Role of Hydrocolloids in the Creaming of Oil in Water Emulsions

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The influence of guar gum and xanthan gum on the creaming of 10% oil in water emulsions has been investigated. The presence of very low concentrations of the polysaccharides (typically $< \sim 0.075\%$) was found to induce depletion flocculation of the emulsion droplets and increased the rate of creaming. However, at higher polysaccharide concentrations (typically $> \sim 0.1\%$) the creaming rate was reduced due to the increased viscosity of the aqueous phase. For most systems a delay period was noted before creaming started, which was found to be dependent on the zero shear viscosity of the continuous phase and independent of polysaccharide type. The delay period increased significantly at zero shear viscosities approaching 1 Pa s. A mathematical model has been used to fit the creaming rate profiles and a simple exponential relationship obtained between delay time and polysaccharide concentration.

INTRODUCTION

Polysaccharides are widely used in the food industry to stabilize oil in water emulsions and to control their rheological properties (*1*). Stability against flocculation and coalescence can be achieved by using amphiphilic polysaccharides such as gum arabic (*2*), which adsorb onto the surface of the droplets and prevent aggregation by steric and/or electrosteric forces. In the main most polysaccharides show little surface activity, and their incorporation into oil in water emulsions is to inhibit droplet creaming by increasing the viscosity of the continuous phase. The main thickeners used are xanthan gum, galactomannans (guar gum and locust bean gum), and carboxymethyl cellulose. In recent years, however, it has been noted that the presence of such polymers can in fact lead to flocculation and, hence, enhance creaming. This has been attributed to a "depletion flocculation" mechanism (*3–6*), which arises when polymer molecules are excluded from the space between droplets at close separation. The difference in the osmotic pressure between the pure solvent in the gap and the bulk polymer solution tends to push the droplets together and results in a net attractive force. This phenomenon had been also reported for emulsions stabilized by surfactants, due to micelle depletion, when the surfactant concentration exceeds a critical limit (*7*). The depletion force between two droplets increases with increasing molecular mass of the polymer and is very much greater for polyelectrolytes than for nonionic polymers because of the contribution of their counterions to the osmotic pressure (*8, 9*). Luyten et al. (*4*) studied the creaming of 4–5% *n*-hexadecane emulsions in the presence of low concentrations of xanthan gum. For emulsions with droplet sizes (d_{32}) of 0.22 and 0.83 μm they found that the creaming rate increased at xanthan concentrations of 0.014 and 0.006%, respectively. They calculated the depth of the secondary minimum in the potential energy curves and concluded that for the 0.22 μm droplet emulsion the minimum was not deep enough for flocculation to occur. However, for larger droplets (0.83 μm) the minimum had values of 5–10 kT at xanthan concentrations of 0.015%, supporting the concept that depletion flocculation was occurring. Further evidence was provided by the fact that the concentration of xanthan gum in the bulk phase of the emulsions increased, confirming that negative adsorption had occurred.

A number of workers have reported the occurrence of a delay period before the onset of creaming (*6, 10–16*). This was first discussed by Parker et al. (*6*), who investigated the creaming behavior of model pourable salad dressings at various oil volume fractions and in the presence of various concentrations of xanthan gum. They concluded that the xanthan gum induced the droplets to flocculate at concentrations $>0.01\%$. This resulted in the formation of a three-dimensional network and

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was the major factor responsible for the delay period and the inhibition of creaming.

The purpose of this paper is to investigate further the role of polysaccharides in the stabilization of oil in water emulsions and to compare the influence of xanthan gum and guar gum on the creaming behavior. The concentrations of polysaccharide used are much higher than those by other workers in model studies (*4*) and are more typical of those employed in commercial dressing formulations (*6*).

EXPERIMENTAL PROCEDURES

Materials. Guar gum is obtained from the seed endosperm of the leguminous plant *Cyamopsis tetragonoloba* and consists of linear chains of β1,4-linked mannose residues with 1,6-linked galactose units present on average on every other mannose. Samples (referred to as GG1−3) were obtained from Meyhall Chemical AG, and their molecular masses were determined by capillary viscometry. Measurements were made on aqueous solutions using a Cannon Ubbelohde viscometer immersed in a water bath at 25 °C. The viscosity average molecular masses were calculated from the intrinsic viscosities taking K and a values of 3.8×10^{-4} and 0.723, respectively (*17*). The values obtained for the three samples were GG1= 790000, GG2 = 1500000, and GG3 = 2700000.

