Influence of Dextran Sulfate and NaCl on the Flocculation of Oil-in-Water Emulsions Stabilized by a Nonionic Surfactant

Kyros Demetriades and David Julian McClements*

Food Biopolymers and Colloids Research Laboratory, Department of Food Science,
University of Massachusetts, Amherst, Massachusetts 01003

The creaming stability and viscosity of 10 wt % soybean oil-in-water emulsions stabilized by Tween 20 were monitored as a function of 500 kDa dextran sulfate (DS) concentration (0–5 wt %) and NaCl concentration (0–1 wt %). In the absence of salt, DS increased the apparent viscosity of the emulsions and promoted droplet flocculation above a critical concentration (CFC ∼ 0.08 % DS). Above the CFC, the creaming rate decreased with increasing DS because of the enhanced viscosity of the continuous phase. The addition of salt decreased the apparent viscosity of emulsions, increased the CFC, and increased the creaming rate above the CFC. These results can be explained by the reduction in the effective radius of DS molecules due to electrostatic screening by the salt. Emulsions with specific physicochemical properties can be developed by carefully controlling salt and biopolymer concentration.

Keywords: *Emulsions; flocculation; rheology; colloidal interactions; dextran sulfate; electrolyte*

INTRODUCTION

Polysaccharides are added to food emulsions to modify their textural properties and to stabilize emulsion droplets against creaming (Hibberd et al., 1986; Dickinson, 1992). They achieve this by either enhancing the viscosity or forming a gel network in the continuous phase (Dickinson et al., 1994). Nevertheless, the addition of polysaccharides can sometimes accelerate the rate and extent of creaming through two mechanisms: depletion and bridging flocculation (Walstra, 1996; Dickinson and Pawlosky, 1997). Whether a polysaccharide increases or decreases emulsion stability depends on its concentration, the rheology of the aqueous phase, and the strength and nature of the colloidal interactions in the system (Dickinson et al., 1995). Bridging flocculation involves the adsorption of a macromolecule onto two neighboring emulsion droplets, with the macromolecule acting as a bridge between the droplets (Walstra, 1993). Depletion flocculation occurs as a result of the osmotic pressure that arises when nonadsorbing biopolymer molecules are excluded from a narrow region surrounding the droplets (Vincent et al., 1986; Seeberg and Berg, 1994; Jenkins and Snowden, 1996).

Several researchers have investigated the influence of the size and concentration of biopolymers and emulsion droplets on depletion flocculation (Sperry et al., 1981; Jones and Vincent, 1989; Smith and Williams, 1995; Ogden and Lewis, 1996). Far less is known about the role that electrolytes play in depletion flocculation. Nevertheless, a number of thickening agents used in food products are ionic, and therefore their properties are strongly influenced by electrolytes. For this reason, we study the influence of NaCl on the stability and rheology of oil-in-water emulsions containing dextran sulfate (DS).

* Author to whom correspondence should be addressed [fax (413) 545-1262; e-mail mcclements@foodsci.umass.edu].

Dextran and its derivatives are highly branched polysaccharides that are widely used in the food industry as thickening agents (Gekko, 1981; de Belder, 1993). DS is a negatively charged derivative of dextran; its conformation and solution properties are therefore dependent on electrolyte concentration. Our ultimate objective is to show that food emulsions with specific physicochemical properties can be created by carefully controlling both the salt and biopolymer concentrations.

BACKGROUND

The stability of an emulsion to flocculation depends on the relative magnitude and range of the attractive and repulsive interactions between the droplets (Israelachvilli, 1992; McClements 1998). The colloidal interactions that play an important role in a particular food emulsion depend on the nature of the emulsifier and the composition of the continuous phase. We assume that the overall interaction potential (V_{TOT}) of the emulsions used in this study can be described by the sum of van der Waals (V_{VDW}), steric (V_{steric}), electrostatic (V_{elec}), and depletion (V_{dep}) interactions

$$V_{TOT}(h) = V_{VDW}(h) + V_{steric}(h) + V_{elec}(h) + V_{dep}(h) \tag{1}$$

where h is the surface-to-surface droplet separation.

van der Waals Interactions. This type of interaction is relatively strong, long-range, and attractive (Israelachvilli, 1992). At close droplet–droplet separations (i.e., $h \ll r_D$), the van der Waals interaction potential between two similarly sized droplets can be approximated by the following expression:

$$V_{VDW}(h) = -Ar_D/12h \tag{2}$$

In eq 2 A is the Hamaker function and r_D is the droplet radius. The Hamaker function comprises a zero-frequency component ($A_{f=0}$) and a frequency-dependent

($A_{f>0}$) component: $A = A_{f=0} + A_{f>0}$ (Israelachvilli, 1992). The zero-frequency component can be reduced by as much as 40% when electrolyte is added to the aqueous phase because of electrostatic screening (Mahanty and Ninham, 1976). As a result, the van der Waals attraction between oil droplets is reduced considerably when salt is added to an oil-in-water emulsion.

