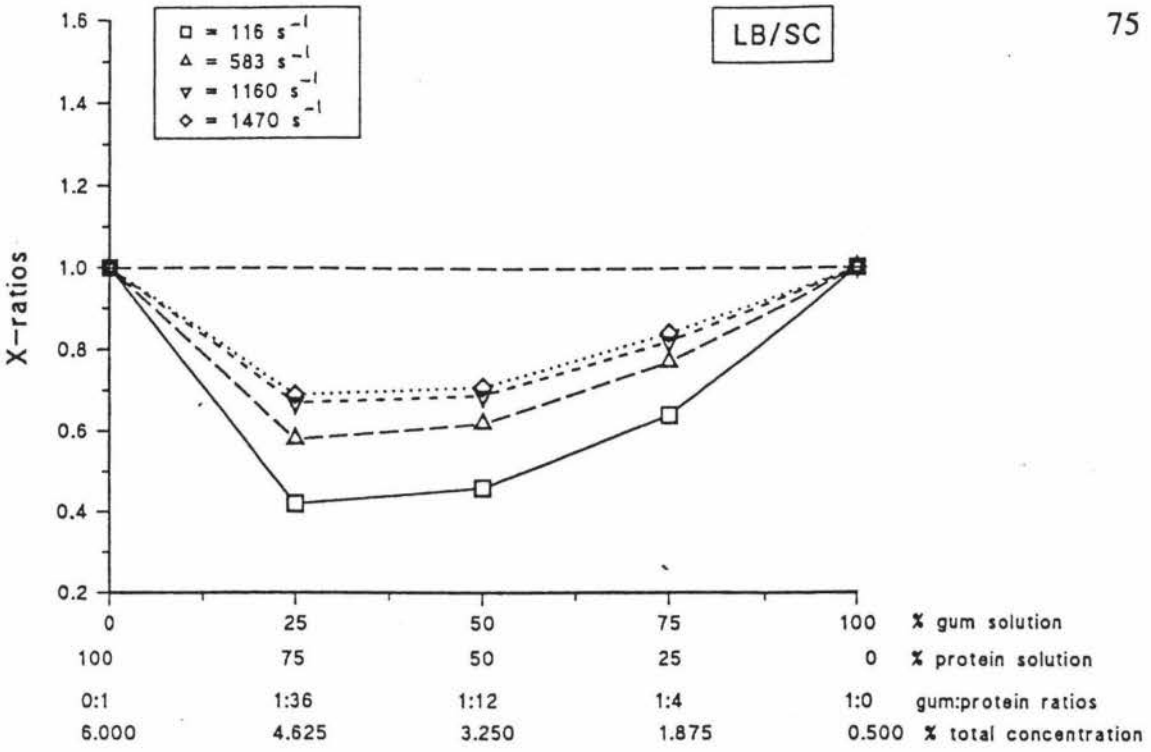


Fig. 6.7a. X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown.

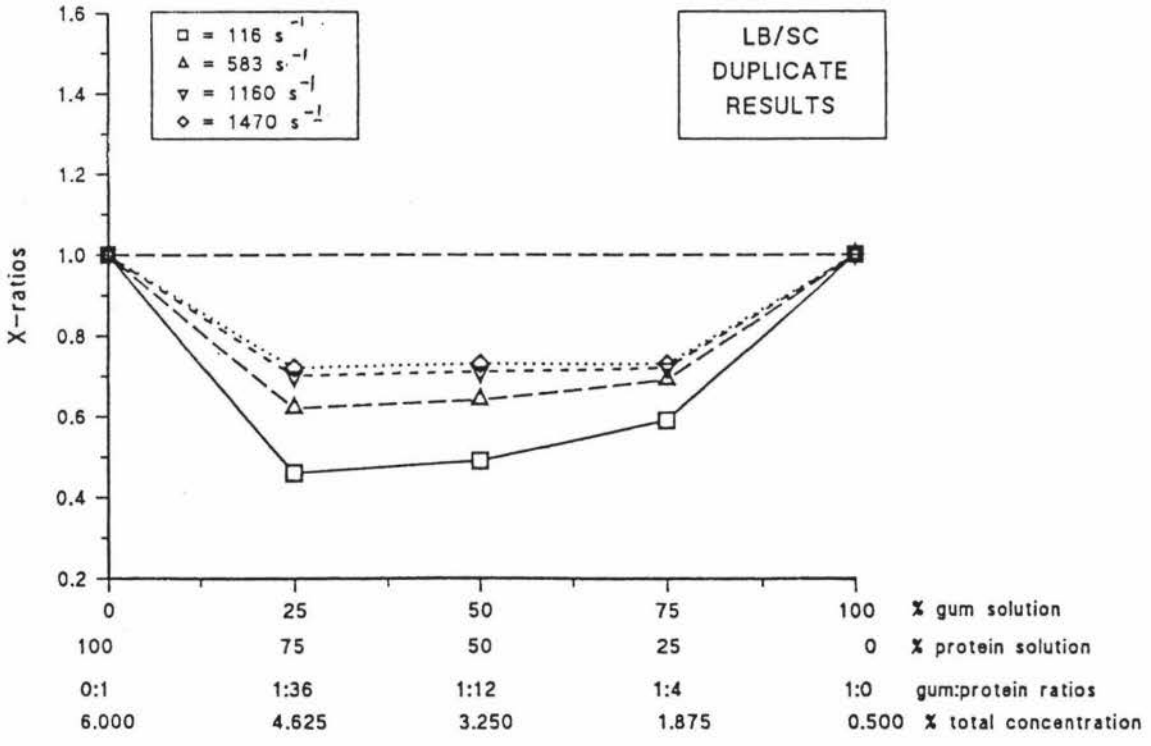


Fig. 6.7b. X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown.

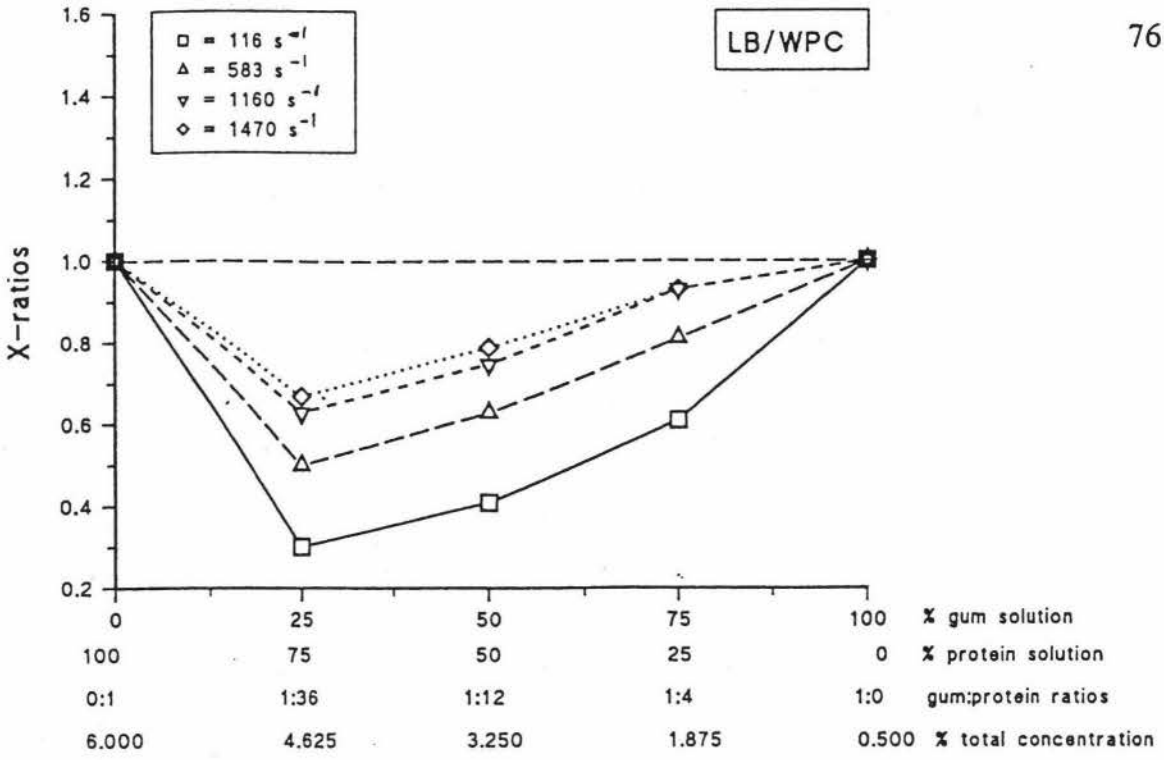


Fig. 6.7c. X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown.

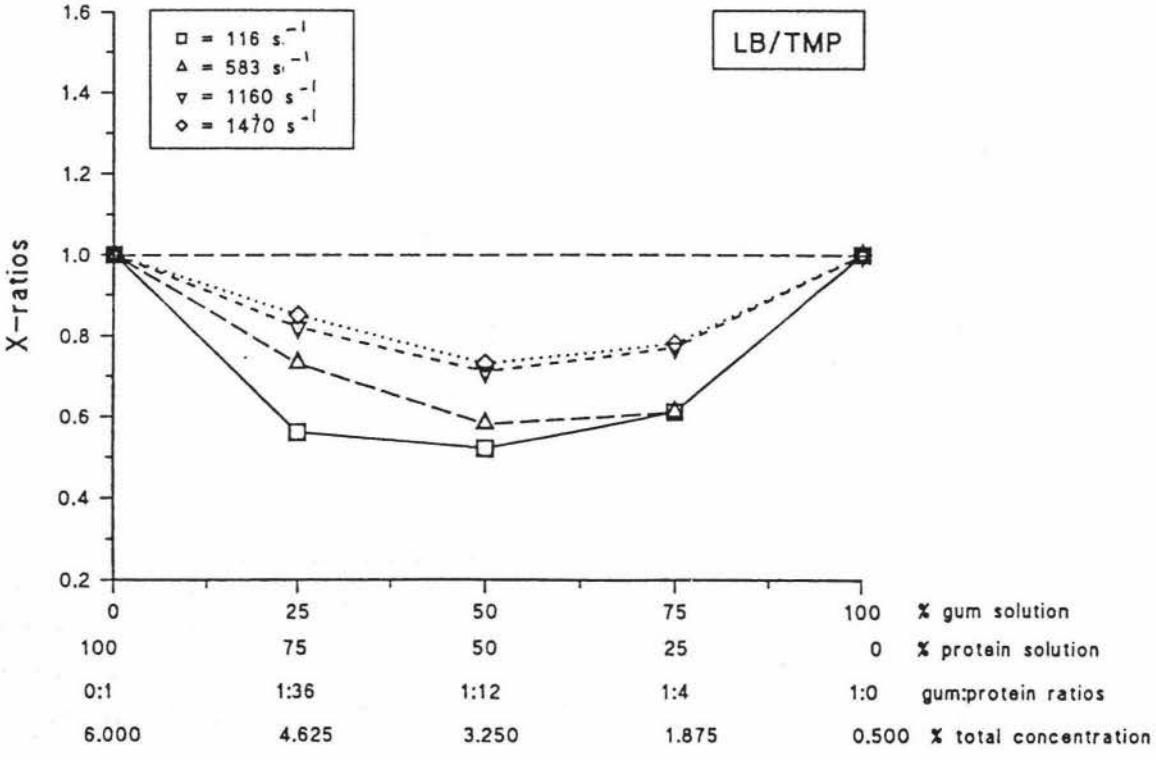


Fig. 6.7d. X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown.

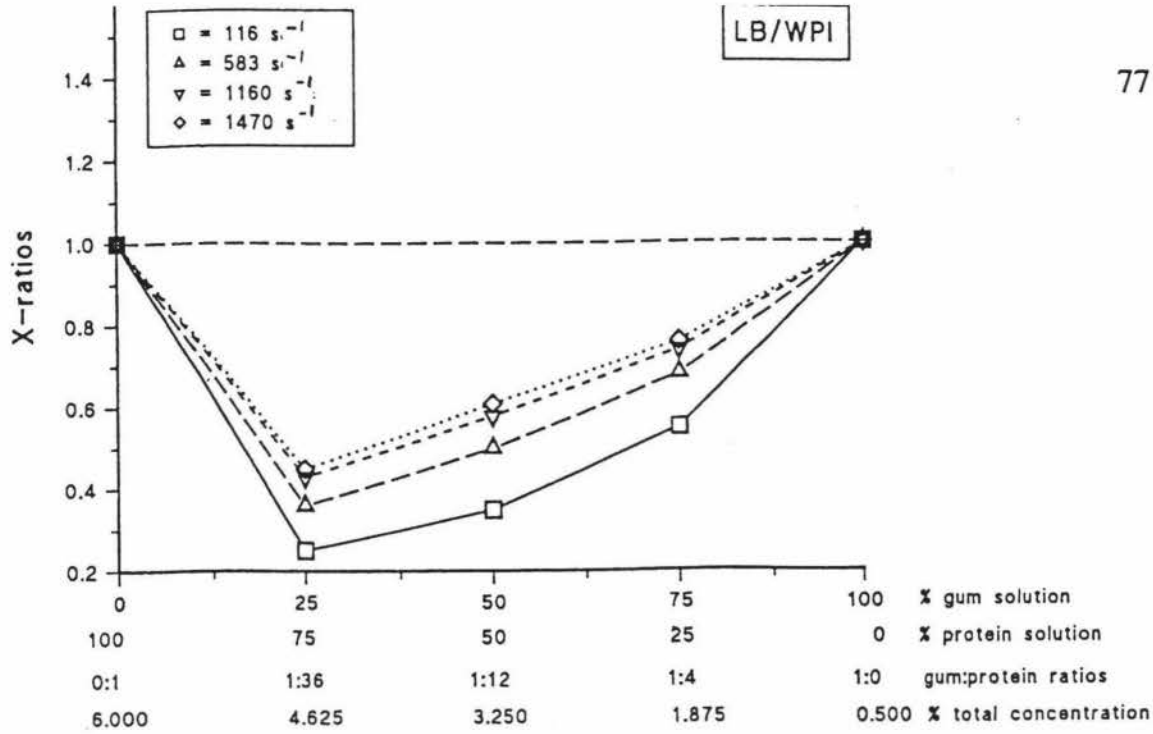


Fig. 6.7e. X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown.

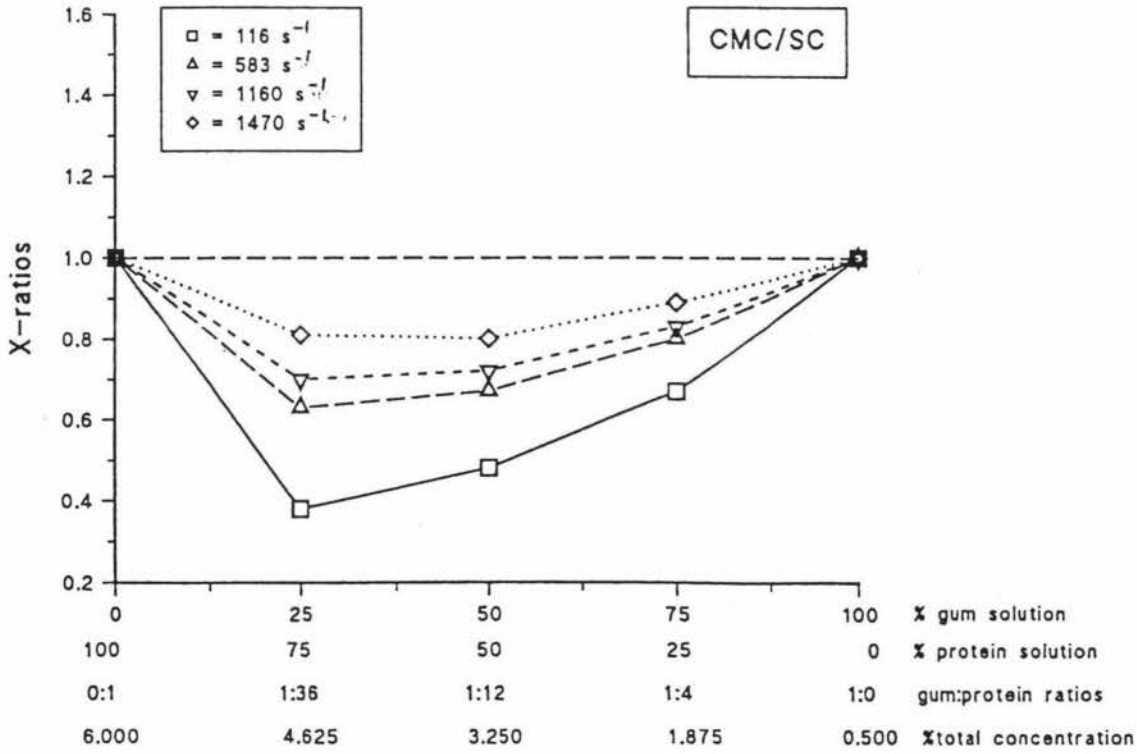


Fig. 6.8a. X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown.

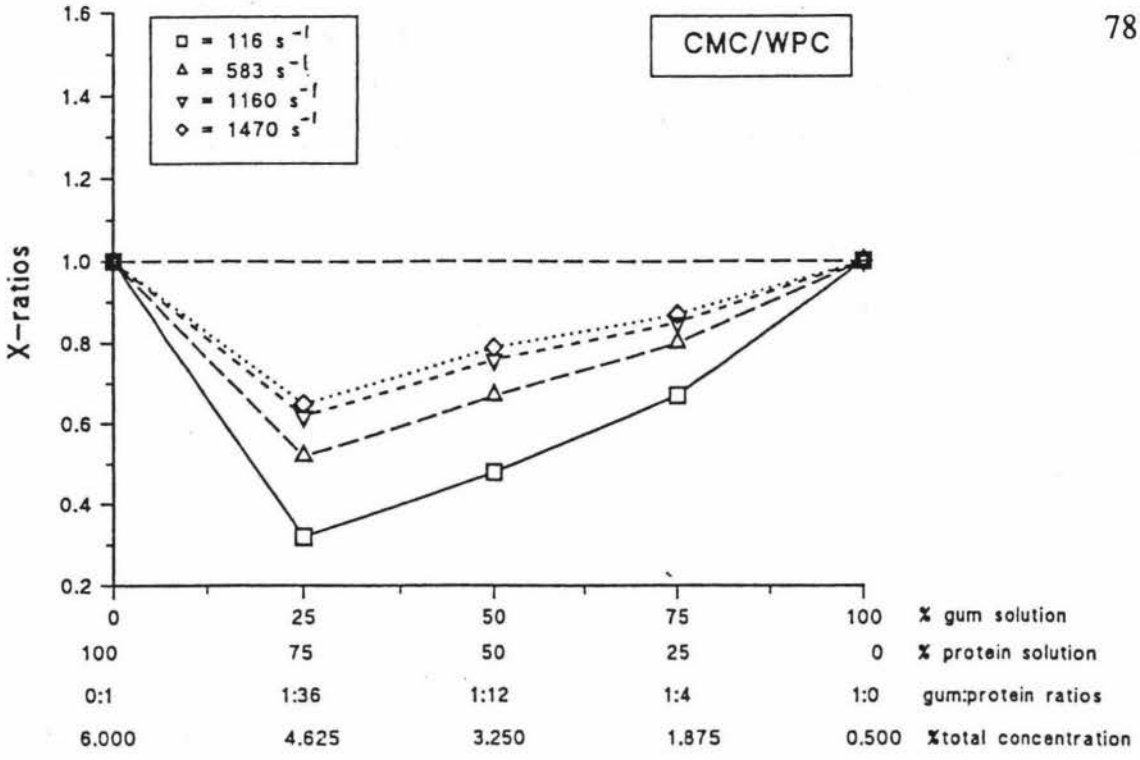


Fig. 6.8b. X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown.

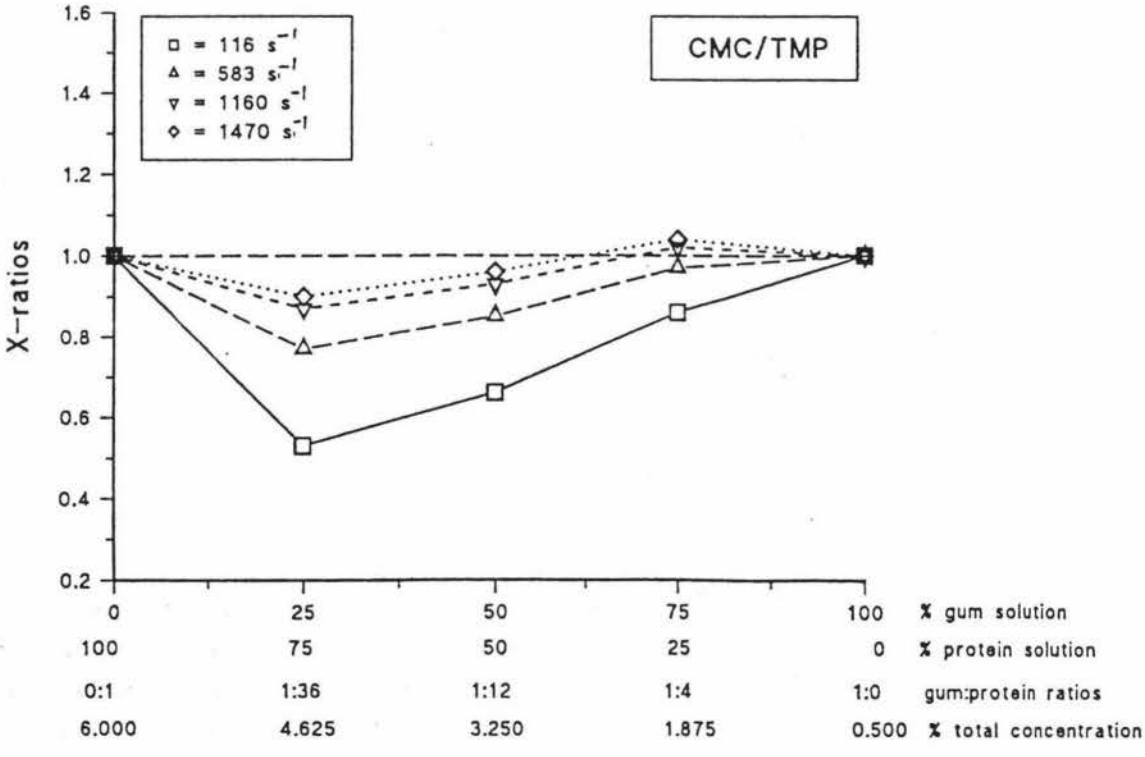


Fig. 6.8c. X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown.

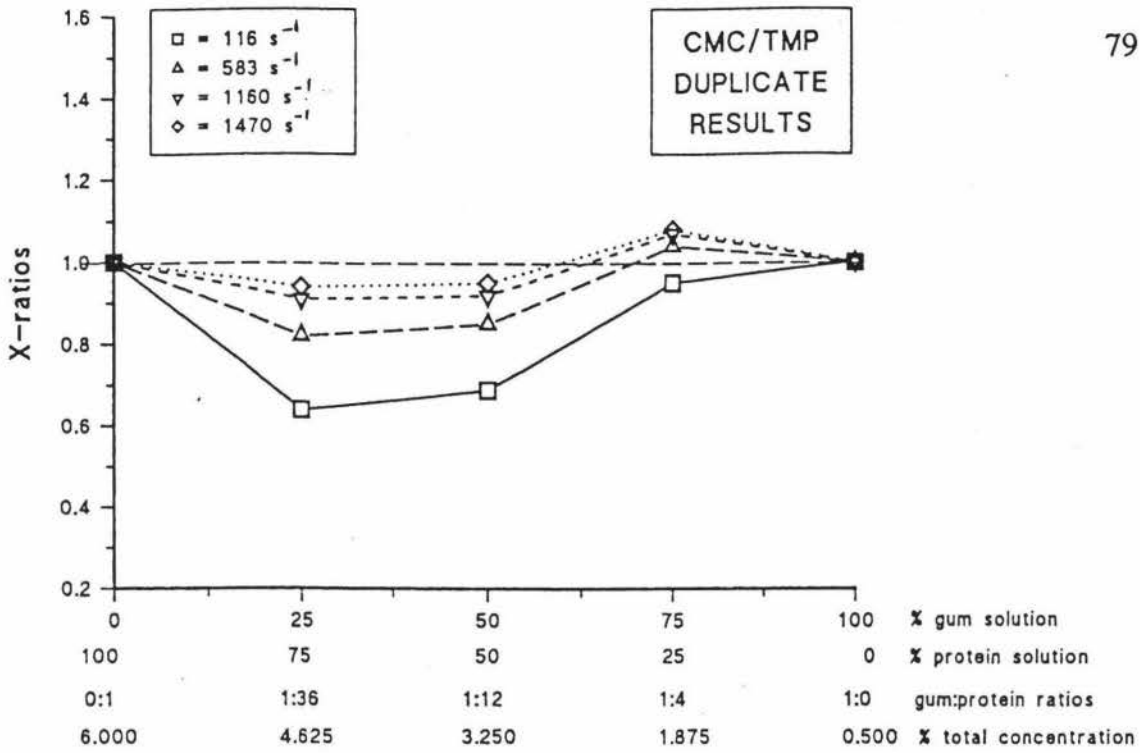


Fig. 6.8d. X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown.

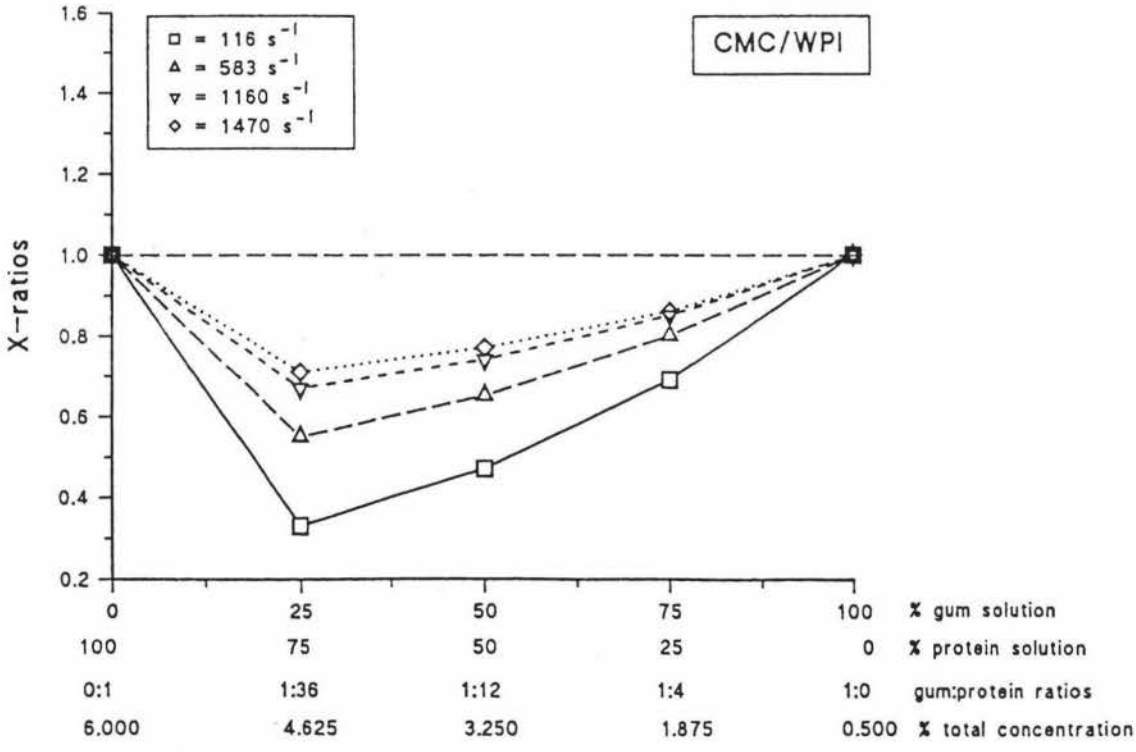


Fig. 6.8e. X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown.

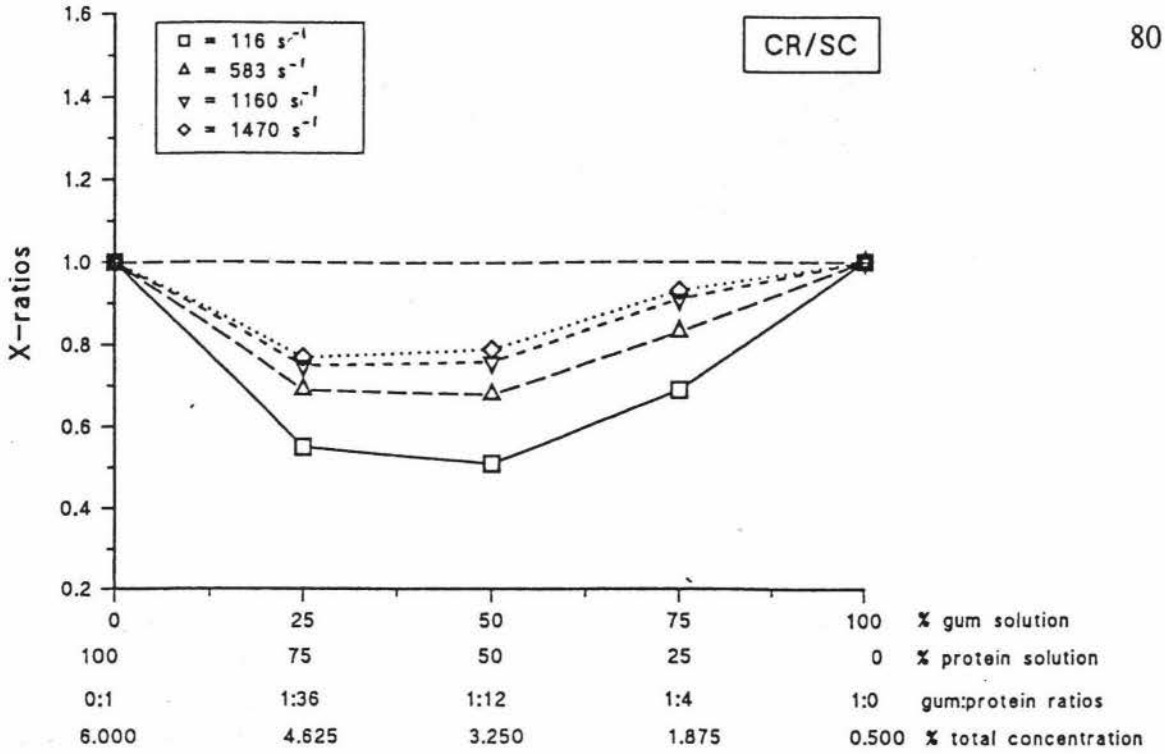


Fig. 6.9a. X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown.

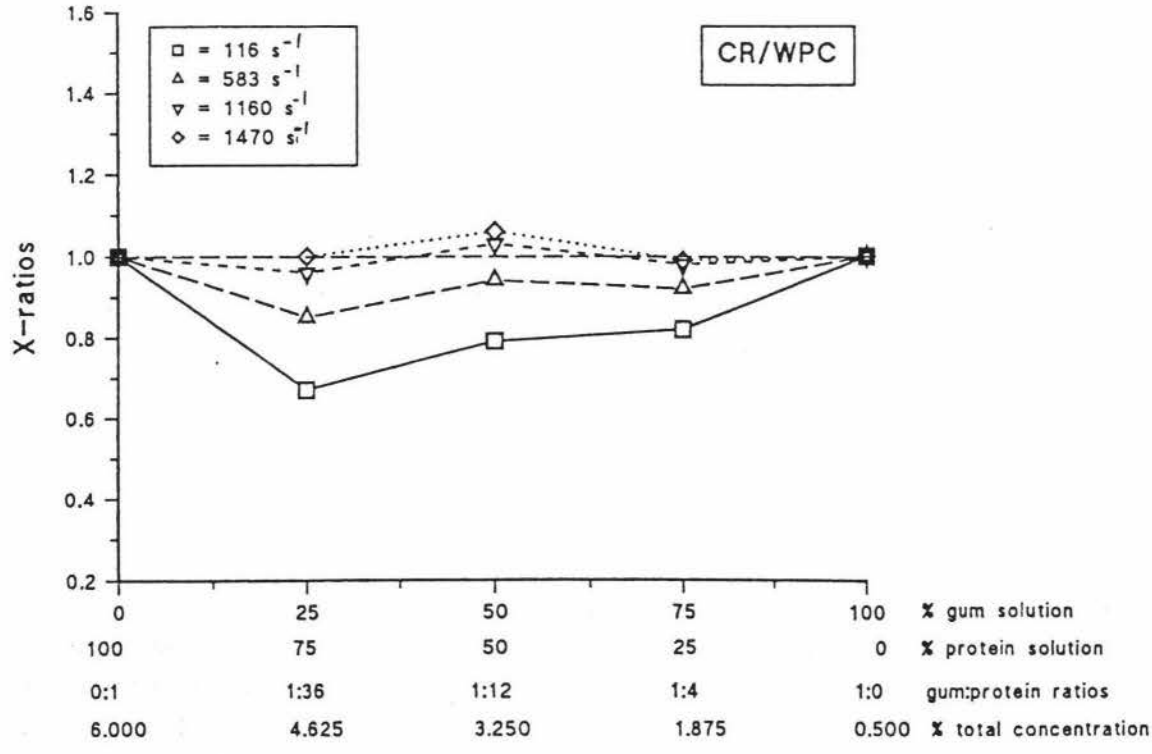


Fig. 6.9b. X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown.

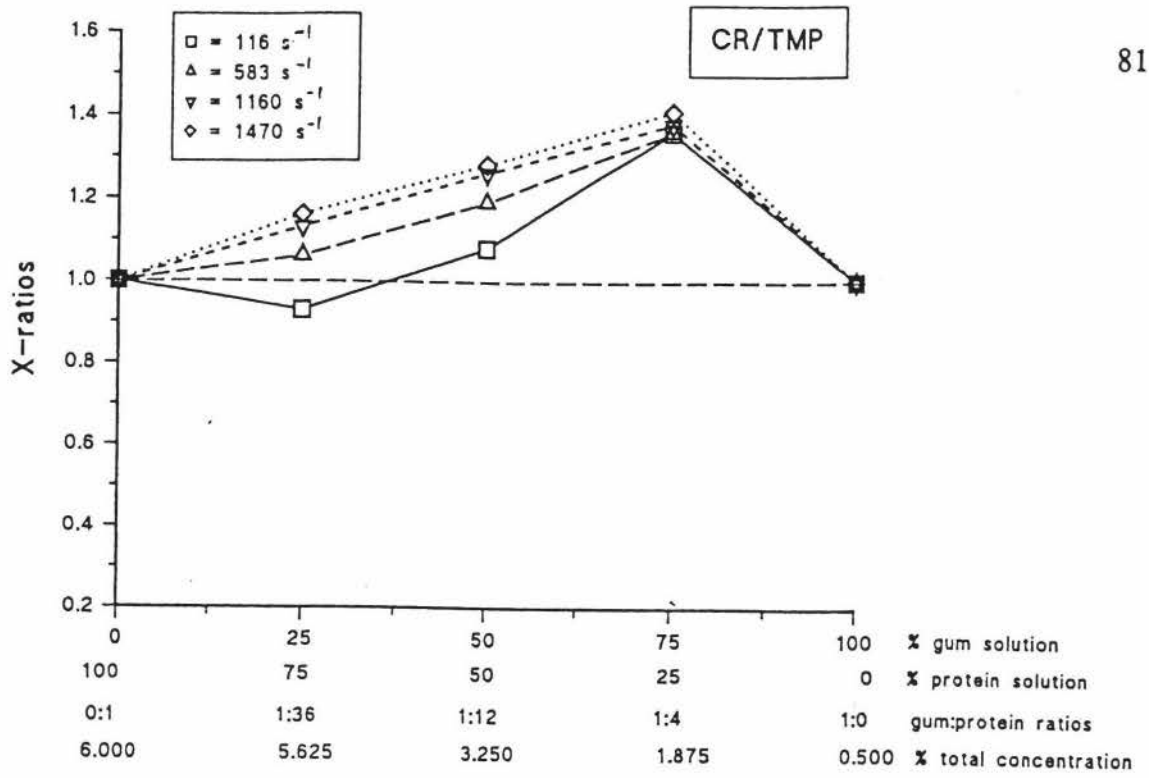


Fig. 6.9c. X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown.

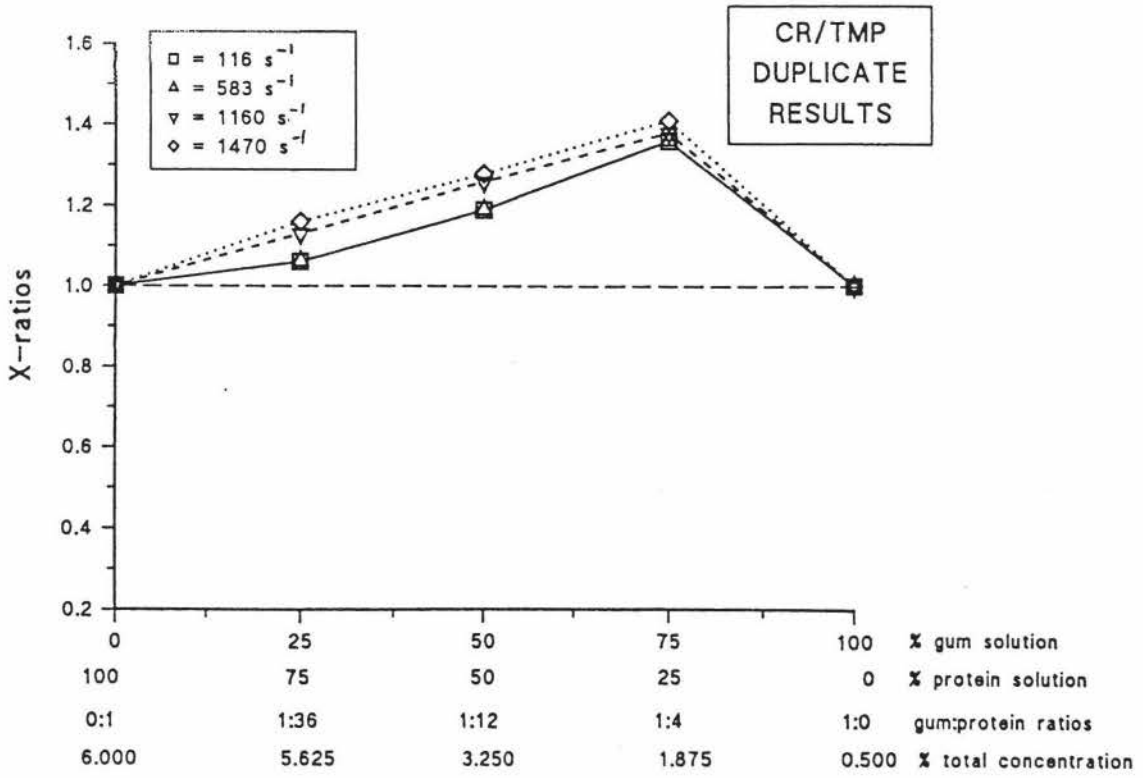


Fig. 6.9d. X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown.

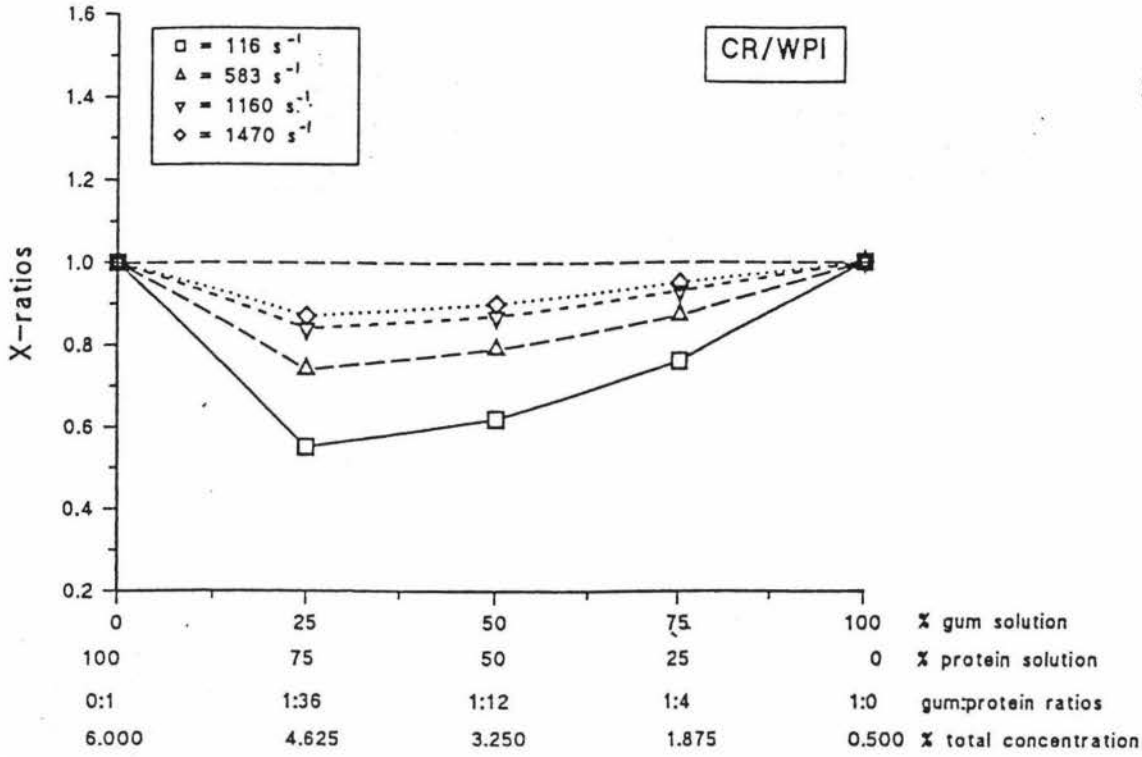


Fig. 6.9e. X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown.

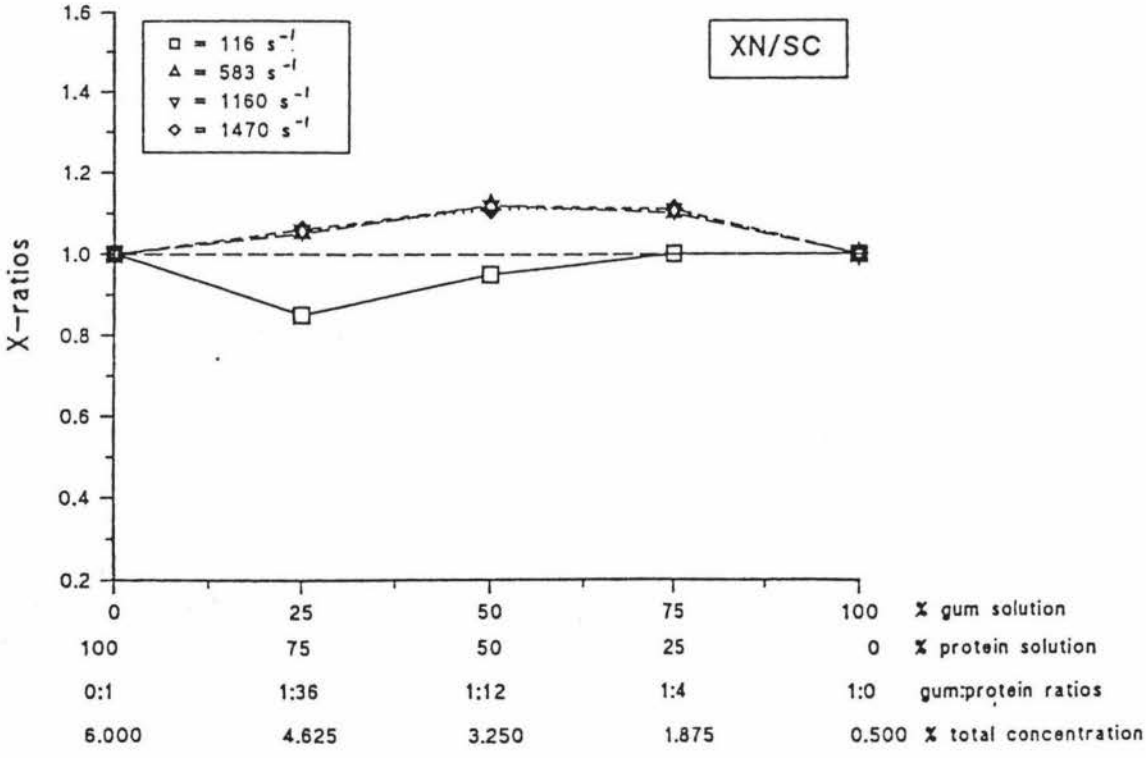


Fig. 6.10a. X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown.

