INSTITUTE OF FOOD, NUTRITION AND HUMAN HEALTH,
MASSEY UNIVERSITY,
PALMERSTON NORTH,
NEW ZEALAND.

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FORMATION AND STABILITY OF OIL-IN-WATER CASEINATE EMULSIONS

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BY
MAGESH SRINIVASAN

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Dedication

To my Parents

ABSTRACT

The main objective of this study was to gain a better understanding of the formation, stability and microstructure of oil-in-water emulsions stabilized by commercial sodium (ALANATE 180) and calcium caseinates (ALANATE 380). The study also determined the effects of heat treatment and NaCl addition on the formation and stability of these emulsions.

Emulsions were prepared using various concentrations of sodium or calcium caseinate solutions (0.5 to 5.0%) and 30% soya oil. Surface protein coverage (mg/m^2) in freshly prepared emulsions was determined from analysis of the aqueous phase after centrifugation of emulsions at 45,000 *g* for 40 minutes, using the Kjeldahl method. SDS-PAGE was used to identify the adsorbed protein components in the cream phase. Creaming stability was determined after storage of emulsions for 24 hours at 20°C by a low speed centrifugation method. The microstructure of these emulsions was determined using confocal laser scanning microscopy. The aggregation state of caseins in sodium and calcium caseinate solutions was determined by successive centrifugation, gel permeation chromatography and multi-angle laser light scattering techniques.

For emulsions stabilized with sodium caseinate, the surface protein concentration increased gradually with protein concentration up to 3%, but the increase was much smaller at higher concentrations. By comparison, the surface protein coverage in emulsions stabilized with calcium caseinate showed an almost linear increase with protein concentration (0.5 to 5.0%). At all protein concentrations, the surface protein coverage of emulsions stabilized with calcium caseinate was higher than that of sodium caseinate emulsions. β-Casein was adsorbed in preference to other caseins in emulsions made using ≤ 2.0% sodium caseinate, but α_s-casein (α_{s1}- + α_{s2}-) appeared to adsorb in preference to other caseins when emulsions were made using > 2.0% sodium caseinate. In calcium caseinate-stabilized emulsions, α_s-casein was found to

adsorb in preference to other caseins at all protein concentrations used.

Heat treatment (121°C for 15 min) of sodium caseinate emulsions or heat treatment of sodium caseinate solutions prior to emulsion formation, at all caseinate concentrations, resulted in an increase in surface protein coverage and altered the proportions of individual caseins at the droplet surface. The surface protein coverage of emulsions formed with calcium caseinate solutions increased markedly when the emulsions were heated (121°C for 15 min) or when calcium caseinate solutions were heated prior to emulsion formation. The preferential adsorption of α_s-casein, observed in the unheated calcium caseinate emulsions, diminished after heating, which was due to polymerization of α_s-casein during heating and/or degradation of this casein.

In sodium caseinate emulsions, the surface protein coverage and the composition of emulsion droplets were influenced by the presence of NaCl prior to emulsion formation. The surface protein coverage in emulsions made with 1 and 3% sodium caseinate increased with an increase in NaCl concentration up to 40 mM, with a large increase in the adsorption of α_s-casein at the droplet surface. Addition of NaCl beyond 40 mM had no further effects on surface coverage and composition. Similar trends were observed when NaCl was added to the emulsions after they were formed. By contrast, in calcium caseinate emulsions, the surface protein coverage decreased with increase in NaCl concentration up to 40 mM, but with further increase in NaCl concentration the surface protein coverage increased slightly. In these emulsions, the composition of the interface remained largely unafffected by NaCl addition; α_s-casein was adsorbed in preference to other caseins.

Creaming stability of calcium caseinate emulsions, after storage at 20°C for 24 hours, increased with an increase in protein concentration. However, the creaming stability of sodium caseinate emulsions decreased markedly as the protein concentration was increased above 2%. This decrease in stability was attributed to the reversible flocculation arising from a 'depletion flocculation'

mechanism. This flocculation in turn resulted in enhanced creaming at high caseinate concentrations. In sodium caseinate emulsions, the appearance of the droplets in the confocal micrographs was dependent on the concentration of protein used for making emulsions. Emulsions formed with low concentrations of sodium caseinate (0.5 and 1.0%) appeared to be homogenous with no sign of flocculation. However the emulsions made with > 2% sodium caseinate showed some irregular flocs, which appeared to be forming a network structure at higher concentrations of protein. In contrast, confocal micrographs of emulsions formed with calcium caseinate at all protein concentrations showed individual droplets. The creaming stability of these emulsions improved, when the emulsions were heated or when emulsions were made using heated sodium or calcium caseinate solutions. The presence of 200 mM NaCl prior to emulsion formation resulted in improved creaming stability and a reduced degree of flocculation.

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TABLE OF CONTENTS