Electrostatic Interactions. Electrostatic interactions play an important role in colloidal dispersions containing electrically charged droplets (Hunter, 1986). Although a nonionic surfactant was used to stabilize the droplets in this study, a small electrical charge was still measured on the droplets (~ -4 mV). The most likely cause of this negative charge is the preferential absorption of OH^- ions from the aqueous phase onto the droplets (Ivanov et al., 1997). For this reason, we included electrostatic interactions in our analysis. The electrostatic repulsion between two similarly charged emulsion droplets can be described by the equation (Walstra, 1996)

$$V_{elec}(h) = 4.3 \times 10^{-9} r_D \psi^2 \ln(1 + e^{-\kappa h}) \qquad (3)$$

where ψ is the droplet surface potential and κ^{-1} is the Debye screening length, which is given by the following relationship for water at room temperature:

$$\kappa^{-1} = 0.31 \times 10^{-9} I^{-1/2} \qquad (4)$$

In eq 4 I is the ionic strength of the aqueous phase (Walstra, 1996). The Debye screening length can be thought of as a measure of the "thickness" of the electrical double layer as it corresponds to the distance from the charged surface where the electrical potential falls to $1/e$ of its value at the surface (Rosen, 1978; Israelachvilli, 1992). The addition of salt to an emulsion increases the ionic strength of the aqueous phase, which decreases the thickness of the double layer and therefore leads to a reduction in the electrostatic repulsion between droplets.

Steric Interactions. This type of interaction is normally short-range and repulsive and arises because of the interpenetration of interfacial layers that occurs when two droplets come into close contact (Hunter, 1986). In our system, the absorbed layer comprises a nonionic surfactant (Tween 20). McClements and Dungan (1997) recently gave an expression for the steric interaction between droplets coated by Tween 20

$$V_{steric}(h) = 64\pi r_D L^2 \frac{kT}{s^3} \left[\frac{1}{5}\left(\frac{2L}{h}\right)^{1/4} + \frac{3}{35}\left(\frac{h}{2L}\right) - \frac{1}{77}\left(\frac{h}{2L}\right)^{11/4} - \frac{3}{11}\right] \qquad \text{for } h < 2L \quad (5)$$

where L is the distance the surfactant headgroups protrude into the aqueous phase and s is the average distance between the surfactant headgroups. In theory, steric interactions are independent of the concentration of electrolyte in the aqueous phase. Nevertheless, they may be indirectly influenced if the salt concentration is high enough to dehydrate the headgroups and therefore reduce their effective size (Israelachvilli, 1992).

Depletion Interactions. An attractive force arises between droplets when there is a nonabsorbing polymer present in the continuous phase of an emulsion because of the exclusion of polymer molecules from a narrow region (approximately equal to their radius) surrounding each of the droplets (Asakura and Oosawa, 1954,
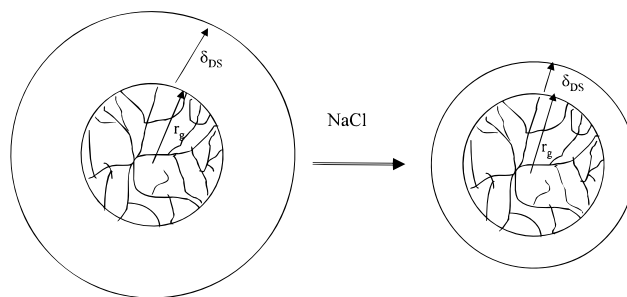

Figure 1. Addition of electrolyte (NaCl) to an aqueous solution of charged polysaccharide molecules (DS) results in a decrease in the effective radius of the molecules due to electrostatic screening effects.

1958; Jenkins and Snowden, 1996). The strength of this attraction increases as the concentration difference between the polymer-depleted region and the bulk aqueous phase increases and as the volume of the polymer-depleted region increases (Donath et al., 1996; Jenkins and Snowden, 1996). When the surface-to-surface separation between two droplets is small compared to their size ($h \ll r_D$), the depletion attraction is given by the following expressions (Sperry, 1982):

$$V_{dep}(h) = -\frac{2}{3}\pi(r_D + L)^3 P_{OSM}\left[2\left(1 + \frac{r_{eff}}{(r_D + L)}\right)^3 + \left(1 + \frac{h - 2L}{2(r_D + L)}\right)^3 - 3\left(1 + \frac{r_{eff}}{(r_D + L)}\right)^2\left(1 + \frac{h - 2L}{2(r_D + L)}\right)\right]$$
$$\text{for } h < 2r_{eff} \quad (6)$$

$$V_{dep}(h) = 0 \qquad \text{for } h \geq 2r_{eff} \qquad (7)$$

r_{eff} is the effective radius of the polymer, and P_{OSM} is the osmotic pressure due to the excluded polymers. The osmotic pressure difference is given by the equation

$$P_{OSM} = \frac{CRT}{M}\left(1 + \frac{2N_A Cv}{M}\right) \qquad (8)$$

where M is the molecular weight of the polymer, N_A is Avogadro's number, C is the polymer concentration, and v is the excluded volume of the polymer.

