

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Characterisation of the rehydration behaviour of milk protein concentrates in the presence of sugar

M.Phil Thesis

Ghulam Mohi Uddin Paracha

**Characterisation of the rehydration behaviour of milk protein
concentrates in the presence of sugar**

A thesis presented in partial fulfilment of the requirements for the degree of
Master of Philosophy
in
Food Science and Technology

at Massey University, Manawatu campus
New Zealand.

Ghulam Mohi Uddin Paracha

2011

Abstract:

The main focus of this study was to characterize the hydration of milk protein in high protein powders to provide insights and strategies that might improve the use of these powders in foods. While the majority of hydration studies reported in the literature have been conducted on systems where there is an excess of water there has been little research characterising hydration in models that more closely approximate powder hydration in real food systems. This study investigates the impact on protein powder hydration of one of the most common ingredients in food systems: sugar. Results from this study show that rehydration of MPC85 powders is much more sensitive to aging compared to rehydration in water. An aged MPC85 powder was found to have the same solubility profile with respect to temperature in pure water compared to the fresh powder. However the degree of solubility was markedly reduced when the same powder was rehydrated in water containing sugar (20%). This should also be kept in mind while calculating the solubility of milk powders during the processing as other ingredients will interfere with them to affect solubility of milk powders which in turn will affect the shelf life of the food products.

It was also shown that the specific volume of the insoluble material sedimented during solubility studies increased as the solubility of the overall increased to about 50%. At higher degrees of solubility the specific volume of the sediment material decreased. Microscopy showed that in the lower solubility range predominantly small particles dissolved and the large particles retained their structural integrity through centrifugation and thus the volume of sediment was relatively unchanged despite material dissolving and becoming part of the supernatant. At higher levels of solubility the large particles dissolve primarily through the outer particle surface which therefore resulted in a progressive decrease in volume with solubility. The rate of change in the specific volume of the sediment and mass of the sediment with the increase in the solubility and temperature was also dependent on the solvent. The rate of change in water was higher than in the 20% sugar solution.

A new mechanism for MPC powder rehydration was also proposed wherein water ingress into the particles occurs over a very short time scale. Water ingress equilibrium was assumed to occur when the concentration of sodium ions reached equilibrium on the assumption that all sodium salts are highly soluble and that the sodium salts are evenly dispersed throughout the primary powder particle. This occurred over a time-period of a

couple of minutes compared with about thirty minutes for the bulk total soluble solids as measured through centrifugation. Increases in solubility with increasing rehydration temperature is proposed to result from shrinkage of the micelles in the particles due to increased hydrophobic bonding that in turn separates the micelles from each other allowing further ingress of water and solubilisation.

Table of Contents

1	INTRODUCTION	1
1.1	RESEARCH PROBLEM	2
2	LITERATURE REVIEW.....	4
2.1	COMMERCIALY AVAILABLE LIMITED MOISTURE ENVIRONMENT IN FOODS	4
2.1.1	QUALITY ISSUES IN LIMITED MOISTURE FOODS.....	4
2.1.2	AN EXAMPLE OF A CHANGES IN THE QUALITY ATTRIBUTES IN A LIMITED MOISTURE FOOD – THE PROTEIN BAR SYSTEM	9
2.2	PROTEIN	14
2.3	PROTEIN CHEMISTRY	14
2.3.1	AMINO ACIDS COMMONLY FOUND IN PROTEINS	14
2.3.2	CLASSIFICATION OF AMINO ACIDS	15
2.3.3	PROTEIN STRUCTURE.....	16
2.3.4	INTERACTIONS IN THE PROTEIN STRUCTURE STABILITY	22
2.3.5	PROTEIN FOLDING	26
2.3.6	FOOD PROTEINS	26
2.3.7	MILK PROTEINS.....	26
2.4	TYPES OF MILK PROTEINS	27
2.4.1	CASEIN CHEMISTRY AND STRUCTURE	27
2.4.2	WHEY PROTEIN CHEMISTRY AND STRUCTURE.....	31
2.5	TYPES OF COMMERCIALY AVAILABLE PROTEIN POWDER	33
2.5.1	DIFFERENCES IN COMPOSITION AND STRUCTURE OF DIFFERENT POWDERS	36
2.6	MANUFACTURING OF MILK POWDER & PROTEIN INTERACTIONS	37
2.6.1	MILK PRE-TREATMENT	37
2.6.2	SEPARATION AND PASTEURIZATION.....	38
2.6.3	PREHEAT TREATMENT.....	38
2.6.4	EVAPORATION.....	40
2.6.5	HOMOGENIZATION	41
2.6.6	HEAT TREATMENT.....	41
2.6.7	SPRAY DRYING.....	41
2.6.8	INSTANTIZATION	44
2.6.9	SUMMARY OF PROCESSING OPERATIONS DURING MANUFACTURING OF POWDERED MILK PROTEIN PRODUCTS	45
2.6.10	MILK PROTEIN INTERACTIONS INVOLVED IN THE MANUFACTURING OF MPC	45
2.7	FUNCTIONAL PROPERTIES OF DAIRY PROTEIN	47
2.7.1	SOLUBILITY	49
2.8	REHYDRATION PROCESS	51