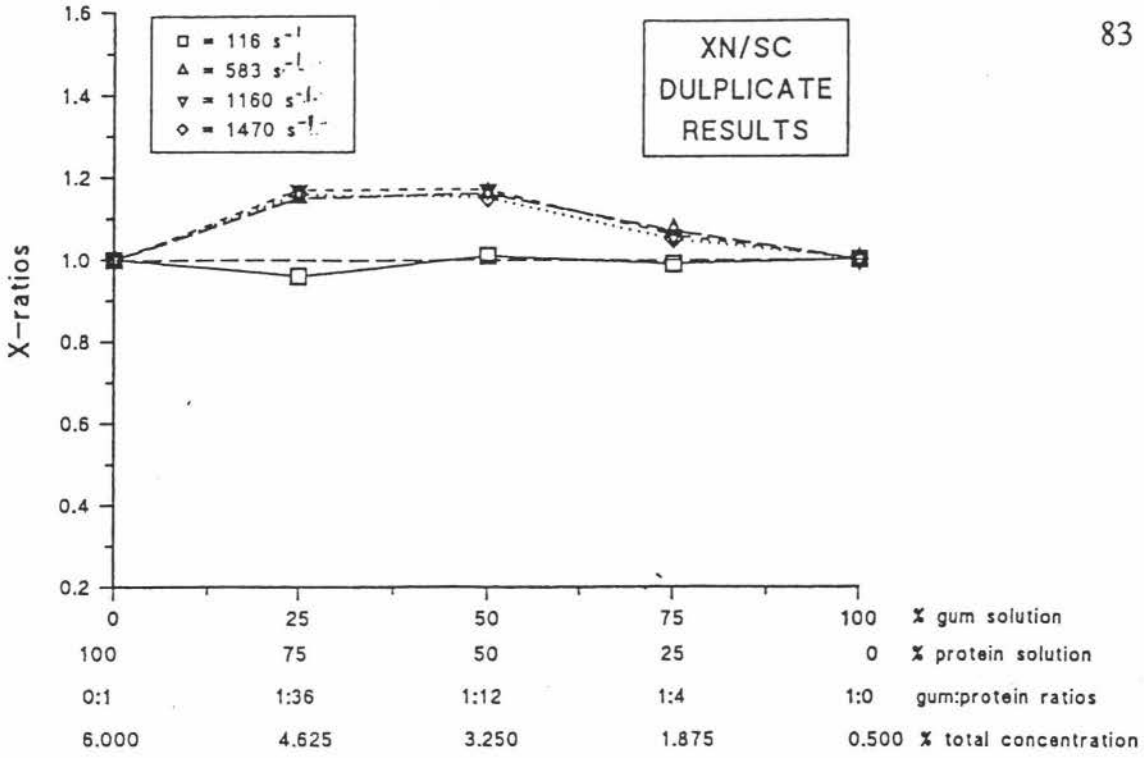


Fig. 6.10b. X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown.

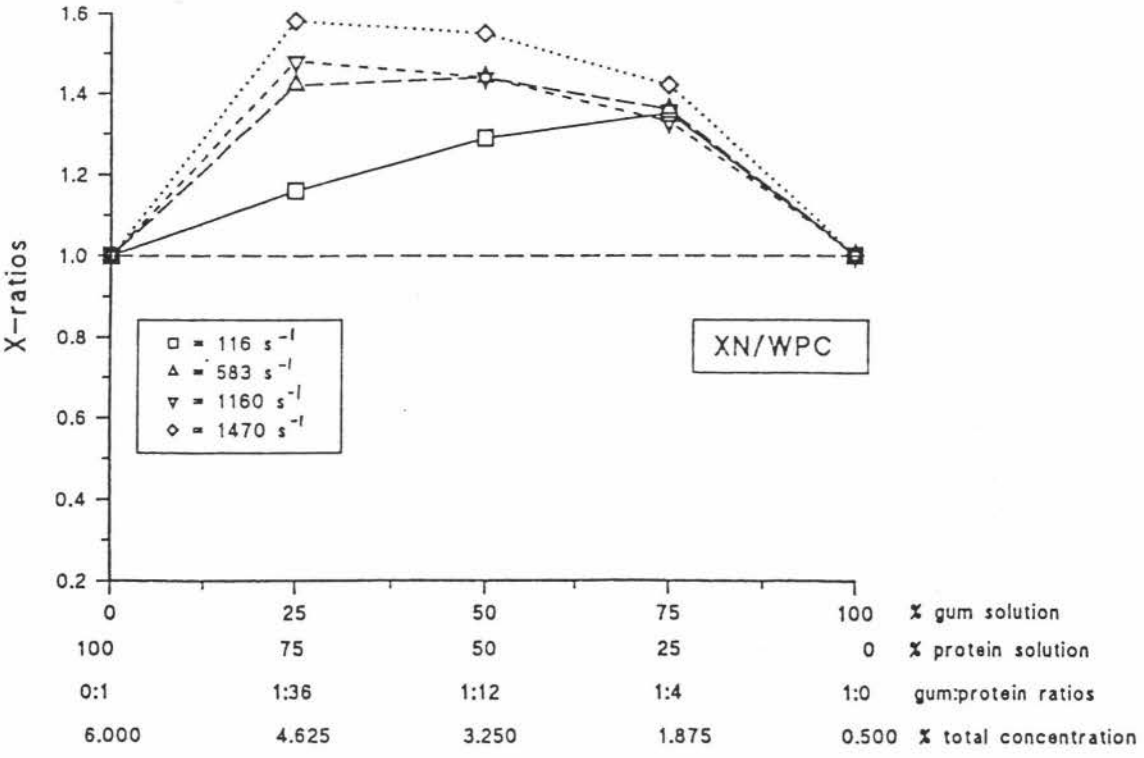


Fig. 6.10c. X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown.

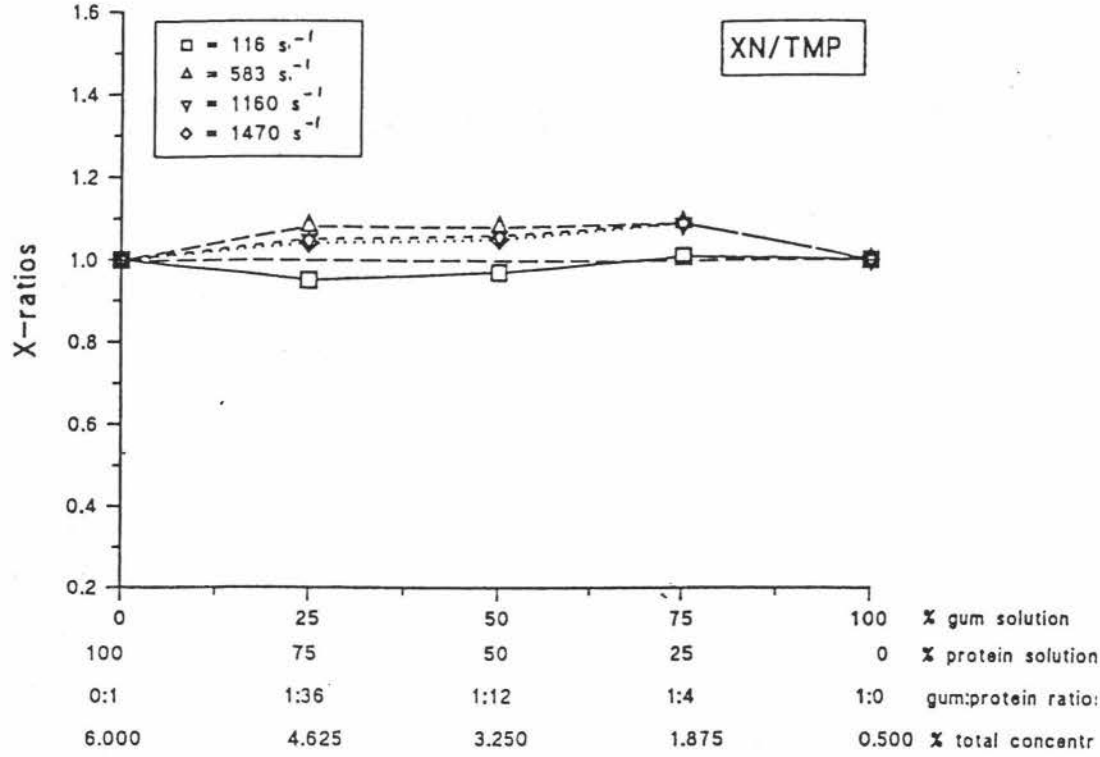


Fig. 6.10d. X-ratio versus mixture composition for mixtures of 0.5 % XN a 6.0 % TMP solutions. Gum : protein ratios and total concentrati are also shown.

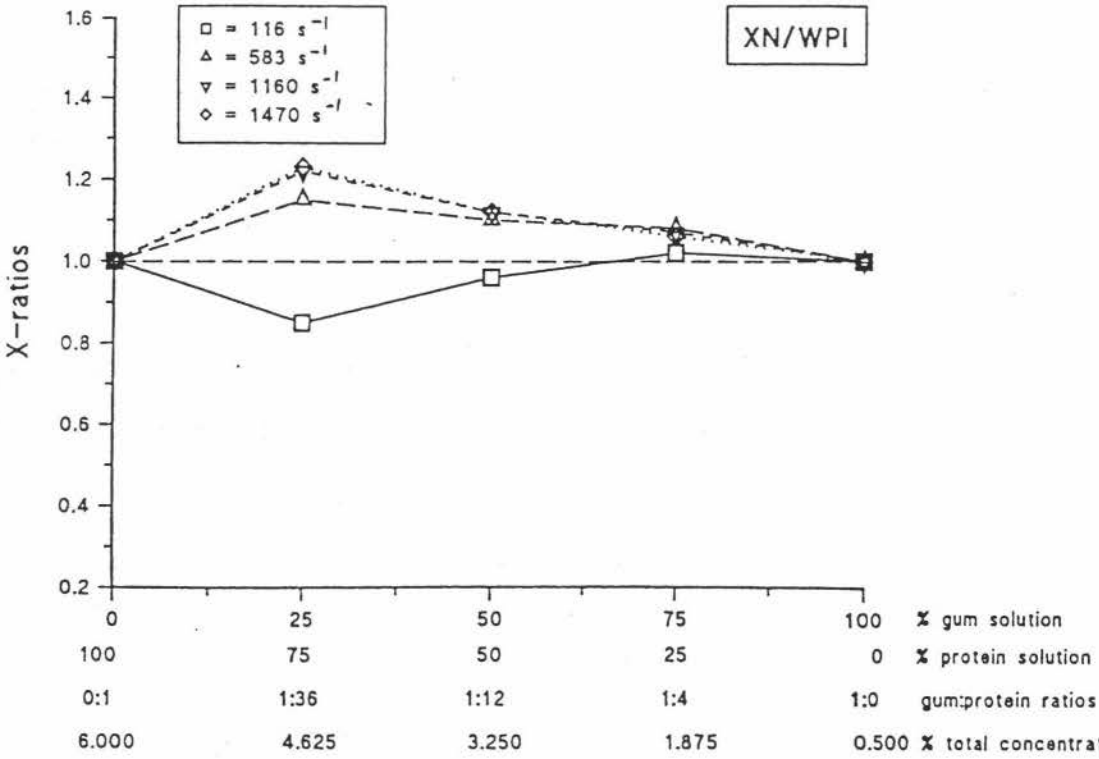


Fig. 6.10e. X-ratio versus mixture composition for mixtures of 0.5 % XN a 6.0 % WPI solutions. Gum : protein ratios and total concentratic are also shown.

available (Norrish (1967)). Using data from Norrish, the expected viscosity of the mixed (i.e. 30%) solution can be predicted using equation (6.1).

Expected viscosity of 30% sucrose solution = b

= (0.5 * 1.695) + (0.5 * 5.164)

= 0.8475 + 2.582

= 3.4295 mPa.s

Norrish's data show that the viscosity of a 30% sucrose solution is actually 2.735 mPa.s. Thus the expected viscosity is 25.4% higher than the true value. The reason for this is made clear by Fig. 6.11 which is a plot of viscosity versus concentration for pure sucrose solutions made using Norrish's data. It can be seen that viscosity varies in a non-linear way with concentration and that, consequently, a viscosity predicted by equation (6.1), which assumes a linear relationship, will be incorrect.

From this it follows that the X-ratio plots for gum-dairy protein mixtures shown in Figs. 6.7 to 6.10 cannot of themselves indicate synergism/antagonism ; they must be compared with X-ratio plots representing the results of mixing 0.5% gum solution with water (as opposed to dairy protein solution). Such plots, which have been computed using equation (6.1) (with P put equal to 0.92 mPa.s, the viscosity of water at 25 °C), equation (6.2) and the viscosity-concentration data presented in Chapter 5, are presented for the four gums studied in Fig. 6.12.

A quantitative measure of gum-protein interaction has been obtained by calculating, for every gum-dairy protein mixture (at each of the four shear rates considered) the following new ratio:

$$\text{X'-ratio} = \frac{(\text{X-ratio})_{g/p} - (\text{X-ratio})_{g/w}}{(\text{X-ratio})_{g/w}} \qquad (6.3)$$

where $(\text{X-ratio})_{g/p}$ = X-ratio for gum-protein mixtures

$(\text{X-ratio})_{g/w}$ = X-ratio for gum-water mixtures

Values of $(\text{X-ratio})_{g/w}$ are tabulated in Appendix 10.

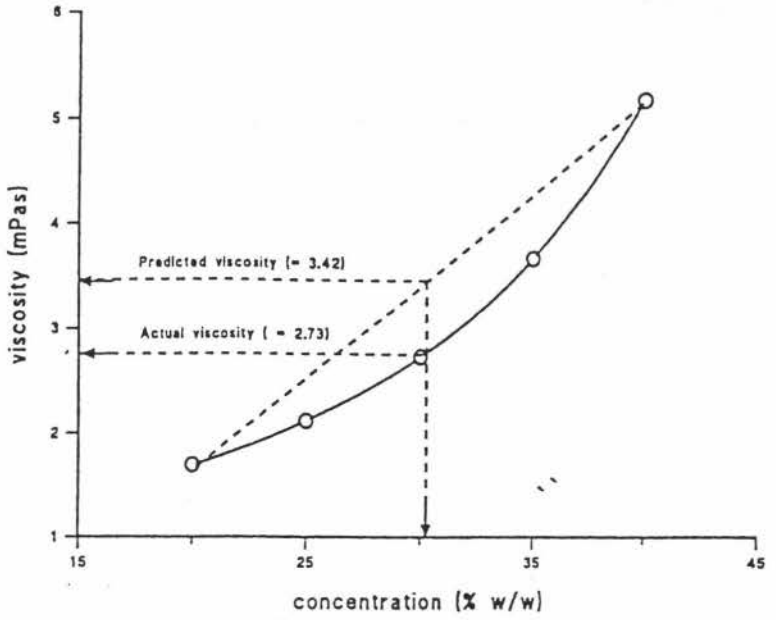


Fig. 6.11 Viscosity versus concentration for aqueous sucrose solutions at 25 °C, showing effect of non-linearity on predicted (expected) viscosity (Data from Norrish (1967)).

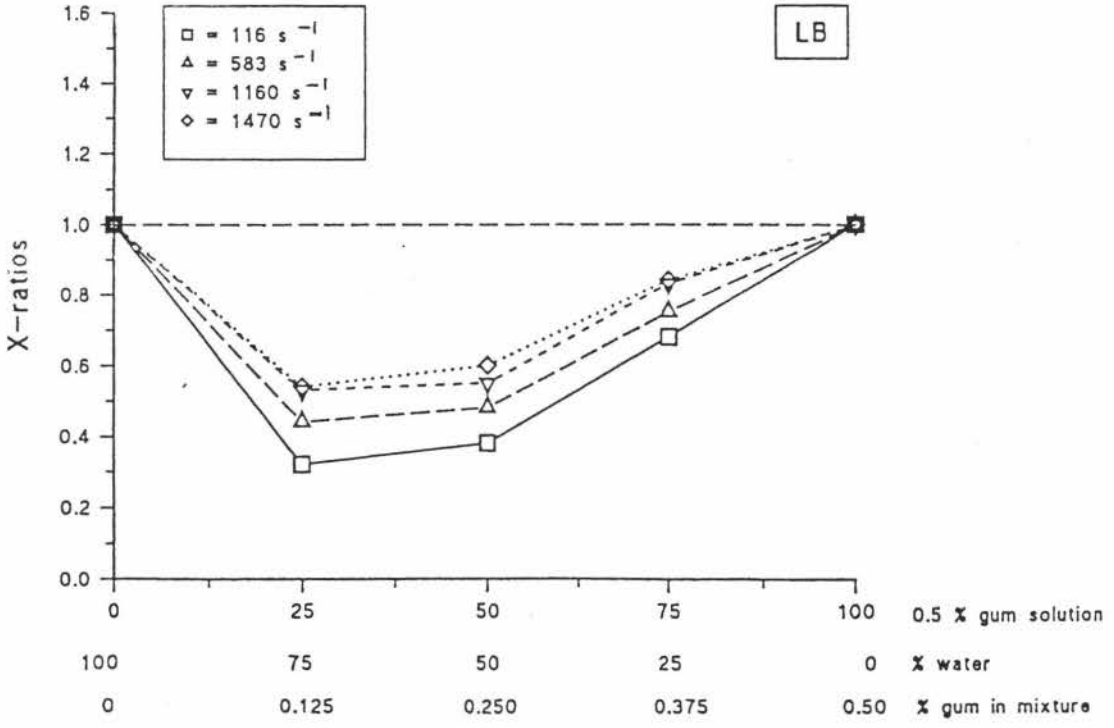


Fig. 6.12a. X-ratio versus mixture composition for mixtures of 0.5 % LB and water.

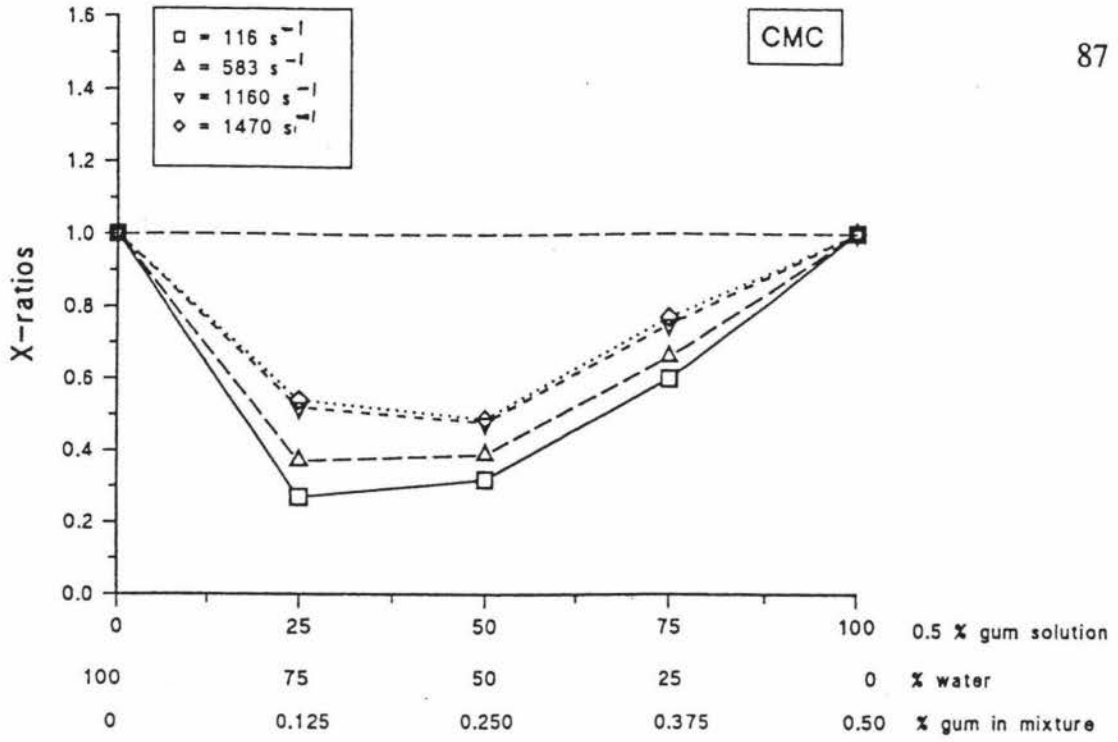


Fig. 6.12b. X-ratio versus composition for mixtures of 0.5 % CMC and water.

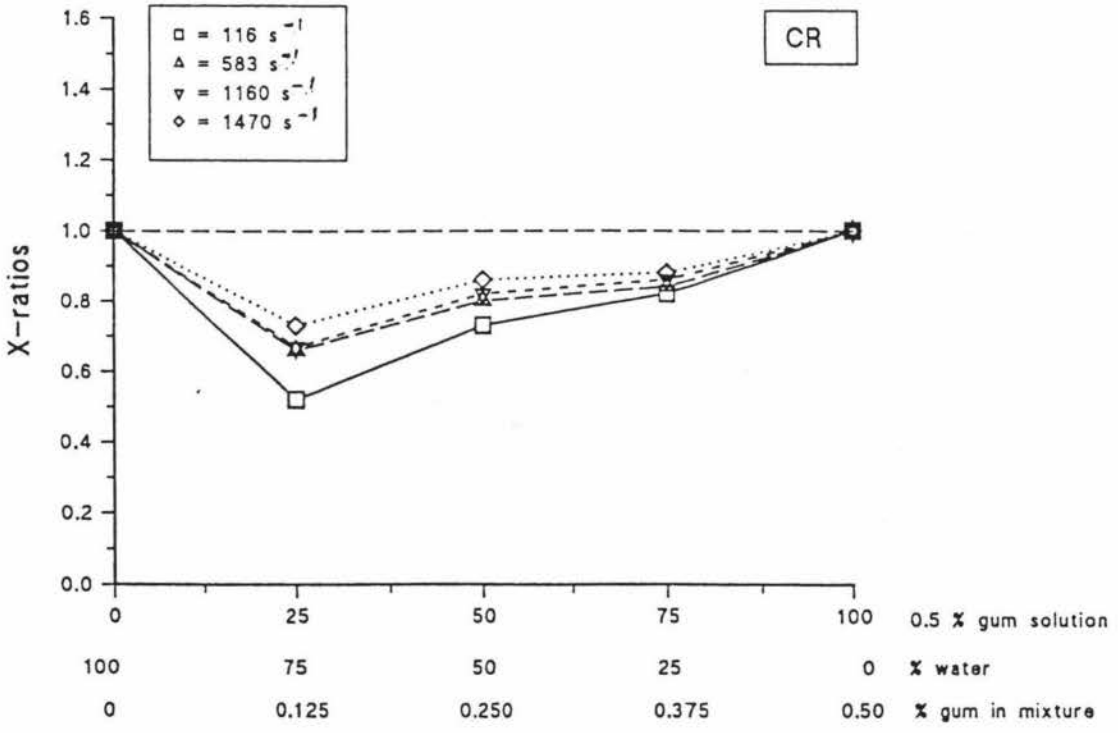


Fig. 6.12c. X-ratio versus mixture composition for mixtures of 0.5 % CR and water.

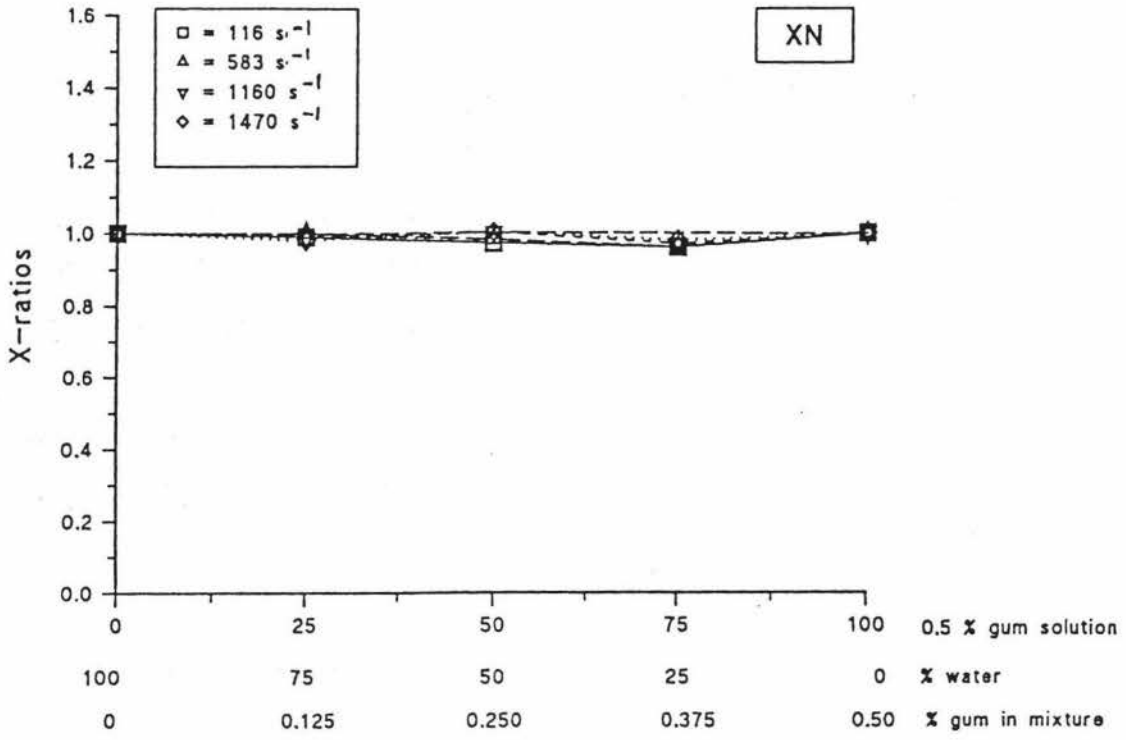


Fig. 6.12d. X-ratio versus mixture composition for mixtures of 0.5 % XN and water.

Now, an X'-ratio greater than zero will indicate synergism, an X'-ratio smaller than zero (i.e. a negative value) will indicate antagonism and an X'-ratio = zero will indicate no interaction. X'-ratio plots for all the gum-dairy protein combinations studied are shown in Figs. 6.13 to 6.16. X'-ratios themselves are tabulated in Appendix 11, Table A11.1 to A11.4.

This development assumes that the variation of viscosity with gum concentration in gum solution-dairy protein solution mixtures is of the same form as for gum-solution water mixtures unless interaction occurs between gum and dairy protein. This development ignores the effect of how the viscosity of the protein solution varies with protein concentration. This is considered reasonable because at the level of protein concentration concerned ($\leq$ 6.0%) the dependence of viscosity upon concentration is very much smaller than is the case for gum solutions.

Sedimentation results for all sixteen gum-dairy protein combinations are presented in Table 6.2. Some duplicate results are included in the table.

6.4 RESULTS

6.4.1 The flow properties of mixed gum-protein solutions

All mixtures were pseudoplastic with n values lower than 1 (Figs. 6.1, 6.2, 6.3 and 6.4). The differences in degree of pseudoplastic behaviour of these mixtures are described by the n values shown in the figures. n value decreased, and k value increased, as the proportion of gum solution in the mixture increased. These results are not surprising in view of the pseudoplastic and relatively viscous nature of the pure gum solutions, and the low viscosity Newtonian behaviour of the dairy protein solutions.

At a shear rate of 116 s^{-1} ,there was an exponential increase in the apparent viscosity of most mixed solutions as the ratio of gum solution in the mixture increased. The apparent viscosity tended to increase more linearly at shear rates higher than 116 s^{-1}. The influence of shear rate on apparent viscosity decreased as shear rate increased.

It was found that the apparent viscosities of XN/SC, XN/TMP and XN/WPI mixtures increased significantly with increase in the gum solution : protein solution ratio at the shear rate of 116 s^{-1}, but were only slightly dependent on this ratio at the shear rate of 1470 s^{-1} (Figs. 6.4a, b, d and e). All XN/protein mixed solutions had a high degree of pseudoplasticity, shown by low n values. This was most likely due to the high degree of pseudoplasticity of the pure xanthan gum solution.

The apparent viscosity of the mixed solution was higher than that of the pure gum solution (at a given shear rate) only in the cases of 75:25 gum solution : dairy protein solution mixtures of CR/TMP (Figs. 6.3c and d) and XN/WPC (Fig. 6.4c).

6.4.2 Synergism and antagonism in mixed solutions

Of the sixteen gum solution-dairy protein solution mixtures studied, seven exhibited synergism at all mixture compositions and all shear rates. These were: all four CMC/dairy protein combinations (Fig. 6.14), CR/WPC (Fig. 6.15b), CR/TMP (Figs.

6.15c and d), XN/WPC (Fig. 6.16c). In the cases of CMC/all dairy proteins, CR/WPC and CR/TMP there is no obvious relationship between the extent of synergism (the X'-ratio) and shear rate. In the case of XN/WPC the X'-ratio increases with increasing shear rate. The X'-ratio was highest at the gum solution : protein solution ratio of 50:50 for CMC/all dairy proteins, but at the ratio of 25:75 for CR/WPC, CR/TMP and XN/WPC. The greatest degree of synergism (X'-ratio = 1.18) was exhibited by CMC/TMP at a solution ratio of 50:50 and a shear rate of 583 s^{-1} (Fig. 6.14c).

Five gum-protein combinations exhibited synergism at shear rates higher than 583 s^{-1} and at all mixture compositions: LB/WPC (Fig. 6.13c), CR/WPI (Fig. 6.15e), XN/SC, XN/TMP, XN/WPI (Figs. 6.16a and b, 6.16d and 6.16e). The X'-ratio was highest at a solution ratio of 50:50 for LB/WPC and at a ratio of 25:75 for XN/WPI. The X'-ratio was substantially independent of mixture composition for XN/SC and XN/TMP. In the case of CR/WPI these was some dependence of the X'-ratio on shear rate; for the other four gum-protein combinations the X'-ratio was essentially independent of shear rate. At the lowest shear rate of 116 s^{-1} the X'-ratio varied slightly about zero for all five combinations as mixture composition changed.

LB/SC (Fig. 6.13a) exhibited synergism at solution ratios of 25:75 and 50:50, but no interaction at the ratio of 75:25. The X'-ratio was independent of shear rate. LB/TMP (Fig. 6.13d) exhibited synergism at the ratios of 25:75 and 50:50, but slight antagonism at the ratio of 75:25. The X'-ratio was slightly dependent on shear rate. CR/SC (Fig. 6.15a) exhibited a mixture of synergism and antagonism depending on the mixture composition and shear rate.

Only one gum-protein combination, LB/WPI (Fig. 6.13e), exhibited antagonism at virtually all mixture compositions and shear rates. The X'-ratios were, however, only slightly less than zero.

Figs. 6.13a and b (LB/SC), Figs 6.14c and d (CMC/TMP), Figs. 6.15c and d (CR/TMP) and Fig. 6.16a and b (XN/SC) show that duplicate results were in good agreement in all cases. This allows some confidence to be placed in the over-all results.

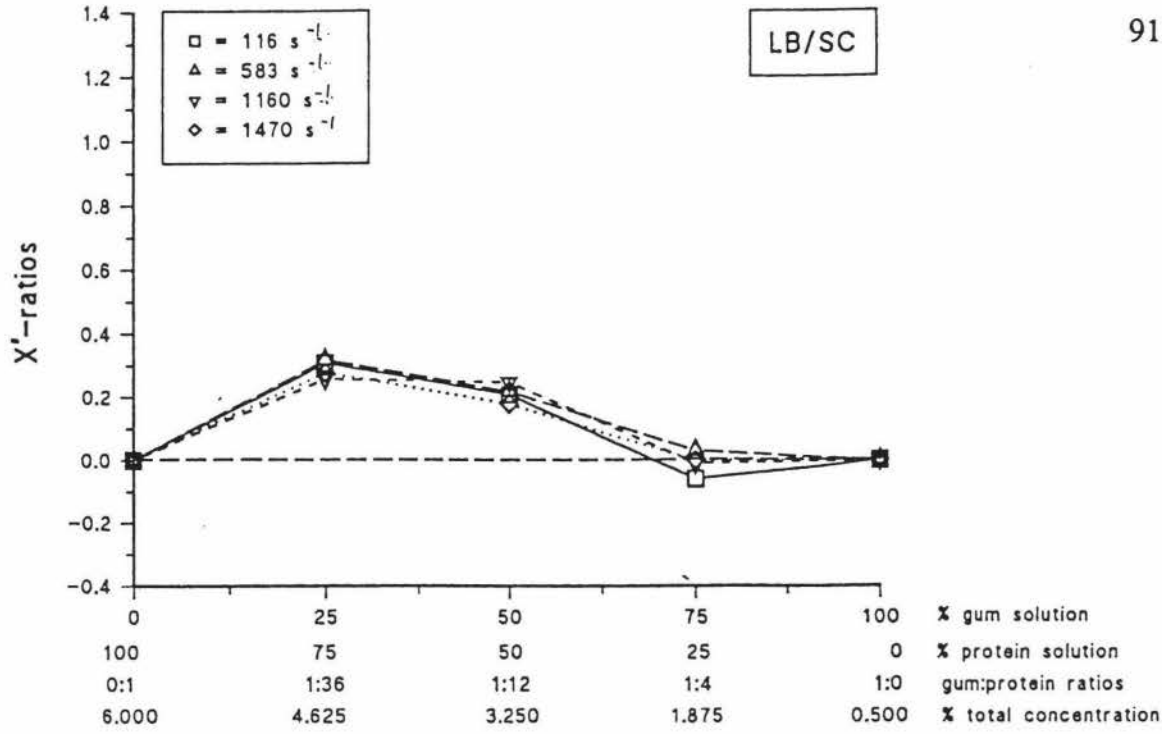


Fig. 6.13a. X'-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown.

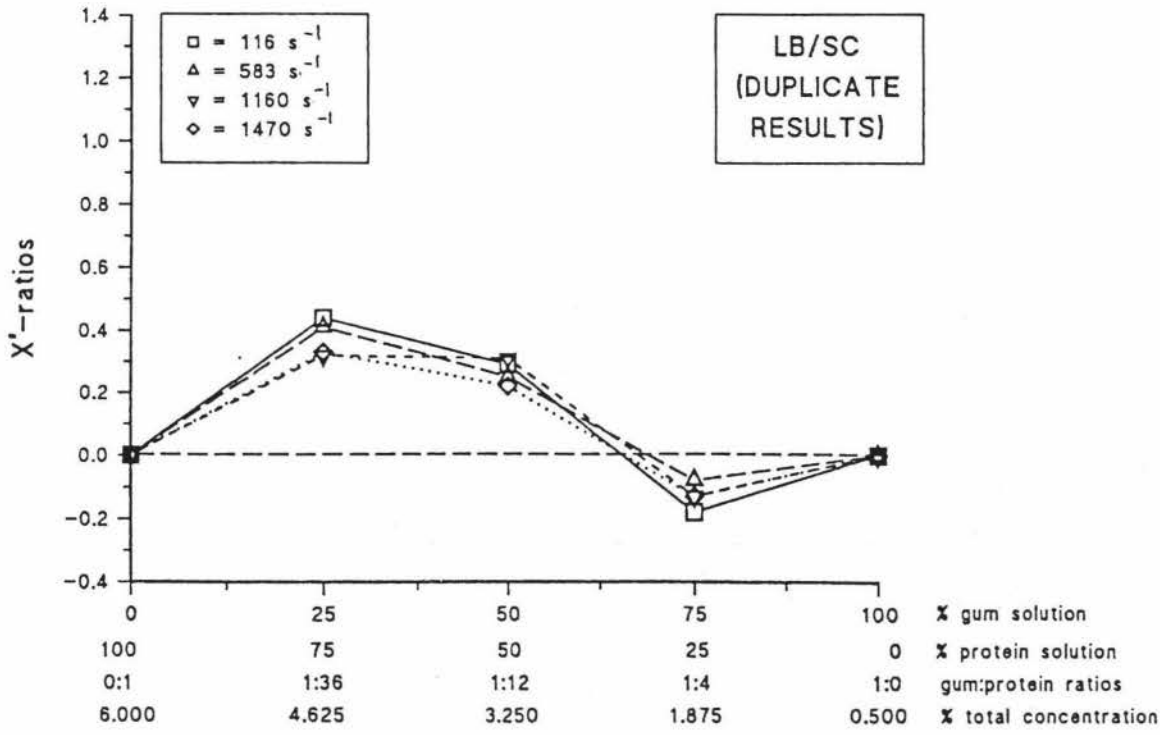


Fig. 6.13b. X'-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown.

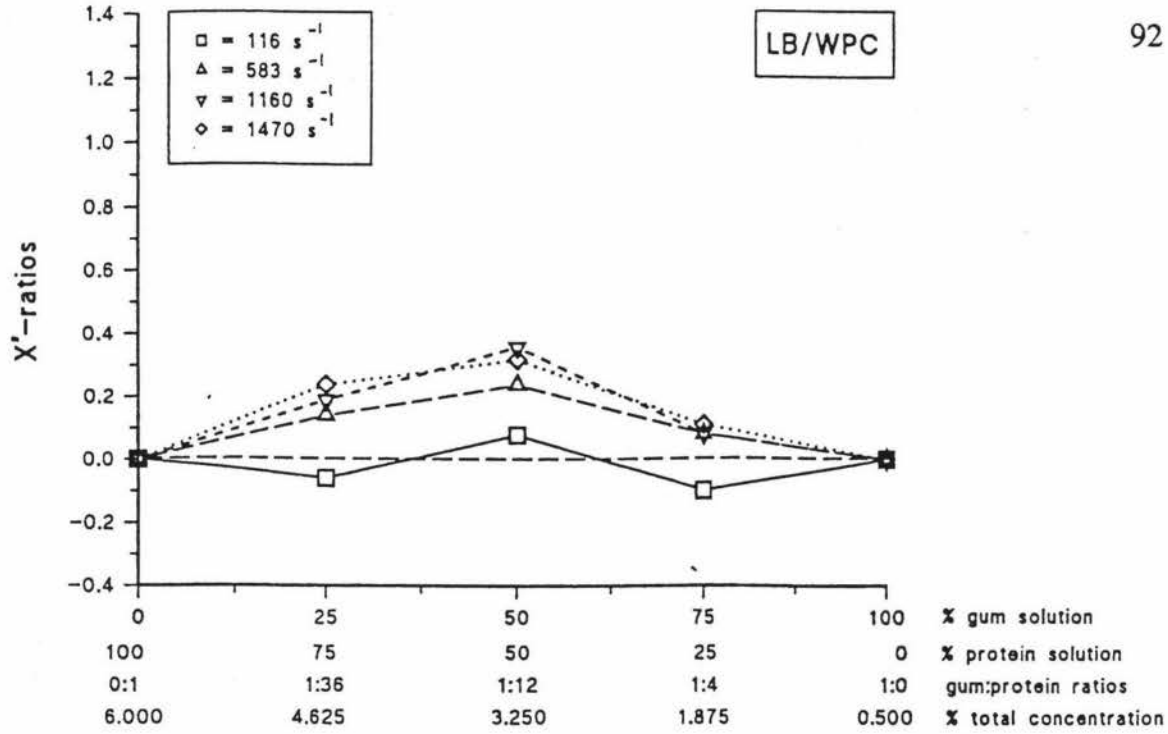


Fig. 6.13c. X'-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown.

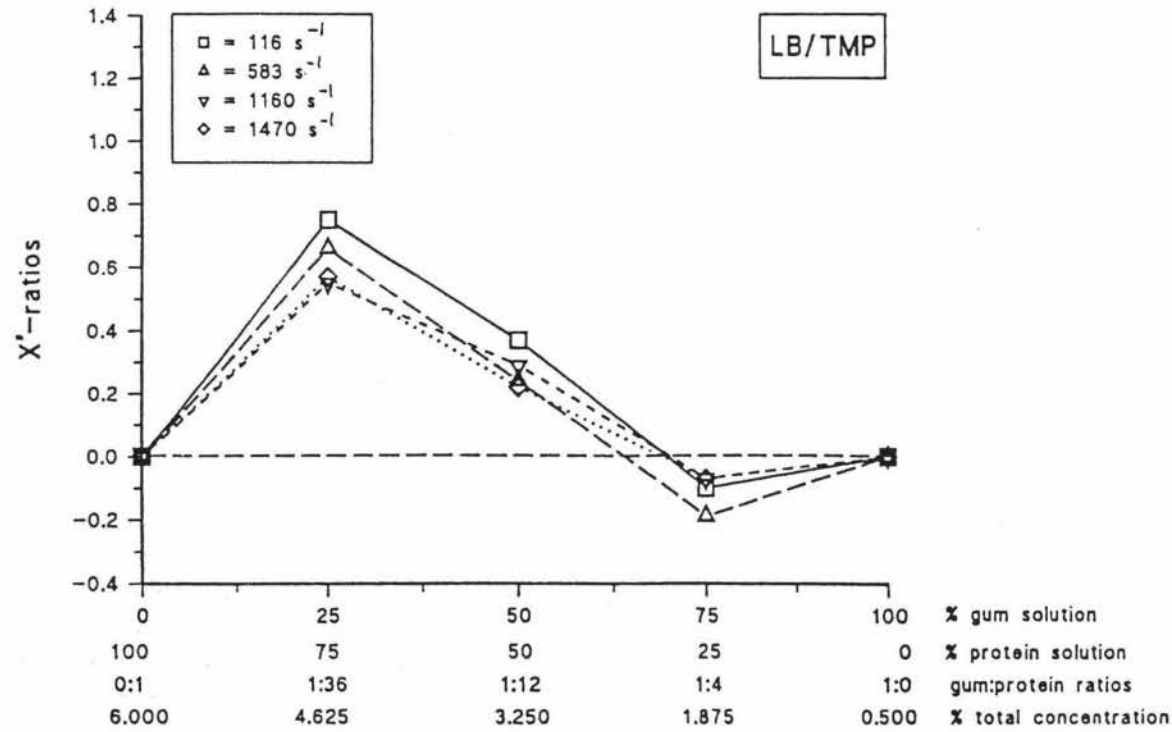


Fig. 6.13d. X'-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown.

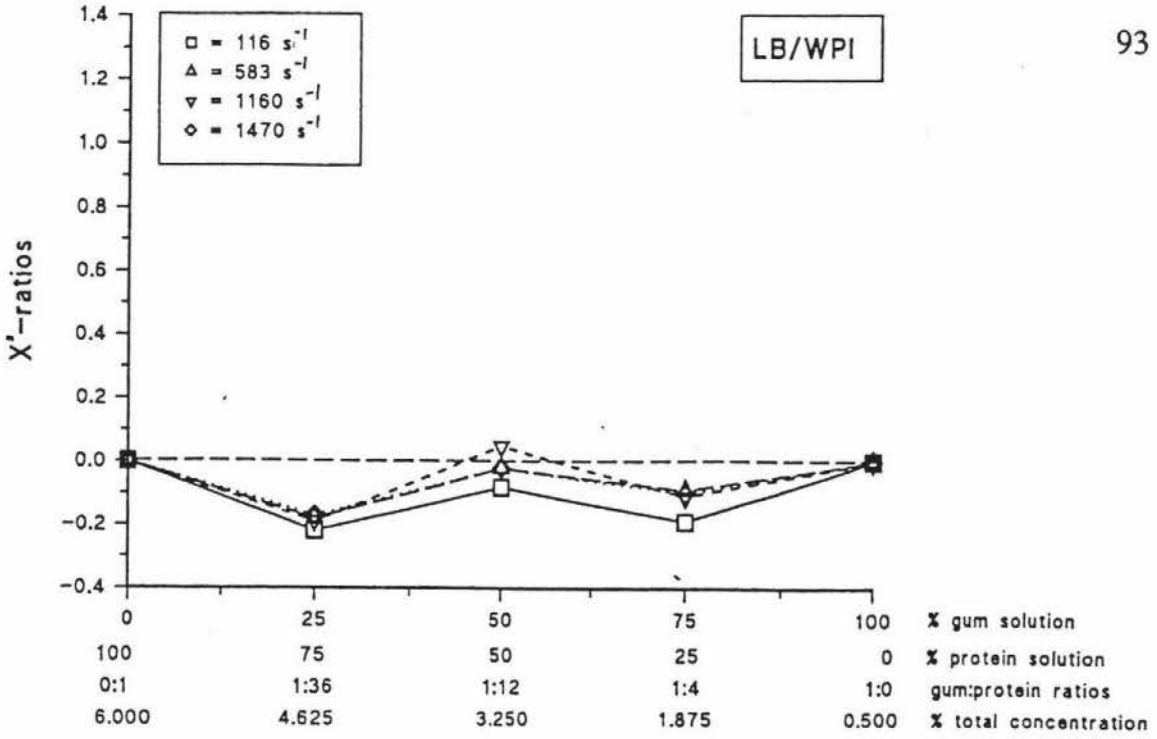


Fig. 6.13e. X'-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown.

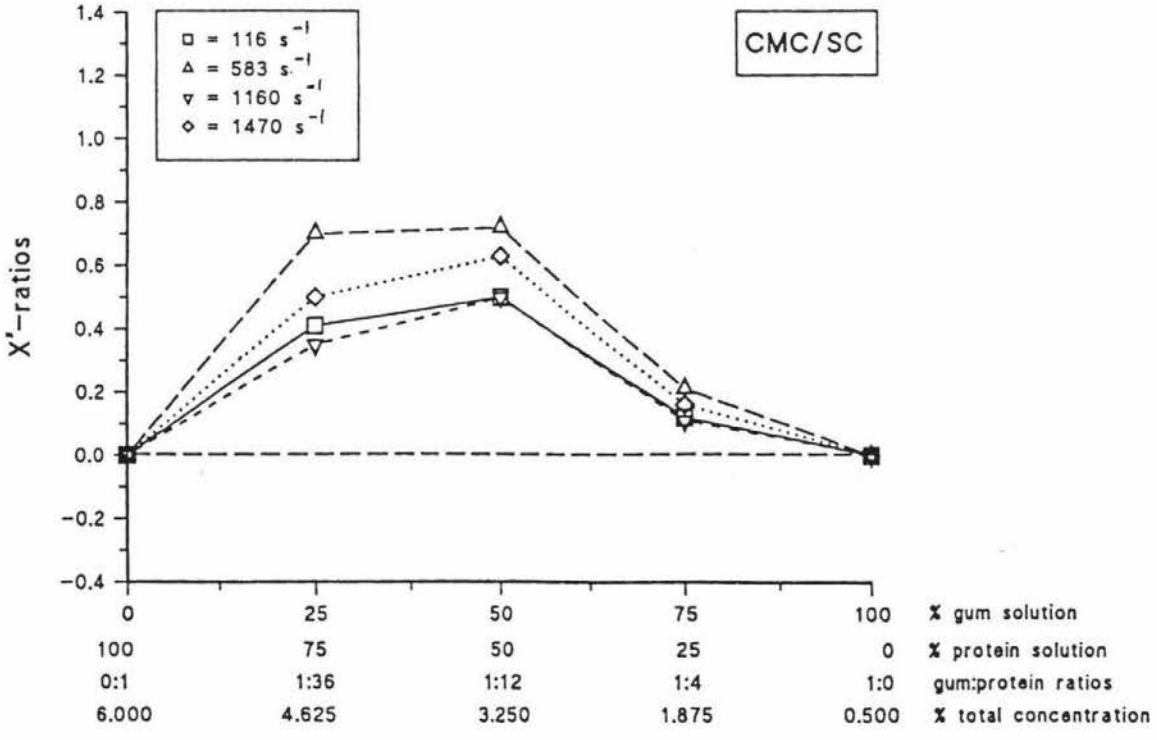


Fig. 6.14a. X'-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown.