Addition of electrolyte to an emulsion containing a charged polymer reduces its effective radius because of electrostatic screening effects (Russel, 1991). A charged polymer can be considered to behave like a "soft sphere" whose effective radius is approximately equal to the sum of the hydrodynamic radius of gyration (r_g) and the Debye screening length (κ^{-1}), that is, $r_{eff} = r_g + \kappa^{-1}$ (Tadros, 1996). There is an electrostatic repulsion between a charged particle and a noncharged interface when they approach each other because the volume available to the counterions is reduced, which is thermodynamically unfavorable (Evans and Wennerstrom, 1994). We therefore expect the Debye screening length to contribute to the thickness of the depletion zone from which the biopolymer is excluded. Addition of an electrolyte causes a decrease in the effective radius of the molecules for two reasons: (i) electrostatic screening reduces κ^{-1} and (ii) electrostatic screening reduces the repulsion between different segments within the molecules and therefore reduces r_g (Figure 1). As a consequence, the volume of the depleted region surrounding the droplets is decreased, which causes a reduction in the strength of the depletion attraction.
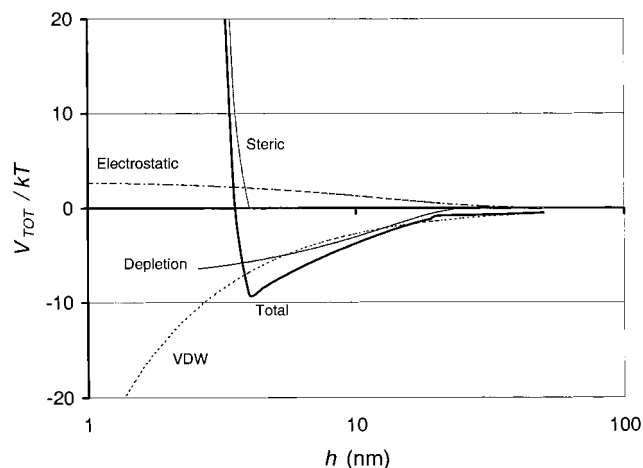
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Figure 2. Changes in total interaction potential ($V_{TOT} = V_{steric} + V_{dep} + V_{VDW} + V_{elec}$) as a function of surface-to-surface droplet separation (h). Calculations were made by assuming 2 wt % DS and an ionic strength of 0.001 mM (i.e., 0.00585 wt % NaCl).

Table 1. Physical Parameters Used To Calculate Droplet−Droplet Interaction Potentials for Oil-in-Water Emulsions Stabilized by Tween 20 at 25 °C[a]

emulsion droplet radius (r_c), μm	0.25
radius of gyration (r_g) of DS, nm	10
thickness of steric layer (L) due to surfactant headgroups, nm	2.1
distance between surfactant headgroups (s), nm	1.4
molecular weight of DS, Da	500000
Hamaker function (nonretarded and nonscreened), J	5.4×10^{-21}

$^a V_{TOT} = V_{steric} + V_{VDW} + V_{dep} + V_{e/s}$.

Numerical Calculation of Overall Interaction Potential. The relative contribution of the various colloidal interactions to the overall interaction potential was calculated using eq 1 (Figure 2). The parameters used in the calculations were chosen to represent the properties of the emulsions used in our experiments in the absence of added electrolyte (Table 1). At low surface-to-surface separations, the repulsive steric and electrostatic forces dominate, whereas at larger separations, the attractive VDW and depletion forces dominate. Overall, there is a minimum in the interaction potential at $h \sim 4$ nm, which is quite deep (~ -9 kT). This attraction should be large enough to cause the droplets to flocculate, which was observed in practice (see later).

We must stress that it is extremely difficult to accurately calculate the magnitude of each of the different contributions to the overall interaction potential because of limitations in the applicability of the mathematical theories developed to describe them and because of a lack of detailed information about the colloidal, interfacial, and physical properties of food emulsions needed to put in the theories (McClements, 1998). Nevertheless, it is still possible to obtain valuable insights into the factors that influence the bulk physicochemical properties of emulsions by examining their influence on the major types of colloidal interaction (see later).

MATERIALS AND METHODS

Materials. Soybean oil (Mazola vegetable oil) was purchased from a local supermarket and used without further treatment. DS (MW = 500 kDa), sodium chloride, sodium

azide, and polyoxyethylene sorbitan monolaurate (Tween 20) were purchased from Sigma Chemical Co. (St. Louis, MO). The supplier reported that the DS powder contained between 0.5 and 2.0% phosphate buffer salts and gave a pH of 6−8 when dissolved in aqueous solution. DS is a highly hydrophilic molecule that does not adsorb to the surface of emulsion droplets (Gekko, 1981). Distilled and deionized water was used for the preparation of all solutions and emulsions.

Emulsion Preparation. A 30 wt % soybean oil-in-water emulsion was prepared by homogenizing oil and a surfactant solution. The surfactant solution consisted of 1.5 wt % Tween 20 (a nonionic surfactant) and 0.02 wt % sodium azide (an antimicrobial agent) dissolved in water. A coarse emulsion was prepared using a high-speed blender (Waring, model 33BL79, New Hartford, CT). A finer emulsion was prepared by passing the coarse emulsion three times through a high-pressure valve homogenizer at a pressure of 8000 psi (APV-Gaulin, model 8.30H Mini-Lab, Wilmington, MA). The emulsion was passed through the homogenizer three times to reduce the particle size and degree of polydispersity. A series of emulsions with a constant final concentration of 10 wt % oil and 0.5 wt % Tween 20, but with various concentrations of DS (0−5 wt %) and NaCl (0−1 wt %), were prepared by diluting the original 30 wt % emulsion with DS and NaCl solutions.

Particle Size and Flocculation. The particle size of the emulsions was determined using a laser light scattering instrument (Horiba LA900, Irvine, CA). This instrument measures the angular dependence of the intensity of the light scattered from the droplets, and then finds the particle size distribution that gives the best fit between the experimental measurements and Mie theory. A relative refractive index of 1.08 was used in the calculations. Before the measurements were carried out, the emulsions were diluted to <0.01 wt % oil using distilled water to eliminate multiple scattering effects. Measurements are expressed as the volume-to-surface area mean diameter: $d_{32} = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$, where n_i is the number of droplets with diameter d_i. The mean diameter of the emulsion droplets used in this study was measured as 0.5 μm.