2.8.1	WETTABILITY	52
2.8.2	SINKABILITY	53
2.8.3	DISPERSIBILITY	53
2.8.4	SOLUBILITY	54
2.9	TYPES OF SOLVENTS	55
2.9.1	ETHANOL	55
2.9.2	OIL/FAT.....	55
2.9.3	WATER	55
2.10	PROTEIN HYDRATION	55
2.10.1	HYDRATION OF CASEIN AND WHEY PROTEIN	57
2.10.2	FACTORS EFFECTING PROTEIN HYDRATION	57
2.11	WATER ACTIVITY	60
2.11.1	MOISTURE SORPTION ISOTHERMS	60
2.12	EXPERIMENTAL TECHNIQUES FOR PROTEIN-WATER INTERACTIONS	61
2.12.1	THERMODYNAMIC	61
2.12.2	KINETIC.....	61
2.12.3	SPECTROSCOPIC	62
2.12.4	DIFFRACTION	62
2.13	TECHNIQUES USED TO MEASURE THE PROTEIN REHYDRATION	62
2.13.1	MONITORING OF TURBIDITY	63
2.13.2	ULTRASONIC SPECTROMETRY.....	63
2.13.3	MONITORING OF VISCOSITY	63
2.13.4	NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY	64
2.13.5	LIGHT MICROSCOPY	64
2.14	SUMMARY, CONCLUSIONS AND DEVELOPMENT OF RESEARCH OBJECTIVES	65
2.15	VALUE OF RESEARCH	66

3 MATERIAL AND METHODS..... 67

3.1	SELECTION OF MILK POWDERS	68
3.2	MODIFICATION OF HYDRATION THROUGH INGREDIENT ADDITION	69
3.3	SELECTION OF EXPERIMENTAL TECHNIQUE	70
3.4	METHODOLOGY	70
3.4.1	REHYDRATION PROCEDURE	70
3.4.2	DETERMINATION OF TOTAL SOLIDS IN REHYDRATED MILK POWDER SOLUTION	71
3.4.3	MEASURING THE ELECTRICAL CONDUCTIVITY.....	73
3.4.4	MEASURING THE ION SELECTIVE ELECTRODE DATA.....	76
3.4.5	CHANGE IN SEDIMENT VOLUME IN COMPARISON WITH THE SOLUBILITY DURING REHYDRATION	79
3.4.6	SAMPLE PREPARATION METHODOLOGY FOR ELECTRON MICROSCOPY	80

4 RESULTS AND DISCUSSION..... 82

4.1	EFFECT OF DIFFERENT TEMPERATURES ON THE SOLUBILITY OF MILK POWDERS	82
4.2	EFFECT OF DIFFERENT TEMPERATURES ON THE ELECTRICAL CONDUCTIVITY OF MILK POWDER DISPERSIONS	85