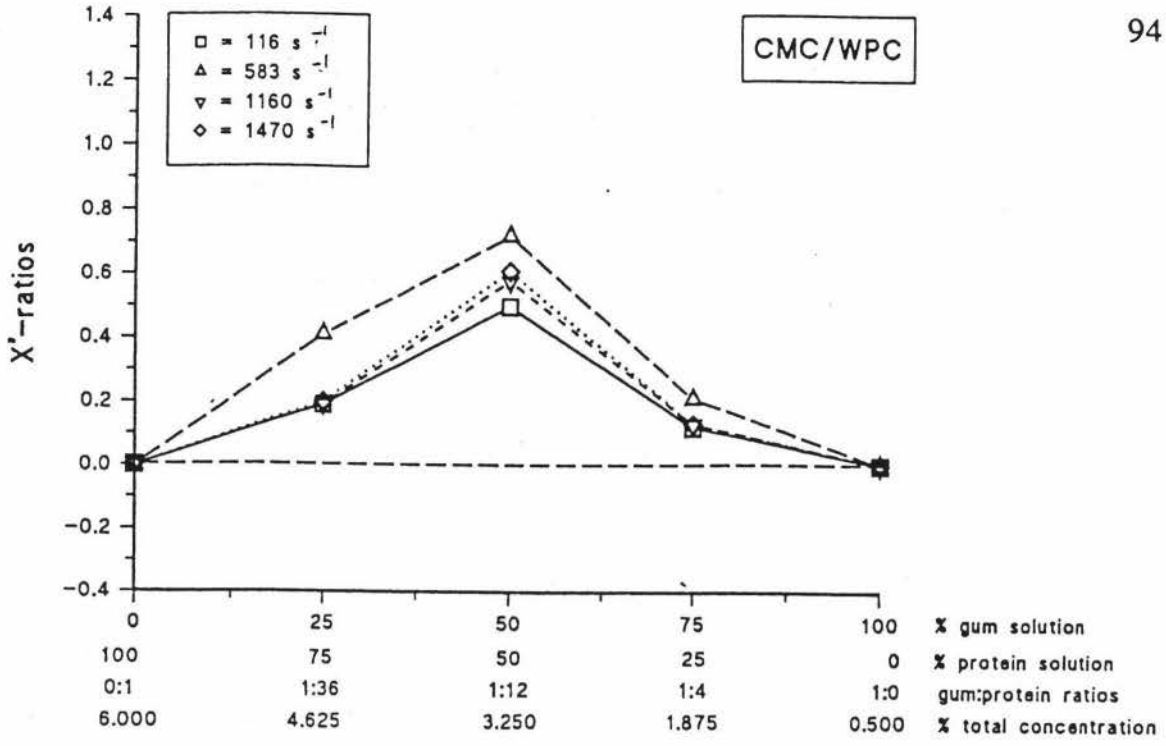


Fig. 6.14b. X'-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown.

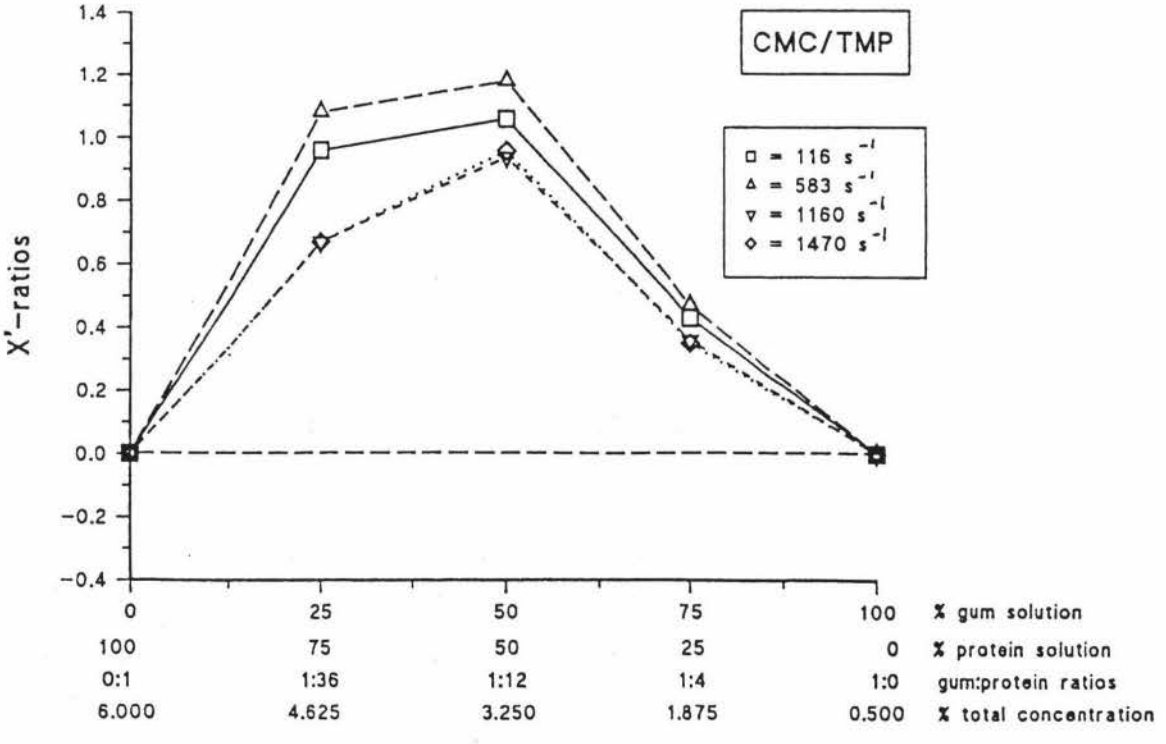


Fig. 6.14c. X'-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown.

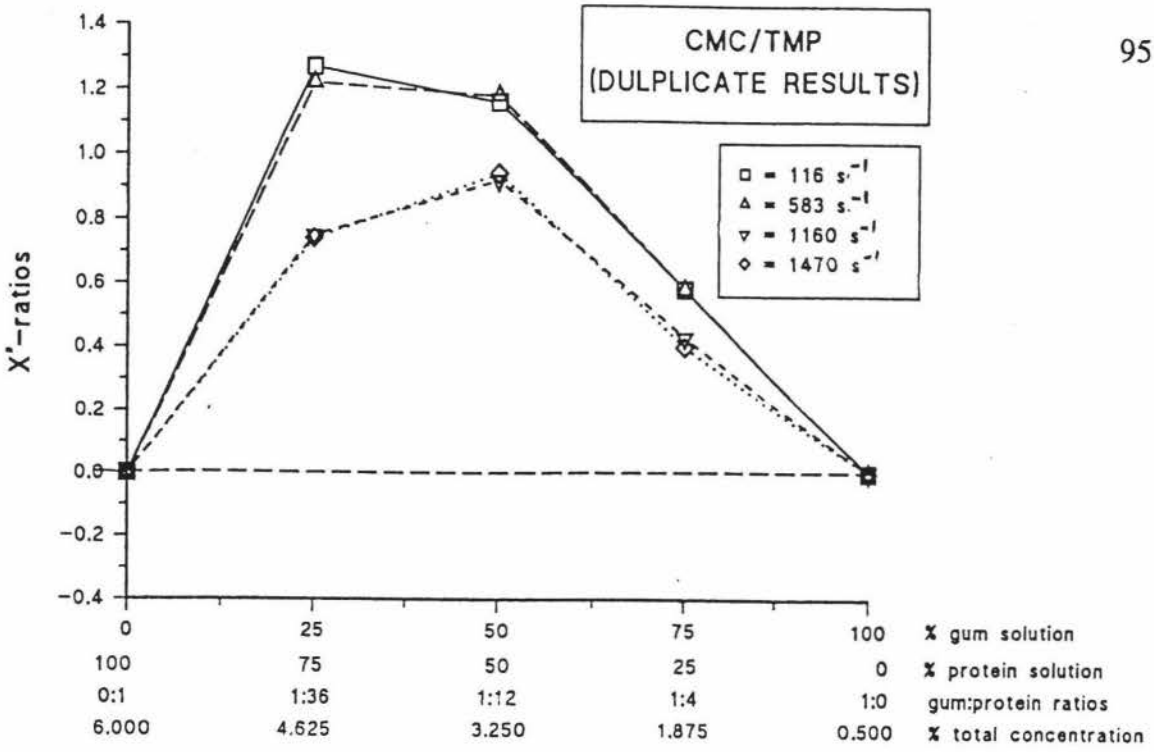


Fig. 6.14d. X'-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown.

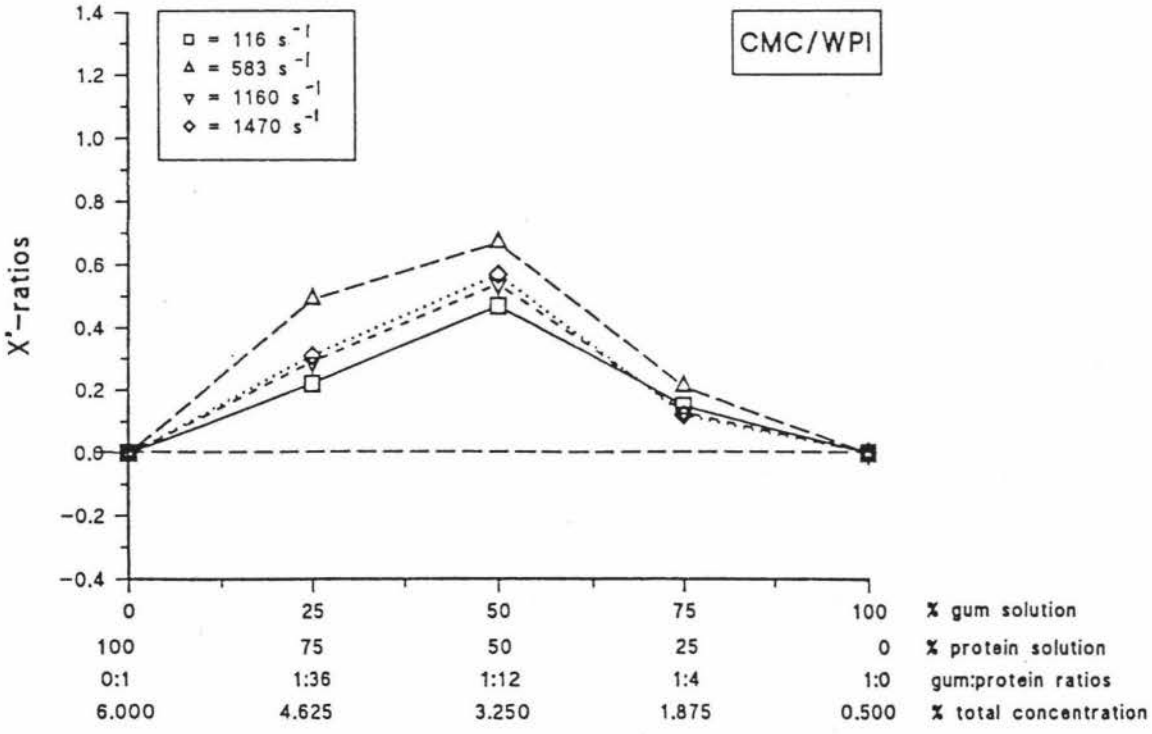


Fig. 6.14e. X'-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown.

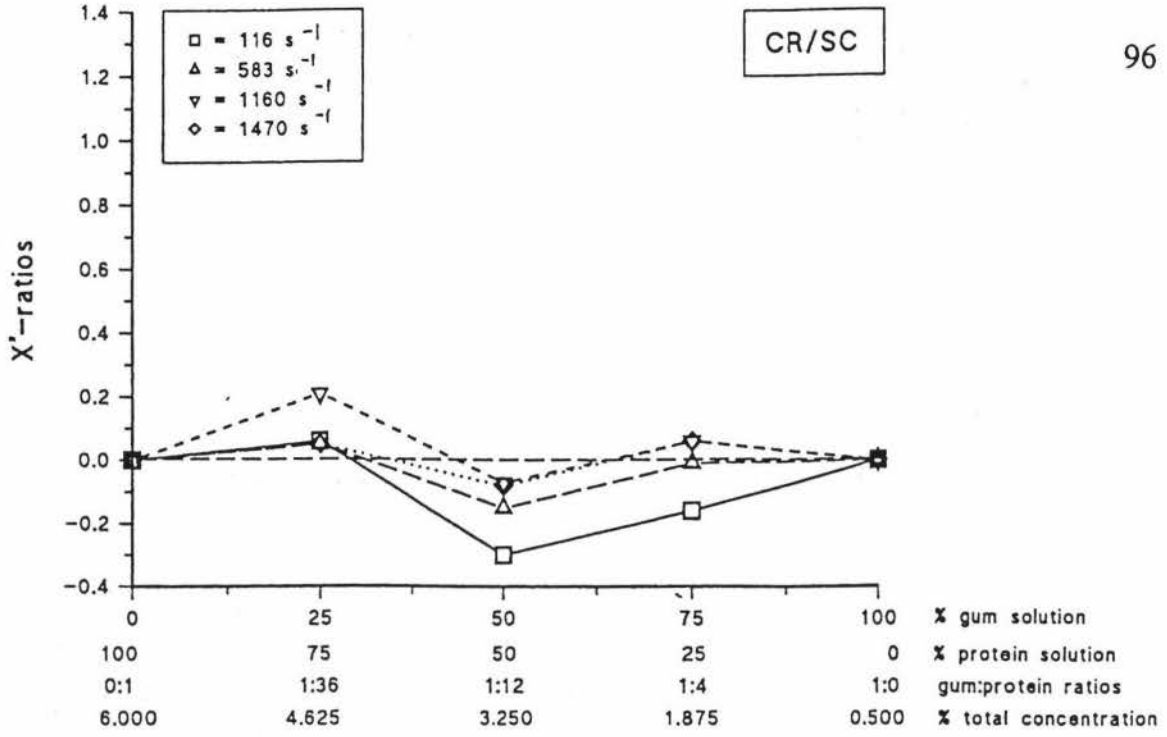


Fig. 6.15a. X'-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown.

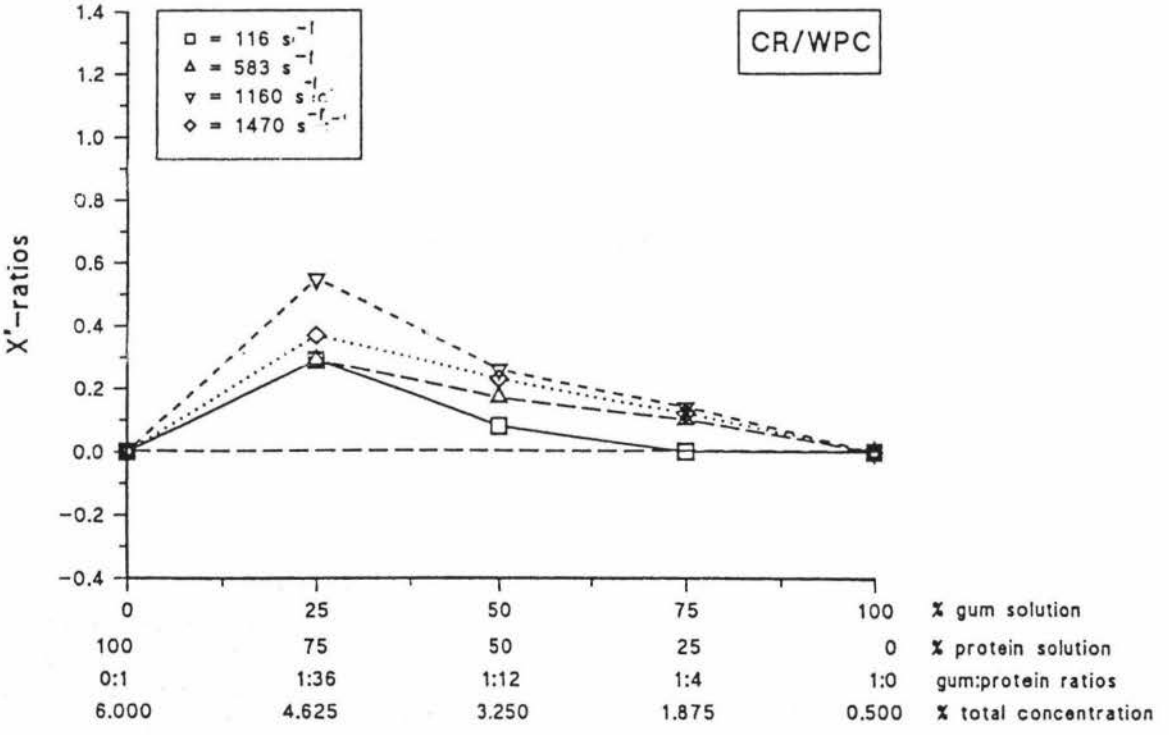


Fig. 6.15b. X'-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown.

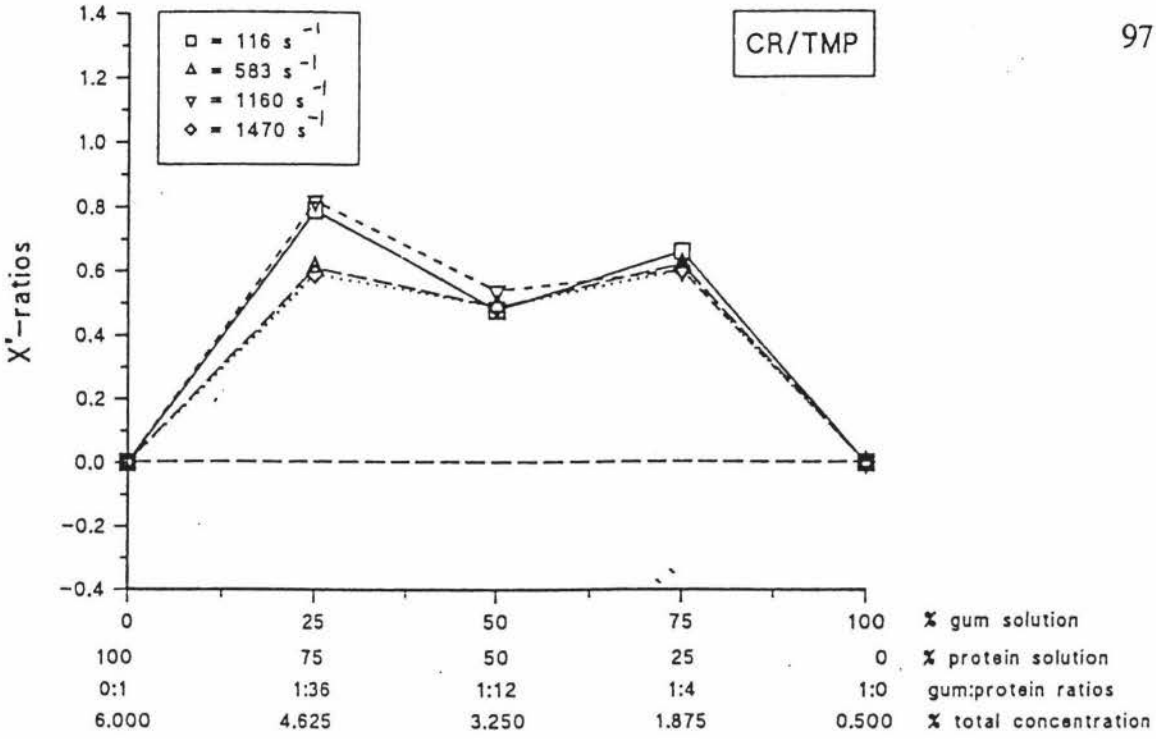


Fig. 6.15c. X'-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown.

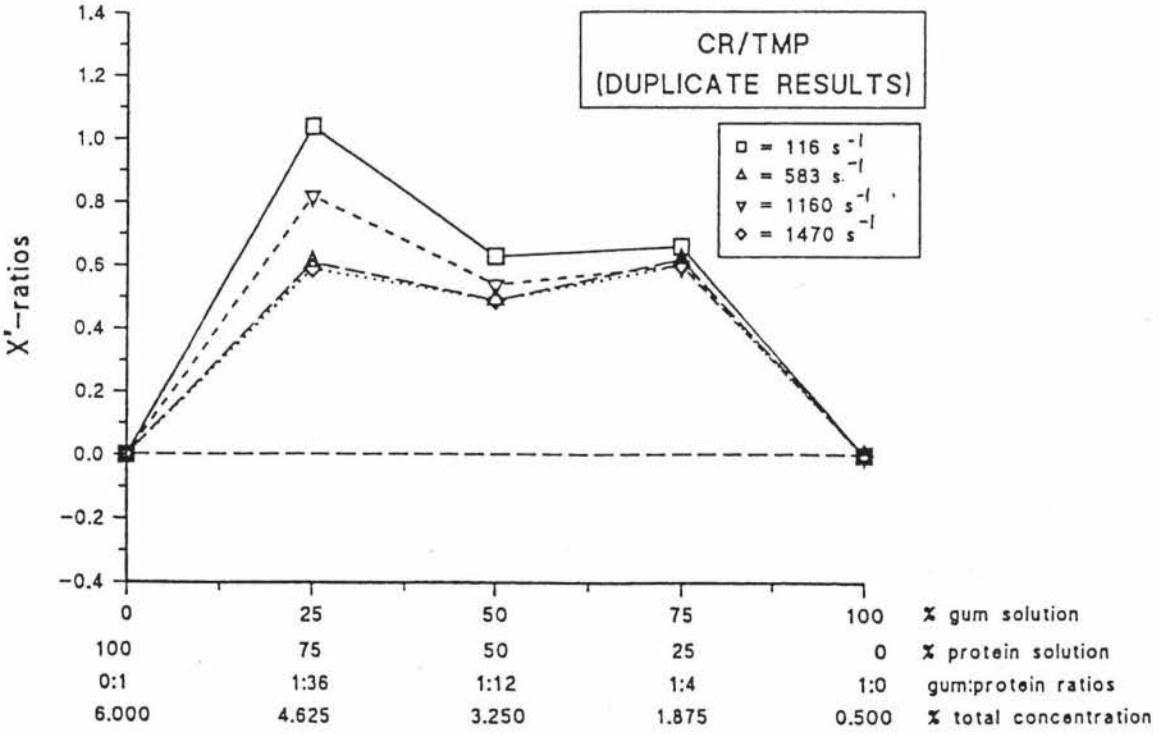


Fig. 6.15d. X'-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown.

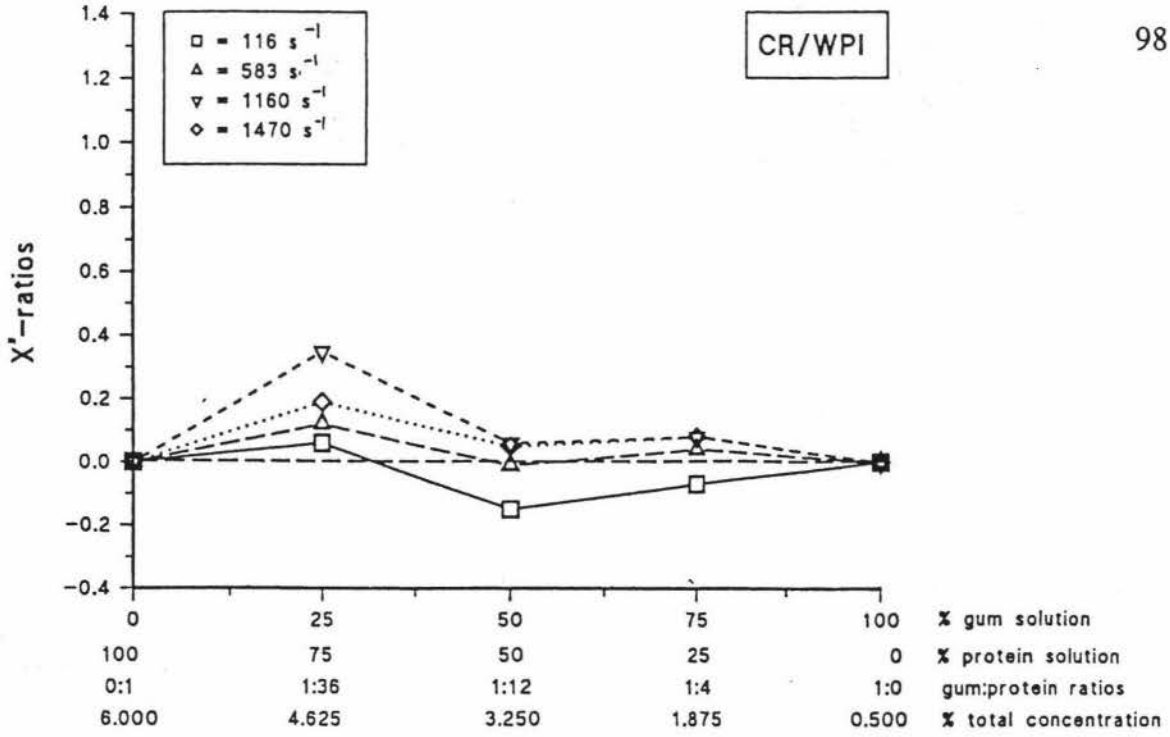


Fig. 6.15e. X'-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown.

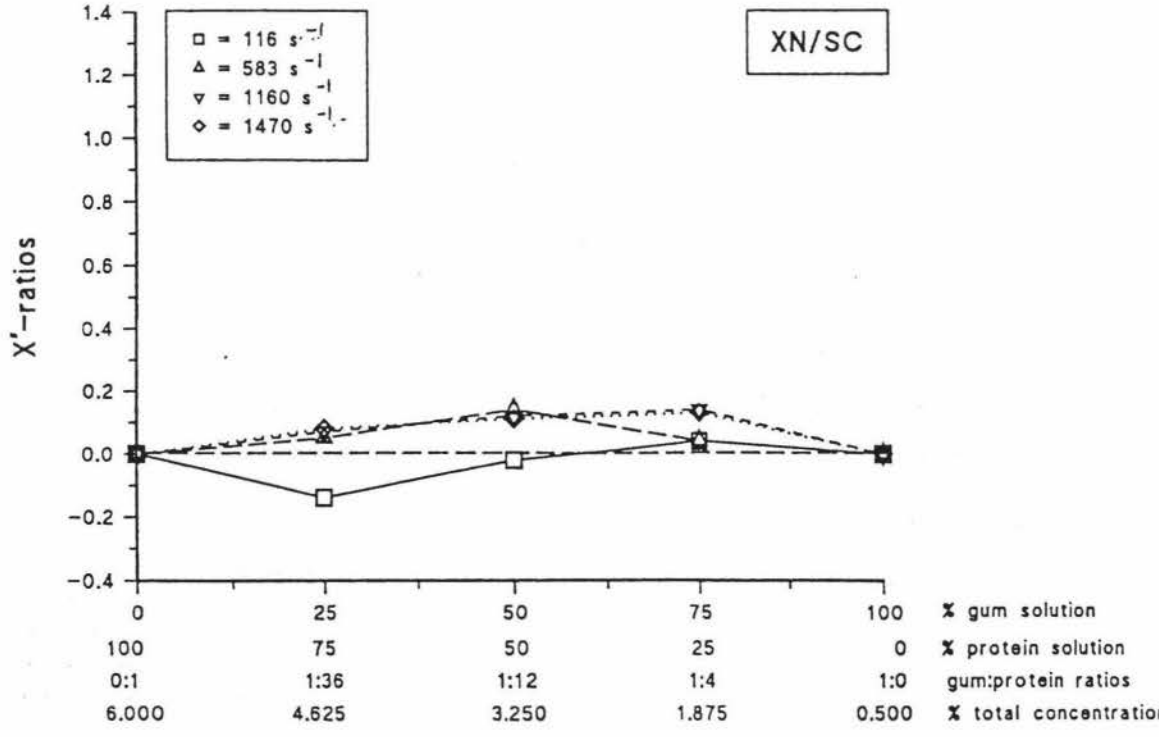


Fig. 6.16a. X'-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown.

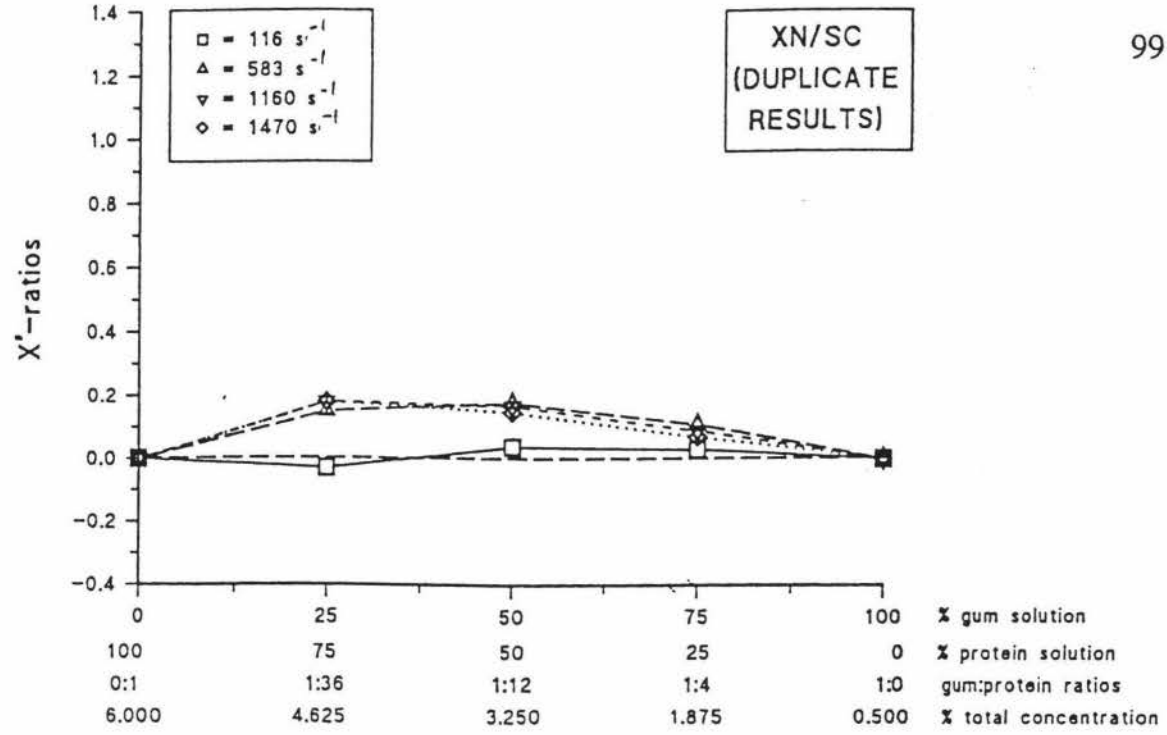


Fig. 6.16b. X'-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions. Gum : protein ratios and total concentrations are also shown.

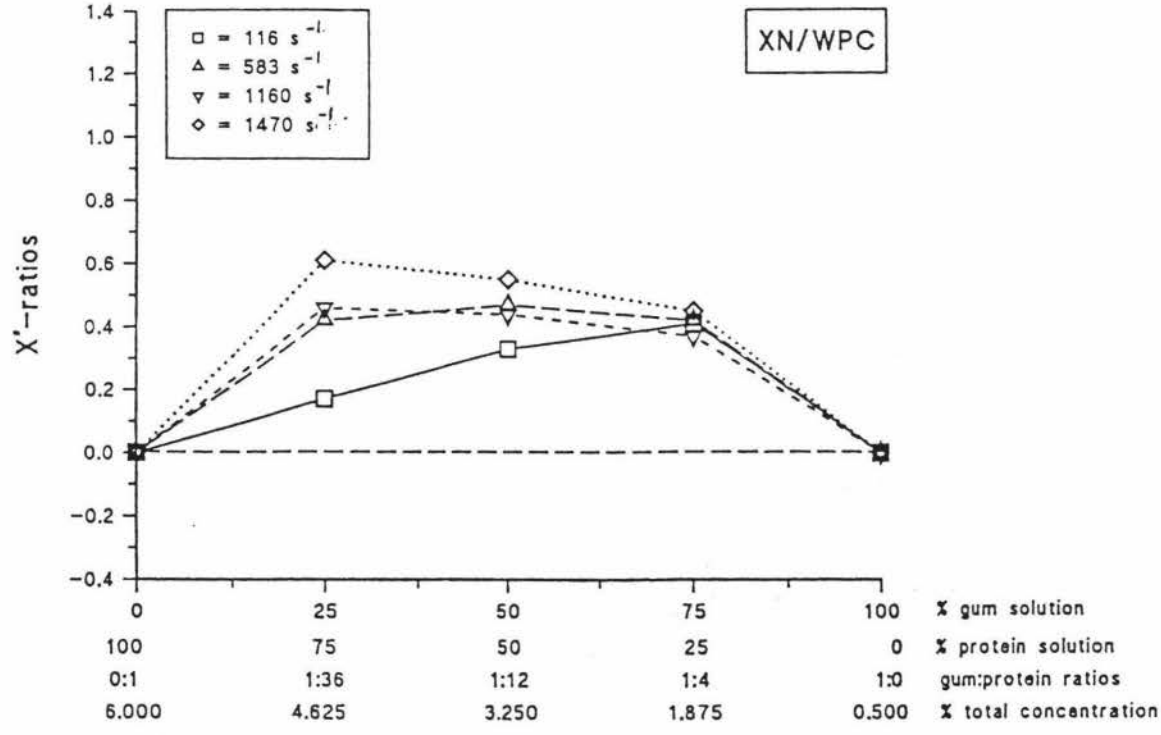


Fig. 6.16c. X'-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPC solutions. Gum : protein ratios and total concentrations are also shown.

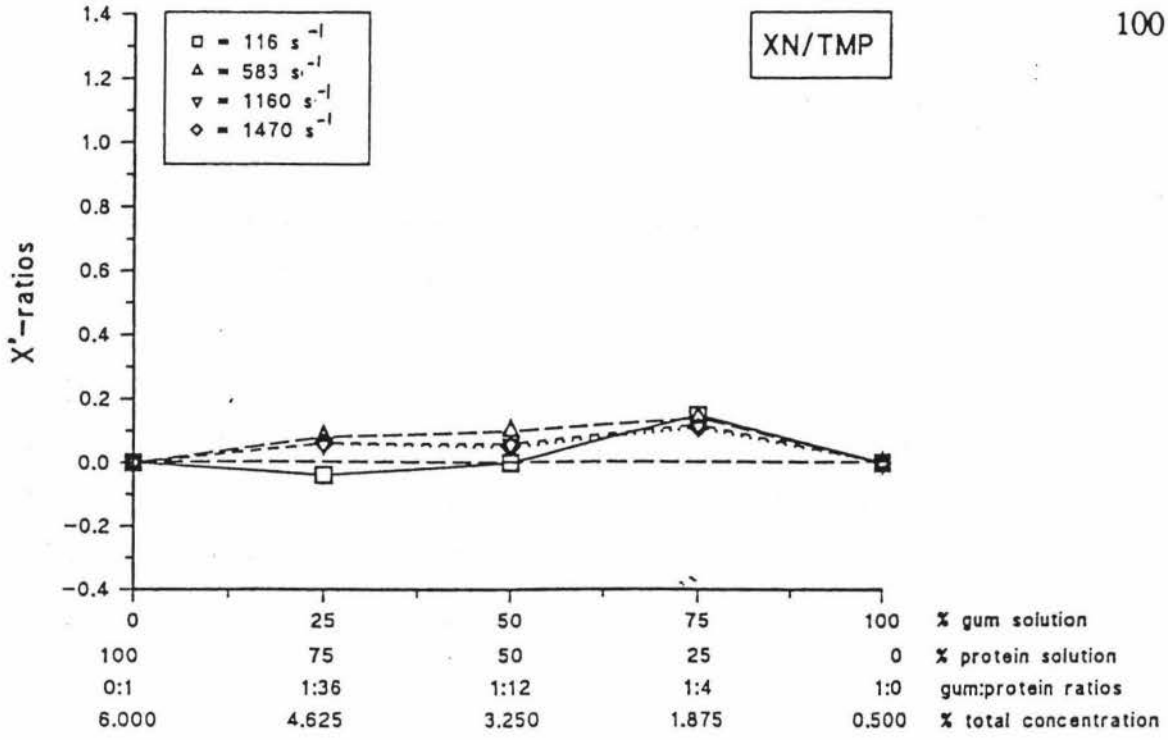


Fig. 6.16d. X'-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % TMP solutions. Gum : protein ratios and total concentrations are also shown.

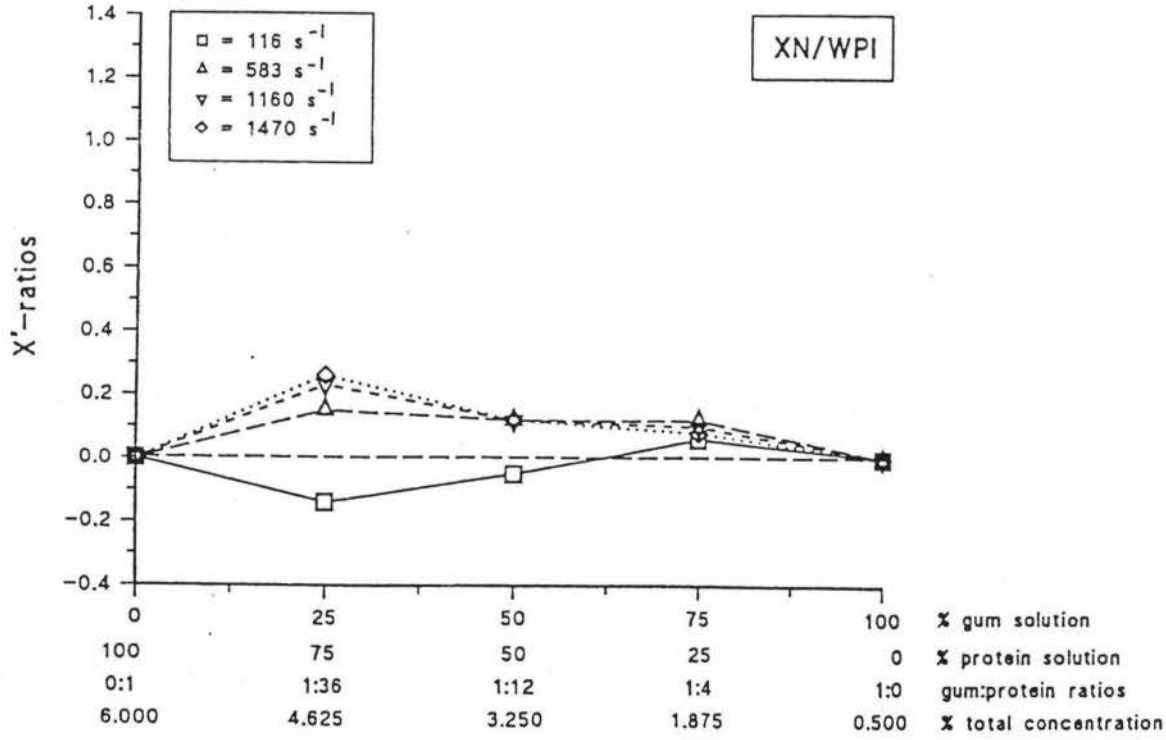


Fig. 6.16e. X'-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPI solutions. Gum : protein ratios and total concentrations are also shown.

6.4.3 Sedimentation study

Two different types of sedimentation were observed. In the first, there was a clear supernatant, good sharpness of separation and fine discrete particles of sediment while in the second there was poor sharpness of separation and the sediment appeared to be a gel-like mass. The first type was observed in CMC/SC (gum solution : dairy protein solution ratio 50:50), CMC/WPC (all ratios), CMC/TMP (ratio 25:75), CR/SC (ratio 75:25) and CR/WPC (ratio 25:75) (Table 6.2). The second type was found in CMC/TMP (ratio 50:50 and 75:25), CR/WPC (ratio 50:50 and 75:25) and CR/TMP (ratio 50:50 and 75:25) (Table 6.2). All LB/dairy protein and all XN/dairy protein mixtures remained homogeneous on centrifugation.

6.5 DISCUSSION

The results presented in Section 6.4.1 show that when 0.5% gum solutions and 6.0% dairy protein solutions were combined, the rheological properties of the mixtures were greatly influenced by the presence of gum, gum concentration and gum type. Both apparent viscosity, and degree of pseudoplasticity (as indicated by the value of n), increased as the proportion of gum solution in the mixture increased. For a given mixture, the level of viscosity and the degree of pseudoplasticity bore direct relationships with these same characteristics (reported in Chapter 5) for a pure solution of the gum concerned.

Because of this, the following discussion considers each gum in turn and how it interacts with each of the four different types of dairy protein.

6.5.1 LB/dairy protein mixed solutions

No sediments were found in any of the LB/dairy protein mixed solutions - indicating that no phase separation of any kind had occurred.

The X'-ratio plots (Fig. 6.13) indicate some synergism with SC and TMP, especially at the lower gum solution : protein solution ratio of 25:75 (i.e. the mixture with the

Table 6.2: Sedimentation results (%) for gum-dairy protein mixed solutions.

sample	gum solution : protein solution		
	25:75	50:50	75:25
LB/SC	N	N	N
LB/WPC	N	N	N
LB/TMP	N	N	N
LB/WPI	N	N	N
CMC/SC	N	*(a)	N
CMC/WPC	5.5(a)	11.1(a)	13.9(a)
CMC/TMP	9.5(a)	4.8(b)	2.17(b)
CMC/WPI	N	N	N
CR/SC	N	N	26.3(a)
CR/WPC	22.8(a)	22.2(b)	16.7(b)
CR/TMP	NG	27.0(b)	23.0(b)
CR/WPI	N	N	N
XN/SC	N	N	N
XN/WPC	NG	NG	NG
XN/TMP	N	N	N
XN/WPI	N	N	N

Notes:

1. N means no sediment was observed.
2. * means sediment (%) is less than 1.35%
3. (a) means a clear supernatant, good sharpness of separation with fine particles of sediment
4. (b) means poor sharpness of separation, with gel-like sediment.
5. NG means no sediment was found but the solution appeared to be a gel-like mass.

highest protein content) (Figs. 6.13a and b, Fig. 6.13d). This could possibly be due to molecular space occupancy competition (but to an extent insufficient to cause thermodynamic incompatibility and hence phase separation). Synergism is twice as great for TMP as for SC. The slight antagonism with SC and TMP at the solution ratio of 75:25 may well be within experimental error; there might be no interaction when the protein content of the mixture is relatively low.

The X'-ratio plots for LB/WPC and LB/WPI (Figs. 6.13c and 6.13e) are of similar shape. However, X'-ratios are generally positive and shear rate-dependent for WPC but generally negative and shear rate-independent for WPI. There does appear to be synergism with WPC at three higher shear rates, while the WPI results may be within experimental error and interaction, in fact, may be insignificant.

It is clear from all the LB results that this gum interacts in a different way with linear proteins (SC and TMP) than it does with globular proteins (WPC and WPI).

6.5.2 CMC/dairy protein mixed solutions

Synergism occurred between CMC and all four dairy proteins, but was significantly greater with TMP than with SC, WPC and WPI: the X'-ratio for TMP is about 50% larger than the X'-ratios for SC, WPC and WPI (which are all approximately equal).

Significant amounts of sediment (Table 6.2) were recovered for CMC/WPC and CMC/TMP but not for CMC/SC and CMC/WPI. These is thus no clear relationship between rheological synergism and phase separation. However, the sediments for CMC/TMP at the solution ratios of 50:50 and 75:25 were of a gel-like character; this, together with the relatively high X'-ratios for TMP, suggest that CMC reacts in a different way with TMP than it does with the other three types of protein. One possible explanation for this is that the Ca^{2+} in TMP forms bridges between CMC molecules (which are anionic and therefore negatively charged) and the protein molecules (which, because the pH of the mixture was well above the protein's isoelectric point, were also negatively charged). Such bridging could perhaps result in partial gelation.

In the mixtures CMC/SC, CMC/WPC and CMC/WPI synergism might be caused by repulsion between the negatively charged gum and protein molecules. In the cases of CMC/SC (slightly) and CMC/WPC such repulsion may have caused some loss of solubility of one of the macromolecular components of the mixtures, resulting in sediment formation. The absence of a sediment with WPI may be due to the fact that the WPI is virtually a pure protein with a low degree of denaturation and thus a greater ability to stay in solution.

6.5.3 CR/dairy protein mixed solutions

In the cases of CR/SC and CR/WPI (Figs. 6.15a and e), the X'-ratio fluctuates about zero as mixture composition changes and no sediments were observed (except with SC at the gum solution : protein solution ratio of 75:25). It seems that no significant interaction occurred with either protein; thus the anionic nature of CR appears to have no influence.

There is significant, synergistic, interaction with WPC (Fig. 6.15b), and sediments were observed in all mixtures - these being gel-like at the two lower protein concentrations. Schmidt and Padua (1982) found that carrageenan can lower the solubility of WPC but has no effect the solubility of sodium caseinate. The sediments could thus possibly consist of WPC of reduced solubility.

A much greater degree of synergism occurred with TMP (Fig. 6.15c and d), and gel-like sediments were found in the two mixtures with the lower protein concentrations. This behaviour is identical with that of CMC/TMP mixtures. It could be due to the same phenomenon : the formation of Ca^{2+} bridges between negatively charged anionic CR molecules and negatively charged protein molecules.

6.5.4 XN/dairy protein mixed solutions

No sediments formed in any of the XN/dairy protein mixtures. The X'-ratio plots suggest that little if any interaction occurred with SC and TMP. Slight synergism occurred with WPI (except at the lowest shear rate) while significant synergism

occurred with WPC. It seems, then, that XN does interact with globular proteins (WPC and WPI) but not with linear proteins (SC and TMP).

The xanthan gum molecule has a 1,4 beta-D-glucose backbone, as cellulose does, with charged trisaccharide sidechains on every second residue (Cottrell et al., 1980). The distribution of negatively charged carboxyl groups along the sidechains tends to keep the XN molecule in an extended form as a disordered coil because electrostatic repulsion produces a weakly structured material (Symes, 1980; Morris, 1988). In a XN/dairy protein mixed solution both the XN and the protein molecules would have been negatively charged. Electrostatic repulsion could thus occur between gum and protein molecules. The XN molecules could undergo a transition to an ordered (helix) form. In this (rod-like) form XN molecules could easily align and form a gel-like structure, thus resulting in a viscosity increase. The significant synergism with WPC may indicate that globular proteins can induce the suggested structural change in XN molecules more readily than can linear proteins (SC and TMP).