Xanthan gum is a bacterial polysaccharide produced by aerobic fermentation of *Xanthamonas campestris*. It has a cellulosic backbone consisting of β1,4-linked glucose residues with a trisaccharide side chain on every other glucose. The side chain consists of two mannose residues on either side of a glucuronic acid residue. The internal mannose may be acetylated, and the external mannose may be pyruvated. It is well-known that xanthan gum undergoes a thermoreversible coil−helix transition in aqueous solution, which is highly dependent on electrolyte concentration. In the ordered form the side chains fold in and stabilize the helices, which are believed to consist of two strands. A sample of xanthan gum (Keltrol) was obtained from Monsanto. Its molecular mass was determined by flow field flow fractionation coupled with refractive index and multiangle light scattering detection and found to be 3200000.

The emulsifiers used were spray-dried egg yolk (SDEY), obtained from Ovosec, and Tween 20 [polyoxyethylene (20) sorbitan mono-laurate], obtained from Aldrich. Sunflower oil was a commercial sample purchased in a local supermarket.

Methods. *Shear Viscosity of Polysaccharide Gum Solutions.* The viscosity of the guar gum and xanthan gum solutions at various concentrations was measured under steady shear at 25 °C as a function of shear rate using the TA Instruments controlled stress rheometer. The zero-shear viscosity was determined by extrapolation of the low-shear Newtonian plateau. The critical shear stress for the onset of shear thinning behavior, σ_{crit}, was estimated from a plot of viscosity against shear stress. In addition, this value was checked from the product of the critical strain rate (obtained from the intercept of the Newtonian plateau and shear thinning region) and the viscosity at the critical strain rate.

Preparation of Emulsions. Twenty percent v/v oil in water emulsions were prepared with 0.50% (w/w) Tween 20 or 0.76% (w/w) SDEY; 18.18 g of oil, together with the emulsifier, was added to water (total volume = 100 mL) contained in a beaker, and emulsification was achieved by shearing for 2 min using an Ultraturrax T-25 mixer. To this 20% v/v emulsion was then added an equal volume of polymer solution at various concentrations ranging from 0 to 1.0% (w/w), thus giving an emulsion with 10% oil and 0−0.5% (w/w) polymer solution.

Determination of Droplet Size Distribution. The emulsions prepared were polydisperse. The droplet size distribution of the emulsions was determined using the Malvern Mastersizer 2000, and the average droplet size was found to be

Sauter's diameter		
d[3,2] (μm)	d[4,3] (μm)	d[v,0.5] (μm)
13.97	32.56	31.23

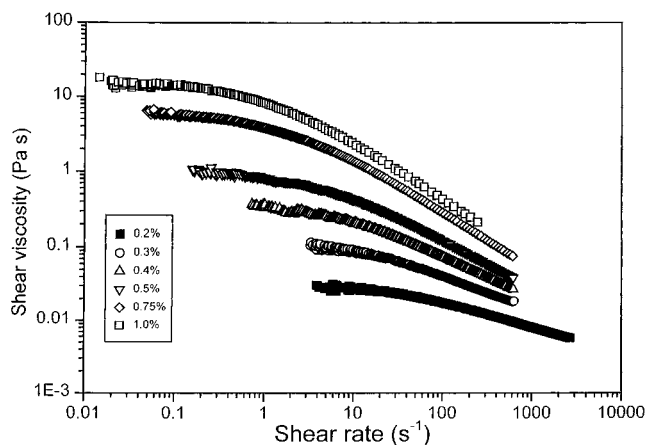*Creaming Experiments.* The emulsions were immediately transferred