4.3	EFFECT OF DIFFERENT TEMPERATURES ON THE IONIC SODIUM SOLUBILITY OF MILK POWDERS	87
4.4	THE SOLUBILITY OF SALTS AS A FUNCTION OF TIME	88
4.5	CHANGE IN SEDIMENT VOLUME IN COMPARISON WITH THE SOLUBILITY DURING REHYDRATION	88
4.6	HIGH CENTRIFUGATION SPEED FOR DISRUPTION OF SEDIMENT	90
4.7	TEXTURAL ANALYZER	90
4.8	EFFECT OF CONCENTRATION ON SOLUBILITY	90
4.9	EFFECT OF CALCIUM ADDITION ON THE SOLUBILITY	91
4.10	SAXS ANALYSIS	92
4.11	MORPHOLOGICAL CHANGES IN UNDISSOLVED MATERIAL	92
4.11.1	LIGHT MICROSCOPY	92
4.11.2	TRANSMISSION ELECTRON MICROSCOPY	93
5	<u>CONCLUSIONS.....</u>	102
6	<u>REFERENCES.....</u>	103

List of Figures

Figure 1. The general structure of an alpha amino acid, with the amino group (left) and the carboxyl group (right)(http://en.wikipedia.org/wiki/File:AminoAcidball.svg).....	17
Figure 2. Representation of an ideal α -helix made up of 16 amino acids (without side chains) linked in a short polypeptide (guweb2.gonzaga.edu/.../CHEM440pub/L05_index.cfm)	19
Figure 3. Casein Micelle (Source: Walstra, 1999).	30
Figure 4. Casein sub micelle model according to Schmidt (1982): A) Sub micelle; B) Casein micelle..	31
Figure 5. Dual Bonding Model of casein micelle structure (Horne, 1998).....	31
Figure 6. Spectrum of application of membrane separation processes in the dairy Industry (Caric et al., 2009)	36
Figure 7. General manufacturing processes for a typical whole milk powder (WMP), skim milk powder (SMP) or milk protein concentrate powder (MPC) (Singh, 2007).	38
Figure 8. Sequence of protein-water interaction for dry protein (Chou and Morr, 1979).....	51
Figure 9. Schematic of dissolution timeline for different types of powder showing the overlaps between different phases with time (Fang et al., 2008).....	52
Figure 10. Effect of pH on solubility of sodium caseinate (A), α_s -/k-casein-enriched caseinate (B) and β -casein-enriched caseinate (C) (Murphy and Fox, 1990)	58
Figure 11. Temperature solubility curve of MPC 85 in water, 10% and 20% sugar solution.....	69
Figure 12. Flow sheet diagram of determination of total solids.....	72
Figure 13. Change in Solubility of ALAPRO 4850, CaCS 380 & CSMPC 85 in 6 hours at $25\pm 1^\circ\text{C}$ in 20% Sugar Solution	73
Figure 14. ProLab 4000 with dual ISE and electrical conductivity electrodes	74
Figure 15. Change during rehydration of ALAPRO 4850 in 30 Min. (a) Electrical Conductivity (b) Sodium Ion Dissolution (c) Calcium Ion Dissolution.	75
Figure 16. Change in Electrical Conductivity in ALAPRO 4850, CSMPC 85 & CaCS 380 in 8 Hrs. at $25\pm 1^\circ\text{C}$	75
Figure 17. Change in Electrical Conductivity in ALAPRO 4850, CSMPC 85 & CaCS 380 in First 5 Min at $25\pm 1^\circ\text{C}$	76
Figure 18. Change in Ion Dissolution in ALAPRO 4850, CSMPC 85 & CaCS 380 in 8 Hrs. at $25\pm 1^\circ\text{C}$ in Na	77
Figure 19. Change in Temperature Over 8 Hours in ALAPRO 4850, CaCS 380 & CSMPC 85	78
Figure 20. Change in Ion Dissolution in ALAPRO 4850, CSMPC 85 & CaCS 380 in First 5 Min at $25\pm 1^\circ\text{C}$ (a) Ca (b) Na	78
Figure 21. Temperature solubility curve - ALAPRO 4850 in Water and 20% Sugar Solution.....	82
Figure 22. Temperature solubility curve (a) ALAPRO 4850 in Water, 10% and 20% Sugar Solution....	83
Figure 23. Temperature solubility curve after 30 Min in CSMPC 85 in Water and 20% Sugar Solution	83
Figure 24. Temperature solubility curve after 30 Min in CaCS 380 in Water and 20% Sugar Solution	84
Figure 25. Relationship between viscosity and solubility of ALAPRO 4850 over a range of temperatures (10°C to 40°C).....	85
Figure 26. Temperature Electrical conductivity curve in Water and 20% Sugar Solution after 60 Min (a) ALAPRO 4850 (b) CSMPC85 (C) CaCS 380.....	86
Figure 27. Effect of temperature on Ionic Sodium in Water and 20% Sugar Solution after 30 Min (a) ALAPRO 4850 (b) CSMPC 85 (c) CaCS 380	87