6.6 CONCLUSION

The rheological properties of the mixed solutions of gums and dairy proteins were dominated by the presence of gum, gum concentration and gum type.

LB interacted synergistically with SC and TMP in mixtures with the two higher protein contents, the interaction being independent of shear rate. Shear rate-dependent synergism occurred between LB and WPC but no significant interaction occurred between LB and WPI. The shapes of the X'-ratio plots indicate that LB interacts in a different way with linear proteins (SC and TMP) than it does with globular proteins (WPC and WPI).

Pronounced synergism, with no obvious shear rate dependence, occurred between CMC and all four dairy proteins, the extent of synergism being relatively much greater with TMP. In the case of TMP synergism may have been caused by Ca^{2+} bridging between CR and protein molecules. In the cases of SC, WPC and WPI synergism may have been caused by electrostatic repulsion.

No significant interaction occurred between CR and SC or between CR and WPI. Some synergism did occur between CR and WPC, the effect increasing with increasing protein content but bearing no obvious relationship to shear rate. A relatively high degree of synergism occurred between CR and TMP. This could be due to the same phenomenon -Ca^{2+} bridging - that is considered likely to have caused synergism in CMC/TMP mixtures.

No significant interaction occurred between XN and SC, or between XN and TMP, or between XN and WPI, but significant synergism occurred between XN and WPC. It is suggested that WPC, alone among the four dairy proteins studied, could possibly have caused a change in the conformation of the XN molecule leading to increased viscosity.

It is evident from the mixture composition data given in the X'-ratio (and other) plots that in these experiments, for any given gum-protein combination, the gum : protein ratio and the total polymer concentration in the mixed solutions changed as the proportion of gum solution to protein solution changed. For this reason it was decided to carry out a further series of experiments in which the gum : protein ratio and total polymer concentration were to be varied independently. It was hoped that the results might help to explain any effects of these two factors and, also, provide confirmation or otherwise of the results reported in this chapter. This new series of experiments, and the results obtained, are described in Chapter 7.

CHAPTER 7

THE EFFECTS OF GUM : PROTEIN RATIO AND TOTAL POLYMER CONCENTRATION ON THE VISCOSITY OF GUM-DAIRY PROTEIN MIXED SOLUTIONS

7.1 INTRODUCTION

In the work reported in Chapter 6, when 0.5% gum solution was mixed with 6.0% protein solution there were large variations in both gum : protein ratio and total concentration with gum solution : protein solution ratio. These variations are shown in Fig. 7.1. The work reported in this chapter was carried out to determine the effects of varying independently the gum : protein ratio and the total polymer concentration in the mixed solutions.

7.2 EXPERIMENTAL PLAN

For each gum-dairy protein combination, mixed solutions with the gum : protein ratios and total concentrations shown in Table 7.1 were prepared (according to the method described in Section 4.2.4) by mixing together 1.2 %w/w gum solution, 10 %w/w protein solution and (where required) distilled water.

Each mixed solution was divided into two batches. The first was kept overnight at room temperature and then centrifuged to recover any sediment as described in Section 4.3. Sediments were measured and recorded as described in Section 4.4. The second was kept for 3 hours at room temperature, deaerated centrifugally (as described in Section 4.3), and then subjected to rheological measurement. A flow curve was obtained using the method described in Section 4.5.

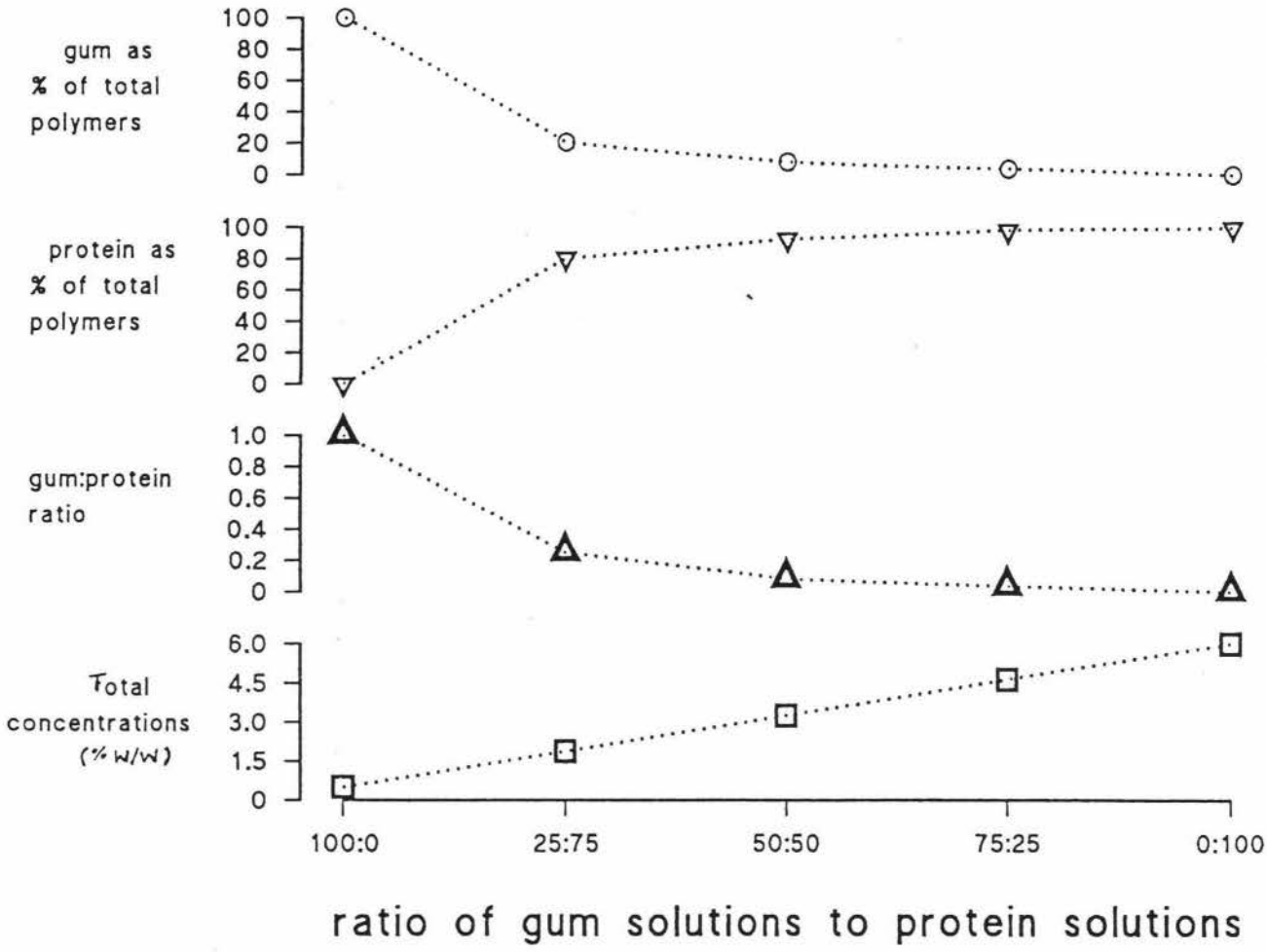


Fig. 7.1. Compositions of the mixed gum-dairy protein solutions studied in Chapter 6.

Table 7.1: Compositions of the gum-dairy protein mixtures studied.

Total conc.	Gum:protein ratio	% gum	% protein
2.0%	1:32	0.061	1.939
	1:16	0.118	1.882
	1:8	0.222	1.778
	1:4	0.400	1.600
2.5%	1:32	0.076	2.424
	1:16	0.147	2.353
	1:8	0.278	2.222
	1:4	0.500	2.000
3.5%	1:32	0.106	3.394
	1:16	0.206	3.294
	1:8	0.389	3.111
	1:4	0.700	2.800
4.0%	1:32	0.120	3.880
	1:16	0.240	3.760
	1:8	0.440	3.560
	1:4	0.800	3.200

7.3 PROCESSING AND PRESENTATION OF EXPERIMENTAL DATA

7.3.1 Viscosity

Apparent viscosity (evaluated from the flow curve data at a shear rate of 1160 s^{-1}) is plotted against gum : protein ratio and total polymer concentration in Figs. 7.2a-d (LB/dairy proteins), Figs. 7.3a-d (CMC/dairy proteins), Figs. 7.4a-d (CR/dairy proteins) and Figs. 7.5a-d (XN/dairy proteins).

It was found previously (Chapter 6) that shear rate appeared to have no pronounced effect on gum-protein interaction. This is why the above plots are presented for only one shear rate (which lies within the shear rate range previously studied).

7.3.2 Power law constants

The flow curves obtained for all the gum-protein mixed solutions were each fitted by the power law (equation 4.1). In every case the correlation coefficient was greater than 0.99. n values for all gum-dairy protein mixtures are tabulated in Tables 7.2-7.5, while k values are tabulated in Tables 7.6-7.9.

Plots of flow behaviour index, n, versus gum content (%w/w) of mixed solution are shown in Fig. 7.6a (LB/dairy proteins), Fig. 7.6b (CMC/dairy proteins), Fig. 7.6c (CR/dairy proteins) and Fig. 7.6d (XN/dairy proteins).

Plots of fluid viscosity index, k, versus gum content of mixed solution are shown in Fig. 7.7a (LB/dairy proteins), Fig. 7.7b (CMC/dairy proteins), Fig. 7.7c (CR/dairy proteins) and Fig. 7.7d (XN/dairy proteins).

7.3.3 Z-ratios

Ratios that here will be called Z-ratios and that are essentially the same as the X-ratios presented in Chapter 6 were calculated as follows using the experimental data obtained in this part of the study. The purpose of doing this was to discover whether or not the results obtained here were or were not in agreement with those reported in Chapter 6.

For each gum-protein combination, the same two mixtures were chosen from among those listed in Table 7.1 such that, in each case, values of total polymer concentration, gum : protein ratio (and therefore gum concentration and protein concentration) were identical to or close to those that would exist in a hypothetical mixed solution obtained by mixing together 0.5% gum solution and 6.0% dairy protein solution in the appropriate ratio. (Chapter 6 records and discusses the measurements made on such solution mixtures).

Mixture A

Mixture A had the following composition (Table 7.1):

Total polymer concentration	=	2.5%
Gum : protein ratio	=	1:8
Gum concentration	=	0.278 %
Protein concentration	=	2.222 %

Using viscosity data obtained as described in Section 7.2, and the viscosity-concentration data for gum solutions presented in Chapter 5, the following ratio (called the 'measured Y-ratio') was to be calculated for each of the shear rates 116, 583, 1160 and 1470 s^{-1}:

$$\text{Measured Y-ratio} = \frac{\text{measured apparent viscosity of mixture A}}{\text{apparent viscosity of 0.275\% pure gum solution}}$$

An 'expected Y-ratio' was calculated by considering a hypothetical mixed solution containing 60% (0.5% gum solution) and 40% (6.0% protein solution) (i.e. a gum solution : protein solution ratio of 60:40). Such a mixture has the composition:

Total polymer concentration	=	2.7%
Gum : protein ratio	=	1:8
Gum concentration	=	0.300%
Protein concentration	=	2.4%

This hypothetical mixture has a composition close to that of Mixture A and, in fact, the same gum : protein ratio.

$$\text{Expected Y-ratio} = \frac{\text{expected apparent viscosity of hypothetical mixture}}{\text{apparent viscosity of 0.300 \% pure gum solution}}$$

where expected viscosity was calculated using equation (6.1) and the viscosity of 0.300 % pure gum solution was to be calculated from the viscosity-concentration data presented in Chapter 5.

Finally, a Z-ratio was to be calculated as follows :

$$\text{Z-ratio} = \frac{\text{measured Y-ratio}}{\text{expected Y-ratio}}$$

This Z-ratio is essentially an X-ratio with the numerator and denominator weighted by gum concentration to account for the slight difference in gum concentration between Mixture A and the hypothetical mixture (the gum being the dominant component of the mixtures with respect to viscosity).

This difference is, in fact, so small that the viscosity-concentration data presented in Chapter 5 predict essentially the same viscosity for a 0.278 % gum solution as for a 0.330 % gum solution. The Z-ratio was therefore finally calculated as

$$\text{Z-ratio} = \frac{\text{measured apparent viscosity}}{\text{expected apparent viscosity}}$$

where measured and expected viscosity values were obtained as described above.

The Z-ratio is thus the same as an X-ratio - but is calculated using new experimental data. A comparison of Z-ratios with the X-ratios obtained earlier was therefore expected to demonstrate whether or not the results reported in this Chapter replicated those reported in Chapter 6.

Mixture B

Mixture B had the following composition (Table 7.1) :

Total polymer concentration	=	3.5 %
Gum : protein ratio	=	1:16
Gum concentration	=	0.206 %
Protein concentration	=	3.294 %

$$\text{Measured Y-ratio} = \frac{\text{measured apparent viscosity of mixture B}}{\text{apparent viscosity of 0.206 \% pure gum solution}}$$

The corresponding hypothetical mixed solution consists of 42.7% (0.5 % gum solution) and 57.3% (6.0% protein solution) (i.e. a gum solution : protein solution ratio of 42.7 : 57.3) and has the following composition :

Total polymer concentration	=	3.65 %
Gum : protein ratio	=	1:16
Gum concentration	=	0.213 %
Protein concentration	=	3.438 %

$$\text{Expected Y-ratio} = \frac{\text{expected apparent viscosity of hypothetical mixture}}{\text{apparent viscosity of 0.213 \% pure gum solution}}$$

Assuming 0.206 % and 0.213 % gum solutions have the same viscosity,

$$\text{Z-ratio} = \frac{\text{measured apparent viscosity}}{\text{expected apparent viscosity}}$$

Z-ratios for Mixtures A and B for all gum -dairy protein combinations are tabulated in Appendix 12. They are plotted, together with the X-ratios already presented in Chapter 6, in Figs.7.8 to 7.11. Figs. 7.8 to 7.11 are identical to Fig 6.13 to 6.16 - expect that they display the Z-ratios calculated as described above.

7.3.4 Sedimentation results

The results of sediment measurements are presented in Table 7.10 (LB/dairy proteins), Table 7.11 (CMC/dairy proteins), Table 7.12 (CR/dairy proteins) and Table 13 (XN/dairy proteins).

7.4 RESULTS AND DISCUSSION

7.4.1 The effect of gum : protein ratio and total polymer concentration on the apparent viscosity of gum-dairy protein mixed solutions

The results presented in Figs 7.2 to 7.5 show that, for each gum-protein combination studied, the apparent viscosity of the mixed solution increased both with increasing gum : protein ratio and with increasing total concentration.

For a given gum-protein combination, apparent viscosity increased approximately exponentially with increasing gum : protein ratio at constant total concentration, the dependence of the viscosity upon this ratio becoming greater as concentration increased. This concentration effect was relatively slight for XN/all dairy proteins but relatively pronounced for CR/SC and CR/TMP.

LB/SC

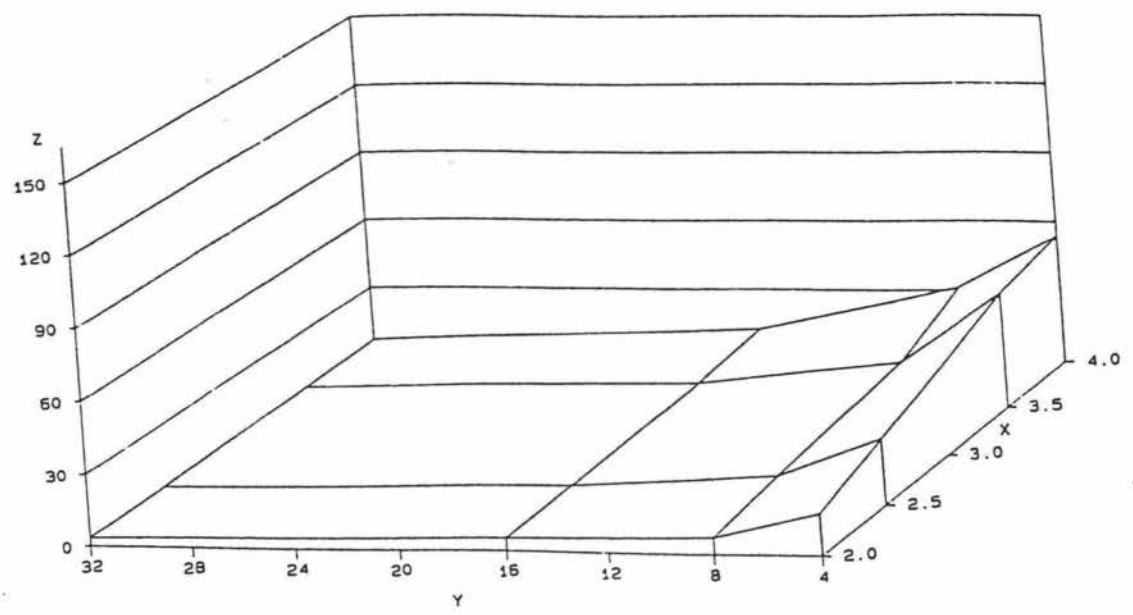


Fig. 7.2a. Apparent viscosity versus gum : protein ratio and total polymer concentration for LB/SC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

LB/WPC

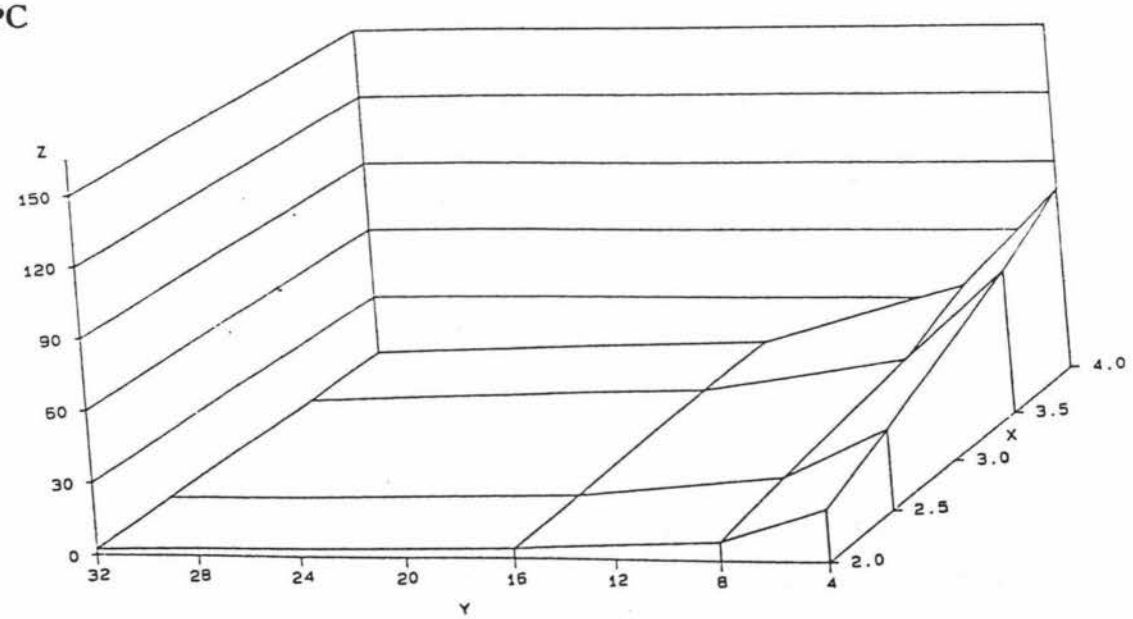


Fig. 7.2b. Apparent viscosity versus gum : protein ratio and total polymer concentration for LB/WPC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

LB/TMP

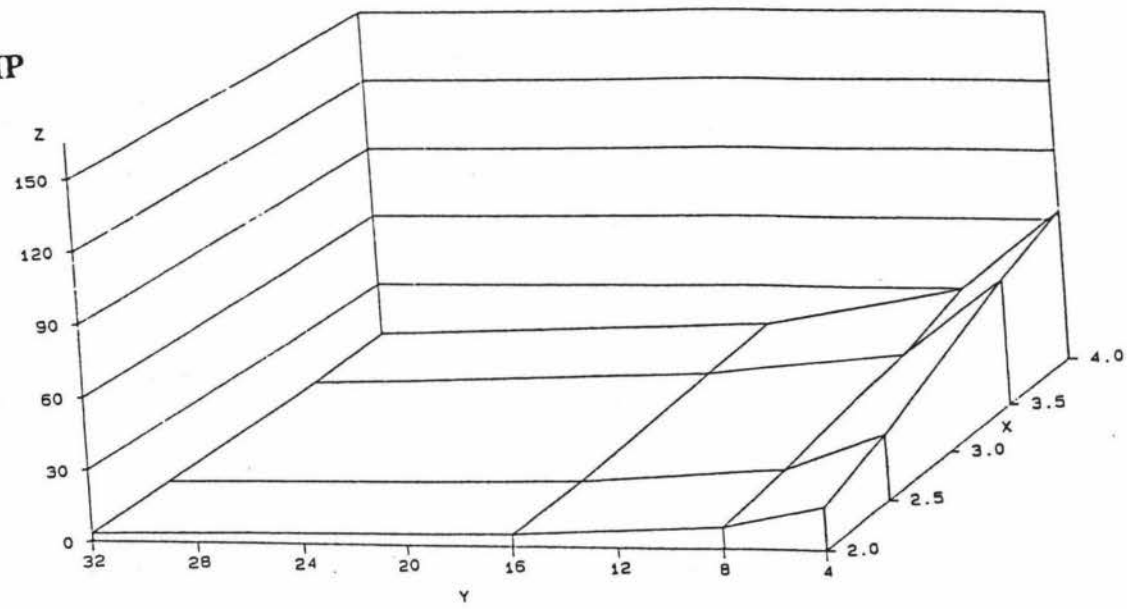


Fig. 7.2c. Apparent viscosity versus gum : protein ratio and total polymer concentration for LB/TMP mixtures. The x-axis is total polymer concentration (%), the y-axis is protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

LB/WPI

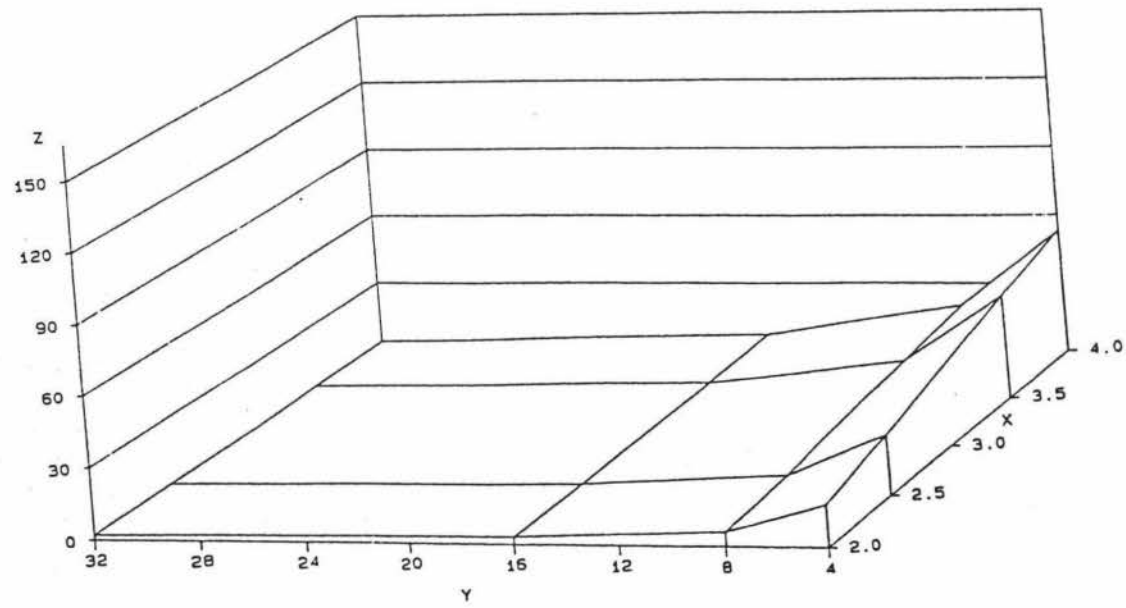


Fig. 7.2d. Apparent viscosity versus gum : protein ratio and total polymer concentration for LB/WPI mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

CMC/SC

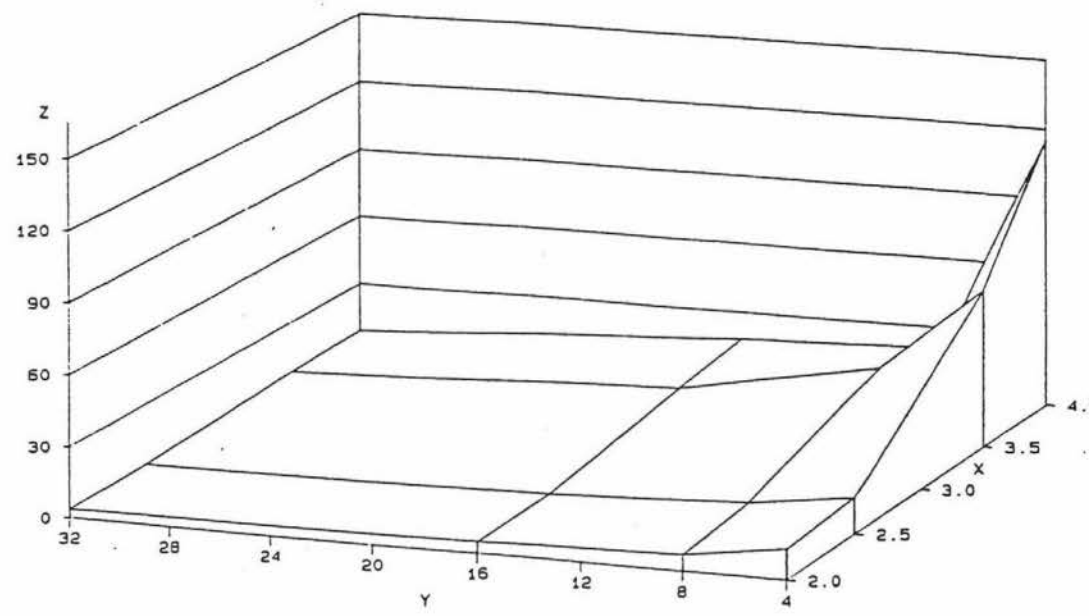


Fig. 7.3a. Apparent viscosity versus gum : protein ratio and total polymer concentration for CMC/SC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

CMC/WPC

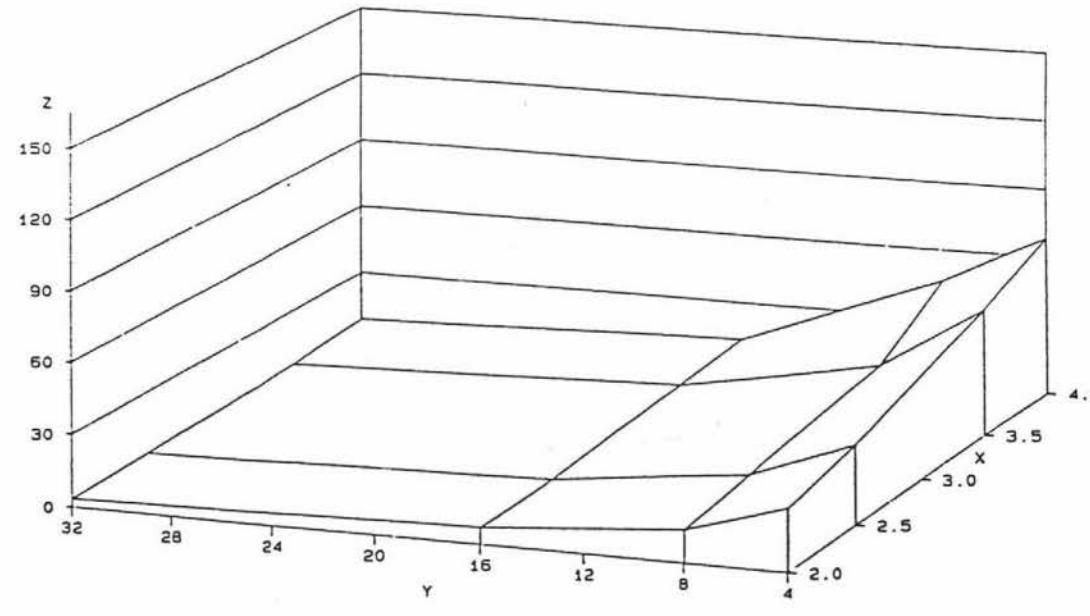


Fig. 7.3b. Apparent viscosity versus gum : protein ratio and total polymer concentration for CMC/WPC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

CMC/TMP

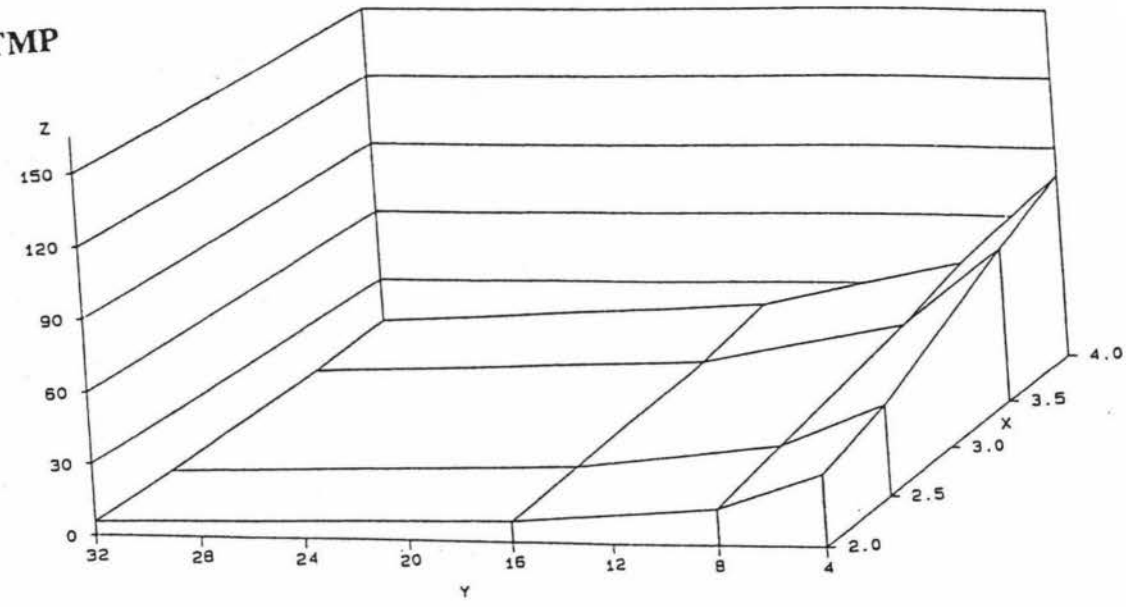


Fig. 7.3c. Apparent viscosity versus gum : protein ratio and total polymer concentration for CMC/TMP mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

CMC/WPI

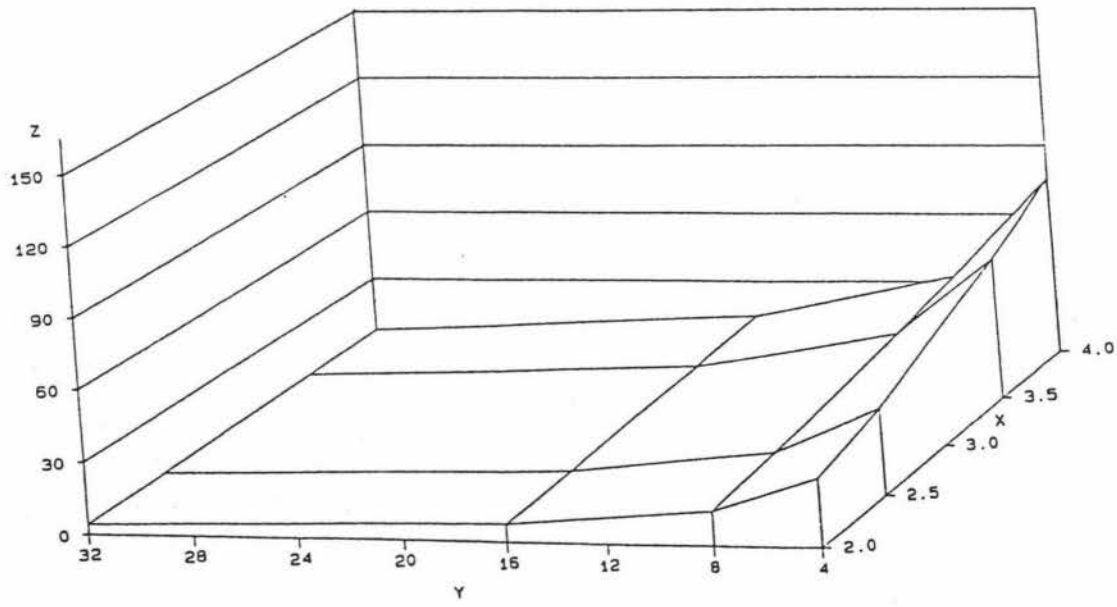


Fig. 7.3d. Apparent viscosity versus gum : protein ratio and total polymer concentration for CMC/WPI mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

CR/SC

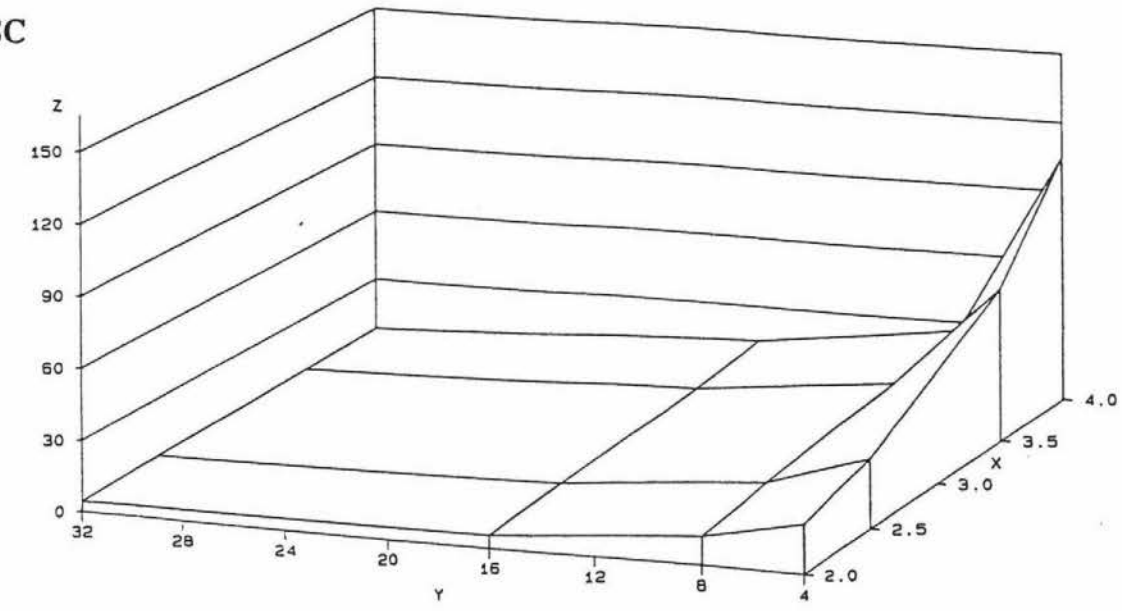


Fig. 7.4a. Apparent viscosity versus gum : protein ratio and total polymer concentration for CR/SC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

CR/WPC

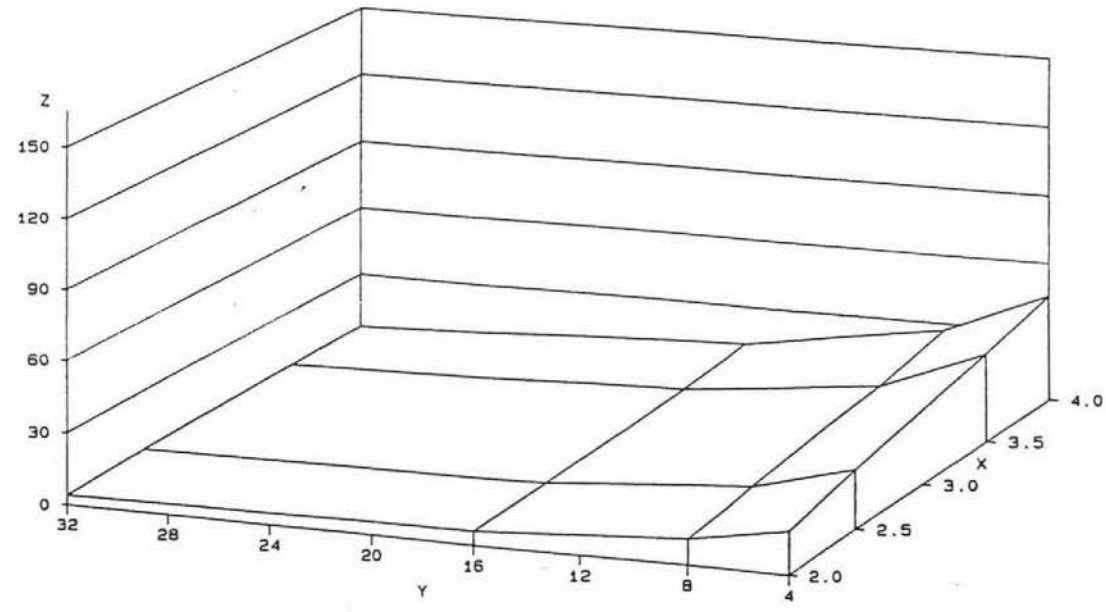


Fig. 7.4b. Apparent viscosity versus gum : protein ratio and total polymer concentration for CR/WPC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

CR/TMP

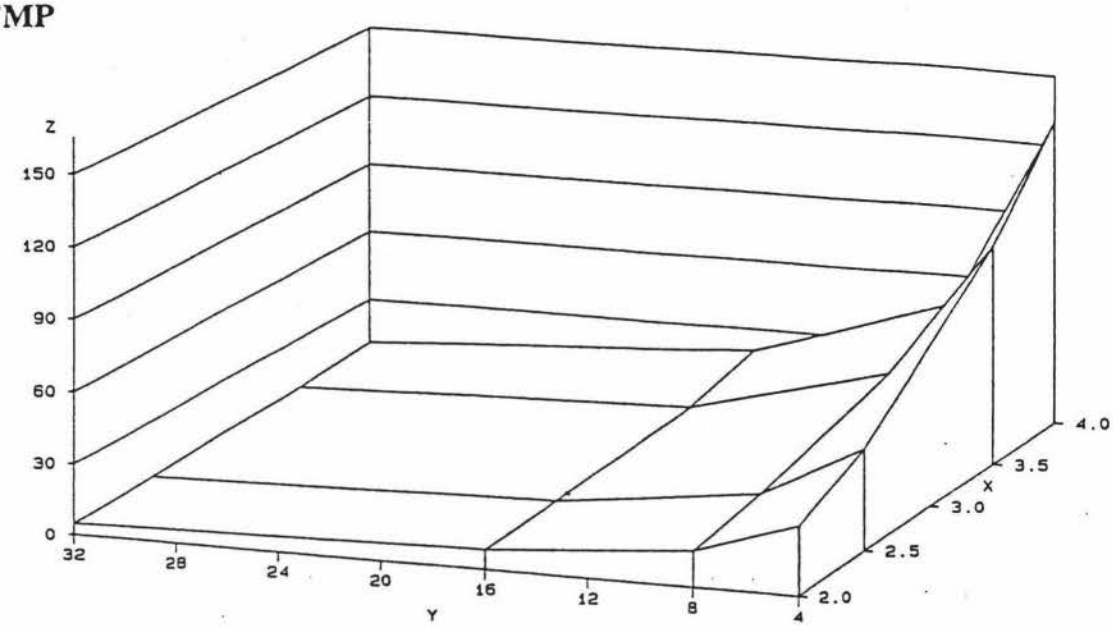


Fig. 7.4c. Apparent viscosity versus gum : protein ratio and total polymer concentration for CR/TMP mixtures. The x-axis is the total polymer concentration (%), the y-axis is protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

CR/WPI

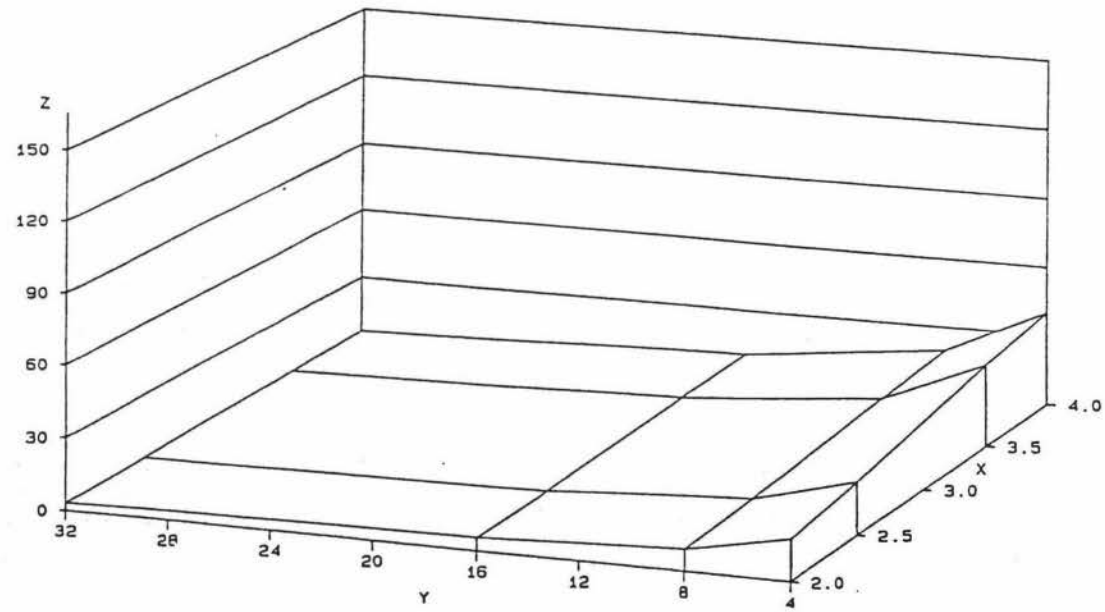


Fig. 7.4d. Apparent viscosity versus gum : protein ratio and total polymer concentration for CR/WPI mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

XN/SC

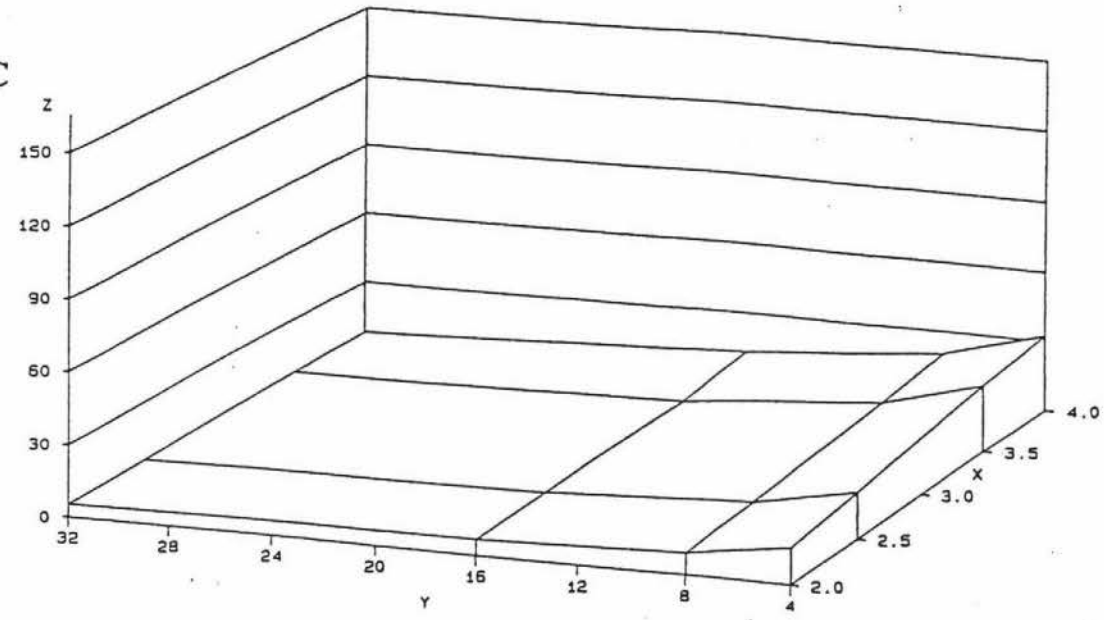


Fig. 7.5a. Apparent viscosity versus gum : protein ratio and total polymer concentration for XN/SC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

XN/WPC

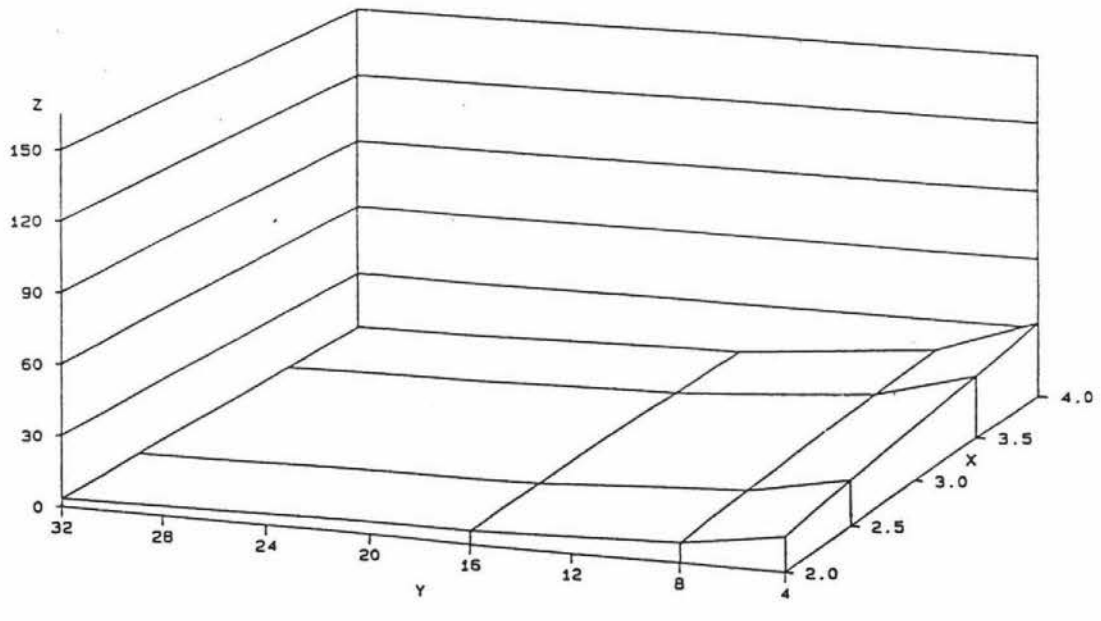


Fig. 7.5b. Apparent viscosity versus gum : protein ratio and total polymer concentration for XN/WPC mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and z-axis is the apparent viscosity (mPa.s).

