

THE INFLUENCE OF XANTHAN AND λ -CARRAGEENAN ON THE CREAMING AND FLOCCULATION OF AN OIL-IN-WATER EMULSION CONTAINING SOY PROTEIN

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Abstract - The effect of polysaccharide content on the stability of an oil-in-water emulsion (20% oil, droplet diameter 6.5 μm , pH = 7) containing soy protein (5 mg/ml) as the emulsifying agent was studied. Flocculation occurs by addition of two depletion flocculants: xanthan (0.01- 0.4%) and λ -carrageenan (0.001- 2%). We report that in both cases the onset of flocculation occurs below the overlap polymer concentration ($c^* = 0.15\%$ for xanthan and $c^* = 0.58\%$ for λ -carrageenan). The strength of depletion interaction is dependent on such factors as polymer concentration, molecular weight and also the presence of other macromolecules.

Profiles of the creaming behaviour of the sample emulsions were obtained by measuring the height of the boundary between the cream phase and the serum as a function of time for each emulsion. The result indicates that creaming kinetics is dependent on polymer concentration in a complex way. The turbidity of the serum gave an indication of whether the system was fully flocculated or contained flocks together with unflocculated droplets. At very low polymer concentrations the droplets cream individually or in small aggregates at the top of the container. At higher concentrations the droplets appear to cream as a single entity, with a sharp lower boundary separating the cream phase from a clear serum. In these emulsions and in some of the coexistent ones, there is a delay before creaming starts. The presence of the polymers at higher concentrations resulted in a stable emulsion with a very high apparent viscosity for the continuous phase and/or a strong emulsion gel network. The length of the delay phase increased with increasing concentration of both polymers.

Keywords: creaming, polysaccharides, soy protein.

INTRODUCTION

Oil-in-water emulsions undergo a number of instability processes, including creaming, flocculation and coalescence. Characterisation and control of these processes are key aspects of the formulation of commercial products.

The dual functionality of added polymers, either stabilisation or flocculation, to emulsion systems has attracted a great deal of attention. It has been observed that the presence of non-absorbing polysaccharide (dextran, xanthan, HEC, etc) induces flocculation of casein stabilised emulsion or emulsions made with low-molecular-weight

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emulsifier by a depletion mechanism (Dickinson et al., 1997; Parker et al., 1995; Manoj et al., 1998). However, it can also be beneficial (above some critical concentration) by increasing the apparent viscosity of the product by forming a continuous network, producing a stabilising effect with the appearance of delay phase (Parker et al., 1995; Manoj et al., 1998). It is well known that concentrated emulsions like mayonnaise do not need stabilising, since the crowding effect of the droplets is sufficient to prevent creaming, but it is difficult to stabilise reduced-fat dressing with xanthan (Parker et al., 1995).

Delayed creaming of soy-protein-stabilised emulsions in the presence of xanthan and λ -carrageenan as flocculants has never been discussed, so the aim of the present study was to study the effect of these polysaccharides on the stability of an oil-in-water emulsion containing soy protein as the emulsifier.

MATERIALS AND METHODS

Materials and Emulsion Preparation

A premix was prepared in a Waring blender using a predetermined shearing cycle by adding corn oil (40%) to a 10 mg/ml solution of soy protein in 10 mM sodium phosphate buffer pH = 7. Soy protein isolate was produced under mild conditions at a pilot plant. The resulting premix was stable to coalescence. The final emulsions were prepared by diluting the premix with a polymer solution to obtain the desired concentration of oil (20%, v/v), soy protein (5 mg/ml) and polymers. The diluents were aqueous solutions of xanthan (X) and λ -carrageenan (C) (SKW Biosystem S.A) and the preservative sodium azide (NaN_3 , Sigma Chemical Company). The molecular weight of the xanthan was 3MD, while the molecular weight of the λ -carrageenan was 1 MD. The polymers were dispersed and hydrated by stirring together the ingredients while heating to 80°C and then allowing the solution to cool to room temperature. After preparation the emulsions were immediately transferred to 100 ml measuring cylinders and kept at 20 °C. The movement of any creaming boundaries was observed over time.

Droplet Size Distribution

The particle size distribution of the premix was measured using a Coulter Counter LS 230. These

size distributions were highly reproducible and did not vary during the study of the creaming measurements. A typical size distribution with a volume mean diameter ($d_{4,3}$) of 6.94 μm is shown in Figure 1. Since the polymers were added after emulsification, they had no effect on droplet size distribution.

Rheological Measurements

Viscosity (steady shear-rate) measurements were obtained using a controlled stress Bohlin Rheometer with a double gap geometry at 20°C. The viscometric measurements were carried out in λ -carrageenan and xanthan solutions. Zero-shear rate viscosity values were obtained for each sample. The specific viscosity (η_{sp} ; poise), which defines the fractional increase in viscosity due to the presence of the polymer, was calculated for each concentration.