Shear Rheology. The rheological properties of biopolymer solutions and emulsions were measured at 30.0 °C using a shear rheometer with a concentric cylinder measurement cell (Constant Stress rheometer, CS-10, Bohlin Instruments, Cranbury, NJ). The diameter of the inner cylinder was 25 mm, and the diameter of the outer cylinder was 27.5 mm. Samples were placed in the temperature-controlled measurement vessel and allowed to equilibrate to the required temperature for 5 min before the measurements were made. The shear-dependent rheological properties of the samples were determined by preshearing them at a constant shear rate of 30 s^{-1} for 5 min, allowing a recovery period of 10 min, and then acquiring the apparent viscosity as a function of shear rate (0.065−518.5 s^{-1}). For many of the samples, the apparent viscosity was measured at a constant shear rate of 30 s^{-1} by taking the average of measurements acquired at this shear rate over a 5 min period. To avoid complications due to phase separation of the emulsions, the rheology of the emulsions was measured using well-stirred samples before any creaming had occurred.

Creaming Experiments. The creaming stability of a series of emulsions containing different concentrations of DS and salt was determined. A total of 12 g of sample (4 g of emulsion + 4 g of DS solution + 4 g of NaCl solution) was poured into a glass test tube (100 mm height, 16 mm i.d.), mixed thoroughly, and then allowed to stand for 168 h. The oil droplets have a lower density than the surrounding aqueous phase and therefore move upward due to gravity. The extent of creaming was assessed by measuring the height of the interface between the opaque, droplet-rich layer at the top of the emulsion and the less opaque, droplet-depleted layer at the bottom, after the samples had been stored at 30 °C. Creaming results are reported as a "creaming index" = 100-(H_D/H_E), where H_D is the height of the droplet-depleted (lower) layer and H_E is the height of the total emulsion. Creaming measurements were made periodically over the 168 h.
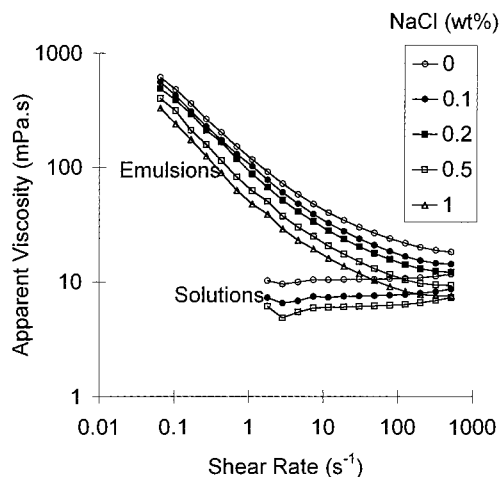
Figure 3. Dependence of apparent viscosity on shear rate and NaCl concentration for 2 wt % DS solutions and for 10 wt % oil-in-water emulsions containing 2 wt % DS.
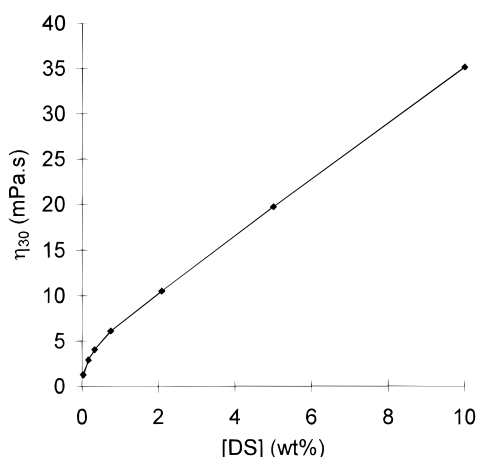

Figure 4. Dependence of apparent viscosity (at a shear rate of 30 s^{-1}) on the DS concentration of aqueous solutions.
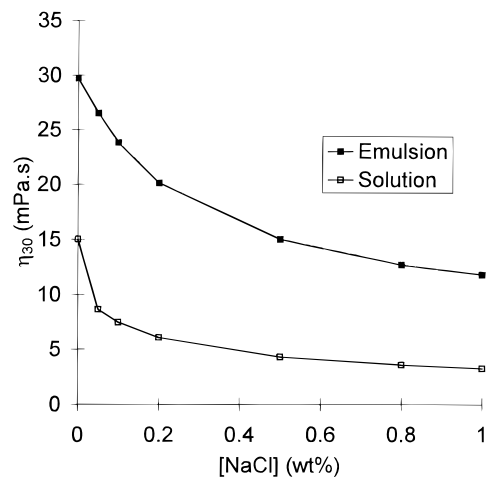

Figure 5. Dependence of apparent viscosity (at a shear rate of 30 s^{-1}) on NaCl concentration for 2 wt % DS solutions and for 10 wt % oil-in-water emulsions containing 2 wt % DS.

RESULTS AND DISCUSSION

Rheology of DS Solutions. Both the creaming stability and the rheology of emulsions are strongly influenced by the viscosity of the continuous phase, and so it was important to characterize the rheological characteristics of DS solutions. The viscosity of a series of solutions containing different concentrations of DS and NaCl was measured (Figures 3–5). The viscosity of the DS solutions was relatively insensitive to shear rate over the range 1–300 s^{-1} (Figure 3). In the absence of electrolyte, the apparent viscosity (η_{30}) of the solutions increased with increasing DS concentration (Figure 4). The dependence of solution viscosity on DS concentration could be divided into two regions: (i) between 0 and 0.75 wt % DS, where there was a steep increase in viscosity with biopolymer concentration, and (ii) above 0.75 wt % DS, where there was an approximately linear increase in viscosity with biopolymer concentration. The most likely reason for the change in the slope of η with DS is an alteration in the degree of biopolymer–biopolymer interactions due to coil overlapping (Morris, 1995).