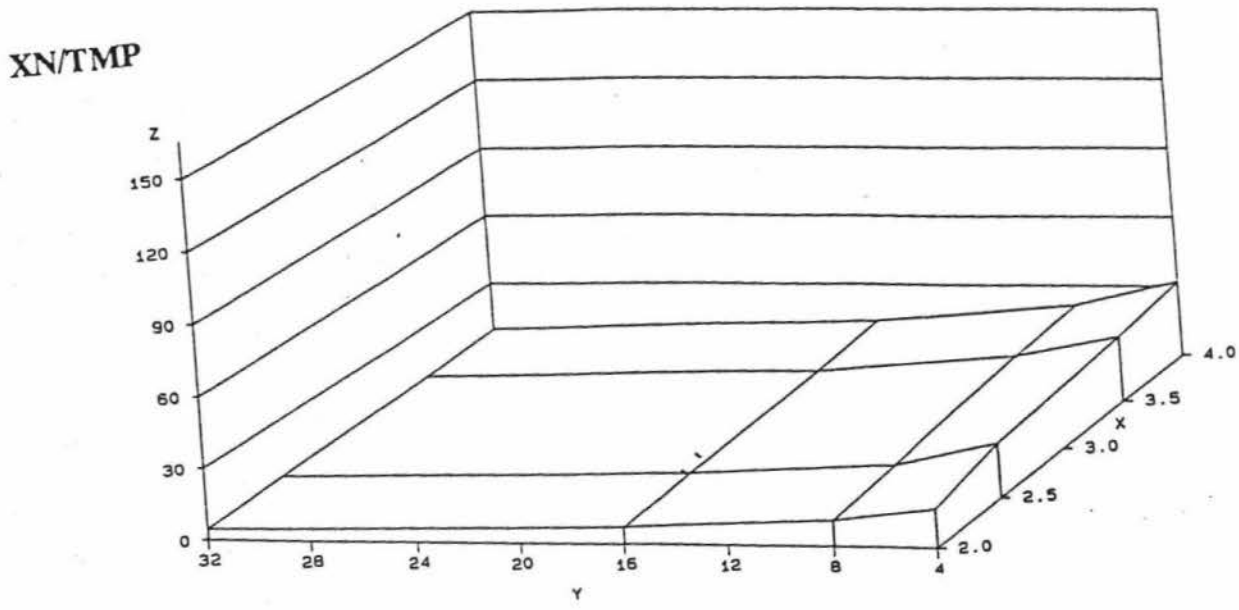


Fig. 7.5c. Apparent viscosity versus gum : protein ratio and total polymer concentration for XN/TMP mixtures. The x-axis is total polymer concentration (%), the y-axis is protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

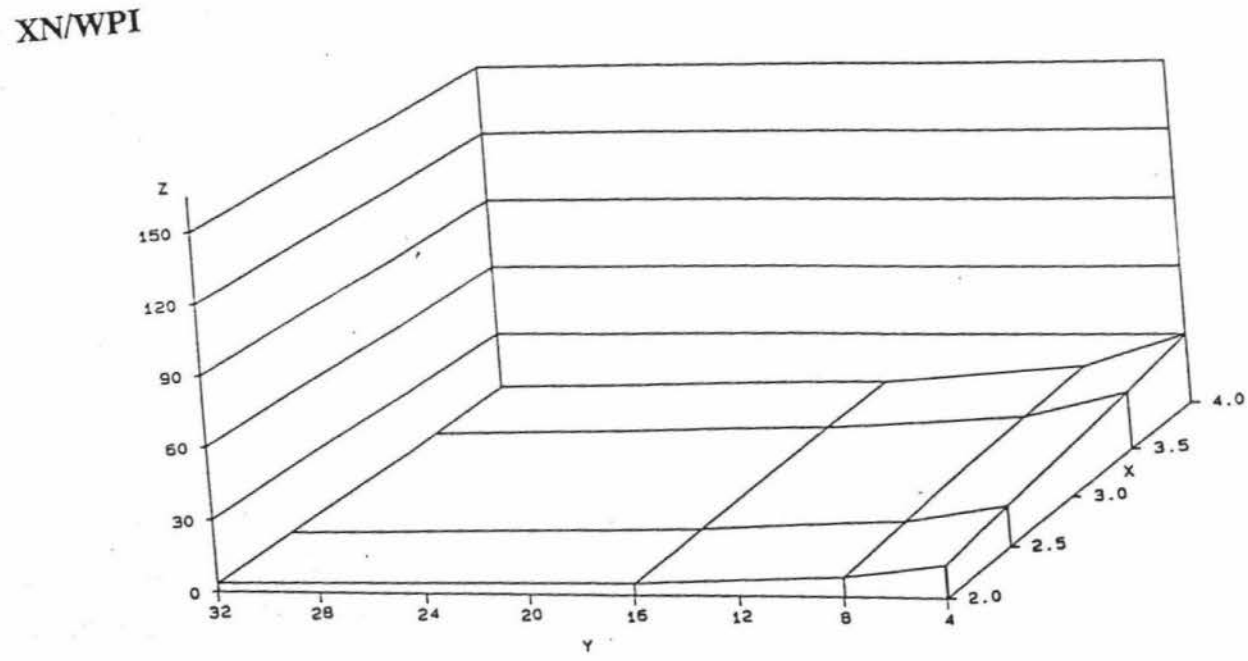


Fig. 7.5d. Apparent viscosity versus gum : protein ratio and total polymer concentration for XN/WPI mixtures. The x-axis is total polymer concentration (%), the y-axis is the protein figure of the gum : protein ratio and the z-axis is apparent viscosity (mPa.s).

For XN/all dairy proteins, viscosity increased linearly with total concentration at constant gum : protein ratio for all values of this ratio. For CMC/SC, CMC/WPC, CR/SC and CR/TMP viscosity tended to increase linearly with total concentration at low gum : protein-ratio but exponentially at high. For all other gum-protein combinations, the increase of viscosity with total concentration was approximately linear at all ratios.

All the plots shown in Figs. 7.2 to 7.5, expect those for CMC/SC, CR/SC and CR/TMP, demonstrate regularity in the way in which viscosity increases with both increasing gum : protein ratio and total concentration. In the case of each of these three gum-protein combinations there is some perturbation of the response surface in the high gum : protein ratio-high total concentration region. This is not felt to be of significance; it could possibly be a result of experimental error.

Over-all these results indicate that, because apparent viscosity increases with gum : protein ratio and because this effect increases with total polymer concentration, the main determinant of viscosity is the gum concentration in the mixed solution. That this is so can be seen also from a qualitative comparison between Figs. 7.2-7.5 and the viscosity-concentration data for gum solutions presented in Chapter 5, Figs. 5.5a-d. This shows that the viscosity of a gum-protein mixed solution at a given gum : protein ratio and a given total concentration was strongly influenced by gum type.

7.4.2 The effect of gum : protein ratio and total polymer concentration on the rheological character of gum-dairy protein mixed solutions

The rheogical properties of the gum-protein mixtures studied, as represented by power law constants n and k, were generally strongly influenced by gum : protein ratio and by total polymer concentration. This can be seen by inspection of the data in Tables 7.2-7.9. For a given gum-protein combination, n decreased (i.e the mixed solution become more pseudoplastic) and k increased (i.e. viscosity increased) as gum:protein ratio increased (for constant total concentration), and as total concentration increased (for constant gum : protein ratio).

The dependence of n and k on these two factors was, in fact, mainly a dependence on gum concentration and gum type. This is demonstrated in Fig. 7.6a-d (for n) and Fig. 7.7a-d (for k). At low gum concentration, the n value is just less than 1.0 (the Newtonian case) for LB, CMC and CR, but less than 0.8 for XN (whose solutions are characterised by a high degree of pseudoplasticity). At high gum concentration the n value is influenced somewhat by dairy protein type in the cases of CR and XN. At lower gum concentration for these two gums, and at all gum concentrations for LB and CMC, the n value is independent of protein type.

For LB, CMC and CR, the dependence of the k value on gum concentration is slight at concentrations less than 0.4% but marked at higher concentrations. For XN, there is an almost exponential dependence over the whole concentration range.

There is an apparent strong effect of protein type on the k value at higher gum concentrations, especially for CR and XN. There is no clear pattern to this effect; it is probably to a significant extent illusory because the units of k ($Pa.s^n$) depend upon the value of n.

7.4.3 Z-ratios

The plots in Figs. 7.8-7.11 show that there is generally very good agreement between the Z-ratios calculated from the data presented in this chapter and the X-ratios calculated from the data presented in Chapter 6. Only in the case of XN/WPC is there a large discrepancy between the two, the Z-ratios being much lower than the X-ratios in this case.

The Z-ratios thus represent excellent replication of the X-ratios. It follows that, indirectly, they represent equally good replication of the X'-ratios presented in Chapter 6 and thus provide confirmation of the findings on rheological interactions between gums and dairy proteins presented in that chapter.

Table 7.2: n values for locust bean gum (LB) and dairy protein mixed solutions.

Gum:protein ratio	Total conc.	LB/SC	LB/WPC	LB/TMP	LB/WPI
1:4	2.0%	0.807	0.739	0.801	0.778
	2.5%	0.701	0.653	0.733	0.718
	3.5%	0.590	0.514	0.575	0.582
	4.0%	0.550	0.447	0.540	0.526
1:8	2.0%	0.953	0.909	0.979	0.939
	2.5%	0.880	0.884	0.892	0.912
	3.5%	0.802	0.729	0.802	0.840
	4.0%	0.730	0.624	0.755	0.778
1:16	2.0%	1.010	0.990	1.020	0.970
	2.5%	1.020	0.938	1.020	1.000
	3.5%	0.937	0.930	0.973	0.961
	4.0%	0.951	0.895	0.922	0.949
1:32	2.0%	1.010	1.000	0.943	1.030
	2.5%	1.020	0.948	0.976	0.954
	3.5%	1.020	0.967	0.997	0.980
	4.0%	0.991	0.991	1.010	0.967

Table 7.3: n values for CMC and dairy protein mixed solutions.

gum:protein ratio	Total conc.	CMC/SC	CMC/WPC	CMC/TMP	CMC/WPI
1:4	2.0%	0.822	0.656	0.646	0.631
	2.5%	0.781	0.652	0.604	0.592
	3.5%	0.491	0.494	0.515	0.498
	4.0%	0.311	0.474	0.545	0.457
1:8	2.0%	0.901	0.795	0.756	0.771
	2.5%	0.920	0.751	0.787	0.732
	3.5%	0.654	0.673	0.677	0.652
	4.0%	0.379	0.589	0.647	0.661
1:16	2.0%	0.964	0.878	0.909	0.868
	2.5%	0.979	0.847	0.872	0.842
	3.5%	0.811	0.796	0.862	0.800
	4.0%	0.805	0.783	0.797	0.787
1:32	2.0%	0.999	0.881	0.988	0.918
	2.5%	1.010	0.905	0.947	0.896
	3.5%	0.907	0.928	0.955	0.889
	4.0%	0.914	0.898	0.930	0.867

Table 7.4: n values for lambda-carrageenan (CR) and dairy protein mixed solutions.

Gum:protein ratio	Total conc.	CR/SC	CR/WPC	CR/TMP	CR/WPI
1:4	2.0%	0.812	0.767	0.745	0.810
	2.5%	0.799	0.748	0.670	0.767
	3.5%	0.619	0.677	0.559	0.718
	4.0%	0.545	0.638	0.522	0.725
1:8	2.0%	0.894	0.861	0.840	0.891
	2.5%	0.879	0.831	0.819	0.831
	3.5%	0.828	0.771	0.723	0.792
	4.0%	0.791	0.764	0.682	0.777
1:16	2.0%	0.985	0.894	0.929	0.939
	2.5%	0.943	0.904	0.921	0.906
	3.5%	0.912	0.865	0.876	0.895
	4.0%	0.900	0.852	0.862	0.881
1:32	2.0%	1.020	0.963	0.966	0.903
	2.5%	0.010	0.979	1.000	0.929
	3.5%	0.956	0.916	0.967	0.953
	4.0%	0.947	0.887	0.944	0.925

Table 7.5: n values for xanthan gum (XN) and dairy protein mixed solutions.

Gum:protein ratio	Total conc.	XN/SC	XN/WPC	XN/TMP	XN/WPI
1:4	2.0%	0.325	0.284	0.313	0.291
	2.5%	0.302	0.269	0.325	0.256
	3.5%	0.294	0.225	0.303	0.209
	4.0%	0.287	0.220	0.305	0.198
1:8	2.0%	0.420	0.393	0.430	0.401
	2.5%	0.392	0.368	0.393	0.359
	3.5%	0.375	0.328	0.377	0.307
	4.0%	0.386	0.308	0.372	0.284
1:16	2.0%	0.540	0.527	0.569	0.514
	2.5%	0.515	0.477	0.529	0.483
	3.5%	0.483	0.425	0.477	0.431
	4.0%	0.489	0.392	0.479	0.392
1:32	2.0%	0.690	0.622	0.663	0.671
	2.5%	0.638	0.626	0.629	0.572
	3.5%	0.610	0.540	0.631	0.527
	4.0%	0.607	0.515	0.617	0.542

Table 7.6: k values for locust bean gum (LB) and dairy protein mixed solutions.

Gum:protein ratio	Total conc.	LB/SC	LB/WPC	LB/TMP	LB/WPI
1:4	2.0%	0.069	0.139	0.075	0.087
	2.5%	0.232	0.349	0.184	0.188
	3.5%	0.881	1.930	1.100	0.861
	4.0%	1.310	3.950	1.670	1.550
1:8	2.0%	0.010	0.014	0.010	0.009
	2.5%	0.027	0.030	0.026	0.155
	3.5%	0.078	0.016	0.086	0.049
	4.0%	0.213	0.052	0.170	0.097
1:16	2.0%	0.005	0.004	0.004	0.004
	2.5%	0.006	0.007	0.005	0.004
	3.5%	0.014	0.015	0.014	0.007
	4.0%	0.018	0.022	0.023	0.010
1:32	2.0%	0.003	0.002	0.005	0.002
	2.5%	0.004	0.004	0.005	0.003
	3.5%	0.005	0.005	0.007	0.004
	4.0%	0.007	0.005	0.008	0.004

Table 7.7: k values for CMC and dairy protein mixed solutions.

Gum:protein ratio	Total conc.	CMC/SC	CMC/WPC	CMC/TMP	CMC/WPI
1:4	2.0%	0.045	0.300	0.360	0.382
	2.5%	0.072	0.395	0.621	0.642
	3.5%	2.440	1.950	2.010	2.090
	4.0%	3.840	2.850	3.020	3.530
1:8	2.0%	0.014	0.058	0.114	0.070
	2.5%	0.016	0.101	0.066	0.116
	3.5%	0.350	0.270	0.312	0.317
	4.0%	1.580	0.780	0.475	0.511
1:16	2.0%	0.006	0.017	0.016	0.019
	2.5%	0.007	0.024	0.026	0.025
	3.5%	0.059	0.048	0.040	0.051
	4.0%	0.073	0.065	0.086	0.066
1:32	2.0%	0.004	0.008	0.006	0.007
	2.5%	0.004	0.008	0.009	0.010
	3.5%	0.016	0.010	0.012	0.014
	4.0%	0.017	0.020	0.019	0.019

Table 7.8: k values for lambda-carrageenan (CR) and dairy protein mixed solutions.

Gum:protein ratio	Total conc.	CR/SC	CR/WPC	CR/TMP	CR/WPI
1:4	2.0%	0.080	0.095	0.178	0.068
	2.5%	0.124	0.150	0.466	0.117
	3.5%	0.972	0.378	2.110	0.261
	4.0%	2.640	0.606	3.860	0.287
1:8	2.0%	0.025	0.028	0.047	0.019
	2.5%	0.037	0.045	0.073	0.037
	3.5%	0.072	0.102	0.250	0.074
	4.0%	0.116	0.146	0.452	0.100
1:16	2.0%	0.006	0.012	0.013	0.009
	2.5%	0.012	0.014	0.018	0.012
	3.5%	0.022	0.027	0.034	0.019
	4.0%	0.031	0.038	0.055	0.026
1:32	2.0%	0.004	0.005	0.006	0.006
	2.5%	0.005	0.006	0.006	0.006
	3.5%	0.010	0.011	0.011	0.007
	4.0%	0.012	0.014	0.016	0.010

Table 7.9: k value for xanthan gum (XN) and dairy protein mixed solutions.

Gum:protein ratio	Total conc.	XN/SC	XN/WPC	XN/TMP	XN/WPI
1:4	2.0%	1.660	2.170	1.940	1.880
	2.5%	2.550	3.110	2.500	3.020
	3.5%	3.860	6.010	3.620	6.140
	4.0%	4.700	7.500	4.110	8.150
1:8	2.0%	0.499	0.566	0.558	0.504
	2.5%	0.755	0.878	0.871	0.849
	3.5%	1.330	1.640	1.450	1.710
	4.0%	1.470	2.120	1.720	2.330
1:16	2.0%	0.163	0.149	0.135	0.136
	2.5%	0.215	0.239	0.228	0.210
	3.5%	0.350	0.459	0.432	0.416
	4.0%	0.455	0.618	0.517	0.591
1:32	2.0%	0.046	0.047	0.046	0.033
	2.5%	0.067	0.054	0.077	0.071
	3.5%	0.105	0.013	0.107	0.127
	4.0%	0.120	0.171	0.138	0.142

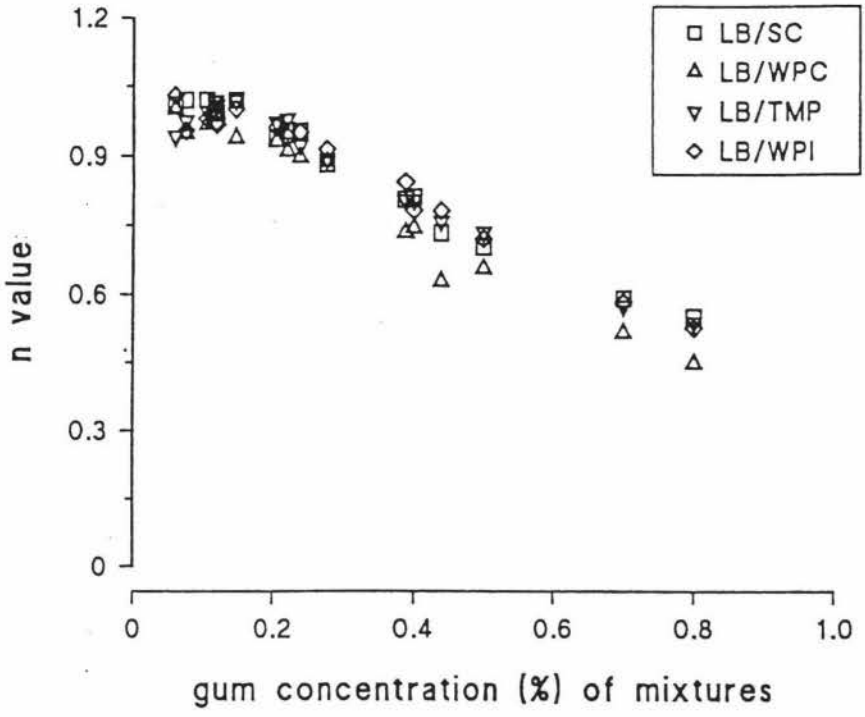


Fig. 7.6a. n value versus gum concentration for LB/dairy protein mixed solutions.

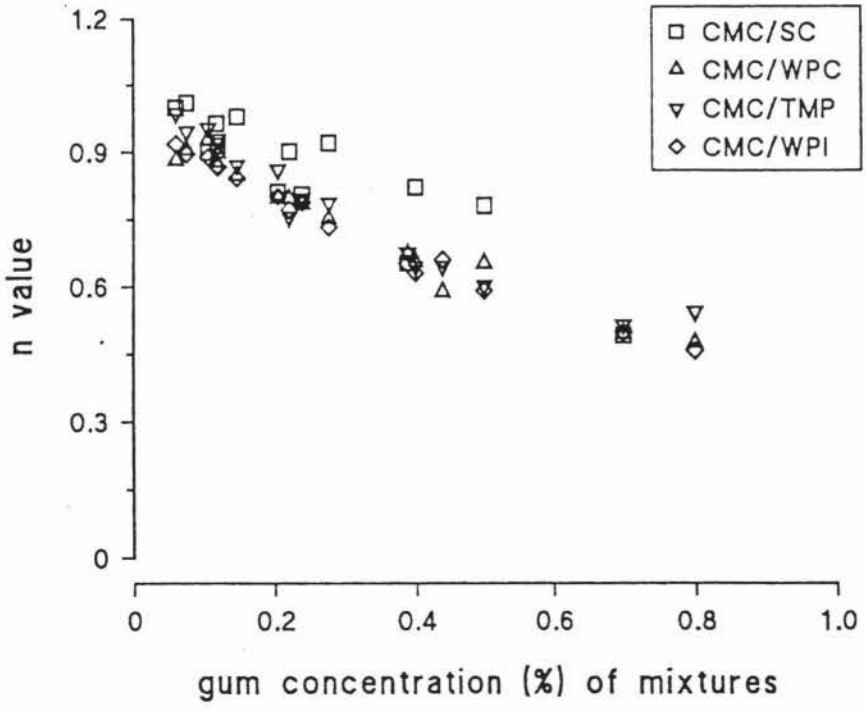


Fig. 7.6b. n value versus gum concentration for CMC/dairy protein mixed solutions.

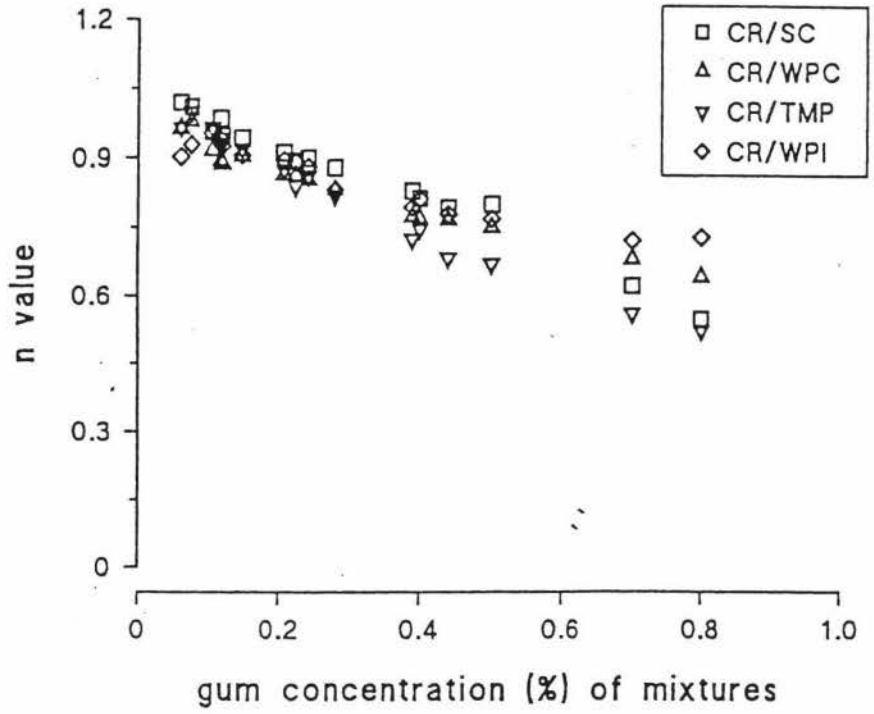


Fig. 7.6c. n value versus gum concentration for CR/dairy protein mixed solutions.

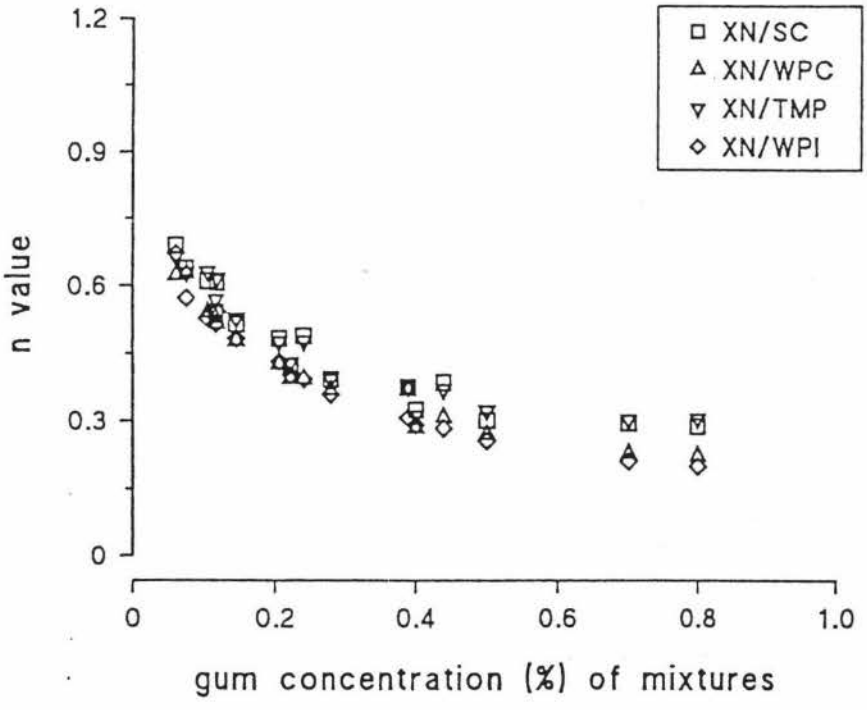


Fig. 7.6d. n value versus gum concentration for XN/dairy protein mixed solutions.

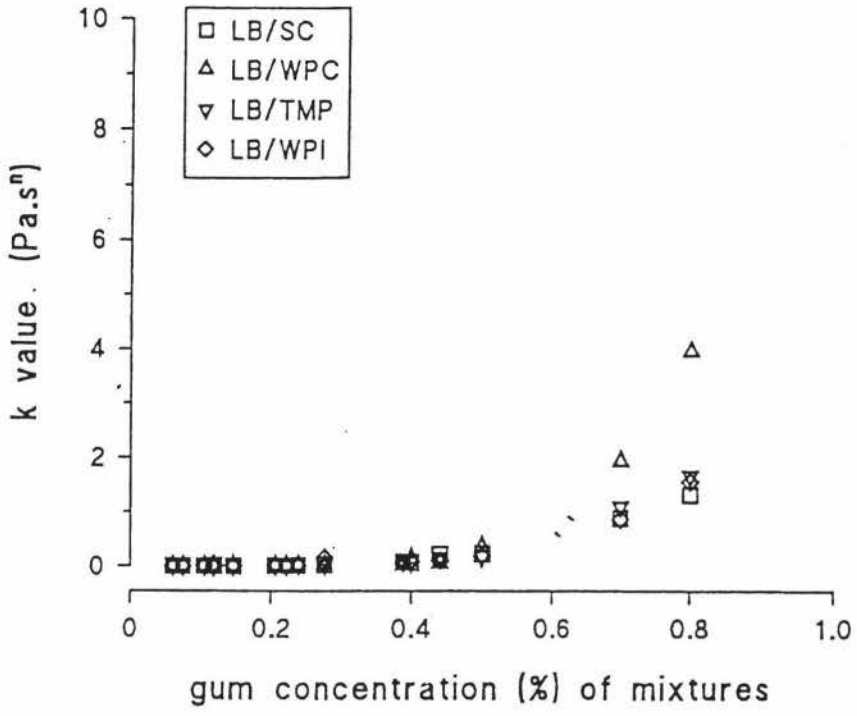


Fig. 7.7a. k value versus gum concentration for LB/dairy protein mixed solutions.

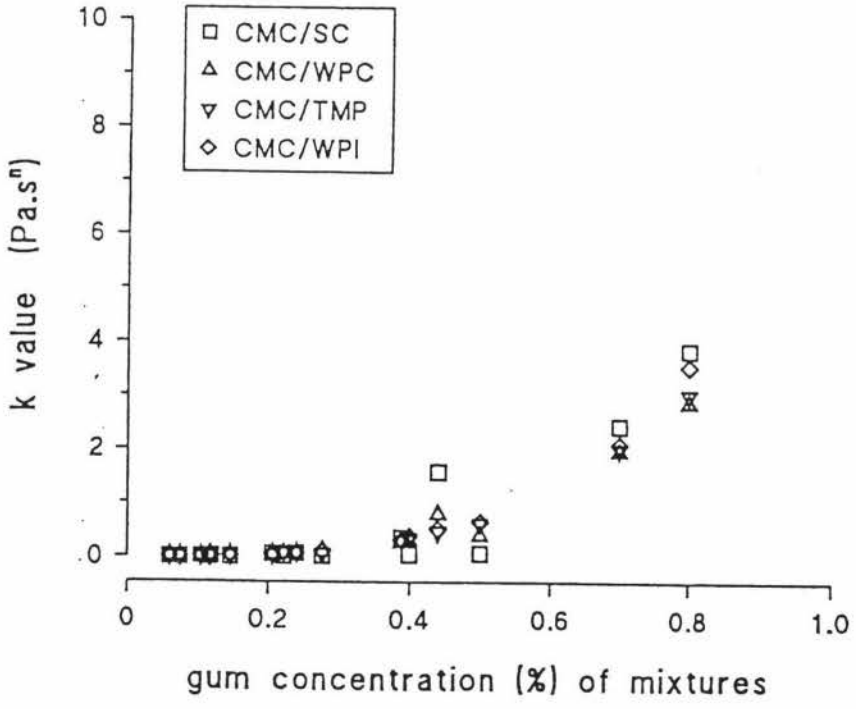


Fig. 7.7b. k value versus gum concentration for CMC/dairy protein mixed solutions.

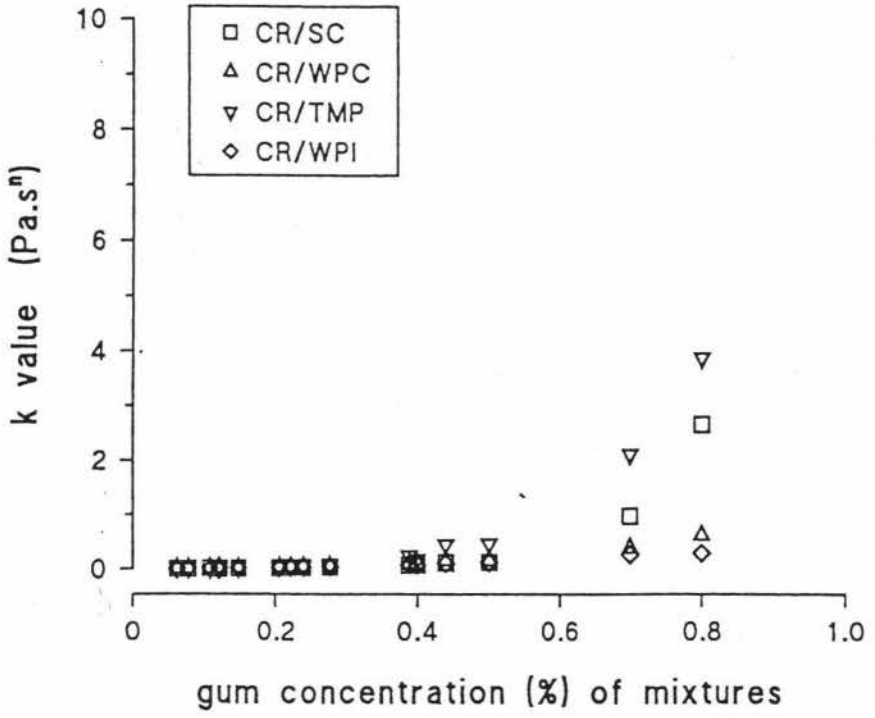


Fig. 7.7c. k value versus gum concentration for CR/dairy protein mixed solutions.

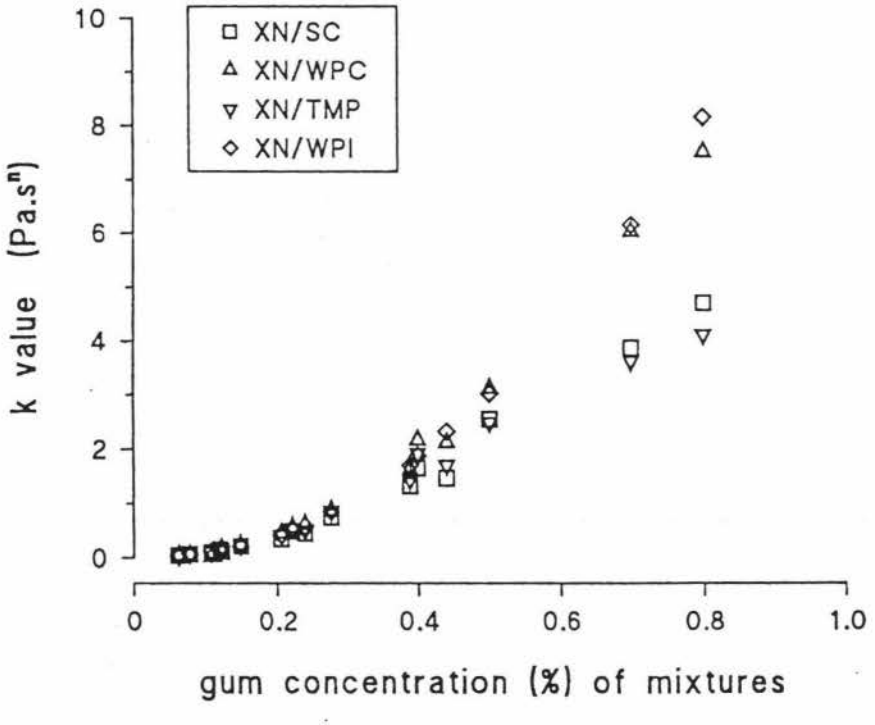


Fig. 7.7d. k value versus gum concentration for XN/dairy protein mixed solutions.

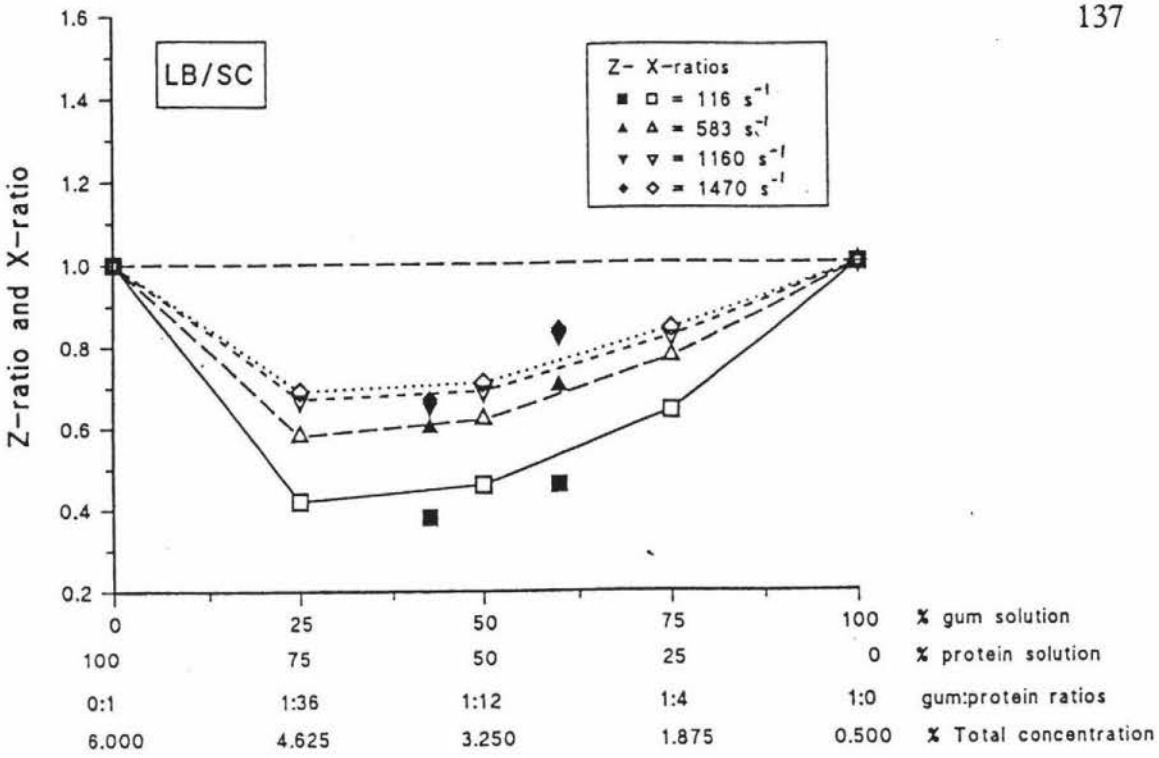


Fig. 7.8a. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % SC solutions.

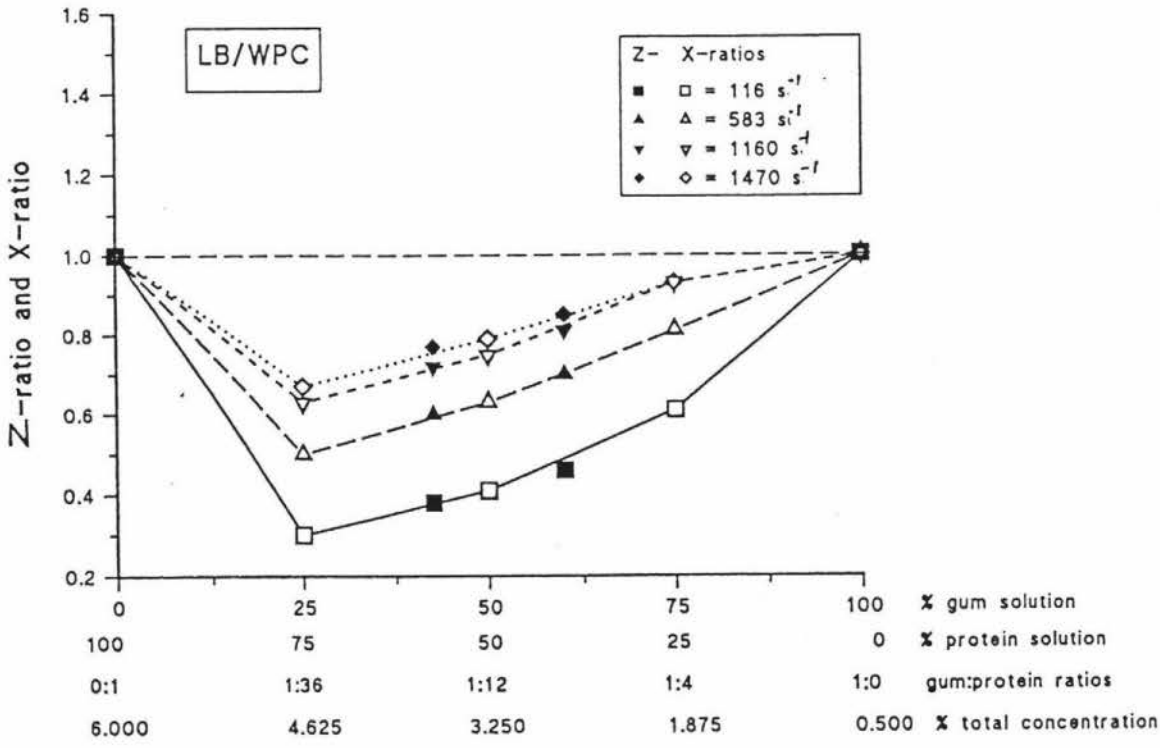


Fig. 7.8b. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPC solutions.

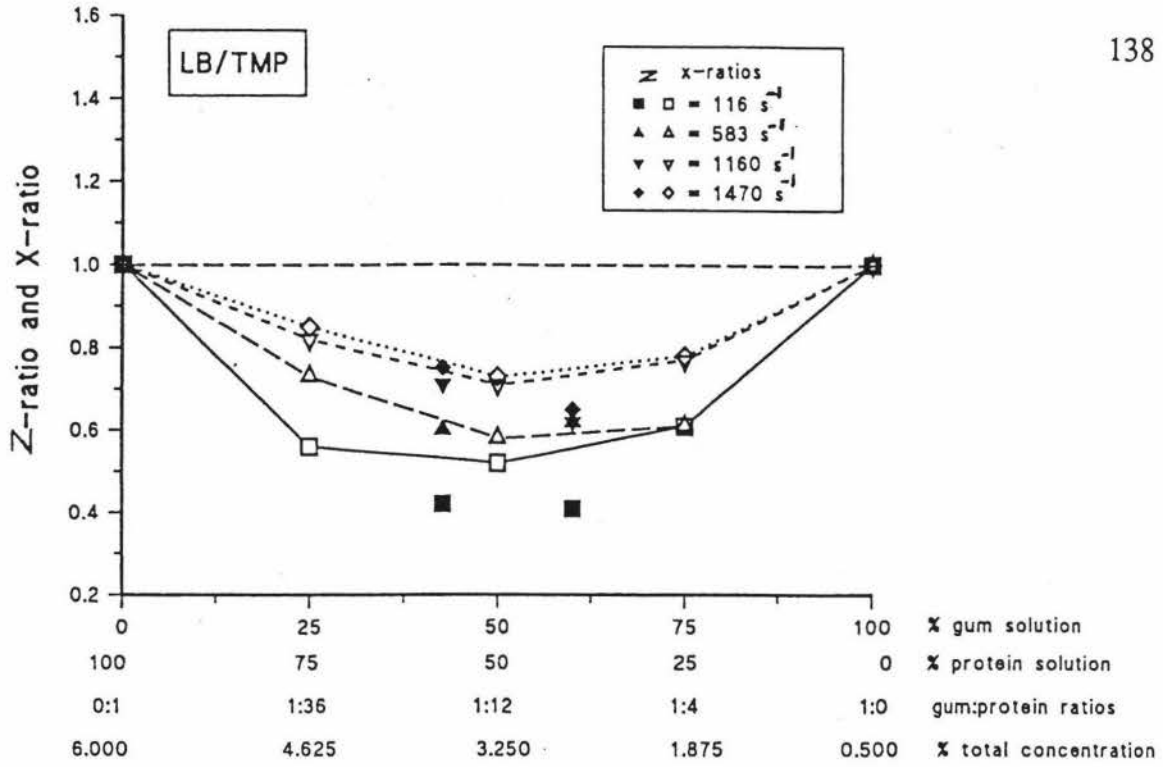


Fig. 7.8c. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % TMP solutions.

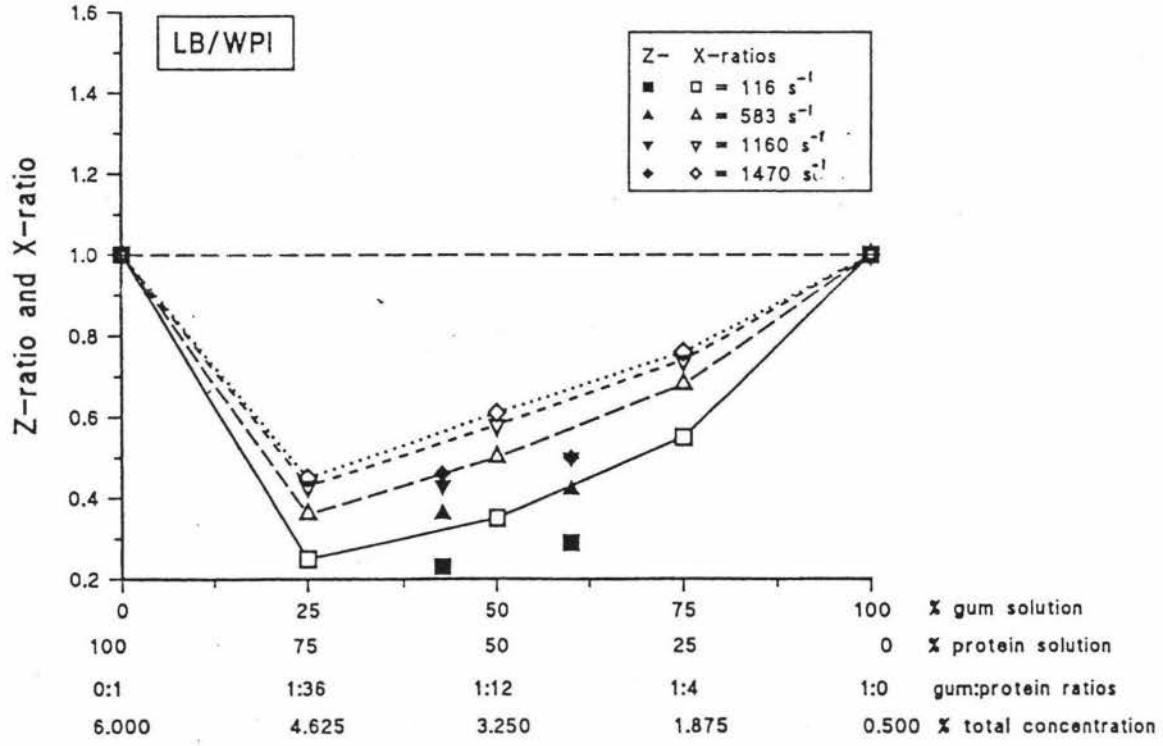


Fig. 7.8d. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % LB and 6.0 % WPI solutions.