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} \quad (1)$$

where η_s (poise) is the solvent viscosity. A log-log chart of η_{sp} vs polymer concentration (Figure 2) shows the critical polymer overlap concentration (C^*) to be $C^*=0.15\%$ (w/w) for xanthan and $C^*=0.58\%$ (w/w) for λ -carrageenan. The behaviour of specific viscosity as a function of concentration was as expected.

Calculation of the Delay Time

Profiles of the creaming behaviour of the sample emulsions were obtained by measuring the height of the boundary between cream and the serum as a function of time for each emulsion. Once started, the rate of creaming was constant, but a delay was sometimes evident before creaming began. The delay could be quantified by extrapolation of the boundary height to zero movement.

RESULTS

Creaming Behaviour

Two distinct modes of creaming were observed in emulsions containing non-absorbing polysaccharides. In type I creaming, emulsions remain opaque at the base of the sample for a significant period of time, while a concentrated cream layer develops at the top of the sample. The

thickness of the cream layer gradually increases over time. There is no clear interface between the creaming emulsion and serum. Accurate visual observations of this type were not possible. In type II creaming there is a sharp interface between the creaming phase and the serum below. Creaming occurs rapidly and the remaining serum can be clear or turbid. This type of creaming is easily monitored visually.

Type I: The addition of xanthan (0.01-0.4%) and λ -carrageenan (0.001-2%) caused a significant change in the visual creaming behaviour of the emulsions. At low concentrations of both polymers (0.01% xanthan and 0.001% λ -carrageenan), there were diffuse boundaries and the serum remained turbid. This behaviour is characteristic of polydisperse emulsions in the presence of little or no polymer, where individual droplets or small aggregates move independently to the top of the container (Manoj et al., 1998; Fillery-Travis et al., 1993). For unflocculated emulsions, the creaming velocity depends on the zero-shear rate viscosity of the serum but also on the emulsion concentration, due to the hinderance of particles. In this case, a modified version of Stokes law applies (Robins, 1991).

Type II: At 0.025% xanthan and 0.01% λ -carrageenan sharp interfaces and a turbid remaining serum were observed. The turbidity of the serum varied with the presence or absence of residual droplets. The initial turbidity gave an indication of whether the system was fully flocculated or contained flocks together with unflocculated droplets. At higher polymer concentrations the boundary lines were sharp from the start, leaving a clear serum which indicated that the emulsion was completely flocculated. The same behaviour was observed in previous studies of xanthan and hydroxyethyl cellulose (HEC) thickened emulsions, but using Tween 60 or BRIJ35 as emulsifiers (Parker et al., 1995; Manoj et al., 1998). Droplets flocculate by a depletion mechanism when there is a secondary minimum in their interaction potential. The depth of the secondary minimum, and hence the strength of the depletion flocculation, is highly dependent on the ratio of particle radius to polymer radius of gyration, the concentration of particles and the concentration of the dispersed polymer. It has been shown that the onset of flocculation occurs above some critical polymer concentration C^* (Robins, 1991; Dickinson et al., 1997). In our case, it was observed by optical microscopy that the emulsions were flocculated at $C = 0.025\%$ for xanthan and $C = 0.01\%$ for λ -carrageenan. Emulsions with both types of

polysaccharides were flocculated by the mechanism of depletion because we have enough protein in the continuous phase to assure monolayer coverage and avoid bridging flocculation.

Figure 3 shows the height of the sharp boundary between flocculated emulsion and the clear serum as a function of time for 20 % (v/v) corn oil, 5 mg/ml soy protein and xanthan (0.025%, 0.10%, 0.18% and 0.25%) and Figure 4 shows the creaming behaviour for 20% (v/v) corn oil, 5 mg/ml soy protein and λ -carrageenan (0.01%, 0.10%, 0.25% and 1%). We found that for a concentration $\geq 0.025\%$ xanthan or 0.01% λ -carrageenan there was an initial delay before creaming started, followed by linear creaming and then as slow continual compression of the concentrated cream.

In both cases the creaming rate (V_c) decreased when the polymer concentration increased, fitting a linear equation (for λ -carrageenan: $R^2 = 0.9612$, slope = -0.1179 and for xanthan: $R^2 = 0.9969$, slope = -0.3206) (Figure 5). Furthermore the creaming rate for λ -carrageenan was faster than that for xanthan. These results may be explained by assuming that the lower molecular weight of the λ -carrageenan produced a lower attraction potential due to the excluded polymer and hence a lower strength of flocculation. However, more studies should be done to explain these results.