The influence of electrolyte on the viscosity of 2 wt % DS solutions was measured (Figure 5). There was a pronounced decrease in apparent viscosity (η_{30}) with an increase in NaCl concentration, which can be explained

in terms of the reduction in the effective radius of the DS molecules in solution caused by electrostatic screening. A decrease in the effective radius of the biopolymer molecules leads to a decrease in solution viscosity because the degree of biopolymer–biopolymer interactions is reduced (Morris, 1995). As mentioned earlier, the overall reduction in r_{eff} when salt is added is due to a decrease in the hydrodynamic radius of gyration (r_g), as well as to a decrease in the Debye screening length (κ^{-1}). We expect the majority of the reduction in the effective radius to be caused by the decrease in κ^{-1}, because DS is a highly branched molecule and therefore steric hindrance effects are likely to prevent extensive shrinkage in r_g.

Rheology of Emulsions. The rheological behaviors of a series of 10 wt % soybean oil-in-water emulsions containing different concentrations of dextran sulfate and electrolyte were measured (Figures 3 and 5). In the absence of DS and NaCl, the emulsions had relatively low viscosities and exhibited Newtonian behavior ($\eta = \sim1.5$ mPa s). In the presence of 2 wt % DS, the emulsions had relatively high viscosities and exhibited pronounced shear thinning behavior (Figure 3). This behavior is in contrast to DS solutions, which have the same DS concentration but which exhibit Newtonian behavior (Figure 3). This suggests that the shear-thinning behavior observed in the emulsions is due to the disruption of flocculated droplets. In addition, the apparent viscosity of emulsions decreased with increasing NaCl concentration.

To a first approximation the viscosity of a suspension containing spherical particles is given by the expression (Hunter, 1986)

$$\eta = \eta_0(1 + 2.5\phi + 6.2\phi^2 + \ldots) \qquad (9)$$

where η is the suspension viscosity, η_0 is the viscosity of the continuous phase, and ϕ is the disperse phase volume fraction. This equation indicates that the viscosity of an emulsion should be proportional to the viscosity of the continuous phase and should increase as the droplet concentration is increased. The observed decrease in emulsion viscosity with salt concentration can therefore be attributed to the decrease in the viscosity of the DS solutions (η_0) caused by electrostatic screening effects (Figure 3).
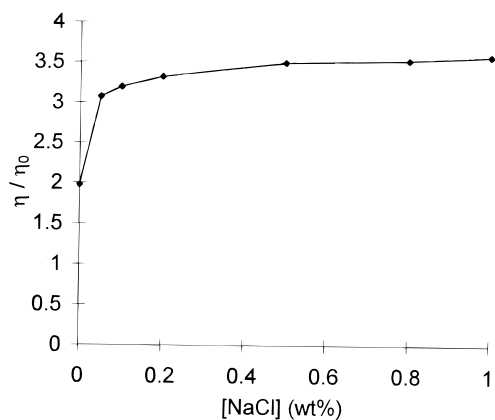
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Figure 6. Dependence of the ratio of the emulsion viscosity (η) to the biopolymer solution viscosity (η_0) on NaCl for a concentration of 2 wt % DS.
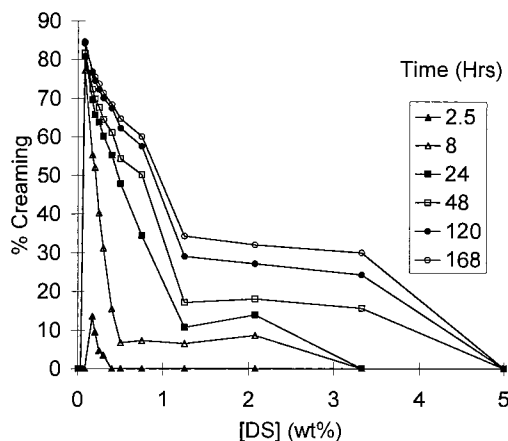

Figure 7. Time dependence of the creaming index of emulsions in the absence of electrolyte. Rapid creaming is observed at ~0.083 wt % DS.

Figure 8. Theoretical calculations of the effect of DS concentration on the total interaction potential in the absence of added salt. Increasing DS leads to a deeper energy minimum. Calculations were made using eq 1 and the physical parameters listed in Table 1.

For a 10 wt % oil-in-water emulsion, the above equation predicts that the viscosity of an emulsion should be ~1.3 times greater than that of a solution with the same biopolymer concentration (i.e., $\eta/\eta_0 \approx 1.3$). In practice, we found that η/η_0 was ~1.9 in the absence of salt and that it increased to a constant value of ~3.2 for NaCl > 0.05 wt % (Figure 6). The most likely reason for the fact that the normalized emulsion viscosity (η/η_0) is greater than that predicted by eq 9 is that the droplets are flocculated, which leads to an increase in their effective volume fraction (Hunter, 1986). Optical microscopy studies on a similar system have shown that extensive droplet flocculation does indeed occur above a critical biopolymer concentration (Chanamai et al., 1998). At 2 wt % DS all of the emulsions contained flocculated droplets; however, the increase in normalized viscosity that occurred when the NaCl concentration was increased from 0 to 0.05 wt % was probably caused by a change in the nature of the flocs in the emulsion, due to an alteration in the strength of the attractive forces and/or the spatial organization of the droplets within the flocs.