Figure 1. Shear viscosity of guar gum solutions (GG3) at various concentration as a function of shear rate.
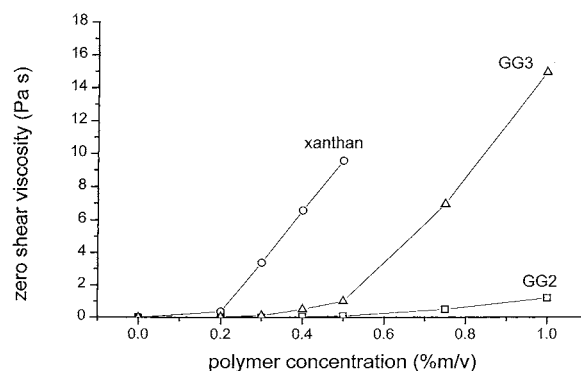

Figure 2. Zero-shear viscosity of xanthan gum and guar gum solutions as a function of polymer concentration.
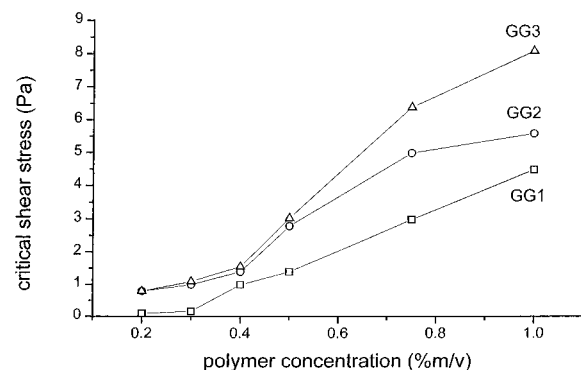

Figure 3. Critical shear stress of guar gum solutions as a function of polymer concentration.

to a 10 mL graduated test tube, and the evolution of the creamed volume was monitored visually over a period of time.

RESULTS

The viscosity−shear rate profiles obtained for all samples were similar; that is, each had a characteristic Newtonian plateau at low shear rate followed by a shear thinning region. This is illustrated in **Figure 1** for GG3. The zero-shear viscosities of GG2, GG3, and xanthan are plotted as a function of concentration in **Figure 2** and the values for σ_{crit} for the guar gum samples in **Figure 3**. Both parameters increase markedly with increasing concentration and molecular mass.