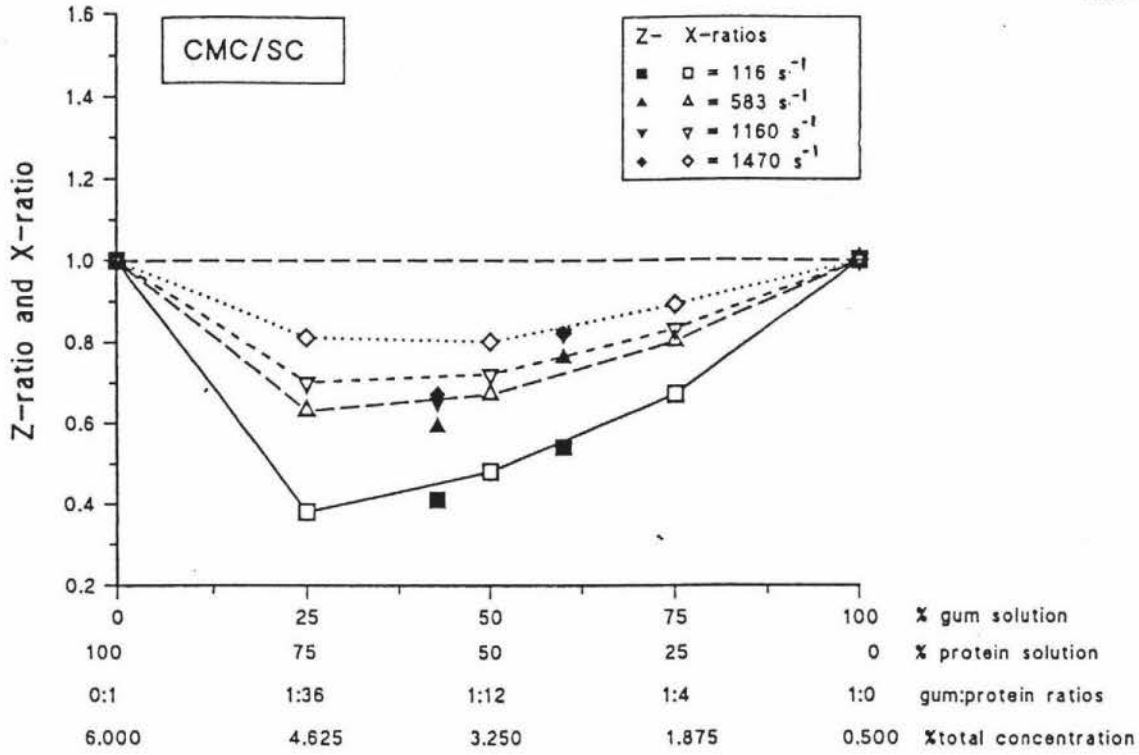


Fig. 7.9a. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % SC solutions.

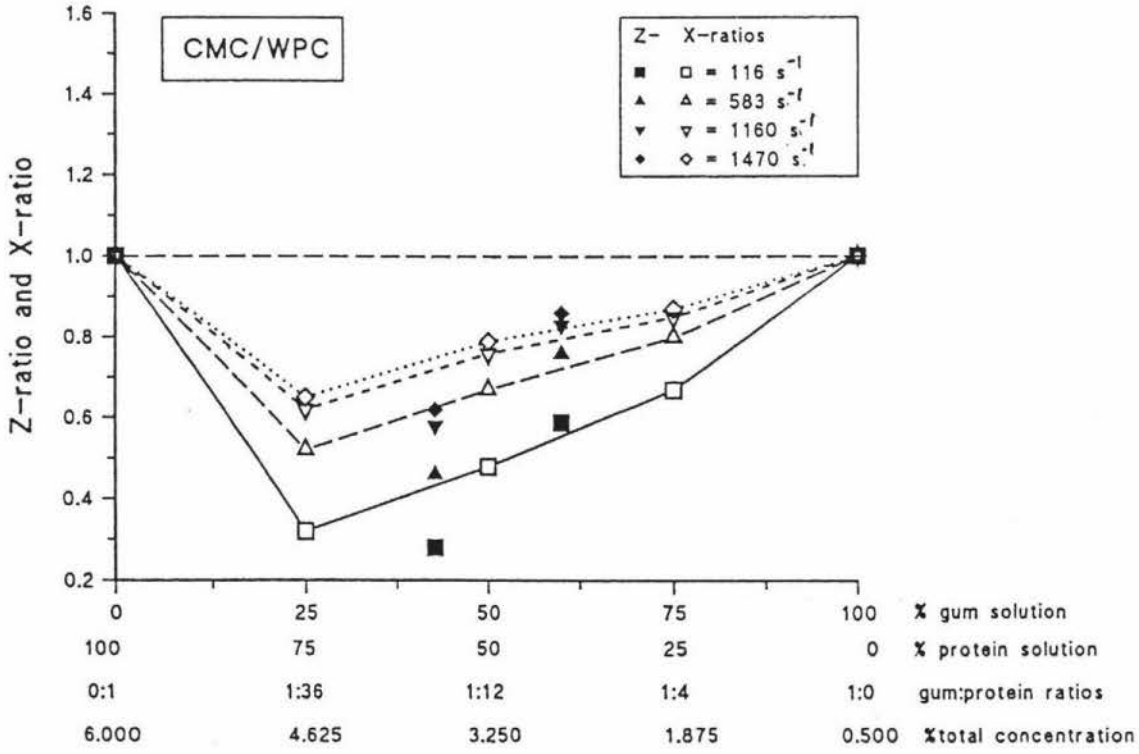


Fig. 7.9b. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPC solutions.

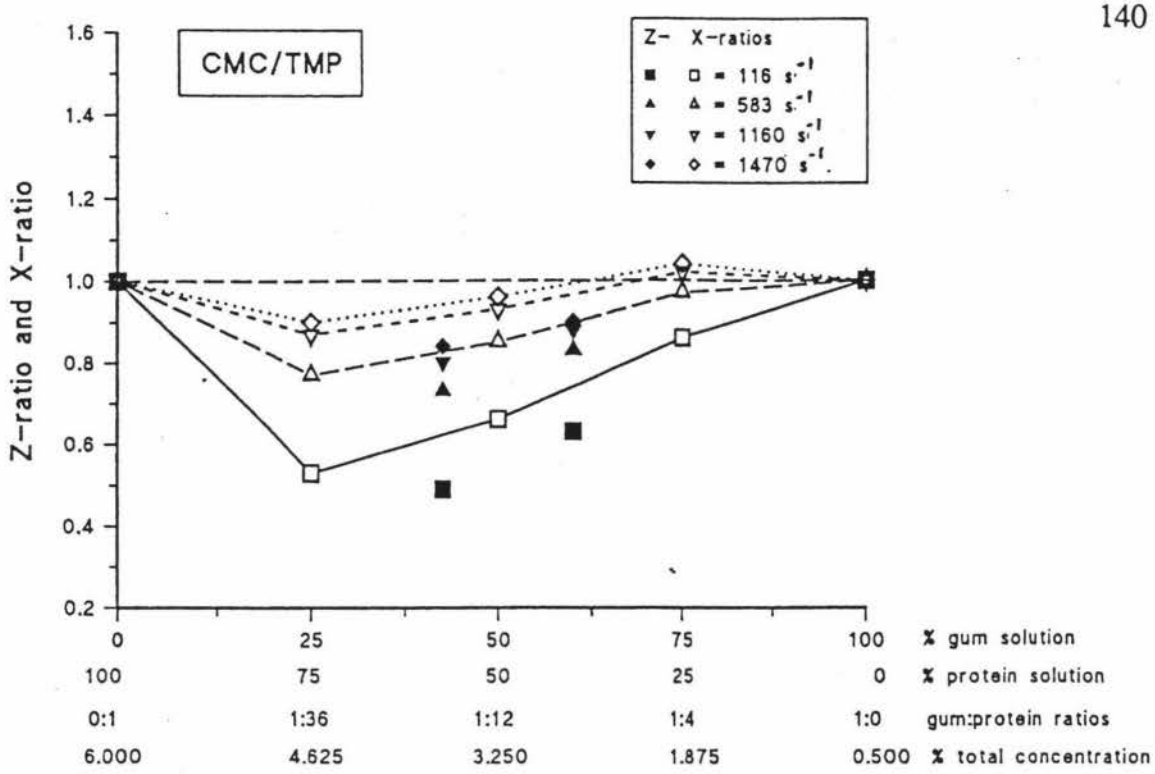


Fig. 7.9c. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % TMP solutions.

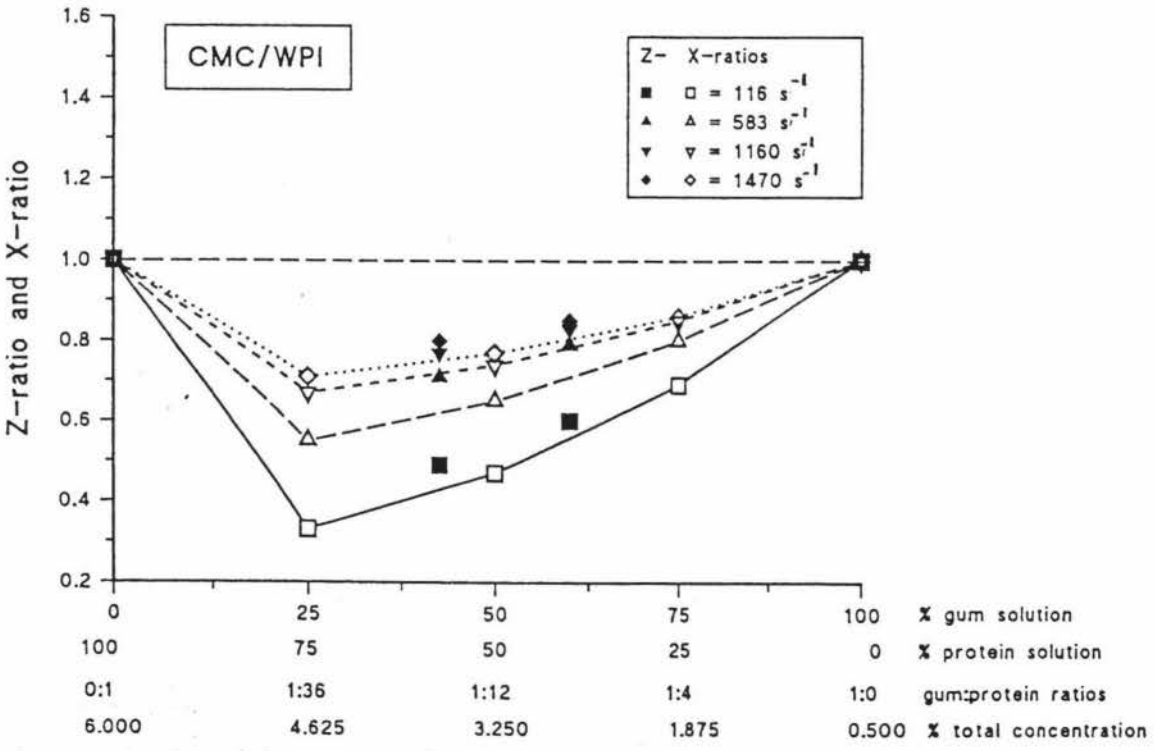


Fig. 7.9d. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CMC and 6.0 % WPI solutions.

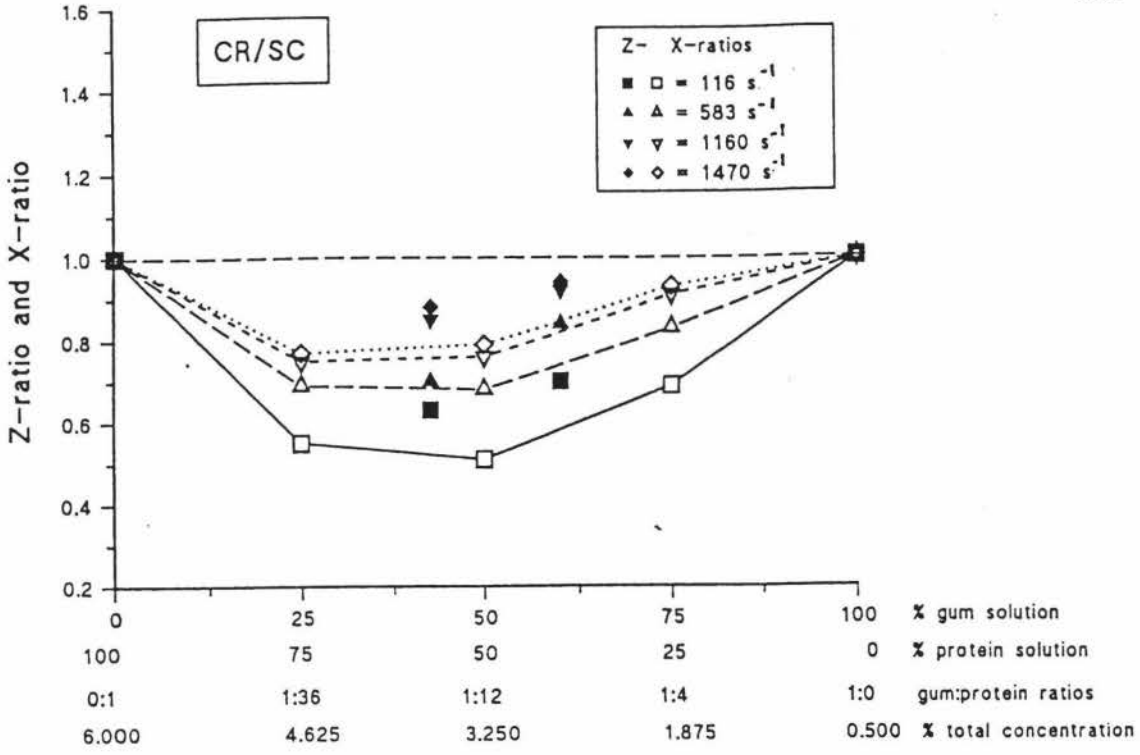


Fig. 7.10a. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % SC solutions.

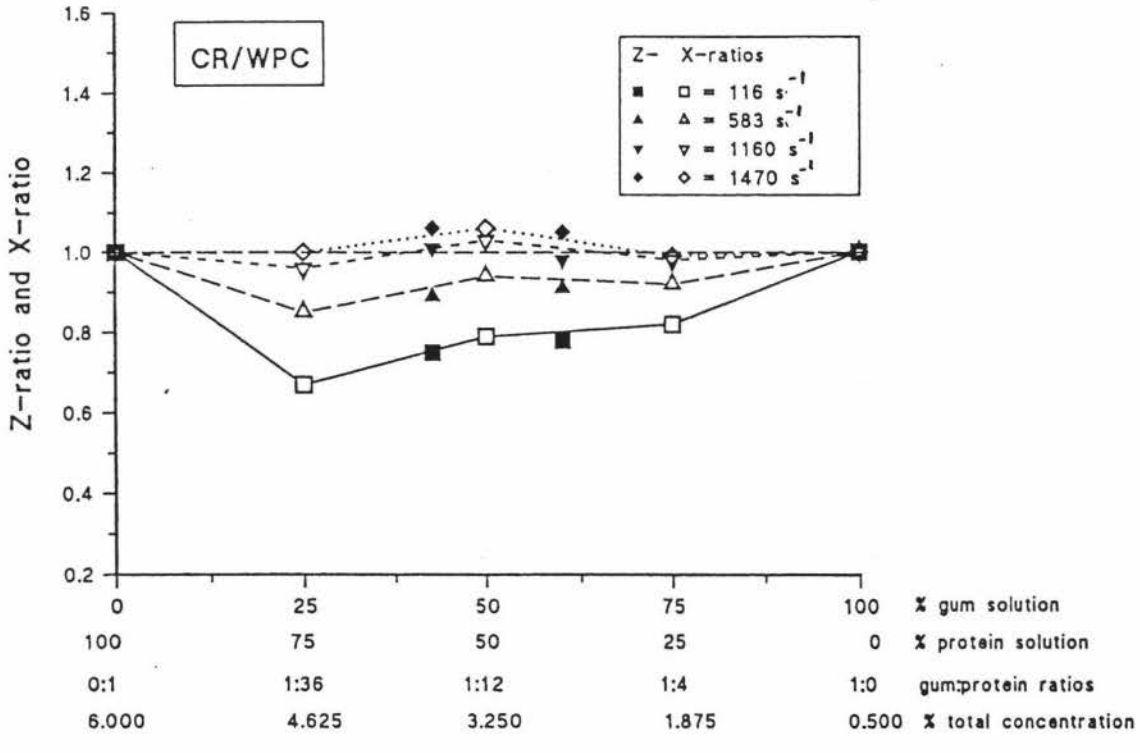


Fig. 7.10b. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPC solutions.

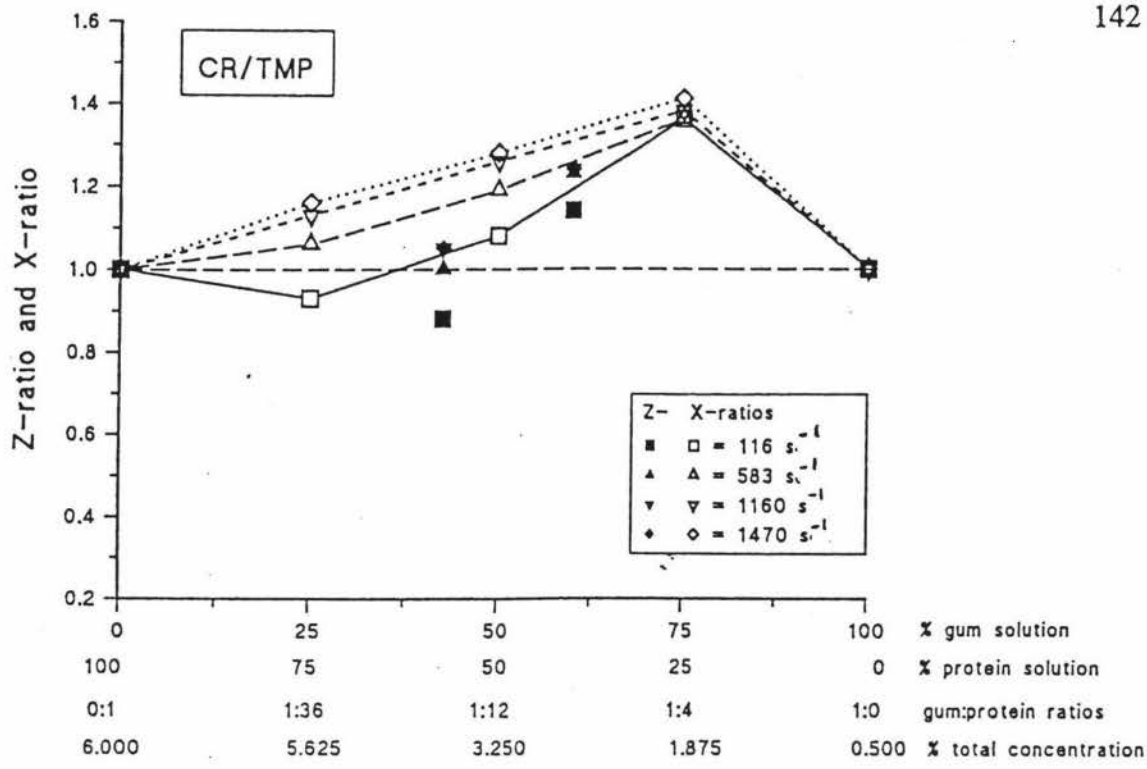


Fig. 7.10c. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % TMP solutions.

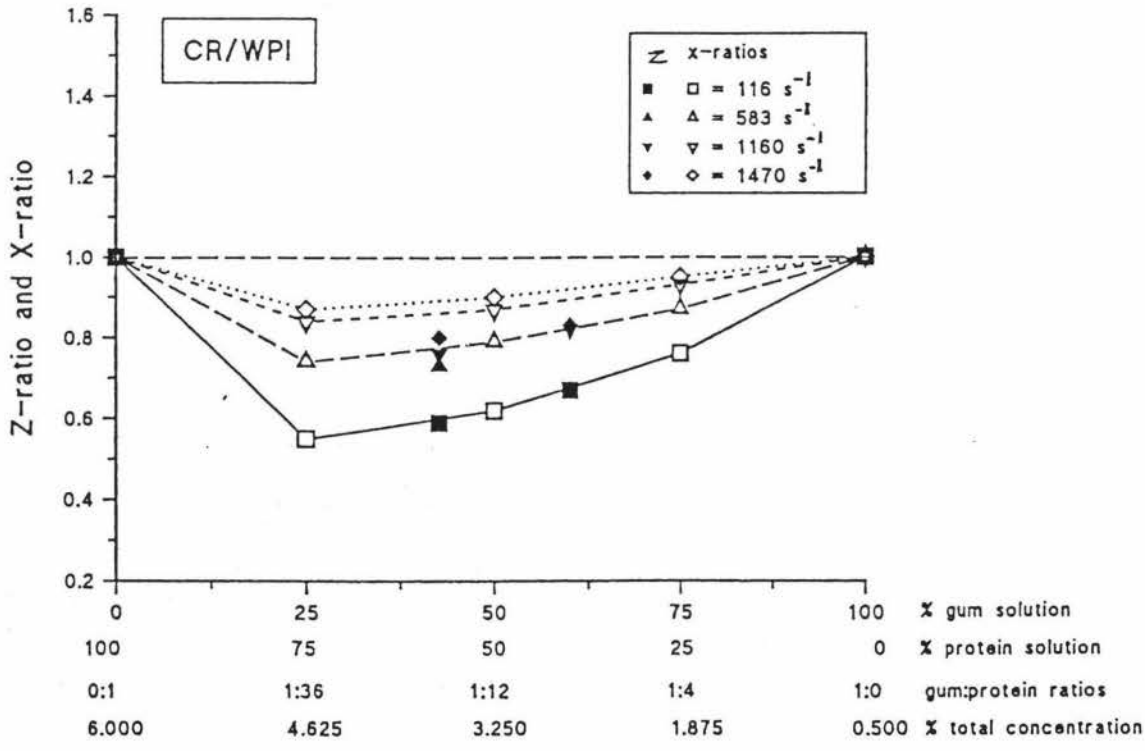


Fig. 7.10d. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % CR and 6.0 % WPI solutions.

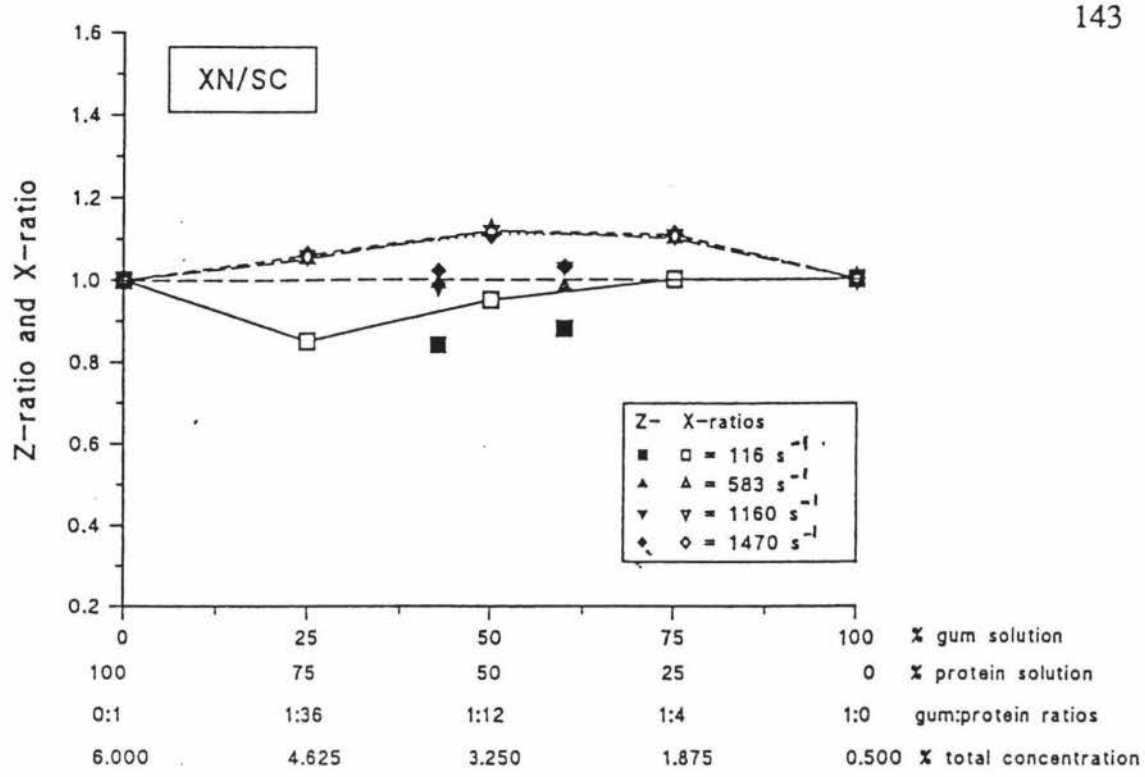


Fig. 7.11a. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % SC solutions.

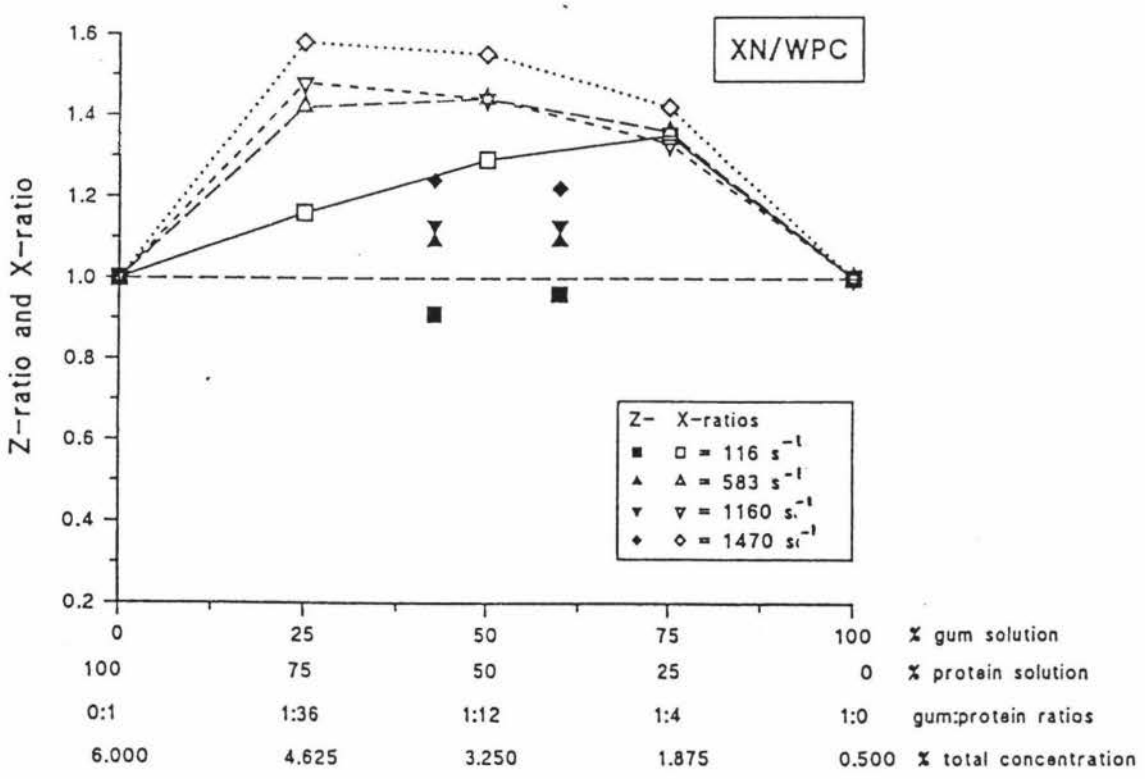


Fig. 7.11b. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPC solutions.

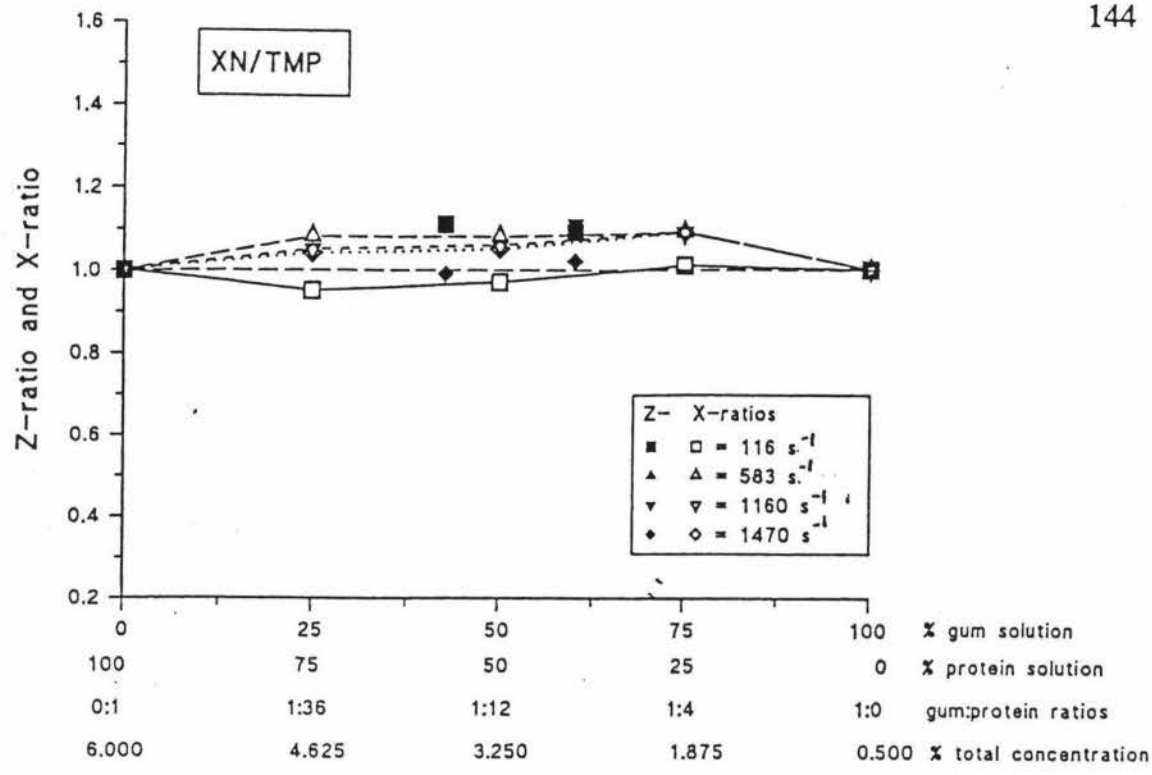


Fig. 7.11c. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % TMP solutions.

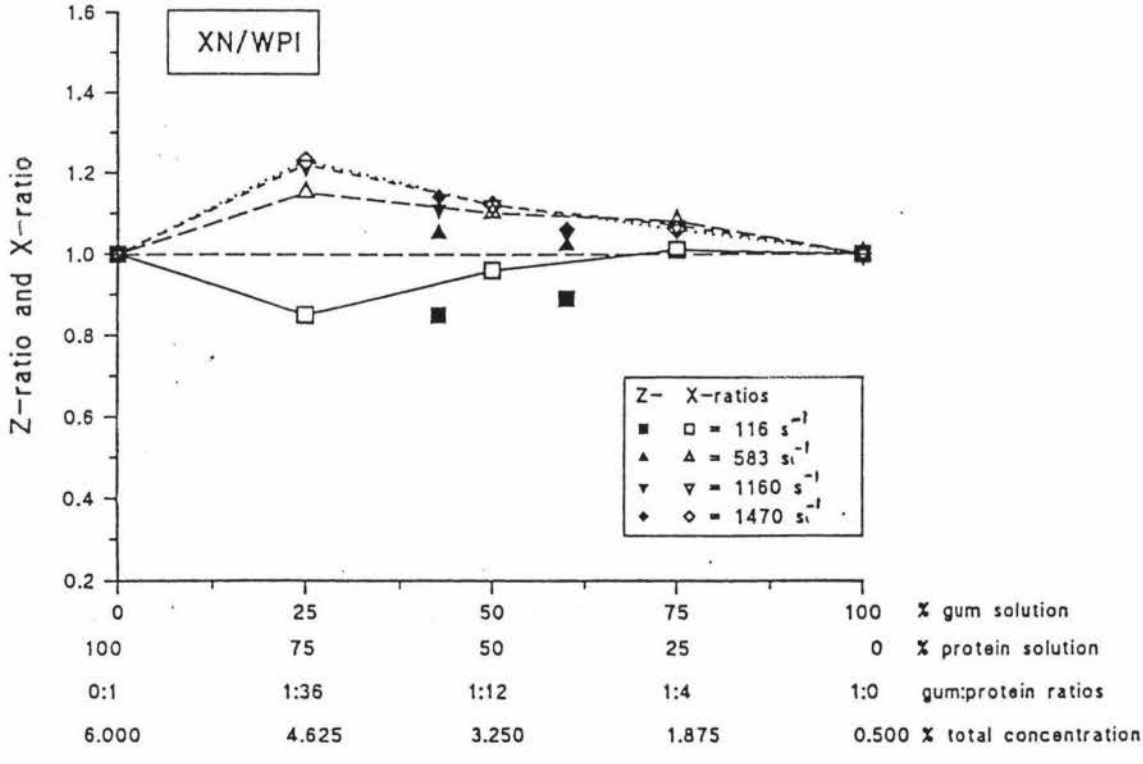


Fig. 7.11d. Z-ratio and X-ratio versus mixture composition for mixtures of 0.5 % XN and 6.0 % WPI solutions.

7.4.4 Sedimentation results

The sedimentation results presented in Tables 7.10-7.13 are discussed in turn by gum type, and compared with the sedimentation results presented in Chapter 6, Table 6.2.

LB

Sediments were found in LB/SC at all gum : protein ratios at the two lower total polymer concentrations, and at all concentrations at the two lower gum : protein ratios (Table 7.10). Sediments were in trace amounts except at the gum : protein ratios of 1:32 at concentrations 3.5 % and 4 %. No sediments were found in LB/SC previously (Table 6.2).

Sediment was found in LB/WPC at nearly all concentrations at gum : protein ratios of 1:8 and 1:16 (Table 7.10). Again, no sediments were found previously (Table 6.2). It is noted that the gum : protein ratio-concentration combinations for which sediments were found here are similar to those for which no sediments were found previously.

CMC

Sediments were found in CMC/SC in the two mixtures with the highest gum : protein ratio and highest concentrations (Table 7.11). Previously, only a trace of sediment was found in one CMC/SC mixture (at a comparable concentration but a lower gum : protein ratio)(Table 6.2).

Trace amounts of sediment were found in all except two CMC/WPC mixtures (Table 7.11), whereas significant amounts of sediment were found previously in this gum-protein combination (Table 6.2).

For both CMC/SC and CMC/WPC the characters of the sediments were the same as found previously.

No sediments were found in CMC/TMP or CMC/WPI (Table 7.11). Previously, significant amounts of sediment were found in CMC/TMP (Table 6.2) but none for CMC/WPI.

Table 7.10: Sedimentation results (%) for LB/dairy protein mixed solutions.

Type	Total conc.	gum:protein ratio 1:4	1:8	1:16	1:32
LB/SC	2.0%	*(a)	*(a)	*(a)	*(a)
	2.5%	*(a)	*(a)	*(a)	*(a)
	3.5%	N	N	*(a)	8.4(a)
	4.0%	N	N	*(a)	6.9(a)
LB/WPC	2.0%	N	*(a)	*(a)	N
	2.5%	N	9.8(a)	*(a)	N
	3.5%	N	11.4(a)	11.4(a)	N
	4.0%	N	N	*(a)	N
LB/TMP	2.0%	N	N	N	N
	2.5%	N	N	N	N
	3.5%	N	N	N	N
	4.0%	N	N	N	N
LB/WPI	2.0%	N	N	N	N
	2.5%	N	N	N	N
	3.5%	N	N	N	N
	4.0%	N	N	N	N

Notes:

1. N means no sediment was observed.
2. * means sediment (%) is less than 1.35%
3. (a) means a clear supernatant, good sharpness of separation with fine particles of sediment

Table 7.11: Sedimentation results (%) CMC/dairy protein mixed solutions

Type	Total conc.	gum:protein ratio 1:4	1:8	1:16	1:32
CMC/SC	2.0%	N	N	N	N
	2.5%	N	N	N	N
	3.5%	8.1(a)	N	N	N
	4.0%	36.7(a)	N	N	N
CMC/WPC	2.0%	*(a)	*(a)	*(a)	*(a)
	2.5%	*(a)	*(a)	*(a)	*(a)
	3.5%	N	*(a)	*(a)	*(a)
	4.0%	N	*(a)	*(a)	*(a)
CMC/TMP	2.0%	N	N	N	N
	2.5%	N	N	N	N
	3.5%	N	N	N	N
	4.0%	N	N	N	N
CMC/WPI	2.0%	N	N	N	N
	2.5%	N	N	N	N
	3.5%	N	N	N	N
	4.0%	N	N	N	N

Notes:

1. N means no sediment was observed.
2. * means sediment (%) is less than 1.35%
3. (a) means a clear supernatant, good sharpness of separation with fine particles of sediment

Table 7.12: Sedimentation results (%) for CR/dairy protein mixed solutions.

Type	Total conc.	gum:protein ratio 1:4	1:8	1:16	1:32
CR/SC	2.0%	N	N	N	N
	2.0%	57.9(a)	N	N	N
	3.5%	71.5(a)	N	N	N
	4.0%	84.2(a)	N	N	N
CR/WPC	2.0%	15.3(b)	12.5(b)	12.5(a)	5.5(a)
	2.5%	19.5(b)	25.0(b)	19.5(b)	15.3(a)
	3.5%	30.5(b)	34.7(b)	30.5(b)	34.7(a)
	4.0%	40.3(b)	35.0(b)	35.0(b)	33.4(a)
CR/TMP	2.0%	N	5.9(b)	N	N
	2.5%	N	49.4(b)	N	N
	3.5%	66.7(b)	50.6(b)	*(b)	N
	4.0%	61.9(b)	58.8(b)	9.5(b)	N
CR/WPI	2.0%	N	N	N	N
	2.5%	*(a)	N	N	N
	3.5%	5.4(a)	*(a)	N	N
	4.0%	8.6(a)	*(a)	N	N

Notes:

1.N means no sediment was observed.
2.* means sediment (%) is less than 1.35%
3.(a) means a clear supernatant, good sharpness of separation with fine particles of sediment
4.(b) means poor sharpness of separation, with gel-like sediment.

Table 7.13: Sedimentation results (%) of XN/dairy protein mixed solutions.

Type	Total conc.	gum:protein ratio 1:4	1:8	1:16	1:32
XN/SC	2.0%	N	N	N	N
	2.5%	N	N	N	N
	3.5%	N	N	N	N
	4.0%	N	N	N	N
XN/WPC	2.0%	N	N	N	N
	2.5%	N	N	N	N
	3.5%	N	N	N	N
	4.0%	N	N	N	N
XN/TMP	2.0%	N	N	N	N
	2.5%	N	N	N	N
	3.5%	N	N	N	N
	4.0%	N	N	N	N
XN/WPI	2.0%	N	N	N	N
	2.5%	N	N	N	N
	3.5%	N	N	N	N
	4.0%	N	N	N	N

Notes:

N means no sediment was observed.

CR

Relatively large amounts of sediment were found in CR/SC at the gum : protein ratio of 1:4 at the three highest concentrations (Table 7.12). Previously, sediment was found at the same gum : protein ratio but at the lower concentration of 1.875 % (Table 6.2). The character of the sediments was the same as that found previously.

Sediments, again relatively large in many cases, were found in all CR/WPC mixtures (Table 7.12) - as they were previously. Type (a) sediments were found at the lowest gum : protein ratio for all concentrations and at the two lower ratios for lower concentrations. These results are the same as found previously (Table 6.2).

Sediments were found in CR/TMP at all concentrations at the gum : protein ratio of 1:8, and at the two highest concentrations at the ratios 1:4 and 1:16 (Table 7.12). The character of the sediments was the same as that observed previously (Table 6.2).

Some sediments were found in CMC/WPI at lower gum : protein ratio-higher concentration (Table 7.12). No sediments were found previously.

XN

In these experiments, as in the previous ones (Chapter 6), no sediments of any kind were found in any of the XN/dairy protein mixtures.

The differences between the sedimentation results reported here and those reported in Chapter 6 may have been due to the different methods of preparation of the mixed solutions: for the Chapter 6 work, mixed solutions were prepared by combining 0.5% gum solution with 6.0% protein solution, while for this work, mixed solutions were prepared by combining 1.2% gum solution, 10% protein solution and (where necessary) distilled water.

7.5 CONCLUSIONS

The following conclusions were drawn on the basis of the work reported in this chapter.

The apparent viscosity of gum-dairy protein mixtures varies in a regular way with gum : protein ratio and total polymer concentration, and is dependent mainly on the gum concentration.

The rheological character of the mixtures depends mainly on gum concentration and gum type.

The data reported in this chapter are in very good agreement with those reported in Chapter 6. The Chapter 6 data was in effect successfully replicated, and the findings on gum-dairy protein rheological interactions thus confirmed.

This good agreement, and the discrepancies between the sedimentation results reported here and in Chapter 6, suggested once again that there was no clear link between rheological interaction and the extent of phase separation. In order to discover if there was, however, a link between interaction and sediment (and supernatant) compositions, the work reported in the next chapter was carried out.

CHAPTER 8

FURTHER SEDIMENTATION EXPERIMENTS

8.1 INTRODUCTION

It was found in the experimental studies reported in Chapters 6 and 7 that, while phase separation occurred in some gum-dairy protein mixed solutions, there was no obvious relationship between the extent of phase separation (as measured by the amount of sediment recoverable centrifugally) and the degree of rheological interaction as characterised by the X'-ratio. The experiments reported in this chapter were carried out to determine, firstly, whether or not a relationship existed between type and composition of sediment and composition of supernatant on the one hand and rheological interaction on the other and, secondly, whether or not the method of preparing the mixed solution influenced the extent and type of phase separation.

8.2 EXPERIMENTAL PLAN

The first part of the experimental plan is shown diagrammatically in Fig. 8.1. Mixture 1 was prepared by mixing 0.5 % gum solution with 6.0 % protein solution in the proportions shown in Table 8.1 for each of the 16 gum-dairy protein combinations. These were thus 48 mixtures designated Mixture 1. The mixture compositions shown in Table 8.1 are identical to those shown in Table 6.1.

Table 8.1 Compositions of mixtures designated Mixture 1.

Ratio of 0.5 % gum to 6.0% protein solution	Gum:protein ratio	Gum conc. (%)	Protein conc. (%)	Total polymer conc.(%)
25:75	1:36	0.125	4.5	4.625
50:50	1:12	0.250	3.0	3.250
75:25	1:4	0.375	1.5	1.875

Mixture 2 was prepared, for each of the 16 gum-dairy protein combinations, by mixing 1.2% gum, 10% protein and distilled water to give a mixed solution with a gum : protein ratio of 1:12 and a total polymer concentration of 3.5% (Table 8.2). These were thus 16 mixtures designated Mixture 2.

Table 8.2 Compositions of mixtures designated Mixture 2.

Gum: protein ratio	Gum conc. (%)	Protein conc (%).	Total polymer conc. (%)
1:12	0.250	3.0	3.250

All mixtures designated Mixture 1 or Mixture 2 were treated as shown in Fig. 8.1. Sediments were measured as described in Section 4.4.

The second part of the experimental plan is shown in Fig. 8.2. All mixtures designated Mixture 1 which exhibited sediment formation to an extent greater than 1.35% as a result of the treatment shown in Fig. 8.1 were prepared again (using the same stock solutions of 0.5% gum and 6.0% protein) and subjected to the treatment shown in Fig. 8.2. All the experimental methods used are described in Chapter 4.

8.3 PROCESSING AND PRESENTATION OF EXPERIMENTAL DATA

Sedimentation results for batches 1, 2.1 and 2.2 (Mixture 1) are shown in Tables 8.3, 8.4 and 8.5.

Sedimentation results for batches 3, 4.1 and 4.2 (Mixture 2) are shown in Table 8.6. Sedimentation results, supernatant total solids (%), supernatant protein (%) and supernatant viscosity at 1160 s^{-1} (mPa.s) for batch 5 (Mixture 1) are shown in Table 8.7. The sediment figures for batch 5 were exactly the same as those for batch 1.