Figure 28. Change in the ratio of sediment volume and solubility in ALAPRO 4850.....	89
Figure 29. Specific volume under same conditions with different particle population	89
Figure 30. Effect of Concentration on Solubility of ALAPRO 4850 at 25±1°C	90
Figure 31. ALAPRO 4850 rehydrated in 20% sugar solution at 20°C and 30°C observed under light microscope with different magnifications	93
Figure 32. ALAPRO 4850 rehydrated in water at 10°C and 35°C observed under TEM with same magnifications.....	94
Figure 33. ALAPRO 4850 rehydrated in water at 10°C and 35°C observed under TEM with same magnifications.....	94
Figure 34. ALAPRO 4850 rehydrated in water at 10°C and 35°C observed under TEM with same magnifications.....	95
Figure 35. ALAPRO 4850 rehydrated in water at 10°C and 35°C observed under TEM with same magnifications.....	95
Figure 36. ALAPRO 4850 rehydrated in water at 10°C and 35°C observed under TEM with same magnifications.....	96
Figure 37. ALAPRO 4850 rehydrated in water at 10°C and 35°C observed under TEM with same magnifications.....	96
Figure 38. ALAPRO 4850 rehydrated in water at 10°C and 35°C observed under TEM with same magnifications.....	97
Figure 39. ALAPRO 4850 rehydrated in water at 10°C and 35°C observed under TEM with same magnifications.....	97
Figure 40. ALAPRO 4850 rehydrated in water at 10°C and 35°C observed under TEM with same magnifications.....	98
Figure 41. ALAPRO 4850 rehydrated in water at 10°C and 35°C observed under TEM with same magnifications.....	98
Figure 42. ALAPRO 4850 rehydrated in water at 10°C observed under TEM with same magnifications	99
Figure 43. ALAPRO 4850 rehydrated in water at 35°C observed under TEM with same magnifications	100

List of Tables

Table 1. Formulation of Protein Bar Recipe.....	9
Table 2. Proteinogenic Amino Acids (Milewski, S., 2001)	15
Table 3. Classification of Amino Acids	16
Table 4. Proteins in Milk (Walstra et al., 2006).....	27
Table 5. Range of Dried Dairy Products (Fox and McSweeney, 2003).....	33
Table 6. Principal food applications of skim and whole milk powders (Fox and McSweeney, 2003) ..	34
Table 7. Milk Powders (Fonterra Co-operative Groups)	35
Table 8. Functional properties of milk proteins in food systems (Singh, 2002)	48
Table 9. Important functional properties of milk protein products and milk powders in food systems (Singh, 2002)	48
Table 10. Composition table of ALAPRO 4850, CSMPC 85 and CaCS 380.....	68
Table 11. Overall Preview of Experiments in ALAPRO 4850, CSMPC 85 and CaCS 380.....	71