The volume of the creamed layer as a function of time for 10% emulsions stabilized by Tween 20 in the presence of GG2,
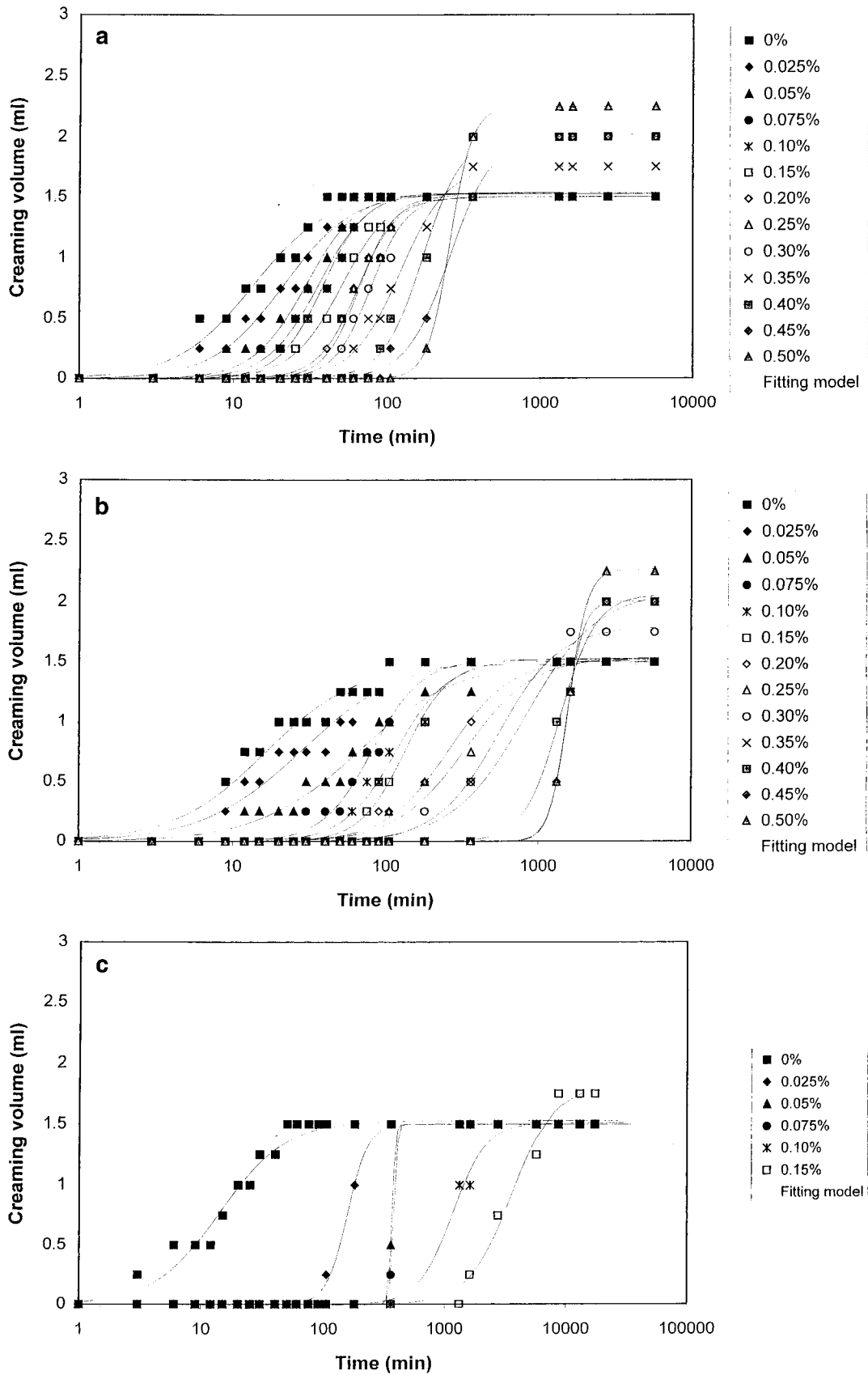
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Figure 4. Volume of the creamed layer for 10% emulsions stabilized by Tween 20 in the presence of various concentrations of (a) GG2, (b) GG3, and (c) xanthan gum. Symbols represent experimental data points; lines have been drawn using eq 1.

GG3, and xanthan gum is given in **Figure 4**. Similar profiles were obtained for emulsions prepared using SDEY (data not shown). For emulsions containing GG1 and GG2 the rate of formation of the creamed layer increased up to concentrations of 0.075 and 0.025%, respectively, and then decreased. For all other emulsions the rate of creaming decreased. The continuous
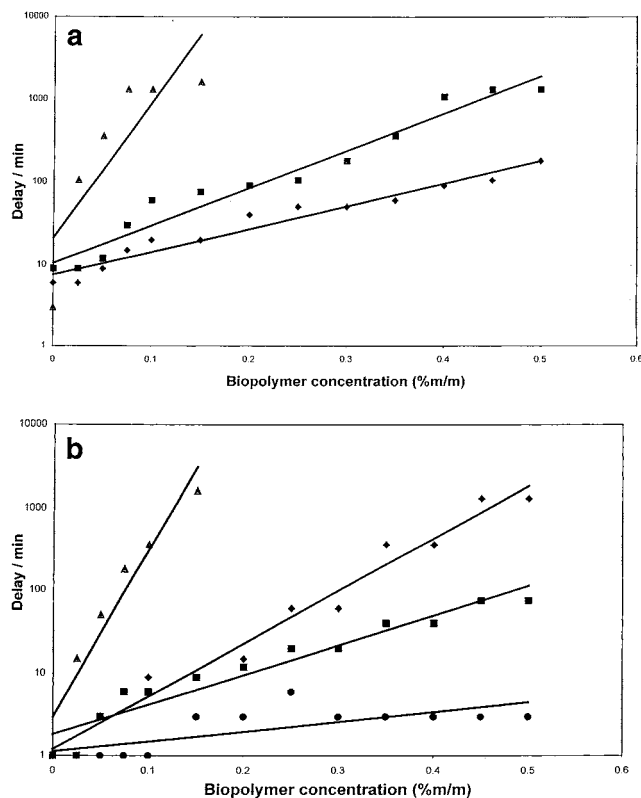
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Figure 5. Delay time as a function of polymer concentration: (a) 10% emulsions stabilized by Tween 20 in the presence of xanthan (triangles), GG3 (squares), and GG2 (diamonds); (b) 10% emulsions stabilized by SDEY in the presence of xanthan (triangles), GG3 (diamonds) GG2 (squares), and GG1 (circles).

