By using static light-scattering we have studied the binary (polymer–solvent) and ternary (polymer1–polymer2–solvent) solutions of a number of individual biopolymers whose structure in aqueous medium are strongly different and well known. These include dextrans, pectinate, alginate, carboxymethyl cellulose, 11S globulin, ovalbumin and fibrinogen. Molecular weight and size of the biopolymers were obtained in the binary solutions. Second virial coefficients characterizing the nature and intensity of the pair interactions polymer–polymer and polymer–solvent were calculated from light scattering data. The correspondence between the character of biopolymer interactions and the phase state of the mixture solutions at moderate concentration was observed. The relationship between the conformations of the biopolymers and the character of their interactions was determined. The coordinates of the critical points of the phase separation in systems were calculated. Systematic correlations of the difference of the affinity biopolymers to the aqueous medium with the intensity of the polymer1–polymer2 interactions and the biopolymer's concentration at the critical point were carried out.

## THE INFLUENCE OF BIOPOLYMERS ON EMULSION STABILITY

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The correlation between the phase behaviour of aqueous solutions of caseinate + guar gum and the stability of oil-in-water emulsions stabilized by caseinate and containing guar gum has been investigated in the presence and absence of added salt at pH 6·7. The aqueous phase behaviour of sodium caseinate + dextran T40, T500 or T2000, in the presence and absence of added salt, was also investigated as a comparative model system.

The water–caseinate–guar system displayed visible phase separation in 0·2 M NaCl at 20°C and pH 6·7. The system maintained homogeneity in the absence of added salt. Tubidity measurements supported the observed phase behaviour and provided evidence for phase separation in the presence of salt.

Oil-in-water emulsions prepared with 10 wt% oil and 2 wt% caseinate displayed extensive creaming. A self-depletion mechanism is proposed. The presence of unadsorbed guar gum (0·001–0·2 wt%) in 10 wt% oil emulsions prepared with 1 wt% caseinate gave rise to enhanced creaming and serum separation due to depletion flocculation. Relative rates and extents of emulsion creaming were determined over a 50-day period at 5°C. The effects of ionic strength on creaming and flocculation were investigated.

In the absence of aqueous phase separation, emulsion stability was reduced with respect to creaming and flocculation by the mechanism of depletion. The concentration of guar gum required to destabilize the emulsion was much lower than that required to cause thermodynamic phase separation in the absence of oil at the same ionic strength and caseinate concentration. Relationships between aqueous phase behaviour and emulsion stability are discussed with a view to developing a predictive model to enable future biopolymer selection to be made on the basis of rheological and emulsion destabilization properties.

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## PROTEIN–POLYSACCHARIDE INTERACTIONS AT THE OIL/WATER INTERFACE

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Electrophoretic mobilities of emulsion droplets of di-*n*-butyl phthalate formed in the presence of methemoglobin alone, methemoglobin plus alginate or carboxymethyl cellulose have been measured. At pHs below the protein isoelectric points addition of the polysaccharide conferred a net negative charge on the emulsion droplets. For pHs up to approximately 2 units above the isoelectric point the mobilities of the polysaccharide containing emulsion droplets were substantially more negative than for the protein covered droplets. At higher pHs the observed mobilities were similar for both systems. Measurements of alginate surface loadings confirmed that polysaccharide was located at the surface of the oil droplets stabilised with methemoglobin at pHs above the protein isoelectric point. The surface concentration of alginate was approximately 2 mg/m$^2$, independent of pH in the region pH 5·0–8·0 (Ward-Smith *et al.*, 1994).

Creep measurements were done on hemoglobin, hemoglobin–alginate and hemoglobin–CMC emulsions at 3 pHs and oil volume fractions up to 60%. The instantaneous elastic compliance, due to deformation within a floc, decreased with increasing oil concentration, and provides a useful method of studying how flocculated a system actually is. The point at which the oil volume fraction is large enough to cause bridging flocculation can be easily determined.

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## EFFECT OF THE HYDROCARBON–DECANE AND FATTY ACID SALT–SODIUM DECANOATE ON THE THERMODYNAMIC PROPERTIES OF THE PROTEINS IN THE AQUEOUS MEDIUM

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Proteins, polysaccharides and lipids are the main components of real foods. It is well known that the mechanisms of food structure formation are mainly dictated by the nature and intensity of interactions between food biopolymers in the bulk and on the interfaces of the food system. The main low molecular weight components of food can affect food structure formation by interacting with biopolymers and acting on the charge, conformation, molecular weight, size and other physical–chemical properties of the food biopolymers as well as on thermodynamic quality of the aqueous medium thereby radically altering biopolymer interactions.