Creaming Stability of Emulsions Containing DS. The time dependence of the creaming index of emulsions depended strongly on the concentration of DS in the continuous phase (Figure 7). In the absence of DS, the creaming rate was so slow that no phase separation was observed over the course of the experiment (168 h). When DS was added to the emulsions, rapid creaming
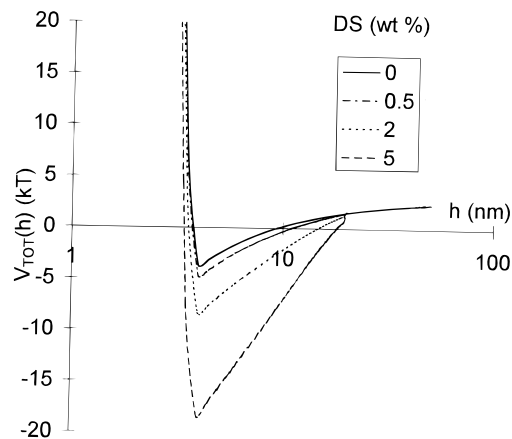
was observed above a certain concentration (DS > 0.08 wt %), which was followed by a decrease in creaming rate on a further increase of the biopolymer concentration (Figure 7). These results can be explained in terms of the influence of DS on the nature of the droplet–droplet interactions and on the rheology of the continuous phase.

In the absence of DS, the repulsive forces between the droplets (principally steric and electrostatic) are strong enough to prevent them from flocculating. As the DS concentration is increased, the depletion attraction between the droplets becomes stronger because of an increase in the concentration difference between the bulk aqueous phase and the depletion zone surrounding the droplets (Jenkins and Snowdon, 1996). Eventually, the attractive forces become stronger than the repulsive forces and so the droplets flocculate, which leads to an enhanced creaming rate because of the increase in the effective size of the particles. A further increase in DS concentration causes a decrease in creaming rate because of the enhancement of the viscosity of the continuous phase or because of the formation of a three-dimensional network of aggregated droplets (Parker et al., 1995). Similar results have been observed for other types of biopolymer (Dickinson et al., 1994; Parker et al., 1995).

A numerical calculation of the overall interaction potential (calculated using eq 1) clearly shows the increase in attraction between the droplets as the DS concentration increases (Figure 8). Nevertheless, it also suggests that there is a relatively weak attraction (~ −4 kT) between the droplets in the absence of DS, which would be expected to cause the droplets to flocculate. In practice, flocculation was not observed in the emulsions in the absence of DS. The discrepancy between the theoretical predictions and the experimental observations is probably because a number of factors that are expected to reduce the attraction between the droplets have been ignored, for example, hydration forces, thermal energy fluctuation forces, and the influence of the interfacial layer on the VDW forces (Israelachvili, 1992).

The creaming behavior of an emulsion containing DS can be characterized by two parameters: (a) the *critical flocculation concentration* (CFC), which is the minimum amount of polymer that must be added to the aqueous
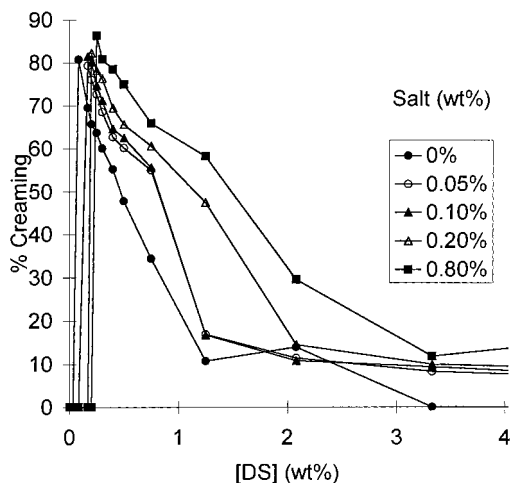
Figure 9. Influence of DS and NaCl on the creaming index of emulsions stored at room temperature for 24 h.
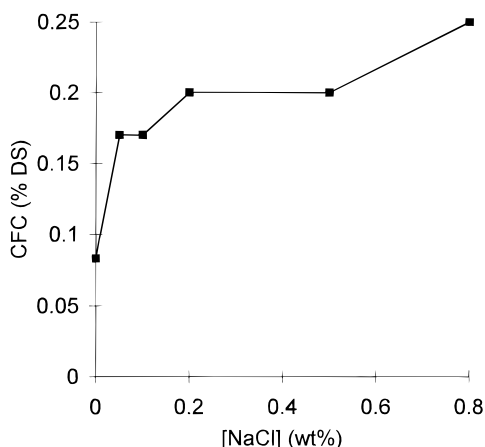

Figure 10. Dependence of CFC on NaCl concentration for 10 wt % oil-in-water emulsions.

phase to cause rapid creaming, and (b) the creaming rate above the CFC. The CFC gives an indication of the influence of DS on the colloidal interactions between the droplets, whereas the creaming rate above the CFC gives an indication of the influence of DS on the rheology of the aqueous phase. Previous work has shown that it takes ~8−10 h for an emulsion containing biopolymer to reach osmotic pressure equilibrium (Dickinson et al., 1994). For this reason, the CFC is reported after 24 h in the following studies to ensure that equilibrium conditions have been established.