lines also plotted in **Figure 4** correspond to the mathematical model

$$V_t = V_{\text{final}}/[1 + (t_0/t)^p] \qquad (1)$$

where V_t is the creaming volume at certain time, t, V_{final} is the final creaming volume, t_0 is the time at which $0.5 V_{\text{final}}$ is attained, and p is a parameter proportional to the slope of the steepest part of the sigmoidal curve. An experimental delay time was defined as the time at which 0.25 mL of oil had creamed. This parameter can also be successfully estimated from the mathematical model. The semilogarithmic plots of delay time against polysaccharide concentration are given in parts a and b of **Figure 5** for emulsions stabilized by Tween 20 and SDEY, respectively, and for all of the polymers a reasonably linear relationship was observed. When the delay time was plotted as a function of the log zero-shear viscosity of the continuous phase, the data for the systems containing the different polysaccharides superimposed reasonably well onto a single curve as shown in **Figure 6**. The delay time was found to increase dramatically when the zero-shear viscosity approached ~1 Pa s.

It is interesting to note also in **Figure 4** that the final creamed volume increased at higher polysaccharide concentrations, which is consistent with enhanced droplet flocculation. Flocculation could be readily observed visually in some of the samples. The droplet size distribution for flocculated emulsions with GG3 present was determined using the Malvern Mastersizer. The GG3 concentration was kept constant when measurements were made because depletion flocculation is reversible to dilution (*9*). Interestingly, there did not appear to be any significant difference in the distribution profiles for the emulsions with and without
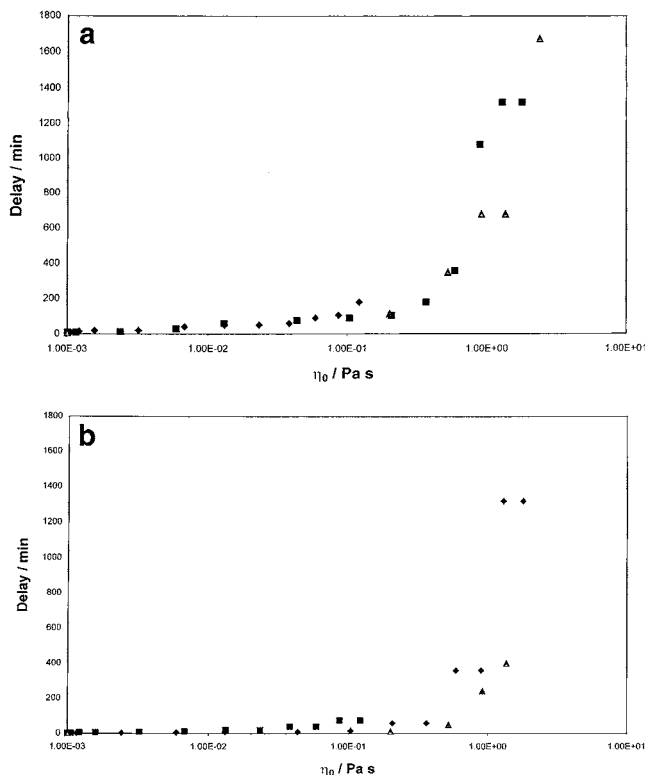

Figure 6. Delay time as a function of zero-shear viscosity for 10% emulsions stabilized by (a) Tween 20 in the presence of xanthan gum (triangles), GG3 (squares), and GG2 (diamonds) and (b) SDEY in the presence of xanthan gum (triangles), GG3 (diamonds), and GG2 (squares).