In this connection the objective of research is the elucidation of the effect of lipophilic molecules (models of the lipid and flavour food components) on the thermodynamic properties of proteins in binary and more complex aqueous solutions. Two lipophilic molecules of the same chain length, non polar decane and polar sodium decanoate were employed. The proteins investigated were ovalbumin and 11S globulin.

The thermodynamic parameters of the different types pair interactions (the second virial coefficients) were estimated using static light scattering data in the binary and ternary aqueous solutions of the biopolymers without and with lipophilic molecules. The limit of thermodynamic stability of the systems (spinodal curve) and the co-ordinates of the critical point were calculated. Experimental data were in good agreement with the calculated results.

The influence of lipophilic molecules on the conformational state of proteins in aqueous medium was characterized by differential scanning calorimetry. Comparison of the effect of unpolar and polar lipophilic molecules on the thermodynamic properties of proteins was carried out.

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## PROTEIN/PROTEIN AND PROTEIN/SURFACTANT INTERACTIONS IN EMULSION SYSTEMS

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Mixed biopolymer interactions have been investigated in the bulk aqueous phase and in oil-in-water emulsion systems. The interactions between oppositely charged β-lactoglobulin and gelatin in aqueous phase is clearly observed in electrophoretic mobility measurement, where the calculated zeta potential is changed from approximately −12 mV in pH 7·0 buffer solution to about −3 mV in the presence of 0·8 wt% gelatin. The addition of gelatin to β-lactoglobulin stabilized emulsions (0·4 wt% β-lactoglobulin, 20 wt% n-hexadecane, 20 mM bis-tris-propane, pH 7·0) induces bridging flocculation at a suitable dosage of gelatin. The most favourable flocculation is observed at a gelatin concentration of 0·3 wt%, a concentration corresponding to approximately half coverage and a very small emulsion droplet electrophoretic mobility. Competitive adsorption experiments in emulsions containing mixed proteins show that the proteins are more strongly packed at the interface and less easy to displace in the presence of Tween 20. This trend is also confirmed by surface shear viscosity experiments. The addition of Tween 20 to 1-day-old mixed β-lactoglobulin + gelatin film reduces the surface shear viscosity to lower steady values over a period of 24 h, whereas the introduction of Tween 20 to a 1-day-old individual β-lactoglobulin or gelatin film brings the surface shear viscosity down to zero in just a few minutes. We suppose that the negatively charged β-lactoglobulin and positively charged gelatin are strongly interacting with each other and so form a more closely packed and more highly cross-linked complex at the interface. This kind of complexed adsorbed protein film most probably has fewer interaction sites available for the non-ionic surfactant, and it may provide a diffusional barrier slowing down the rate of penetration of surfactant towards the oil–water interface. The experimental results suggest that there may be a synergistic effect occurring between two different kinds of protein at the oil–water interface which may be relevant to food emulsion stability in systems containing mixed food biopolymers.

## THE EFFECT OF COUNTER IONS ON THE PARTITIONING OF BIOMOLECULES IN UCON–DEXTRAN AND UCON–WATER SYSTEMS

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Ucon–dextran is an aqueous polymer two-phase system, formed at room temperature, which can be used for protein partitioning (Harris *et al.*, 1991). Ucon is a water-soluble random copolymer of equal amounts of weight of ethylene oxide and propylene oxide. The observed partition coefficient of a charged protein in a Ucon–dextran system is an average value as a result of contributions from the partitioning of the single protein and its counter ions. Perchlorate and triethyl ammonium are two hydrophobic ions which have been used to direct the partitioning of albumin and lysozyme in Ucon–dextran systems.

In water solutions containing the hydrophobic Ucon-polymer a two-phase system is formed after temperature increase (Johansson *et al.*, 1993). This polymer–water system has been used to study the effect of the relative hydrophobicity of the amino acid side chains and different counter ions. Tryptophan (Trp) was found to be strongly partitioned to the hydrophobic polymer rich phase. The partitioning of Trp in a Ucon–water system can be directed to the polymer rich phase at low pH (pH 2 or less) with $NaClO_4$ present in the system. At this pH the counter ion of Trp is $ClO_4^-$. At high pH (pH 10 or higher) $NaClO_4$ will drive the partitioning of Trp to the water rich phase. $Na^+$ is the counter ion of Trp in this case. $ClO_4$ and $Na^-$ have different affinities to the polymer rich phase which explains why Trp partitions differently at low or high pH. The effect of hydrophobic ions on Trp in Ucon–water systems is qualitatively the same for protein partitioning in Ucon–dextran systems.

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