The results presented in Tables 8.3-8.5 are retabulated in Table 8.8 where they are ranked according to the amount of sediment in batch 1 (Table 8.3). The mixed solutions are arbitrarily divided into three groups : Group A (sediment < 4%), Group

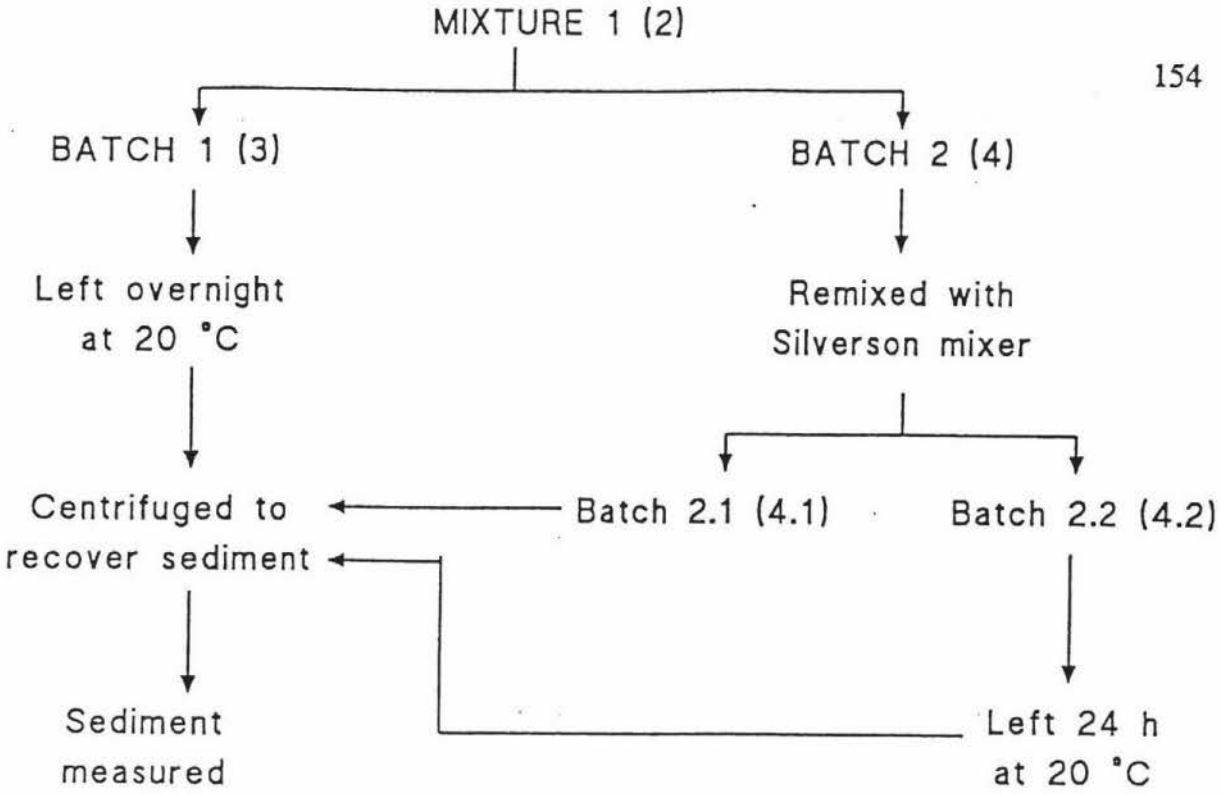


Fig. 8.1. Sedimentation experiments carried out on Mixtures 1 and 2.

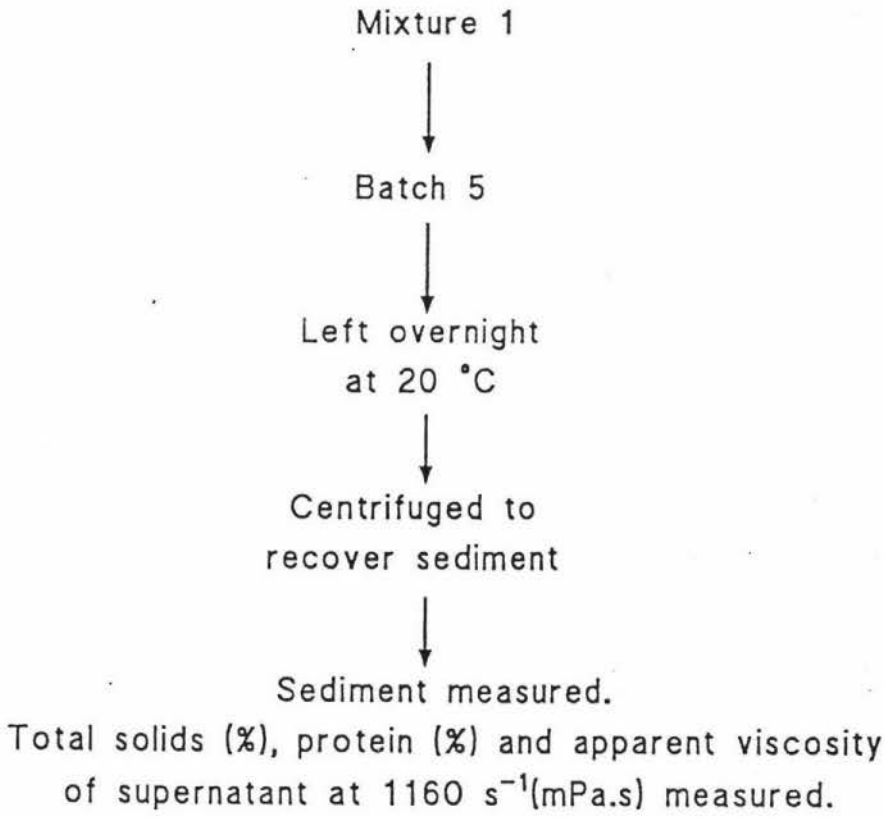


Fig. 8.2. Sedimentation measurement and analyses carried out on batch 5 (Mixture 1).

B (sediment = 4-10%) and Group C (sediment >10%). Table 8.8 includes for comparison the sedimentation results previously presented in Table 6.2.

The results presented in Table 8.6 are retabulated in Table 8.9 where they are ranked and grouped in the same way as those in Table 8.8 (i.e. on the basis of the sedimentation results for batch 1).

The analytical results presented in Table 8.7 have been processed as shown in Appendix 13. This appendix contains a full calculation for the LB/WPC mixture by way of example. The exact compositions of the remaining mixed solutions (before sedimentation) are shown in Appendix 13.

The data processing illustrated in Appendix 13 yielded the following information for each mixture:

1. Gum remaining in supernatant (after sedimentation) expressed as a percentage of the gum content of the whole mixture (supernatant plus sediment).
2. Dairy protein remaining in supernatant expressed as a percentage of the protein content of the whole mixture.
3. "Expected" apparent viscosity of supernatant at 1160 s^{-1} (mPa.s). This viscosity was defined as the viscosity of a pure gum solution with a concentration equal to the gum concentration of the supernatant. It was obtained form the viscosity-concentration data for the gums presented in Chapter 5.

Finally, all the information presented in Table 8.7 (except for % total solids and % soluble protein) has been retabulated in Table 8.10 together with the three factors listed just above and the X'-ratios presented in Chapter 7 for identical mixed solutions. The data in Table 8.10 are ranked in descending order of the figure for the percentage of total gum in the mixed solution remaining in the supernatant after sedimentation.

The data in Table 8.10 are retabulated in Table 8.11, but this time they are ranked in ascending order of the amount of sediment recovered centrifugally.

8.4 RESULTS AND DISCUSSION

8.4.1 Sedimentation results

The sedimentation results for batch 1 (Table 8.3) may be compared to those in Table 6.2 since the starting solutions (0.5% gum and 6.0% dairy protein), the mixed solution preparation method and the method of centrifuging were the same in each case.

Over-all, the two sets of results are in good agreement. Exceptions are, as shown in Table 8.3, the formation of small sediments in two LB/WPC mixed solutions, the lower sediment amounts for CMC/WPC and some differences (between Table 8.3 and 6.2) in sediment amounts among CR/dairy protein mixed solutions.

Once again, no sediment was found in any XN/dairy protein or in any gum/WPI mixed solutions.

In the sedimentation study reported in this chapter, careful observation was made of the character of any mixtures where sediment was not recovered on centrifugation. Some of these mixtures, identified by the letter 'NG' in Tables 8.3-8.6, were qualitatively observed to be homogeneous, but to have an unexpectedly high viscosity or even a gel-like character. If any particle formation had occurred in these mixtures it is possible that the character of the mixture prevented particles being recoverable as sediment under the centrifugation conditions used. (Type (b) sediments might very well have been the result of the centrifugation conditions used having an effect on 'NG' type mixed solutions.)

It can be seen (Table 8.3) that XN/WPC was the only XN/dairy protein combination to exhibit 'NG' type mixtures. An inspection of X'-ratio data for XN/dairy proteins tabulated in Appendix 11, Table A11.4 shows that XN/WPC had positive X'-ratios (indicating synergistic rheological interaction) at least 60% greater than those of any of the other XN/dairy protein mixtures. This suggests a connection between rheological synergism and the qualitative nature of the mixture referred to above. However, a comparison of both 'N' and 'NG' sedimentation results in Table 8.3 with X'-ratios (Appendix 11) shows that some 'N' mixtures have X'-ratios as high or even

Table 8.3: Sedimentation results (%) for batch 1.

Sample	gum : protein ratios		
	1:36	1:12	1:4
LB/SC	N	N	N
LB/WPC	N	*(a)	1.9(a)
LB/WPC(R)	N		1.7(a)
LB/TMP	N	N	N
LB/WPI	N	N	N
CMC/SC	N	*(a)	N
CMC/WPC	*(a)	NG	*(a)
CMC/WPC(R)		*(a)	
CMC/TMP	2.7(a)	4.0(b)	1.4(a)
CMC/TMP(R)		4.0(b)	
CMC/WPI	N	N	N
CR/SC	N	N	25.7(a)
CR/SC(R)			25.0(a)
CR/WPC	31.1(a)	28.4(b)	9.5(b)
CR/WPC(R)	31.1(a)	25.7(b)	8.5(b)
CR/TMP	NG	9.5(b)	58.1(b)
CR/TMP		9.5(b)	60.0(b)
CR/WPI	N	N	N
XN/SC	N	N	N
XN/WPC	NG	NG	NG
XN/TMP	N	N	N
XN/WPI	N	N	N

Notes:

1. N means no sediment was observed.
2. * means sediment (%) is less than 1.35%
3. (a) means a clear supernatant, good sharpness of separation with fine particles of sediment
4. (b) means poor sharpness of separation, with gel-like sediment.
5. NG means no sediment was found but the solution appeared to be a gel-like mass.

Table 8.4: Sedimentation results (%) for batch 2.1.

Sample	gum : protein ratios		
	1:36	1:12	1:4
LB/SC	N	N	N
LB/WPC	N	*(a)	*(a)
LB/WPC(R)			*(a)
LB/TMP	N	N	N
LB/WPI	N	N	N
CMC/SC	N	N	N
CMC/WPC	*(a)	NG	N
CMC/WPC(R)		N	
CMC/TMP	NG	*(b)	NG
CMC/TMP(R)	*(b)		
CMC/WPI	N	N	N
CR/SC	N	N	NG
CR/SC(R)			NG
CR/WPC	12.4(a)	9.5(b)	*(b)
CR/WPC(R)	12.2(a)	10.0(b)	*(b)
CR/TMP	NG	*(b)	NG
CR/TMP(R)		*(b)	NG
CR/WPI	N	N	N
XN/SC	N	N	N
XN/WPC	NG	NG	NG
XN/TMP	N	N	N
XN/WPI	N	N	N

Notes:

1. N means no sediment was observed.
2. * means sediment (%) is less than 1.35%
3.(a) means a clear supernatant, good sharpness of separation with fine particles of sediment
4.(b) means poor sharpness of separation, with gel-like sediment.
5. NG means no sediment was found but the solution appeared to be a gel-like mass.

Table 8.5: Sedimentation result (% w/w) for batch 2.2.

Sample	gum : protein ratios		
	1:36	1:12	1:4
LB/SC	N	N	N
LB/WPC	N	*(a)	*(a)
LB/WPC(R)			*(a)
LB/TMP	N	N	N
LB/WPI	N	N	N
CMC/SC	N	N	N
CMC/SC(R)			N
CMC/WPC	*(a)	NG	NG
CMC/TMP	NG	2.7(b)	NG
CMC/TMP(R)	2.7(b)	N	
CMC/WPI	N	N	N
CR/SC	N	N	NG
CR/SC(R)			NG
CR/WPC	24.3(a)	20.3(b)	NG
CR/WPC(R)	26.8(a)	21.5(b)	NG
CR/TMP	NG	31.1(b)	NG
CR/TMP(R)		35.0(b)	NG
CR/WPI	N	N	N
XN/SC	N	N	N
XN/WPC	NG	NG	NG
XN/TMP	N	N	N
XN/WPI	N	N	N

Notes:

1. N means no sediment was observed.
2. * means sediment (%) is less than 1.35%
3. (a) means a clear supernatant, good sharpness of separation with fine particles of sediment
4. (b) means poor sharpness of separation, with gel-like sediment.
5. NG means no sediment was found but the solution appeared to be a gel-like mass.

Table 8.6: Sedimentation results (%) for Mixture 2.

Sample	Batch 3	Batch 4.1	Batch 4.2
LB/SC	N	N	N
LB/WPC	N	*(a)	N
LB/WPC(R)	N	*(a)	N
LB/TMP	N	N	N
LB/WPI	N	N	N
CMC/SC	N	N	N
CMC/WPC	NG	NG	NG
CMC/TMP	NG	*(b)	2.7(b)
CMC/TMP(R)NG	*(b)		2.5(b)
CMC/WPI	N	N	N
CR/SC	N	N	N
CR/WPC	27.0(b)	*(b)	28.0(b)
CR/WPC(R)	26.4(b)	*(b)	26.0(b)
CR/TMP	10.0(b)	*(b)	16.0(b)
CR/TMP(R)	8.6(b)	*(b)	11.0(b)
CR/WPI	N	N	N
XN/SC	N	N	N
XN/WPC	NG	NG	NG
XN/TMP	N	N	N
XN/WPI	N	N	N

Notes:

1. N means no sediment was observed.
2. * means sediment (%) is less than 1.35%
3.(a) means a clear supernatant, good sharpness of separation with fine particles of sediment
4.(b) means poor sharpness of separation, with gel-like sediment.
5. NG means no sediment was found but the solution appeared to be a gel-like mass.

Table 8.7: Sediment results (%) and analytical results for batch 5.

Sample	Gum:protein ratio	%sediment	Supernatant		
			%TS	%protein	Apparent viscosity at 1160 s^{-1}(mPa.s)
LB/WPC	1:4	1.9(a)	1.91	1.16	12.6
CMC/TMP	1:36	2.7(a)	5.09	4.55	13.3
CMC/TMP	1:12	4.0(b)	3.53	3.00	18.5
CMC/TMP	1:4	1.3(a)	2.12	1.50	27.4
CR/SC	1:4	25.7(a)	1.85	1.33	18.9
CR/WPC	1:36	31.1(a)	4.10	3.00	3.8
CR/WPC	1:12	28.4(b)	2.80	1.97	8.5
CR/WPC	1:4	9.5(b)	1.71	1.06	12.3
CR/TMP	1:12	9.5(a)	3.24	2.66	13.8
CR/TMP	1:4	58.1(b)	1.87	1.20	19.4

higher than those of 'NG' mixtures. There seems therefore to be no obvious relationship between rheological interaction and the quanlitatively observed characters of mixed solutions remaining homogeneous after centrifugation.

A comparison between the results for batch 2.1 (Table 8.4) and those for batch 1 (Table 8.3) shows that a second vigorous mixing of the gum-protein mixed solution just before centrifugation had the effect of reducing or preventing sediment recovery (if not sediment formation), but not of changing sediment type (where sediments were recovered). The effect was greatest at high gum : protein ratio, least at low. This suggests that the second mixing broke up particles or particle aggregates into smaller ones which sedimented more slowly -particularly in the more viscous higher gum : protein ratio solutions - during centrifugation.

A comparison of the sedimentation results for batch 2.2 (Table 8.5) with those for batch 2.1 (Table 8.4) and batch 1 (Table 8.3) shows that a 24 hour rest period after the second mixing resulted in almost complete recovery of sediment amounts at the gum : protein ratios of 1:36 and 1:12, but no recovery at the ratio of 1:4. At this last ratio, all mixtures in which sediment was found in batches 1 and 2.1 were observed

to be 'NG'. It is possible that the relatively high viscosities of these 1:4 mixtures hampered reaggregation of particles and that the presence of well-dispersed small particles resulted in a change in the character of the mixtures.

Referring back to the XN/WPC results for batch 1 (Table 8.3) it is possible that XN does react with WPC to form insoluble particles but that these could not aggregate, and could not be recovered by centrifugation, because of the relatively high viscosity imparted to the XN/WPC mixtures by the xanthan gum. Further, xanthan gum solutions are known to possess a yield stress - a characteristic that tends to keep small particles suspended (and that is exploited for this purpose in foods).

The results for batches 3, 4.1 and 4.2 (Mixture 2) shown in Table 8.6 may be compared with the results for the gum : protein ratio of 1:12 shown in Tables 8.3, 8.4 and 8.5. Such a comparison shows that preparing the gum-protein mixed solutions in the form of Mixture 2 as opposed to Mixture 1 had only a very small effect on the sedimentation results obtained - and no effect on sediment type. Sediment amounts thus depend principally on the gum-protein ratio (and the total polymer concentration) of the mixed solution, and the way in which the mixed solution is treated after preparation.

The information in Table 8.8, where the data from Tables 8.3-8.5 are ranked by sediment amount, shows that for batch 1 small sediment amounts (<4%) were of type (a), medium amounts (4-10%) of type (b) and large amounts (>10%) of either type (a) or type (b). This pattern was the same for batches 2.1 and 2.2.

The information in Table 8.9 (which is analogous to Table 8.8) demonstrates once again that the sedimentation results for Mixture 2 are very similar to those for mixture 1.

Ranking of data by sediment amount (Table 8.8) shows that of the two anionic gums (CMC and CR) that form sediments with the dairy proteins SC, TMP and WPC, CR resulted in consistently larger amounts of sediment.

Table 8.8: Sedimentation results (%) for Mixture 1 (Data from Tables 8.3-8.5).

Group	Sample	Gum: protein ratio	Batch 1	Batch 2.1	Batch 2.2	Results from Chapter 6 Table 6.2
A	LB/WPC	1:12	*(a)	*(a)	*(a)	N
	CMC/SC	1:12	*(a)	N	N	*(a)
	CMC/WPC	1:4	*(a)	N	N	13.9(a)
	CMC/WPC	1:4(R)	*(a)	N	N	
	CMC/WPC	1:36	*(a)	*(a)	*(a)	5.5 (a)
	CMC/TMP	1:4	1.4(a)	N	N	2.17(b)
	LB/WPC	1:4	1.9(a)	*(a)	*(a)	N
	LB/WPC	1:4(R)	1.7(a)	*(a)	*(a)	
	CMC/TMP	1:36	2.7(a)	N	N	9.5(a)
B	CMC/TMP	1:12	4.0(b)	*(b)	2.7(b)	4.8(b)
	CMC/TMP	1:12(R)	4.0(b)	*(b)	2.7(b)	
	CR/WPC	1:4	9.5(b)	*(b)	N	16.7(b)
	CR/WPC	1:4(R)	8.5(b)	*(b)	N	
	CR/TMP	1:12	9.5(b)	*(b)	31.1(b)	27.0(b)
	CR/TMP	1:12(R)	9.5(b)	*(b)	35.0(b)	
C	CR/SC	1:4	25.7(a)	N	N	26.3(a)
	CR/SC	1:4(R)	25.0(a)	N	N	
	CR/WPC	1:12	28.4(b)	9.5(b)	20.3(b)	22.2(b)
	CR/WPC	1:12(R)	25.7(b)	10.0(b)	21.5(b)	
	CR/WPC	1:36	31.1(a)	12.4(a)	24.3(a)	22.8(a)
	CR/WPC	1:36(R)	31.1(a)	12.2(a)	26.8(a)	
	CR/TMP	1:4	58.1(b)	N	N	27.0(b)
	CR/TMP	1:4(R)	60.0(b)	N	N	

Notes:

1. N means no sediment was observed.
2. * means sediment (%) is less than 1.35%
3. (a) means a clear supernatant, good sharpness of separation with fine particles of sediment
4. (b) means poor sharpness of separation, with gel-like sediment.
5. NG means no sediment was found but the solution appeared to be a gel-like mass.
6. R means dulplicate results

Table 8.9: Sedimentation results (%) for Mixture 2 (Data from Table 8.6)

group	Sample	Gum: protein ratio	Batch 3	Batch 4.1	Batch 4.2
A	LB/WPC	1:12	N	*(a)	N
	LB/WPC	1:12(R)	N	*(a)	N
B	CMC/TMP	1:12	N	*(b)	2.7(b)
	CMC/TMP	1:12(R)	N	*(b)	2.5(b)
	CR/TMP	1:12	10.0(b)	*(b)	16.0(b)
	CR/TMP	1:12(R)	8.6(b)	*(b)	11.0(b)
C	CR/WPC	1:12	27.0(b)	*(b)	28.0(b)
	CR/WPC	1:12(R)	26.4(b)	*(b)	26.0(b)

Notes:

1. N means no sediment was observed.
2. * means sediment (%) is less than 1.35%
3. (a) means a clear supernatant, good sharpness of separation with fine particles of sediment
4. (b) means poor sharpness of separation, with gel-like sediment.
5. NG means no sediment was found but the solution appeared to be a gel-like mass.
6. R means dulplicate results

8.4.2 Supernatant and sediment compositions

The data in Table 8.10 show that, when the proportion of total gum in the mixed solution that remains in the supernatant after centrifugation was at or close to 100%, the character of the sediment was type (a). When the proportion dropped to less than 90% the sediment character changed to type (b).

The data in Table 8.11 show that as sediment amount increased, the proportion of the total dairy protein in the mixed solution that remained in the supernatant after centrifugation decreased - i.e. the proportion of the total protein that end up in the sediment increased.

These observations indicate that the amount of sediment depends on the proportion of the total protein that is in the sediment while the character of the sediment depends on the proportion of the total gum that is in the sediment. Both of these effects appear to be largely independent of mixture type and gum : protein ratio, although mixtures containing CR gave consistently higher amounts of sediment than mixtures containing CMC.

It is noted that for all batch 5 mixtures the proportions of the total amounts of gum and protein present that remained in the supernatant were in all cases greater than 50% (Table 8.10 or 8.11).

8.4.3 Rheology

The following discussion focuses on the rheological data presented in Tables 8.10 and 8.11

It was expected that as the proportion of the total protein left in the supernatant decreased the percentage difference between the measured supernatant viscosity and the viscosity expected on the basis of the supernatant gum concentration would decrease - especially for supernatant gum concentrations at or close to 100%.

Table 8.10: Sedimentation results, compositions, supernatant viscosities and X'-ratios for batch 5 mixed solutions. (Data ranked in descending order of the figure for the percentage of total gum in the mixed solution remaining in the supernatant after centrifugation).

Type	gum: protein ratio	sediment (%)	% of total in supernatant		Viscosity of supernatant		% diff*	X'-ratio (Chapter 6)
			Gum	Protein	Measured (mPa.s)	Expected (mPa.s)		
CMC/TMP	1:36	2.7(a)	100.0	98.3	13.30	3.90	241.0	0.67
CR/TMP	1:12	9.5(a)	100.0	79.5	13.80	9.50	45.3	0.54
CR/SC	1:4	25.7(a)	100.0	62.7	18.92	14.00	35.1	0.06
CR/WPC	1:36	31.1(a)	100.0	56.8	3.80	4.40	-13.6	0.55
CMC/TMP	1:4	1.3(a)	94.7	98.3	27.40	28.00	-2.1	0.36
LB/WPC	1:4	1.9(a)	93.3	93.2	12.60	13.00	-3.1	0.08
CMC/TMP	1:12	4.0(b)	83.3	95.8	18.50	8.20	125.0	0.94
CR/WPC	1:4	9.5(b)	68.7	78.0	12.27	9.30	31.9	0.14
CR/TMP	1:4	58.1(b)	56.2	52.8	19.43	17.00	14.3	0.60
CR/WPC	1:12	28.4(b)	54.5	58.1	8.51	6.60	28.9	0.26

$$* \ \% \text{ diff} = \frac{(\text{measured viscosity} - \text{expected viscosity}) * 100}{\text{expected viscosity}}$$

Table 8.11: Sedimentation results, compositions, supernatant viscosities and X'-ratios for batch 5 mixed solutions. (Data ranked in ascending order of the figure for the sediment %).

Type	gum: protein ratio	sediment (%)	% of total in supernatant		Viscosity of supernatant		% diff*	X'-ratio (Chapter 6)
			Gum	Protein	Measured (mPa.s)	Expected (mPa.s)		
CMC/TMP	1:4	1.3(a)	94.7	98.3	27.40	28.00	-2.1	0.36
LB/WPC	1:4	1.9(a)	93.3	93.2	12.60	13.00	-3.1	0.08
CMC/TMP	1:36	2.7(a)	100.0	98.3	13.30	3.90	241.0	0.67
CMC/TMP	1:12	4.0(b)	83.3	95.8	18.50	8.20	125.0	0.94
CR/TMP	1:12	9.5(a)	100.0	79.5	13.80	9.50	45.3	0.54
CR/WPC	1:4	9.5(b)	68.7	78.0	12.27	9.30	31.9	0.14
CR/SC	1:4	25.7(a)	100.0	62.7	18.92	14.00	35.1	0.06
CR/WPC	1:12	28.4(b)	54.5	58.1	8.51	6.60	28.9	0.26
CR/WPC	1:36	31.1(a)	100.0	56.8	3.80	4.40	-13.6	0.55
CR/TMP	1:4	58.1(b)	56.2	52.8	19.43	17.00	14.3	0.60

$$* \ \% \text{ diff} = \frac{(\text{measured viscosity} - \text{expected viscosity}) * 100}{\text{expected viscosity}}$$

It was expected also that a relationship might exist between this percentage difference and the X'-ratio; a larger than expected supernatant viscosity (i.e. a large percentage difference), especially for mixed solutions where the gum and protein concentrations of the supernatant both were at or near their maxima possible, might have been expected to coincide with a high (positive) X'-ratio (indicating rheological synergism).

An inspection of the data in Tables 8.10 and 8.11 shows that neither of these expected patterns exists. Further, there are apparently no relationships between the X'-ratio on the one hand and sediment amount, proportion of gum left in supernatant or proportion of protein left in supernatant on the other.

The absence of expected patterns, while difficult to interpret, is consistent with the earlier findings reported in Chapters 6 and 7 that there was apparently no relationship between sediment formation (and type) and rheological interaction (as measured by the X'-ratio). Yet the X'-ratio data presented in Chapter 6 (and which are indirectly replicated by the Z-ratio data presented in Chapter 7) show that rheological interaction does occur in several of the gum-dairy protein mixtures studied. It seems that rheological interaction as measured in homogeneous gum-dairy protein mixtures is independent of the presence of sedimentable material provided this material is evenly dispersed at the time of rheological measurement.

8.5 CONCLUSION

The following conclusions are drawn.

1. The sedimentation behaviour of the gum-dairy protein mixed solutions studied is unaffected by varying the compositions of the starting pure gum and pure protein solutions.
2. For a given gum : protein combination, sedimentation behaviour (but not sediment type) is very much affected by the treatment the mixed solution receives after initial preparation.
3. The amount of recoverable sediment depends on the proportion of total protein present that ends up in the sediment.

4. The character of the sediment depends on the proportion of total gum present that ends up in the sediment.
5. Sediment amount and type seem to be largely independent of mixture type (gum-dairy protein combination) and gum : protein ratio, but mixtures containing CR gave consistently greater amounts of sediment that those containing CMC.
6. No discernible relationships exist between the X'-ratios reported in Chapter 6 and any of the sedimentation and rheological data presented in this chapter.
7. Rheological interaction is independent of the amount of sedimentable material and of the composition of such material provided this material is evenly dispersed in the mixed solution.

CHAPTER 9

FINAL DISCUSSION AND CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

This study was an attempt to measure and to understand rheological interactions between selected gums and selected dairy proteins though viscometric measurements on mixed solutions. The gums were locust bean gum (LB), sodium carboxymethycellulose (CMC), lambda-carrageenan (CR) and xanthan gum (XN). The dairy proteins, which were all commercial protein products, were sodium caseinate (SC), whey protein concentrate (WPC), coprecipitate (TMP) and whey protein isolate (WPI).

Pure solutions of the gums were found to be viscous and pseudoplastic. This behaviour is typical of gums and is a consequence of their hydrophillic nature and long random-coil molecules. Solution viscosity increased with gum concentration. At a given shear rate apparent viscosity increased exponentially with concentration for LB, CMC and CR, but increased in a nearly linear manner for XN. The degree of pseudoplasticity of the solutions also increased with increasing concentration. At a given concentration the degree of pseudoplasticity (departure from Newtonian behaviour) increased in the order CR > LB > CMC > XN. The simple power law fitted the viscometric data closely in all cases.

Pure 6.0 % SC, WPC and WPI solutions were found to be of low viscosity and to be Newtonian, while 6.0% TMP was somewhat more viscous and exhibited slight pseudoplasticity at low shear rate. Solutions of the linear proteins SC and TMP were over twice as viscous as solutions of the globular proteins WPC and WPI. This was probably a consequence of differences in molecular shape and degree of hydration.

Gum-dairy protein interactions were studied by mixing pure gum solutions and pure protein solutions in various proportions and measuring the steady shear rheological

properties of the mixed solutions. These properties were found to depend very much on gum concentration and gum type.

The presence or absence of rheological interaction was detected by processing viscometric data in a way similar to that reported in the literature by previous workers. However, the data processing method used in the present work is considered to be an improvement over that used previously because it takes into account non-linear dependence of viscosity upon concentration for the gums (the rheologically-dominant component of the mixed solutions).

Rheological synergism was found at all shear rates in LB/SC and LB/TMP mixed solutions with the two lower gum:protein ratios, and in LB/WPC at all gum : protein ratios at the three higher shear rates. Synergism was found also, at all gum : protein ratios and all shear rates, in CMC/all dairy proteins, CR/WPC, CR/TMP and XN/WPC.

Synergism was relatively much greater with TMP than with the other dairy proteins. In the cases of CMC/TMP and CR/TMP synergism could have been the result of Ca^{2+} bridging between the negatively-charged anionic gum molecules and the net negatively charged protein molecules.

Synergism in LB/TMP and in the other gum-dairy protein mixed solutions identified above may have been the result of electrostatic or molecular space occupancy effects or both. In the case of synergism in XN/WPC it is suggested that WPC, alone among the four dairy proteins studied, might possibly cause a change in the conformation of the XN molecule leading to increased viscosity. However, the interaction results for this particular gum-protein combination were not successfully replicated.

In all cases of synergism, the effect of shear rate was found to be small and indeterminate.

No significant interaction was found in any of following combinations: LB/WPI, CR/SC, CR/WPI, XN/SC, XN/TMP and XN/WPI. XN was the "most unreactive" gum

and WPI was the "most unreactive" dairy protein.

The rheological interaction experimental results (except those for XN/WPC) were replicated closely by two quite separate series of experiments. Some confidence can thus be placed in them. The second series of experiments showed that the apparent viscosity of gum-dairy protein mixed solutions varies in a regular way with gum : protein ratio and total concentration.

Phase separation resulting in centrifugally-recoverable sediments occurred in a number of gum-dairy protein mixed solutions studied, but it proved impossible to establish even a qualitative relationship between this phenomenon and the measured degrees of rheological interaction. However, it was established that the sedimentation behaviour of the solutions depends on the treatment they receive after initial preparation (but not on the concentrations of pure gum and protein solutions from which they are made). It was established further that the amount and type of sediment depend respectively on the proportion of total protein present and on the proportion of total gum present that end up in the sediment.

Sediments were of two types. The first consisted almost entirely of protein, suggesting that the presence of gum had altered the solubility of the protein causing some of it to precipitate. The second consisted of both protein and gum and had a viscous or even gel-like character. This second kind of "sediment" may have been the result of thermodynamic incompatibility.

It is concluded

- that rheological synergism can be detected by steady shear viscometric measurements,
- that such synergism exists in a number of non-Newtonian gum-dairy protein mixed solutions (at natural pH and natural ionic strength) in which the concentrations of the components are at typical food use levels,
- that the degree of synergism is dependent on the gum : protein ratio and on the total polymer concentration,
- that the degree of synergism is independent of shear rate and is also

independent of phase separation provided the phases remain intimately mixed.

It is considered that quantitative measurement of rheological synergism between gums and dairy proteins of the kind reported here could be used to optimise the proportions and types of these ingredients used in food systems - so as to maximise functionality and minimise cost. Since gums are generally good stabilisers and proteins are generally good emulsifiers suitably chosen gum-dairy protein combinations could have dramatically-improved dual functionality in foods.

It is recommend that father work be carried out

- to investigate more fully the phase separation phenomena discussed above and how they affect the functionality of gum-dairy protein mixtures,
- to extend the work reported here to different temperatures, different pHs and different ionic strengths,
- to determine the emulsifying capacity and emulsion stabilizing capacity of gum-dairy protein mixtures,
- to investigate the effects of other water soluble food components (for example, sugars) on the functional properties of gum-dairy protein mixtures.

Oscillatory rheometry, as well as steady shear viscometry, should be used to measure rheological properties in order to gain a more complete understanding of these. This in turn should lead to a greater ability to exploit the rheologically-functional characteristics of gum-dairy protein mixtures.

REFERENCES

Antonov, Y.A., Grinberg, V.Y. and Tolstoguzov, V.B.(1977) "Phase equilibria in water-protein-polysaccharide systems II. Water-casein-neutral polysaccharide systems." Colloid and Polymer Science, 255(10) :937-947.

Antonov, Y.A., Losinskaya, N.V., Grinberg, V.Y., Dianova, V.T. and Tolstoguzov, V. B. (1979) "Phase equilibria in water-protein-polysaccharide systems III. Water-soy bean globulins-polysaccharide systems." Colloid and Polymer Science, 257(11) :1159-1171.

Antonov, Y.A. and Grinberg, V.Y. (1980) "Liquid two phase water-protein-polysaccharide systems and their processing into textured protein products." Journal of Texture Studies, 11:199-215.

Antonov, Y.A., Grinberg, V.Y., Zhuravskaya, N.A. and Tolstoguzov, V.B.(1982) "Concentration of the proteins of skimmed milk by membraneless, isobaric osmosis." Carbohydrate Polymers, 2:81-90.

Arnaud, J.P., Choplin, L. and Lacrox, C. (1989) "Rheological behaviour of kappa-carrageenan/locust bean gum mixed gels." Journal of Texture Studies, 19:419-430.

Asano, Y. (1970) "Interaction between casein and carboxylmethylcellulose in the acidic condition." Agr. Biol. chem., 34(1) :102-107.

Aspinall G.O. (1983) The Polysaccharides Vol 2. Academic Press, New York.

Balmaceda, E., Rha, C.and Huang, F. (1973) "Rheological properties of hydrocolloids." Journal of Food Science, 38:1169-1173.

Batdorf J.B. (1957) "Sodium Carboxymethylcellulose." In: Industrial Gums. Academic Press, New York and London.

Campbell, L.B. and Pavlasek, J. (1987) "Dairy products as ingredients in chocolate and confections." Food Technology, (October) :78-85.

Castelain, C.,Goncalves, M.P., Doublier, J. L. and Lefebvre, J. (1986) "Protein-Polysaccharide Interactions: Rheological Evidénce for Aggregation Processes in Aqueous Cellulose Derivatives-BSA Systems." In: Gum and Stabilisers for the Food Industry 3. Pergamon Press, New York.

Castelain, C., Lefebvre, J.and Doublier, J.L. (1988) "Rheological behaviour of BSA-cellulose derivative mixtures in neutral aqueous medium." Food Hydrocolloids, 1(2) :141-151.

Clark, R.C. (1987) "Viscoelastic Response of Xanthan gum/Guar gum Gum Blends." In: Gum and Stabilisers for the Food Industry 4. Pergamon Press, New York.

Cluskey, F.J., Thomas, E.L. and Coulter, S.T. (1969) "Precipitation of milk proteins by sodium carboxymethylcellulose." Journal of Dairy Science, 52(8) :1181-1185.

Cottrell, I.W., Kang, K.S. and Kovacs, P. (1980) "Xanthan gum." In: Handbook of Water-Soluble Gums and Resins. McGraw-Hill Book company, New York.

Dalgleish, D.G. and Morris, E.R. (1988) "Interactions between carrageenans and casein micelles: electrophoretic and hydrodynamic properties of the particles." Food Hydrocolloids, 2(4) :311-320.

de wit, J.N. (1987) "Empirical observations and theoretical considerations on whey protein functionality in food products". Milk-The Vital Force, 779-789, Reidel Publishing company.

de wit, J.N., Klarenbeek and Hontelez-Backx E.(1983) "Evaluation of functional properties of whey protein concentrates and whey protein isolates 1. Isolation and characterization." Neth. Milk Dairy J., 37:37-49.

de wit, J.N., Hontelez-Backx, E. and Adamse, M. (1988) "Evaluation of functional properties of whey protein concentrates and whey protein isolates 3. Functional properties in aqueous solution." Neth. Milk Dairy J., 42:155-172.

Descamps, O., Langevin, P.and Combs, D.H. (1986) "Physical Effect of starch/carrageenan interactions in water and milk." Food Technology, 40(4) :81-86,88.

Elfak, A.M., Pass, G., Phillips, G.O. and Morley, R.G. (1977) "The viscosity of dilute solutions of guar gum and locust bean gum with and without added sugars." J. Sci. Fd Agric., 28:895-899.

Elfak, A.M., Pass, G. and Phillips, G.O. (1978) "The viscosity of dilute solutions of kappa-carrageenan and sodium carboxylmethylcellulose." J. Sci. Fd Agric., 29:557-562.

Elfak, A.M., Pass, G. and Phillips, G.O. (1979a) "The effect of shear rate on the viscosity of solutions of guar gum and locust bean gum." J. Sci. Fd Agric., 30:439-444.

Elfak, A.M., Pass, G. and Phillips, G.O. (1979b) "The effect of shear rate on the viscosity of solutions of sodium carboxymethylcellulose and kappa-carrageenan." J. Sci. Fd Agric., 30:724-730.

Elfak, A.M., Pass, G. and Phillips, G.O. (1979c) "The effect of casein on the viscosity of solutions of hydrocolloids." J. Sci. Fd Agric., 30:994-998.

Elfak, A.M., Pass, G. and Phillips, G.O. (1980) "Rheological properties of hydrocolloids in the presence of sucrose and milk." Journal of Texture Studies,

:271-279.

Evans, E.W. (1982) "Used of milk proteins in formulated foods." In: Developments in food protein -1. Applied science publishers, London and New Jersey.

Ganz, A.J. (1973) "Some effects of gums derived from cellulose on the texture of foods." Cereal Science Today, 18(12) :398-403, 415-416.

Ganz, A.J. (1974) "How cellulose gum reacts with proteins." Food Engineering, (June) :67-69.

Gencer, G. (1989) "Effect of selected additives on the flow parameters of 1:1 mixtures of carrageeanan-guar and CMC-locust bean gum." Journal of Texture Studies, 20:473-478.

Glahn, P.E. (1982) "Hydrocolloid stabilization of protein suspensions at low pH." Prog. Fd. Nutr. Sci., 6:171-177.

Glicksman, M. (1980a) "Comparative Properties of Hydrocolloids." In: Food Hydrocolloids. CRC Press, Inc., Boca Raton, Florida.

Glicksman, M. (1980b) "Xanthan." In: Food Hydrocolloids. CRC Press, Inc., Boca Raton, Florida.

Glicksman, M. (1982) "The hydrocolloids industry in the'80s -problems and opportunities" Pro. Fd. Nutr. Sci. Vol 6, 299-321

Glicksman, M. (1983) "Red Seaweed Extracts (Agar, Carrageenan, Furcellaran)." In: Food Hydrocolloids. CRC Press, Inc., Boca Raton, Florida.

Glicksman, M. (1986a) "Locust/Carob Bean Gum and Guar Gum." In: Food Hydrocolloids. CRC Press, Inc., Boca Raton, Florida.

Glicksman, M. (1986b) "Sodium Carboxymethylcelluluse (CMC)." In: Food Hydrocolloids. CRC Press, Inc., Boca Raton, Florida.

Greminger, G.K. and Krumel, K.L. (1980) "Carboxymethylcellulose." In: Handbook of Water-Soluble Gums and Resins. McGraw-Hill Book company, New York.

Grinberg V.Y. and Tolstoguzov, V.B. (1972) "Thermodynamic compatibility of gelatin with some D-glucans in aqueous media." Carbohydrate research, 25:313-321.

Grindrop, J. and Nickerson, T.A. (1967) "Effect of various gums on skimmilk and purified milk proteins." Journal of Dairy Science, 51(6) :834-841.

Guiseley, K.B., Stanley, N.F. and Whitehouse, P.A. (1980) "Carrageenan." In: Handbook of Water-Soluble Gums and Resins. McGraw-Hill Book company, New York.

Gurov, A.N. and Tolstoguzov, V.B. (1988) "Equilibrium and non-equilibrium complexes between bovine serum albumin and dextran sulfate II. Equilibrium complexes in solution." Food Hydrocolloids, 2(4) :285-296.

Gurov, A.N., Wajnerman, E.S. and Tolstoguzov, V.B. (1974a) "On the interaction of some proteins with sulfonated dextran in an aqueous medium." Die Nahrung, 26:172-174.

Gurov, A.N., Wajnerman, E.S. and Tolstoguzov, V.B. (1974b) "Interaction of proteins with dextransulfate in an aqueous medium II. nonequilibrium phenomena." Die Starke, 29:186-190.

Gurov, A.N., Leontiev, Poteshnikh, A.V. and Tolstoguzov, V.B. (1979) "Interaction of casein with diethyaminoethyl- dextran in aqueous solutions : isolation of alpha-s- caseins." Journal of Dairy Science, 64(3) :380-383.

Gurov, A.N., Gurova, N.V., Leontiev and Tolstoguzov, V.B. (1988a) "Equilibrium and

non-equilibrium complexes between bovine serum albumin and dextran sulfate I. Complexing conditions and composition of non-equibrium complexes." Food Hydrocolloids, 2(4) :267-283.

Gurov, A.N., Nuss, P.V., Gurova, N.V. and Dotdaev, S.H. (1988b) "Equilibrium and non-equilibrium complexes between bovine serum albumin and dextran sulfate II. Methylene blue binding by equilibrium complexes." Food Hydrocolloids, 2(4) :297-310.

Haggitt, B.D. (1989) New Zealand Dairy Board New Zealand. Personal communication.

Hansen, P.M.T. (1968) "Stabilization of alpha-s1-casein by carrageenan." Journal of Dairy Science, 51(2) :192-195.

Hansen, P.M.T. (1982) "Hydrocolloid-protein interactions: relationship to stabilization of fluid milk products. A review." Prog. Fd. Nutr. Sci., 6:127-138.

Hansen, P.M.T. and Black, D.H. (1972) "Whipping properties of spray-dried complexes from whey protein and carboxylmethylcellulose." Journal of Food Science, 37:452-456.

Hansen, P.M.T. and Crauer, L.S. (1971) "Production of complexes between whey proteins and food stabilizers." Journal of Dairy Science, 54(5) :756-757.

Hansen, P.M.T., Hidalgo, J. and Gould, I.A. (1971) "Reclamation of whey protein with carboxymethylcellulose." Journal of Dairy Science, 54(6) :830-834.

Harper, W.J.(1984) "Whey proteins" Food Technology in New Zealand 19(3) 21,23,26-27,29

Harper, W.J. and McKinlay (1983) "Coffee whiteners model system" N. Z. Dairy Res. Inst., Palmerston North, New Zealand. Unpublished data.

Harper, W.J., Peltonen, J.R. and Hayes, J (1980) "Model food systems yield clearer utility evaluations of whey protein" Food Prod. Dev. 14(10):52

Hayes, J.F. and Muller, L.L. (1961) "Factors affecting the viscosity of solutions of acid-precipitated caseins." The Australian Journal of Dairy Technology, 16:265-269.

Hayes, J.F., Southby, P.M. and Muller, L.L. (1968) "Factors affecting the viscosity of caseinates in dispersions of high concentrations." Journal of Dairy Research, 35:31-47.

Hayes, J.F., Dunkerley, J. and Muller, L.L. (1969) "Studies on co-precipitates of milk proteins Part 4 - Solubility and whiteness of ground co-precipitates in aqueous dispersions." The Australian Journal of Dairy Technology, (June) :69-74.

Hermamsson, A.M. (1975) "Functional properties of food-flow properties" Journal of Texture Studies, 5:425-437.

Hidalgo, J., and Hansen, P.M.T. (1969) "Interactions between food stabilizers and beta-lactoglobulin." J. Agri. Fd Chem., 17(5) :1989-1092.

Hidalgo, J., and Hansen, P.M.T. (1971) "Selective precipitation of whey proteins with carboxymethylcellulose." Journal of Dairy Science, 54(9) :1270-1274.

Hill, R.D. and Zadow, J.G. (1974) "The precipitation of whey proteins by carboxymethyl cellulose of differing degrees of substitution." Journal of Dairy Research, 41:373-380.

Hill, R.D. and Zadow, J.G. (1978) "Recovery of whey proteins from precipitated complexes of carboxymethyl cellulose and protein." Journal of Dairy Research, 45:77-83.

Hood, L.F. and Allen, J.E. (1977) "Ultrastructure of carrageenan-milk sols and gels."

Journal of Food Science, 42(2) :1062-1065.

Hughes, L, Ledward, D.A., Mitchell, J.R. and Summerlin C. (1980) "The effect of some meat proteins on the rheological properties of pectate and alginate gels. Journal of Texture Studies, 11,247-256.

Igoe, R.S. (1982) "Hydrocolloid interactions useful in food systems." Food Technology, (April) :72-74.

Imeson, A.P., Ledward, D.A., Mitchell J.R. (1977) "On the nature of the interaction between some anionic polysaccharides and proteins." J. Sci. Fd Agric., 28: 661-667.

Imeson, A.P., Watson, P.R., Mitchell, J.R. and Ledward, D.A. (1978) "Protein recovery from blood plasma by precipitation with polyuronates." J. Fd Technol., 13:329-338.

Inglett, M.J. and Inglett, G.E. (1982) In: Food products formulary. Vol 4. Fabricated foods. p.52-53. Avi Publ. New York, NY.

Kaletunc-Gencer, K. and Peleg, M. (1986) "Rheological characteristics of selected food gum mixtures in solution." Journal of Texture Studies, 17:61-70.

Kinsella J.E. (1984) "Milk protein: Physicochemical and functional properties" CRC critical Reviews in Food Science and Nutrition 21:197-262.

Kirkpatrick, K.J. and Fenwick, R.M. (1987) "Manufacture andgeneral properties of dairy ingredients." Food Technology, (October) :58-65.

Korolczuk, J. (1982) "Effect of temperature on viscosity and hydration of casein in neutral and acidic solutions." New Zealand Journal of Dairy Science and Technology, 17:273-276.

Korolczuk, J. (1984) "Viscosity and hydration of casein derivatives." New Zealand Journal of Dairy Science and Technology, 19:107-118.