GG3. This was believed to be due to the fact that the flocs present were broken up by the shear forces generated while measurements were taken. This is consistent with the emulsion droplets having undergone weak flocculation by polymer depletion forces.

DISCUSSION

The presence of guar gum and xanthan gum was found to induce depletion flocculation of the emulsion droplets even at very low concentrations as has been observed by others (*3−6, 10−16*). In the majority of the emulsions prepared, the rate of creaming was reduced by the presence of polymer in the continuous phase. Parker et al. (*6*) reported that the delay phase for oil in water emulsions increased linearly in a log−log plot with xanthan concentration in the range 0.05−0.7%. Buscall et al. (*18*) had also observed a delay phase in the sedimentation of flocculated particles in the absence of polymer. Parker et al. (*6*) concluded that xanthan gum induced oil droplets to flocculate and form a three-dimensional gel network, which delayed droplet creaming. They acknowledged, however, that the aqueous phase rheology probably also had a contribution to play and cited the work of Buscall et al. (*19*), who noted that for nonflocculated emulsions, creaming depended on the zero-shear viscosity of the continuous phase. Because Parker et al. (*6*) showed that the delay time was not influenced by the oil content (9−36%), it is clear that the influence of the xanthan itself on the aqueous phase rheology must indeed be important at the concentrations used (0.05−1%). More recently, Moates et al. (*16*) reported that for hexadecane emulsions in the presence of hydroxyethyl cellulose (HEC) the delay time increased significantly with oil content. For a 10% emulsion there was no delay time, whereas for a 40% emulsion there was a delay time of

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~450 min. Robins et al. (*15*) and Moates et al. (*16*) showed that the delay was proportional to the product of the complex viscosity of the polymer-thickened emulsion and the strain at the end of linearity. Interestingly, this means that the delay time was proportional to the amplitude of the critical shear stress for the onset of nonlinear viscoelasticity.

In our work using 10% emulsions the contribution of the flocculated droplets to the delay time of the emulsions is expected to be small compared to that of the polymer-thickened continuous phase as indicated by the work of Moates et al. (*16*). This is confirmed by the fact that the plots of delay time against zero-shear viscosity for emulsions containing different molecular mass guar gum samples and xanthan gum superimpose (**Figure 6**). The delay time increases sharply at zero shear viscosities of ~1 Pa s. This presumably corresponds to the transition of the polymer solution from the semidilute to concentrated regime as indicated by the steep rise in the plot of zero-shear viscosity against polymer concentration (**Figure 2**). The delay time, therefore, is the time required for the polysaccharide structure to collapse under the gravitational stress induced by the presence of the droplets. The minimum stress, σ, necessary to overcome creaming is given by (*18*)

$$\sigma = h\phi(\Delta\rho)g \qquad (2)$$

where h is the height of the sample, ϕ is the volume fraction of the droplets, $\Delta\rho$ is the density difference between the oil and water, and g is the gravitational constant (9.81 m s^{-2}). For our system σ has a value of ~7 Pa, which is approximately 2–3 times the value of the σ_{crit} for 0.5% solutions of guar and xanthan gum (**Figure 3**), that is, the maximum value used in the creaming experiments.

CONCLUSIONS

The addition of polysaccharides to oil in water emulsions induces depletion flocculation. The concentration of polysaccharide required is dependent on the droplet size and the molecular mass and charge density of the polymer but is nevertheless very low (typically <0.1%). For low-volume fraction emulsions (<10%) the possibility of the flocs forming a three-dimensional network is low and the creaming rate is controlled principally by the viscosity of the polymer-thickened continuous phase. The delay time before creaming begins is dependent on the zero-shear viscosity of the continuous phase and is largely independent of polymer type. The delay time increases dramatically at zero-shear viscosities approaching 1 Pa s.

LITERATURE CITED

(1) Phillips, G. O., Williams, P. A., Eds. *Handbook of Hydrocolloids*; Woodhead Publishing: Cambridge, U.K., 2000.

(2) Williams, P. A.; Phillips, G. O. Gum arabic. In *Handbook of Hydrocolloids*; Woodhead Publishing: Cambridge, U.K., 2000; pp 155–168.