Creaming Stability of Emulsions Containing DS and Electrolyte. The creaming index of a series of emulsions containing different DS and NaCl concentrations was measured after 24 h (Figures 9 and 10). Increasing the salt concentration in the emulsions caused an increase in the CFC, which meant that more DS had to be added before rapid creaming was observed (Figures 9 and 10). The addition of salt to an emulsion alters the colloidal interactions in a number of ways: (i) it reduces the electrostatic repulsion (which promotes flocculation), (ii) it reduces the VDW attraction (which opposes flocculation), and (iii) it reduces depletion attraction (which opposes flocculation). Our experimental data suggest that the overall effect of adding salt is to reduce the strength of the attractive forces between the droplets because a greater amount of DS had to be added to promote droplet flocculation when the salt
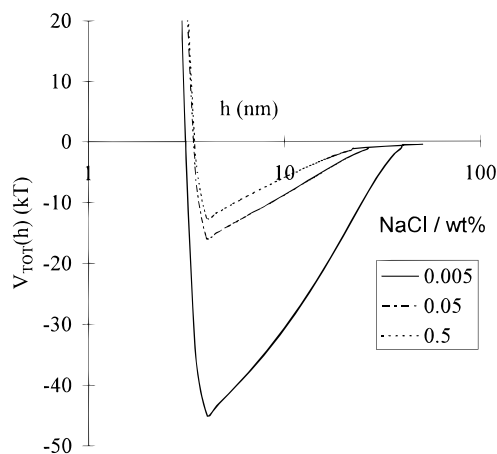

Figure 11. Numerical calculations of the effect of NaCl concentration on the total interaction potential of an emulsion containing 2 wt % DS. Calculations were made using eq 1 and the physical parameters listed in Table 1.

concentration was increased. A numerical calculation of the influence of salt on the interaction potential between droplets supports this observation (Figure 11). We assumed that the effective radius of the biopolymer molecules was given by $r_{eff} = r_g + \kappa^{-1}$, with $r_g = 10$ nm and κ^{-1} given by eq 4. These predictions clearly show that the strength of the attraction between the droplets is reduced with increasing salt concentration, and therefore a greater amount of biopolymer would be needed to cause flocculation at higher salt concentrations.

In those emulsions that exhibited significant creaming, increasing the salt concentration in the emulsions caused an increase in the creaming index above the CFC after 24 h (Figure 9), which could be attributed to the reduction in the aqueous phase viscosity that occurs when salt is present (Figure 5). The largest change in the emulsion viscosity (Figure 5), CFC (Figure 10), and creaming index above the CFC (Figure 9) occurred between 0 and 0.05 wt % NaCl, which suggests that most of the electrostatic screening effects occur over this concentration range. At higher salt concentrations there is little further change in the rheology and stability of the emulsions.

Emulsions that cream extensively within 24 h would be unsuitable for commercial application because they would have very short shelf lives. This study clearly shows that certain combinations of DS and salt lead to rapid creaming and should therefore be avoided in the formulation of shelf-stable products.

Conclusion. Varying the concentration of DS and salt in the aqueous phase can control the rheology and creaming stability of oil-in-water emulsions. Dextran sulfate is normally added to emulsions to enhance the viscosity of the continuous phase and thereby retard creaming. However, it can actually accelerate creaming at certain concentrations because it increases the attraction between droplets through a depletion mechanism, which leads to flocculation. Salt screens the electrostatic interactions within and between electrically charged biopolymer molecules, which reduces their effective radius, thereby reducing the viscosity of the aqueous phase and the strength of the depletion attraction. As a result, salt influences both the rheology and the creaming stability of emulsions containing DS. Salt can also screen VDW and electrostatic interactions

between droplets, and therefore its effects may be quite complex in some systems. In summary, salt and polysaccharides play a complex role in determining the texture and stability of emulsions, which can only be understood by considering the nature of the interactions between the molecules and colloidal particles.

In this study, DS and salt were added to the emulsions after homogenization. During the commercial production of food emulsions, it is more likely that these components would be added prior to homogenization. In this case the DS and salt may influence the efficiency of the homogenization process as well as the long-term stability. For this reason, the influence of these components on the physicochemical characteristics of commercial emulsions may be more complex than that on the model emulsions used in this study. Nevertheless, this study has provided some valuable insights into the role of ingredient interactions on the bulk physicochemical properties of food emulsions.

LITERATURE CITED

Asakura, S.; Oosawa, F. On Interaction Between Two Bodies Immersed in a Solution of Macromolecules. *J. Chem. Phys.* **1954**, *22*, 1255–1256.

Asakura, S.; Oosawa, F. Interaction Between Particles Suspended in Solutions of Macromolecules. *J. Polym. Sci.* **1958**, *33*, 183–192.

Chanamai, R.; Herrmann, N.; McClements, D. J. Ultrasonic Spectroscopy Study of Flocculation and Shear-Induced Floc Disruption in Oil-in-Water Emulsions. *J. Colloid Interface Sci.* **1998**, *203*, in press.

de Belder, A. N. Dextran. In *Industrial Gums Polysaccharides and Their Derivatives*, 3rd ed.; Whistler, R. L., BeMiller, J. N., Eds.; Academic Press: San Diego, CA, 1993; Chapter 14.

Dickinson, E. *Introduction to Food Colloids*; Oxford University Press: Oxford, U.K., 1992.