Krumel, K.L., Sarkar, N. (1975) "Flow properties of gums useful to the food industry." Food Technology, 29(4) :36-44.

Launay, B., Doublier, J.L. and Cuvelier, G. (1986) "Flow Properties of Aqueous Solutions and Dispersions of Polysaccharides." In: Functional Properties of Food Macromolecules. Elsevier Applied Science Publishers, London and New York.

Lawn, M., Cott er, M. and Van Vliet, A. (1989) "Effect of gums on the viscosity of Alanate 180" Report No. CA88501, New Zealand Dairy Research Institude, New Zealand.

Ledward, D.A. (1979) "Protein-Polysaccharide interactions." In: Polysaccharides in Food. Butterworths, London.

Lee C.H. and Rha, C. (1979) "Rheological properties of proteins in solution." In: Food Texture and Rheology. Acadamic Press, London.

Lelievre, J. and Husbands, J. (1989) "Effect of sodium caseinate on the rheological properties of starch pastes." Starch, 41(6) :236-238.

Lim, D.M. (1980) "Functional Properties of milk proteins with particular reference to confectionary products" Scientific and Technical Surveys, No 120, The British Food Manufacturing industries Research Association.

Lin, C.F. (1977) "Interaction of sulfated polysaccharides with proteins." In: Food Hydrocolloids. AVI,

Mangino, M.E. (1984) "Physicochemical aspects of whey protein functionality." Journal of Dairy Science, 67:2711-2722.

Manning, D., Witt, H. and Ames, J. (1983) "Increasing Chesses Yields with Carrageenan." In: Gum and Stabilisers for the Food Industry 3. Pergamon Press, New York.

Marrs, W.M. (1989) "Protein/polysaccharide interactions and their application in food products." Scientific and Technical Surveys No. 168, Leatherhead Food R.A.

Mitchell, J.R. (1979) "Rheology of Polysaccharide Solutions and Gels." In: Polysaccharides in Food. Butterworths, London.

Morley, R.G. (1983) "Utilisation of Hydrocolloids in Formulated Foods." In: Gum and stabilisers for the Food Industry 2. Pergamon Press, New York.

Morr C.V. (1979) "Conformation and functionality of milk proteins" In:Functionality and Protein Structure" ACS Symposium series 92, American Chemical Society, Washington. D.C.

Morr, C.V. (1982) "Functional properties of milk proteins and their use as food ingredients." In: Developments in Dairy chemistry -1. Applied science publishers, London and New Jersey.

Morr, C.V. (1989) "Conformation and functionality of milk protein." American chemical society, Washington D.C.

Morr, C.V., Swenson, P. E., Richter, R. L. (1973) "Functional characteristics of whey protein concentrates." Journal of Food Science, 38:324-330.

Morris, R.S. (1983) "Rheology of Hydrocolloids." In: Gum and stabilisers for the Food Industry 2. Pergamon Press, New York.

Nakamura, I.(1988) Whey protein concentration -gum interaction in an aqueous system and in a ham model. Massey University Palmerston North, New

Zealand.

Ozawa, K., Niki, R. and Arima, S. (1984) "Interaction of beta-casein and kappa-carrageenan. I viscosity and turbidity under non-gelling conditions." Agr. Biol. chem., 48(3) :627-632.

Ozawa, K., Niki, R. and Arima, S. (1985) "Effects of coexistence of beta-casein on gelation of kappa-carrageenan." Agr. Biol. chem., 49(11):3123-3129.

Payen, T.A.J. (1972) "Light scattering of protein reactivity of polysaccharides especially of carrageenans." Journal of Dairy Science, 55(1):141-150.

Pederson, K. (1979) "The selection of hydrocolloids to meet functional requirements." In: Polysaccharides in Food. Butterworths, London.

Pettitt, J. (1979) "Xanthan gum." In: Polysaccharides in Food. Butterworths, London.

Pomeranz, Y. (1975) "Functional Properties of Food Components" Academic Press inc.,London.

Pradipasena, P. and Rha, C. (1977a) "Effect of apparent viscosity of a globular protein solution." Polymer Engineering and Science, 17(12):861-864.

Pradipasena, P. and Rha, C. (1977b) "Pseudoplastic and rheopectic properties of globular protein (beta-lactoglobulin) solution." Journal of Texture Studies, 8:311-325.

Qingnong, T.(1988) Steady shear and oscillatory rheological measurements on solutions of commercially available whey protein concentrates. M. Tech. thesis, Massey University Palmerston North, New Zealand.

Renner, C.,Grogan, C. and Franich, P.(1989) Synergism of gums and caseinates. New Zealand Dairy Research Institute Palmerston North, New Zealand.

Rha, C. (1978) "Rheology of fluid foods." Food Technology, (July) :77-82.

Rha, C. and Pradipasena, P. (1986) "Viscosity of Proteins." In: Functional Properties of Food Macromolecules. Elsevier Applied Science Publishers, London and New York.

Rha, M.A. (1977) "Rheology of liquid foods - Areview." Journal of Texture Studies, 8:135-168.

Rizzotti, R., Tilly, G. and Patterson, R.A. (1983) "The Use of Hydrocolloids in the Dairy Industry." In: Gum and Stabilisers for the Food Industry 2. Pergamon Press, New York.

Roeper, J. and Winter, G.J. (1982) "Viscosity of sodium caseinate solutions at high concentrations." International Dairy Congress XXI, :97-98.

Schmidt, R.H. and Padua, M.R. (1982) "Effects of heat treatment and kappa-carrageenan addition on protein solubility and viscosity of milk protein/peanut flour blends in an ionic environment simulating cow's milk" Journal of food Processing and Preservation 6:243-252.

Schmidt, K.D. and Smith, D.E. (1988) "Milk protein-gum interactions as determined by viscosity." Journal of Dairy Science (Supplement 1), :66.

Schwenke, K.D., Augustat, D. and Bock, W. (1988) "Rapeseed protein-polyanion interactions binding of pectic acid to the main rapeseed protein fractions in insoluble complexes." Sciences Des Aliments, 8:97-112.

Seaman, J.K. (1980) "Locust bean gum." In: Handbook of Water-Soluble Gums and Resins. McGraw-Hill Book company, New York.

Skura, B.J. and Nakai, S. (1980) "Physicochemical Verification of Nonexistence of alpha-s1-casein -kappa-carrageenan interaction in calcium-free systems."

Journal of Food Science, 45:582-591.

Skura, B. J. and Nakai, S. (1981) "Stabilization of alpha-s1-casein by kappa-carrageenan in the presence of calcium." Can. Inst. Food Sci. Technol. J., 14(1) :59-63.

Smith D.R. and Snow, N.S. (1968) "Studies on coprecipitates of milk proteins 3. Factors affecting behaviour in aqueous dispersions" The Australian Journal of Dairy Technology 3:8-14.

Snoeren, T.M., Payens, T.A.J., Jeunink,J. and Both, P. (1975) "Electrostatic interaction between kappa-carrageenan and kappa-casein." Michwissensch, 30(7) :393-396.

Southward, C.R.(1985) "Manufacture and Applications of edible casein products I. Manufacture and properties" New Zealand Journal of Dairy Science and Technology, 20:79-101.

Southward, C.R. (1986) "Utilisation of Milk Components: Casein." In: Modern Dairy Technology Volume 1. Elsvier Applied Science Publishers, New York and London.

Southward, C.R., Goldman, A. (1975) "Co-precipitates - A review." New Zealand Journal of Dairy Science and Technology, 10:101-112.

Southward, C.R. and Aird, R.M. (1978) "Coprecipitate and their application in food products I. observations on the manufacture of coprecipitates" New Zealand Journal of Dairy Science and Technology, 13:77-96.

Southward, C.R. and Goldman, A. (1978) "Coprecipitate and their application in food products II. some properties and applications." New Zealand Journal of Dairy Science and Technology, 13:97-105.

Southward, C.R. and Walker, N.J. (1980) "The manufacture and industrial use of

casein" New Zealand Journal of Dairy Science and Technology, 15:201-217.

Southward, C.R. and Walker, N.J. (1982) In: CRC Handbook of processing and Utilization in Agriculture. Vol.1, p 455-552.

Suchkov, V.V., Grinberg, V.Y. and Tolstoguzov, V.B. (1981) "Steady-state viscosity of the liquid two phase disperse system water-casein-sodium alginate." Carbohydrate Polymers, (1) :39-53.

Szczesniak, A.S. (1985) "Rheological basis for selecting hydrocolloids for specific applications" In: Gum and stabilisers for the Food Industry 3. Pergamon Press, New York.

Takada, N. and Nelson, P.E. (1983) "Pectin-protein interaction in tomato products." Journal of Food Science, 48:1408-1411.

Tokaev, E.S., Gurov, A.N. and Rogov, I.A. and Tolstoguzov, V. B. (1987) "Properties of oil/water emulsions stabilized by casein-acid polysaccharide mixtures." Die Nahrung, 31(8) :826-834.

Tolstoguzov V.B. (1986) "Functional Properties of Protein-Polysaccharide Mixtures." In: Functional Properties of Food Macromolecules. Elsevier Applied Science Publishers, London and New York.

Tolstoguzov, V.B. (1988a) "Concentration and purification of proteins by means of two-phase system: membraneless osmosis process." Food Hydrocolloids, 2(3) :195-207.

Tolstoguzov, V.B. (1988b) "Some physico-chemical aspects of protein processing into foodstuffs." Food Hydrocolloids, 2(3) :339-370.

Tolstoguzov, V.B. (1990) "Proteins as food additives." International Food Ingredients, 2:8-15.

Tolstoguzov, V.B. (1991) "Functional properties of food proteins and role of protein-polysaccharide interaction." Food Hydrocolloids, 6(4):429-468.

Tolstoguzov, V.B. and Braudo, E. (1985) "Proteins and anionic polysaccharides as stabilizers of o/w emulsions" J. Dispers. Sci. Techol., 6:575-603.

Tolstoguzov, V.B., Grinber, V.Y. and Gurov, A.N. (1985) "Some physico-chemical approaches to the problem of protein texturization." J. Agri. Fd Chem., 33(2) :151-159.

Towler, C. (1974) "Rheology of casein solutions." New Zealand Journal of Dairy Science and Technology, 9:155-160.

Towler, C. (1975) "Sodium caseinate-carrageenan reaction." New Zealand Journal of Dairy Science and Technology, :168-169.

Towler, C. (1984) "Sedimentation in a cultured milk beverage." New Zealand Journal of Dairy Science and Technology, 19:205-211.

Towler, C., Creamer, L. K. and Southward, C.R. (1984) "The effect of disulphide-bond reducing agents on the viscosity of casein solutions." New Zealand Journal of Dairy Science and Technology, 16:155-165.

Walker, B. (1983) "Gums and Stabilisers in Food Formulations." In: Gum and stabilisers for the Food Industry 2. Pergamon Press, New York.

Welsby, D., McCarthy, M. and Doolan, D. (1982) "The use of milk proteins as hydrocolloids in food systems." Prog. Fd. Nutr. Sci., 6:221-231.

Whistler R.L. and BeMiller, J.N. (1959) In:Industrial gums - polysaccharides and their Derivative. p.1-14 Academic Press, New York and London.

Whistler R.L. and BeMiller, J.N. (1973) In:Industrial gums - polysaccharides and their

Derivative. p.3-19 Academic Press, New York and London.

Zadow, J.G. (1986) "Utilisation of Milk Components: Whey." In: Modern Dairy Technology Volume 1. Elsvier Applied Science Publishers, New York and London.

Zadow, J.G. and Hill, R.D. (1978) "Complex formation between whey proteins and insoluble cross linked carboxymethyl cellulose." New Zealand Journal of Dairy Science and Technology, 13:162-165.

Zhuravskaya, N.A., Kiknadze, E.V., Antonov, Y.A. and Tolstoguzov, V. B. (1986a) "Concentration of proteins as a result of the phase separation of water-protein-polysaccharide systems I. Phase equilibria in water-milk protein -polysaccharide systems." Die Nahrung, 30(6) :591-599.

Zhuravskaya, N. A., Kiknadze, E. V., Antonov, Y. A. and Tolstoguzov, V. B. (1986b) "Concentration of proteins as a result of the phase separation of water-protein-polysaccharide systems II.Concentration of milk proteins." Die Nahrung, 30(6) :601-613.

APPENDIX 1

THE CONCENTRATIONS AND RATIOS OF DAIRY PROTEINS AND GUMS THAT HAVE BEEN USED IN FOODS.

mixtures	%protein	%gum	products	Reference
sodium caseinate/xanthan	2.0	0.06	Coffee-whitener	Harper and Mckinlay (1983)
sodium caseinate/carrageenan	5.5	0.8	Coffee-whitener	Harper and Mckinlay (1983)
sodium caseinate/carrageenan	0.35	0.1	Stabilized frozen thick snake	Haggitt (1989)
sodium caseinate/gums (carrageenan : guar gum : CMC ratio 1:1:3)	7.0	0.2	Whipped topping	Harper, et al (1982)
WPC/xanthan	2.0	0.1	Salad dressing	Harper et al (1980)
TMP/gums (guar: CMC: carrageenan ratio 60:30:10)	3.0	0.3	Frozen dessert	Inglett and Inglett (1982)
TMP/carrageenan	7.5	1.5	Instant bakery filling	Hagglett (1989)
Whey protein/carrageenan	0.25	0.015	UHT cream	Harper et al (1980)
Dry whey and caseinate/CMC	10	0.1	Strawberry-flavoured shakes	Inglett and Inglett (1982)
WPC/gum (carrageenan or xanthan gum)	6.0	0.09	Hams	Nakamura (1988)

APPENDIX 2

SPECIFICATIONS OF GUMS

Table A2.1: Specification of locust bean gum (Davis Gelatine [N.Z.] Ltd, Christchurch , New Zealand)

Description	White free flowing powder
Particle size	Less than 5% on 0.15mm sieve
Solubility	Dissolves completely above 80 °C
Viscosity	900 - 1200 cps 1% solution @ 25 °C (Brookfield BH 20 RPM)
pH	6-8
Moisture	less than 15%
Heavy Metals	
-Pb	less than 10 ppm
-As	less than 2 ppm

Table A2.2. Specification of CMC (466) (Davis Gelatine [N.Z.] Ltd, Chrischurch , New Zealand)

Description	Cream coloured; free flowing granules
Viscosity	2500 - 3000 cps 1% solution @ 25 °C (Brookfield)
pH	6.5 - 7.5 at 1% solution
Moisture	Max 8.0%
Degree of substitution	0.64 - 0.74

Table A2.3: Specification of Lambda-carrageenan (407) (Davis Gelatine [N.Z.] Ltd, Christchurch , New Zealand)

Description	Light tan to tan coloured; free flowing powder
Viscosity	220 - 350 mPa.s (cps) 1.5% solution @ 75 °C (Brookfield)
Particle size	More than 95% through a US Standard sieve, 180 µm
pH	7.0 - 10.5 at 1% solution
Moisture	less than 12%

Table A2.4: Specification of xanthan gum (N 9753) (Davis gelatine [N.Z.] Limited, Christchurch, New Zealand).

Description	White -to cream- coloured free flowing powder
Viscosity	1300 - 1700 mPa.s (cps) 1.0% solution @ 25 °C (Brookfield LVTD, spindle 3,60 rpm)
pH	6.0 - 8.0 at 1% solution
Moisture	less than 15%

APPENDIX 3

SPECIFICATIONS OF DAIRY PROTEINS

Table A3.1: Specification of sodium caseinate (Alanate 180) (New Zealand Dairy Board, Wellington, New Zealand)

Protein (N* 6.38)	95.4%
Ash	3.6%
Moisture	3.5%
Fat	0.7%
Lactose	0.1%
Sodium	1300 mg/100g
Calcium	20 mg/100g
pH (5% @ 20 °C)	6.6
Colour	white to pale cream
Bulk density	0.50 g/ml
Viscosity	15 P (15% solution @ 25 °C)

Table A3.2: Specification of whey protein concentrate (Alacen 132) (New Zealand Dairy Board, Wellington, New Zealand)

Protein (N * 6.38)	76.6%
Ash	4.2%
Moisture	3.7%
Fat	4.1%

Table A3.3 Specification of total milk protein (TMP 1100) (New Zealand Dairy Board, Wellington, New Zealand)

Protein (N* 6.38)	95.2%
Ash	3.7%
Moisture	3.5%
Fat	0.7%
Lactose	0.2%
Sodium	1300 mg/100g
Calcium	40 mg/100g
pH (5% @ 20 °C)	6.8
colour	white to pale cream
Bulk density	0.51 g/ml

Table A3.4: Specification of whey protein isolate (Bipro) (Bipro is manufactured in the USA and supplied by New Zealand Dairy Research Institute)

Total nitrogen	14.30%
Non-protein nitrogen	0.29%
Moisture	5.66%
Fat	1.24%
Ash	1.60%
Lactose	5.98%

APPENDIX 4

PREPARATION OF GUM SOLUTIONS

The following methods were used for preparing solutions at natural pH and ionic strength. An example of how the required weights of dry gum powder and water were calculated is given as follows:

For a 1.2% CMC solution with a total weight of 1000 g

weight of CMC powder required (g)	=	1.2 * 1000 / %solids
	=	(1.2 * 1000) / 92.94
	=	12.912 g
weight of water required	=	1000 - 12.912 g
	=	987.09 g

LOCUST BEAN GUM

1 The weight of gum required was calculated.
2 The weight of water required was calculated.
3 Water and gum were weighed out.
4 Sodium azide was weighed out to 0.03 % of total weight.
5 Water was added into beaker then sodium azide was added.
6 Water was stirred with a Silverson mixer (Model Laboratory, Machaines, England) at the medium speed.
7 Gum was added into water vortex so that it was all wetted.
8 The speed of the mixer was increased up to the maximum.
9 Gum solution was mixed for 5 min, then the stirrer was removed.
10 The beaker was put in a microwave oven (Samsung, Model RE-630D, Korea)and the gum solution was heated up to about 80 °C at medium high heat setting for 10 min.
11 Solution was stirred again while still hot at the same high speed for 5 mins.
12 The stirrer was stopped and removed.
13 The gum solution was left to cool down at room temperature for 30 mins.
14 The top of the beaker was covered with tissue paper
15 Solution was left overnight at room temperature and then it was covered with foil.
16 The gum solution was mixed with a plastic spatula.
18 37 g of gum solution was put into a centrifuge cup
19 The sample was centrifuged at 5000 rpm for 4 mins.
20 The clear and homogeneous gum solution was used to measure the flow curve and viscosity.

CMC

1 The weight of gum required was calculated.
2 The weight of water required was calculated.
3 Water and gum were weighed.
4 Sodium azide was weighed out to 0.03 % of total weight.
5 Water was added into beaker then sodium azide was added.
6 Water was stired with Silverson mixer at the medium speed.
7 Gum was added into water vortex so that it was all wetted.
8 The speed of the mixer was increased up to the maximum speed.
9 Solution was mixed for 5 min, then the stirrer was removed.
10 The beaker was put in the microwave oven and the gum solution was heated up to about 40 °C at medium high heat setting for 6 min.
11 Solution was stirred again while still hot at the same high speed for 5 mins.
12 The stirrer was stopped and removed.
13 The gum solution was left to cool down at room temperature for 30 mins.
14 The top of the beaker was covered with tissue paper
15 Solution was left overnight at room temperature and then it was covered with foil.
16 The gum solution was mixed with a plastic spatula.
18 37 g of gum solution was put into a centrifuge cup
19 The sample was centrifuged at 5000 rpm for 4 mins.
20 The clear and homogeneous gum solution was used to measure the flow curve and viscosity.

LAMBDA-CARRAGEENAN

1 The weight of gum required was calculated.
2 The weight of water required was calculated.
3 Water and gum were weighed out.
4 Sodium azide was weighed out to 0.03 % of total weight.
5 Water was added into beaker then sodium azide was added.
6 Water was heated up to 85 C by putting the beaker of water into microwave oven at the high heat setting for 10 mins.
7 Water was stired at the medium speed with Silverson mixer.
8 Gum was added into water vortex so that it was all wetted.
9 The speed of the mixer was increased up to the maximum speed.
10 Solution was mixed for 8 min.
11 The stirrer was stopped and removed.
12 The gum solution was left to cool down at room temperature for 30 mins.
13 The top of the beaker was covered with tissue paper
14 Solution was left overnight at room temperature and then it was covered with foil.
15 The gum solution was mixed with a plastic spatula.
16 37 g of gum solution was put into a centrifuge cup
17 The sample was centrifuged at 5000 rpm for 4 mins.
18 The clear and homogeneous gum solution was used to measure the flow curve and viscosity.

XANTHAN GUM

1 The weight of gum required was calculated.
2 The weight of water required was calculated.
3 Water and gum were weighed out.
4 Sodium azide was weighed out to 0.03 % of total weight.
5 Water was added into beaker then sodium azide was added.
6 Water was stired with Silverson mixer at the medium speed.
7 Gum was added into water vortex so that it is all wetted.
8 The speed of the mixer was increased up to the maximum speed.
9 Solution was mixed for 5 min, then the stirrer was removed.
10 The beaker was put in the microwave oven and the gum solution was heated up to about 40 C at medium high heat setting for 6 min.
11 Solution was stirred again while still hot at the same high speed for 3 mins.
12 The stirrer was stopped and removed.
13 The gum solution was left to cool down at room temperature for 30 mins.
14 The top of the beaker was covered with tissue paper
15 Solution was left overnight at room temperature and then it was covered with foil.
16 The gum solution was mixed with a plastic spatula.
18 37 g of gum solution was put into a centrifuge cup
19 The sample was centrifuged at 5000 rpm for 4 mins.
20 The clear and homogeneous gum solution was used to measure the flow curve and viscosity.

APPENDIX 5

PREPARATION OF DAIRY PROTEIN SOLUTIONS

The following methods were used for preparing solutions at natural pH and ionic strength. An example of how the required weights of dry protein powder and water were calculated is given as follows:

For a 10% WPC solution with a total weight of 1000 g

weight of WPC powder required (g)	=	10 * 1000 / %solids
	=	(10 * 1000) / 96.42
	=	103.72 g
weight of water required	=	1000 - 103.72 g
	=	895.75 g

SODIUM CASEINATE (ALANATE 180)

1 The weight of protein power required was calculated.
2 The weight of water required was calculated.
3 Water and dairy protein were weighed out.
4 Sodium azide was weighed out to 0.03 % of total weight.
5 Water was added into beaker then sodium azide was also added.
6 The beaker was put in the microwave oven and the water was heat up to about 70 °C at high heat setting for 6 min.
7 Water was stirred with Silverson mixer at the medium speed.
8 Dairy protein was slowly added into water vortex so that it was all wetted.
9 Solution was mixed for 20 min.
10 The stirrer was stopped and removed.
11 Dairy protein solution was left to cool down at room temperature for 30 min
12 The top of the beaker was covered with tissue paper.
13 Solution was left overnight at room temperature and foam was carefully removed with a spoon.
14 37 g dairy protein solution was poured into a centrifuge tube.
15 The sample was centrifuged at 5000 rpm for 4 mins.
16 The clear and homogeneous solution was used to measured the flow curve and viscosity.

WHEY PROTEIN CONCENTRATE (ALACEN 132) and WHEY PROTEIN ISOLATE (BIPRO)

1 The weight of dairy protein required was calculated.
2 The weight of water required was calculated.
3 Water and dairy protein were weighed out.
4 Sodium azide was weighed out to 0.03 % of total weight.
5 Water was added into beaker then sodium azide was also added.
6 Water was stired with Silverson mixer at the medium speed.
7 Dairy protein was slowly added into water vortex so that it was all wetted.
8 Solution was mixed for 20 min.
9 The stirrer was stopped and was removed.
10 The top of the beaker was covered with tissue paper.
11 Solution was left overnight at room temperature and foam was carefully removed with a spoon.
12 37 g dairy protein solution was poured into a centrifuge tube.
13 The sample was centrifuged at 5000 rpm for 4 mins.
14 The clear and homogeneous solution was used to measured the flow curve and viscosity.

TOTAL MILK PROTEIN (TMP 1100)

1 The weight of dairy protein required was calculated.
2 The weight of water required was calculated.
3 Water and dairy protein were weighed out.
4 Sodium azide was weighed out to 0.03 % of total weight.
5 Water was added into beaker then sodium azide was also added.
6 The beaker was put in the microwave oven and the water was heat up to about 50 C at high heat setting for 4 min.
7 Water was stirred with Silverson mixer at the medium speed.
8 Dairy protein was slowly added into water vortex so that it was all wetted.
9 Solution was mixed for 20 min.
10 The stirrer was stopped and removed.
11 Dairy protein solution was left to cool down at the room temperature for 30 min
12 The top of the beaker was covered with tissue paper.
13 Solution was left overnight at room temperature and foam was carefully removed with a spoon.
14 37 g dairy protein solution was poured into a centrifuge tube.
15 The sample was centrifuged at 5000 rpm for 4 mins.
16 The clear and homogeneous solution is used to measured the flow curve and viscosity.

APPENDIX 6

STORAGE TIME STUDY

Table A6.1 n values for 0.25% gum solution and 3.0% sodium caseinate solution.

Days	batch No.	LB	CMC	CR	XN	SC
1	1	0.90	0.74	0.80	0.43	1.05
	2	0.92	0.72	0.81	0.41	1.05
3	1	0.90	0.74	0.82	0.41	1.03
	2	0.92	0.73	0.84	0.40	1.03
5	1	0.89	0.75	0.81	0.43	1.07
	2	0.91	0.75	0.82	0.42	1.05
7	1	0.93	0.74	0.82	0.42	1.06
	2	0.92	0.75	0.82	0.42	1.06
F-values		2.09	0.88	2.46	0.07	9.00

The F values from statistical tables are 6.59 at $\alpha = 0.05$ and 16.7 at $\alpha = 0.01$, which are much higher than the calculated F-values. Therefore, there is no significant variation in n values (at the 1.0% level of confidence) of any of the solutions over 7 days.

Table A6.2 k values (Pa.s) for 0.25% gum solution and 3.0% sodium caseinate solution.

Days	batch No.	LB	CMC	CR	XN	SC
1	1	0.017	0.089	0.044	0.461	0.0019
	2	0.015	0.101	0.042	0.514	0.0019
3	1	0.016	0.088	0.041	0.500	0.0021
	2	0.015	0.090	0.037	0.533	0.0020
5	1	0.017	0.084	0.043	0.473	0.0018
	2	0.016	0.085	0.040	0.494	0.0019
7	1	0.014	0.090	0.041	0.503	0.0019
	2	0.015	0.085	0.041	0.493	0.0016
F-values		3.80	1.38	3.79	0.15	1.64

The F values from statistical tables are 6.59 at $\alpha = 0.05$ and 16.7 at $\alpha = 0.01$, which are much higher than the calculated F-values. Therefore, there is no significant variation in k values (at the 1.0% level of confidence) of any of the solutions over 7 days.

APPENDIX 7

MEASURED MOISTURE AND SOLIDS CONTENTS OF ALL GUM POWDERS AND DAIRY PROTEIN POWDERS

Sample	% moisture	% solids
LB	6.93	93.07
CMC	7.06	92.94
CR	7.41	92.59
XN	7.41	92.59
SC	3.44	96.56
WPC	3.58	96.42
TMP	4.08	95.92
WPI	6.57	93.43

APPENDIX 8

NATURAL pH VALUES OF 0.5% GUM SOLUTIONS AND 6.0% DAIRY PROTEIN SOLUTIONS

Sample	pH
LB	7.1
CMC	7.2
CR	7.2
XN	6.8
SC	6.6
WPC	6.7
TMP	6.8
WPI	6.8

APPENDIX 9

X-RATIOS FOR MIXTURES OF 0.5% GUM AND 6.0 % DAIRY PROTEIN SOLUTIONS

Table A9.1: X-ratios for mixtures of 0.5% LB and 6.0% dairy protein solutions.

Sample	Gum solution:protein solution ratio	shear rate (s^{-1})			
		116	583	1160	1470
LB/SC	75:25	0.64	0.77	0.82	0.84
LB/SC	50:50	0.46	0.62	0.69	0.71
LB/SC	25:75	0.42	0.58	0.67	0.84
LB/SC	75:25	0.59	0.69	0.72	0.73
LB/SC	50:50	0.49	0.64	0.71	0.73
LB/SC (duplicate result)	25:75	0.46	0.62	0.70	0.72
LB/WPC	75:25	0.61	0.81	0.90	0.93
LB/WPC	50:50	0.41	0.63	0.75	0.79
LB/WPC	25:75	0.30	0.50	0.63	0.67
LB/TMP	75:25	0.61	0.61	0.77	0.78
LB/TMP	50:50	0.52	0.58	0.71	0.73
LB/TMP	25:75	0.56	0.73	0.82	0.85
LB/WPI	75:25	0.55	0.68	0.74	0.76
LB/WPI	50:50	0.35	0.50	0.58	0.61
LB/WPI	25:75	0.25	0.36	0.43	0.45

Table A9.2: X-ratios for mixtures of 0.5% CMC and 6.0% dairy protein solutions.

Sample	Gum solution:protein solution ratio	shear rate (s^{-1})			
		116	583	1160	1470
CMC/SC	75:25	0.67	0.80	0.83	0.89
CMC/SC	50:50	0.48	0.67	0.72	0.80
CMC/SC	25:75	0.38	0.63	0.70	0.81
CMC/WPC	75:25	0.67	0.80	0.85	0.87
CMC/WPC	50:50	0.48	0.67	0.76	0.79
CMC/WPC	25:75	0.32	0.52	0.62	0.65
CMC/TMP	75:25	0.86	0.97	1.02	1.04
CMC/TMP	50:50	0.66	0.85	0.93	0.96
CMC/TMP	25:75	0.53	0.77	0.87	0.90
CMC/TMP	75:25	0.95	1.04	1.07	1.08
CMC/TMP	50:50	0.69	0.85	0.92	0.95
CMC/TMP (dulplicate result)	25:75	0.64	0.82	0.91	0.94
CMC/WPI	75:25	0.69	0.80	0.85	0.86
CMC/WPI	50:50	0.47	0.65	0.74	0.77
CMC/WPI	25:75	0.33	0.55	0.67	0.71

Table A9.3: X-ratios for mixtures of 0.5% CR and 6.0% dairy protein solutions.

Sample	Gum solution:protein solution ratio	shear rate (s^{-1})			
		116	583	1160	1470
CR/SC	75:25	0.69	0.83	0.91	0.93
CR/SC	50:50	0.51	0.68	0.76	0.79
CR/SC	25:75	0.55	0.69	0.75	0.77
CR/WPC	75:25	0.82	0.92	0.98	0.99
CR/WPC	50:50	0.79	0.94	1.03	1.06
CR/WPC	25:75	0.67	0.85	0.96	1.00
CR/TMP	75:25	1.36	1.36	1.38	1.41
CR/TMP	50:50	1.08	1.19	1.26	1.28
CR/TMP	25:75	0.93	1.06	1.13	1.16
CR/TMP	75:25	1.36	1.36	1.38	1.41
CR/TMP	50:50	1.19	1.19	1.26	1.28
CR/TMP (dulplicate result)	25:75	1.06	1.06	1.13	1.16
CR/WPI	75:25	0.76	0.87	0.93	0.95
CR/WPI	50:50	0.62	0.79	0.87	0.90
CR/WPI	25:75	0.55	0.74	0.84	0.87

Table A9.4: X-ratios for mixtures of 0.5% XN and 6.0% dairy protein solutions.

Sample	Gum solution:protein solution ratio	shear rate (s^{-1})			
		116	583	1160	1470
XN/SC	75:25	1.00	1.00	1.11	1.11
XN/SC	50:50	0.95	1.12	1.12	1.11
XN/SC	25:75	0.85	1.05	1.06	1.06
XN/SC	75:25	0.99	1.07	1.06	1.05
XN/SC	50:50	1.01	1.16	1.17	1.15
XN/SC (duplicate result)	25:75	0.96	1.15	1.17	1.16
XN/WPC	75:25	1.35	1.36	1.33	1.42
XN/WPC	50:50	1.29	1.44	1.44	1.55
XN/WPC	25:75	1.16	1.42	1.48	1.58
XN/TMP	75:25	1.01	1.09	1.09	1.09
XN/TMP	50:50	0.97	1.08	1.06	1.05
XN/TMP	25:75	0.95	1.08	1.05	1.04
XN/WPI	75:25	1.01	1.08	1.13	1.06
XN/WPI	50:50	0.95	1.10	1.26	1.12
XN/WPI	25:75	0.84	1.15	1.43	1.23

APPENDIX 10

X-RATIOS FOR MIXTURES OF 0.5% GUM SOLUTION AND WATER

Table A10.1: X-ratios for mixtures of 0.5% gum solution and water.

Gum	0.5 % gum solution and water ratio	shear rate (s^{-1})			
		116	583	1160	1470
LB	75:25	0.68	0.75	0.83	0.84
	50:50	0.38	0.48	0.55	0.60
	25:75	0.32	0.44	0.53	0.54
CMC	75:25	0.60	0.66	0.75	0.77
	50:50	0.32	0.39	0.48	0.49
	25:75	0.27	0.37	0.52	0.54
CR	75:25	0.82	0.84	0.86	0.88
	50:50	0.73	0.80	0.82	0.86
	25:75	0.52	0.66	0.67	0.73
XN	75:25	0.96	0.96	0.97	0.98
	50:50	0.97	0.98	1.00	1.00
	25:75	0.99	1.00	0.99	0.98

APPENDIX 11

X'-RATIOS FOR MIXTURES OF 0.5% GUM AND 6.0% DAIRY PROTEIN SOLUTIONS

Table A11.1: X'-ratios for mixtures of 0.5% LB and 6.0% dairy protein solutions.

Type	Gum solution :protein solution ratio	shear rate (s^{-1})			
		116	583	1160	1470
LB/SC	75:25	-0.06	0.03	-0.01	-0.00
	50:50	0.21	0.22	0.25	0.18
	25:75	0.31	0.32	0.26	0.28
LB/SC	75:25	-0.18	-0.08	-0.13	-0.13
(duplicate result)	50:50	0.29	0.33	0.31	0.22
	25:75	0.44	0.41	0.32	0.33
LB/WPC	75:25	-0.10	0.08	0.08	0.11
	50:50	0.08	0.31	0.36	0.32
	25:75	-0.06	0.14	0.19	0.24
LB/TMP	75:25	-0.10	-0.19	-0.07	-0.07
	50:50	0.37	0.21	0.29	0.22
	25:75	0.75	0.66	0.55	0.57
LB/WP	75:25	-0.19	-0.09	-0.11	-0.10
	50:50	-0.08	0.04	0.05	0.02
	25:75	-0.22	-0.18	-0.19	-0.17

Table A11.2: X'-ratios for mixtures of 0.5% CMC and 6.0% dairy protein solutions.

Type	Gum solution:protein solution ratio	shear rate (s^{-1})			
		116	583	1160	1470
CMC/SC	75:25	0.12	0.21	0.11	0.16
	50:50	0.50	0.72	0.50	0.63
	25:75	0.41	0.70	0.35	0.50
CMC/WPC	75:25	0.12	0.21	0.13	0.13
	50:50	0.50	0.72	0.58	0.61
	25:75	0.19	0.41	0.19	0.20
CMC/TMP	75:25	0.43	0.47	0.36	0.35
	50:50	1.06	1.18	0.94	0.96
	25:75	0.96	1.08	0.67	0.67
CMC/TMP	75:25	0.58	0.58	0.43	0.40
(duplicate result)	50:50	1.16	1.18	0.92	0.94
	25:75	1.37	1.22	0.75	0.74
CMC/WPI	75:25	0.15	0.21	0.13	0.12
	50:50	0.47	0.67	0.54	0.57
	25:75	0.22	0.49	0.29	0.31

Table A11.3: X'-ratios for mixtures of 0.5% CR and 6.0% dairy protein solutions.

Type	Gum solution:protein solution ratio	shear rate (s^{-1})			
		116	583	1160	1470
CR/SC	75:25	-0.16	-0.01	0.06	0.06
	50:50	-0.30	-0.15	-0.07	-0.08
	25:75	0.06	0.05	0.21	0.05
CR/WPC	75:25	-0.00	0.10	0.14	0.12
	50:50	0.08	0.17	0.26	0.23
	25:75	0.29	0.29	0.55	0.37
CR/TMP	75:25	0.66	0.62	0.60	0.60
	50:50	0.48	0.49	0.54	0.49
	25:75	0.79	0.61	0.82	0.59
CR/TMP	75:25	0.66	0.62	0.60	0.60
(duplicate result)	50:50	0.63	0.49	0.54	0.49
	25:75	1.04	0.61	0.82	0.59
CR/WPI	75:25	-0.07	0.04	0.08	0.08
	50:50	-0.15	-0.01	0.06	0.05
	25:75	0.06	0.12	0.35	0.19

Table A11.4: X'-ratios for mixtures of 0.5% XN and 6.0% dairy protein solutions.

Type	Gum solution:protein solution ratio	shear rate (s^{-1})			
		116	583	1160	1470
XN/SC	75:25	0.04	0.04	0.14	0.13
	50:50	-0.02	0.14	0.12	0.11
	25:75	-0.14	0.05	0.07	0.08
XN/SC	75:25	0.03	0.11	0.09	0.07
(duplicate result)	50:50	0.04	0.18	0.17	0.15
	25:75	-0.03	0.15	0.18	0.18
XN/WPC	75:25	0.41	0.42	0.37	0.45
	50:50	0.33	0.47	0.44	0.55
	25:75	0.17	0.42	0.49	0.61
XN/TMP	75:25	0.15	0.14	0.12	0.11
	50:50	-0.00	0.10	0.06	0.05
	25:75	-0.04	0.08	0.06	0.06
XN/WPI	75:25	0.06	0.12	0.10	0.08
	50:50	-0.05	0.12	0.12	0.12
	25:75	-0.14	0.15	0.23	0.26

APPENDIX 12

Z-RATIOS FOR MIXTURES OF GUM-DAIRY PROTEIN SOLUTIONS

Type	Gum:protein ratio	shear rate (s^{-1})			
		116	583	1160	1470
LB/SC	1:16	0.38	0.60	0.72	0.77
	1:8	0.46	0.70	0.81	0.85
LB/WPC	1:16	0.38	0.60	0.72	0.77
	1:8	0.46	0.70	0.81	0.85
LB/TMP	1:16	0.42	0.60	0.71	0.75
	1:8	0.41	0.55	0.62	0.65
LB/WPI	1:16	0.23	0.36	0.43	0.46
	1:8	0.29	0.42	0.48	0.50
CMC/SC	1:16	0.41	0.59	0.65	0.67
	1:8	0.54	0.76	0.82	0.84
CMC/WPC	1:16	0.28	0.46	0.58	0.62
	1:8	0.59	0.76	0.83	0.86
CMC/TMP	1:16	0.49	0.73	0.80	0.84
	1:8	0.63	0.83	0.88	0.90
CMC/WPI	1:16	0.49	0.71	0.77	0.80
	1:8	0.60	0.79	0.83	0.85
CR/SC	1:16	0.63	0.78	0.85	0.88
	1:8	0.70	0.84	0.92	0.94
CR/WPC	1:16	0.75	0.89	1.01	1.06
	1:8	0.78	0.91	0.98	1.05
CR/TMP	1:16	0.88	1.00	1.05	1.06
	1:8	1.14	1.23	1.24	1.31
CR/WPI	1:16	0.59	0.73	0.76	0.80
	1:8	0.67	0.77	0.82	0.83
XN/SC	1:16	0.84	0.98	0.99	1.02
	1:8	0.88	0.98	0.98	1.03
XN/WPC	1:16	0.91	1.09	1.13	1.24
	1:8	0.96	1.09	1.13	1.22
XN/TMP	1:16	0.99	1.11	1.10	1.11
	1:8	1.02	1.11	1.10	1.09
XN/WPI	1:16	0.85	1.05	1.11	1.14
	1:8	0.89	1.02	1.05	1.06

APPENDIX 13

MASS BALANCE AND COMPOSITION DATA

FORMING THE BASIS OF TABLES 8.10 AND 8.11

LB/WPC 1:4

Mixed solution (Batch 5)

Before sedimentation

Nominal gum:protein ratio	= 1:4
Wt. 0.5% gum solution	= 27.75 g
Wt. 6.0% protein solution	= 9.25 g
Wt. mixed solution	= 37.00 g
Actual concentration of gum solution	= 0.53 %
Actual concentration of protein solution	= 6.35 %
Wt. gum in mixed solution	= 0.15 g
Wt. protein in mixed solution	= 0.59 g
Actual gum : protein ratio	= 1:3.93

After sedimentation

Sediment %	= 1.9
Wt. sediment	= 1.9*37.0/100
	= 0.70 g
Wt. supernatant	= 37.0-0.70
	= 36.3 g
Total solids in supernatant	= 1.91 %
Wt. total solids in supernatant	= 1.91*36.3/100
	= 0.69 g
Soluble protein in supernatant	= 1.16 %
Dairy protein in supernatant	= 1.16/0.768*
	= 1.51 %
Wt. protein in supernatant	= 1.51*36.3/100
	= 0.55 g
Percentage of total protein remaining in supernatant	= 0.55*100/0.59
	= 93.2 %
Wt. gum in supernatant	= 0.69-0.55
	= 0.14 g
Percentage of total gum remaining in supernatant	= 0.14*100/0.15
	= 93.3 %
Gum concentration in supernatant	= 0.14*100/36.3
	= 0.38 %
"Expected" viscosity of supernatant at 1160 s^{-1}	= 13.00 mPa.s
(* Protein content of WPC	= 76.8 %)

CMC/TMP 1:4

Mixed solution (Batch 5)

Before sedimentation

Nominal gum:protein ratio	= 1:4
Wt. 0.5% gum solution	= 27.75 g
Wt. 6.0% protein solution	= 9.25 g
Wt. mixed solution	= 37.00 g
Actual concentration of gum solution	= 0.67 %
Actual concentration of protein solution	= 6.47 %
Wt. gum in mixed solution	= 0.19 g
Wt. protein in mixed solution	= 0.60 g
Actual gum : protein ratio	= 1:3.16

CMC/TMP 1:12

Mixed solution (Batch 5)

Before sedimentation

Nominal gum:protein ratio	= 1:12
Wt. 0.5% gum solution	= 18.50 g
Wt. 6.0% protein solution	= 18.50 g
Wt. mixed solution	= 37.00 g
Actual concentration of gum solution	= 0.67 %
Actual concentration of protein solution	= 6.47 %
Wt. gum in mixed solution	= 0.12 g
Wt. protein in mixed solution	= 1.20 g
Actual gum : protein ratio	= 1:10

CMC/TMP 1:36

Mixed solution (Batch 5)

Before sedimentation

Nominal gum:protein ratio	= 1:36
Wt. 0.5% gum solution	= 9.25 g
Wt. 6.0% protein solution	= 27.75 g
Wt. mixed solution	= 37.00 g
Actual concentration of gum solution	= 0.67 %
Actual concentration of protein solution	= 6.47 %
Wt. gum in mixed solution	= 0.06 g
Wt. protein in mixed solution	= 1.80 g
Actual gum : protein ratio	= 1:30

CR/SC 1:4

Mixed solution (Batch 5)

Before sedimentation

Nominal gum:protein ratio	= 1:4
Wt. 0.5% gum solution	= 27.75 g
Wt. 6.0% protein solution	= 9.25 g
Wt. mixed solution	= 37.00 g
Actual concentration of gum solution	= 0.52 %
Actual concentration of protein solution	= 6.40 %
Wt. gum in mixed solution	= 0.14 g
Wt. protein in mixed solution	= 0.59 g

Actual gum : protein ratio	= 1:4.2

CR/WPC 1:4

Mixed solution (Batch 5)

Before sedimentation

Nominal gum:protein ratio	= 1:4
Wt. 0.5% gum solution	= 27.75 g
Wt. 6.0% protein solution	= 9.25 g
Wt. mixed solution	= 37.00 g
Actual concentration of gum solution	= 0.57 %
Actual concentration of protein solution	= 6.35 %
Wt. gum in mixed solution	= 0.16 g
Wt. protein in mixed solution	= 0.59 g
Actual gum : protein ratio	= 1:3.7

CR/WPC 1:12

Mixed solution (Batch 5)

Before sedimentation

Nominal gum:protein ratio	= 1:12
Wt. 0.5% gum solution	= 18.50 g
Wt. 6.0% protein solution	= 18.50 g
Wt. mixed solution	= 37.00 g
Actual concentration of gum solution	= 0.57 %
Actual concentration of protein solution	= 6.35 %
Wt. gum in mixed solution	= 0.11 g
Wt. protein in mixed solution	= 1.17 g
Actual gum : protein ratio	= 1:10.6

CR/WPC 1:36

Mixed solution (Batch 5)

Before sedimentation

Nominal gum:protein ratio	= 1:36
Wt. 0.5% gum solution	= 9.25 g
Wt. 6.0% protein solution	= 27.75 g
Wt. mixed solution	= 37.00 g
Actual concentration of gum solution	= 0.57 %
Actual concentration of protein solution	= 6.35 %
Wt. gum in mixed solution	= 0.05 g
Wt. protein in mixed solution	= 1.76 g
Actual gum : protein ratio	= 1:35.2

CR/TMP 1:4

Mixed solution (Batch 5)

Before sedimentation

Nominal gum:protein ratio	= 1:4
Wt. 0.5% gum solution	= 27.75 g
Wt. 6.0% protein solution	= 9.25 g
Wt. mixed solution	= 37.00 g
Actual concentration of gum solution	= 0.57 %

Actual concentration of protein solution	= 6.57 %
Wt. gum in mixed solution	= 0.16 g
Wt. protein in mixed solution	= 0.61 g
Actual gum : protein ratio	= 1:3.8

CR/TMP 1:12

Mixed solution (Batch 5)

Before sedimentation

Nominal gum:protein ratio	= 1:12
Wt. 0.5% gum solution	= 18.50 g
Wt. 6.0% protein solution	= 18.50 g
Wt. mixed solution	= 37.00 g
Actual concentration of gum solution	= 0.57 %
Actual concentration of protein solution	= 6.57 %
Wt. gum in mixed solution	= 0.11 g
Wt. protein in mixed solution	= 1.22 g
Actual gum : protein ratio	= 1:11.1