(3) Gunning, P. A.; Hibberd, D. J.; Howe, A. M.; Robins, M. M. Gravitational destabilisation of emulsions flocculated by non adsorbed xanthan. *Food Hydrocolloids* **1998**, *2*, 119–129.

(4) Luyten, H.; Jonkman, M.; Kleok, W.; van Vliet, T. Creaming behaviour of dispersed particles in dilute xanthan solutions. In *Food Colloids and Polymers*; Dickinson, E., Walstra, P., Eds.; RSC Special Publication 113; Royal Society of Chemistry: Cambridge, U.K., 1993; pp 24–234.

(5) Dickinson, E.; Ma, J.; Povey, M. J. W. Creaming of concentrated emulsions containing xanthan. *Food Hydrocolloids* **1994**, *8*, 481–497.

(6) Parker, A.; Gunning, P. A.; Ng, K.; Robins, M. M. How does xanthan stabilise salad dressing? *Food Hydrocolloids* **1995**, *9*, 333–342.

(7) Aronson, M. P. Surfactant induced flocculation of emulsions. In *Emulsions—A Fundamental and Practical Approach*; Sjöblom, J., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; pp 75–96.

(8) Snowden, M. J.; Clegg, S. M.; Williams, P. A.; Robb, I. D. Flocculation of silica particles by adsorbing and non adsorbing polymers. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2201–2207.

(9) Smith, N. J.; Williams, P. A. Depletion flocculation of polystyrene latices by water soluble polymers. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1483–1489.

(10) Gouldby, S. J.; Gunning, P. A.; Hibberd, D.; Robins, M. M. Creaming in flocculated oil in water emulsions. In *Food Polymers, Gels and Colloids*; RSC Special Publication 82; Royal Society of Chemistry: Cambridge, U.K., 1991; pp 244–261.

(11) Fillery-Travis, A. J.; Gunning, P. A.; Hibberd, D. J.; Robins, M. M. Coexistent phases in concentrated polydisperse emulsions flocculated by non adsorbing polymer. *J. Colloid Interface Sci.* **1993**, *159*, 189–197.

(12) Manoj, P.; Fillery-Travis, A. J.; Watson, A. D.; Hibberd, D. J.; Robins, M. M. Characterisation of a depletion-flocculated polydisperse emulsion. 1. Creaming behaviour. *J. Colloid Interface Sci.* **1998**, *207*, 283–293.

(13) Manoj, P.; Watson, A. D.; Hibberd, D. J.; Fillery-Travis, A. J.; Robins, M. M. Characterisation of a depletion-flocculated polydisperse emulsion. II. Steady-state rheological investigations. *J. Colloid Interface Sci.* **1998**, *207*, 294–302.

(14) Manoj, P.; Fillery-Travis, A. J.; Watson, A. D.; Hibberd, D. J.; Robins, M. M. Characterisation of a depletion-flocculated polydisperse emulsion. III. Oscillatory rheological measurements. *J. Colloid Interface Sci.* **2000**, *228*, 200–206.

(15) Robins, M.; Manoj, P.; Hibberd, D.; Watson, A.; Fillery-Travis, A. Creaming and rheology of oil-in-water emulsions. In *Food Colloids*; Dickinson, E., Miller, R., Eds.; RSC Special Publication 258; Royal Society of Chemistry: Cambridge, U.K., 2001; pp 144-151.

(16) Moates, G. K.; Watson, A.; Robins, M. M. Creaming and oscillation rheology of weakly flocculated concentrated emulsions. *Colloids Surf. A* **2001**, *190*, 167–178.

(17) Robinson, G.; Ross-Murphy, S. B.; Morris, E. R. Viscosity-molecular weight relationships, intrinsic chain flexibility, and dynamic solution properties of guar galactomannan. *Carbohydr. Res.* **1982**, *107*, 17–32.

(18) Buscall, R. The sedimentation of concentrated colloidal suspensions. *Colloids Surf.* **1990**, *43*, 33–53.

(19) Buscall, R.; Goodwin, J. W.; Ottewill, R. H. The settling of particles through Newtonian and non Newtonian media. *J. Colloid Interface Sci.* **1982**, *85*, 78–86.