Dickinson, E.; Pawlowsky, K. Effect of *i*-Carrageenan on Flocculation, Creaming, and Rheology of a Protein-Stabilized Emulsion. *J. Agric. Food Chem.* **1997**, *45*, 3799–3806.

Dickinson, E.; Ma, J.; Povey, M. J. W. Creaming of Concentrated Oil-in-Water Emulsions Containing Xanthan. *Food Hydrocolloids.* **1994**, *8*, 481–497.

Dickinson, E.; Goller, M. I.; Wedlock, D. J. Osmotic Pressure, Creaming, and Rheology of Emulsions Containing Nonionic Polysaccharide. *J. Colloid Interface Sci.* **1995**, *172*, 192–202.

Donath, E.; Krabi, A.; Allan, G.; Vincent, B. A Study of Polymer Depletion Layers by Electrophoresis: The Influence of Viscosity Profiles and the Nonlinearity of the Poisson–Boltzmann Equation. *Langmuir* **1996**, *12*, 3425–3430.

Gekko, K. Solution Properties of Dextran and its Ionic Derivatives. In *Solution Properties of Polysaccharides*; Brant, D. A., Ed.; American Chemical Society: Washington, DC, 1981.

Hibberd, D. J.; Howe, A. M.; Mackie, A. R.; Purdy, P. W.; Robins, M. M. Measurement of Creaming Profiles in Oil-in-Water Emulsions. In *Food Emulsions and Foams*; Dickinson, E., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1986.

Hunter, R. J. *Foundations of Colloid Science*; Oxford University Press: Oxford, U.K., 1986; Vol. I.

Israelachvilli, J. N. *Intermolecular and Surface Forces*, 2nd ed; Academic Press: San Diego, CA, 1992.

Ivanov, I. B.; Marinova, K. G.; Alargova, R. G.; Denkov, N. D.; Borwankar, R. P. Charge of Emulsion Droplets Covered with Nonionic Surfactant. *Proceedings of the Second World Congress on Emulsions*, Bordaeux, France, 1997.

Jenkins, P.; Snowden, M. Depletion Flocculation in Colloidal Dispersions. *Adv. Colloid Interface Sci.* **1996**, *68*, 57–96.

Jones, A.; Vincent, B. Depletion Flocculation in Dispersions of Sterically-Stabilized Particles: 2. Modifications to Theory and Further Studies. *Colloids Surf.* **1989**, *42*, 113–138.

Mahanty, J.; Ninham, B. W. *Dispersion Forces*; Academic Press: London, 1976.

McClements, D. J. *Food Emulsions: Principles, Practice and Techniques*; CRC Press: Boca Raton, FL, 1998.

McClements, D. J.; Dungan, S. R. Effect of Interactions on the Rate of Interdroplet Heterogeneous Nucleation in Oil-in-Water Emulsions. *J. Colloid Interface Sci.* **1997**, *186*, 17–28.

Morris, R. E. Polysaccharide Rheology and In–Mouth Perception. In *Food Polysaccharides and Their Applications*; Stephen, M. A., Ed.; Dekker: New York, 1995.

Ogden, A. L.; Lewis, J. A. Effect of Nonadsorbed Polymer on the Stability of Weakly Flocculated Suspensions. *Langmuir* **1996**, *12*, 3413–3424.

Parker, A.; Gunning, P. A.; Ng, K.; Robins, M. M. How Does Xanthan Stabilize Salad Dressings? *Food Hydrocolloids* **1995**, *9*, 333–342.

Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley: New York, 1978.

Russel, W. B. *Concentrated Colloidal Dispersions*; MRS Bulletin 27-31; Materials Research Society: Pittsburgh, PA, 1991.

Seeberg, J. E.; Berg, J. C. Depletion Flocculation of Aqueous, Electrosterically-Stabilized Latex Dispersions. *Langmuir* **1994**, *10*, 454–463.

Smith, N. J.; Williams, P. A. Depletion Flocculation of Polystyrene Lattices by Water-Soluble Polymers. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1483–1489.

Sperry, P. R. A Simple Quantitative Model for the Volume Restriction Flocculation of Latex by Water-Soluble Polymers. *J. Colloid Interface Sci.* **1982**, *87*, 375–385.

Sperry, P. R.; Hopfenberg, H. B.; Thomas, N. L. Flocculation of Latex by Water-Soluble Polymers: Experimental Confirmation of a Nonbridging, Nonadsorptive, Volume-Restriction Mechanism. *J. Colloid Interface Sci.* **1981**, *82*, 62–76.

Tadros, Th. F. Correlation of Viscoelastic Properties of Stable and Flocculated Suspensions with their Interparticle Interactions. *Adv. Colloid Interface Sci.* **1996**, *68*, 97–200.

Vincent, B.; Edwards, J.; Emmett, S.; Jones, A. Depletion Flocculation in Dispersions of Sterically-Stabilized Particles ("Soft Spheres"). *Colloids Surf.* **1986**, *18*, 261–281.

Walstra, P. Introduction to Aggregation Phenomena in Food Colloids. In *Food Colloids and Polymers: Stability and Mechanical Properties*; Dickinson, E., Walstra, P., Eds.; The Royal Society of Chemistry: Cambridge, U.K., 1993.

Walstra, P. Dispersed Systems: Basic Considerations. In *Food Chemistry*, 3rd ed.; Fennema, O. N., Ed.; Dekker: New York, 1996.