Figure 6 shows the variation in delay time as a function of xanthan and λ -carrageenan concentration. The delays vary by more than three orders of magnitude from a few minutes to two months. It can be seen that delay time as a function of concentration is linear in a log-log plot, i.e., they are related by a power law. The slope is 2.9 for xanthan and 2.1 for λ -carrageenan. It can be seen that the slope for xanthan is higher than that for λ -carrageenan. Delay time is clearly longer for xanthan than for λ -carrageenan for the same concentration. Parker et al., (1995) reported a slope of 3.9 for xanthan in a 20% alkane emulsion and 3.1 for the same emulsion stabilised by HEC. They discussed two models for stabilisation of salad dressing by xanthan, the traditional one whereby stabilisation is explained by the yield stress of the xanthan solution and the other model whereby the depletion flocculation of the emulsion droplets, induced by the addition of xanthan, leads to the formation of a particle network. It is the time-dependent yield stress of the network which stabilises the dressing. More measurements should be made to evaluate how this slope varies with polymer type, molecular weight, etc.

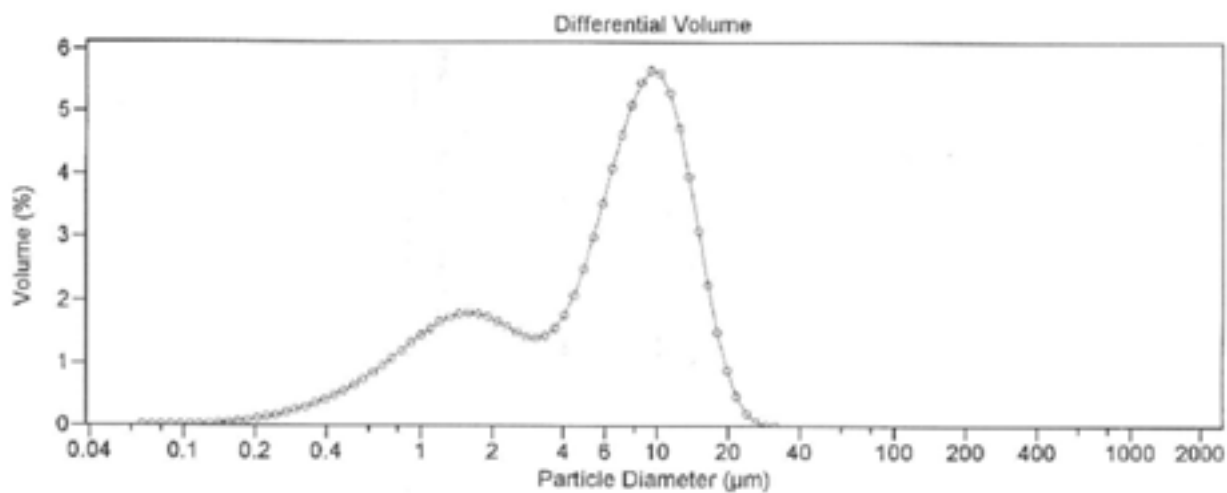


Figure 1: Particle size distribution of the premix.

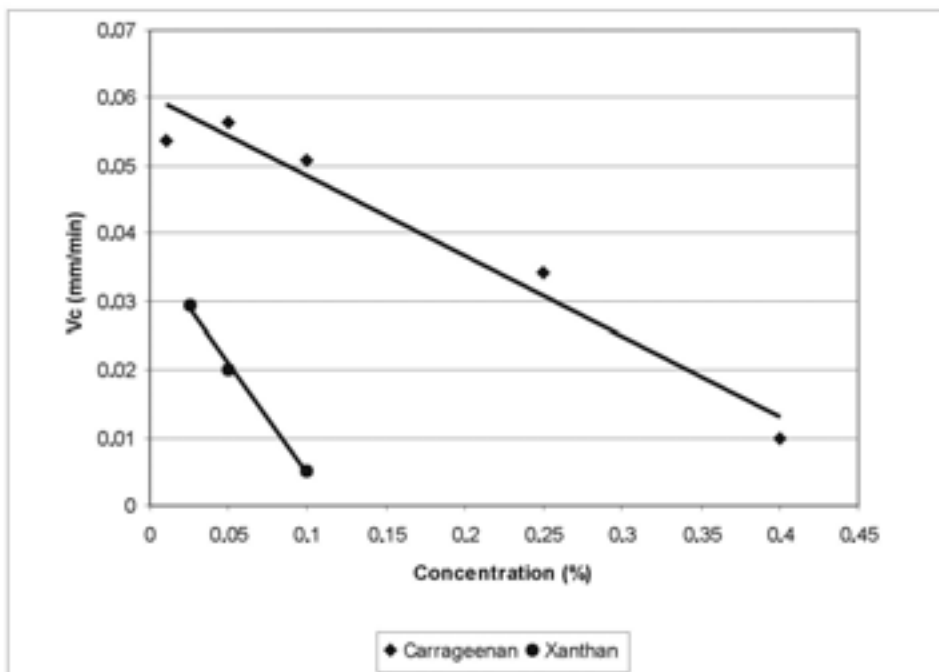
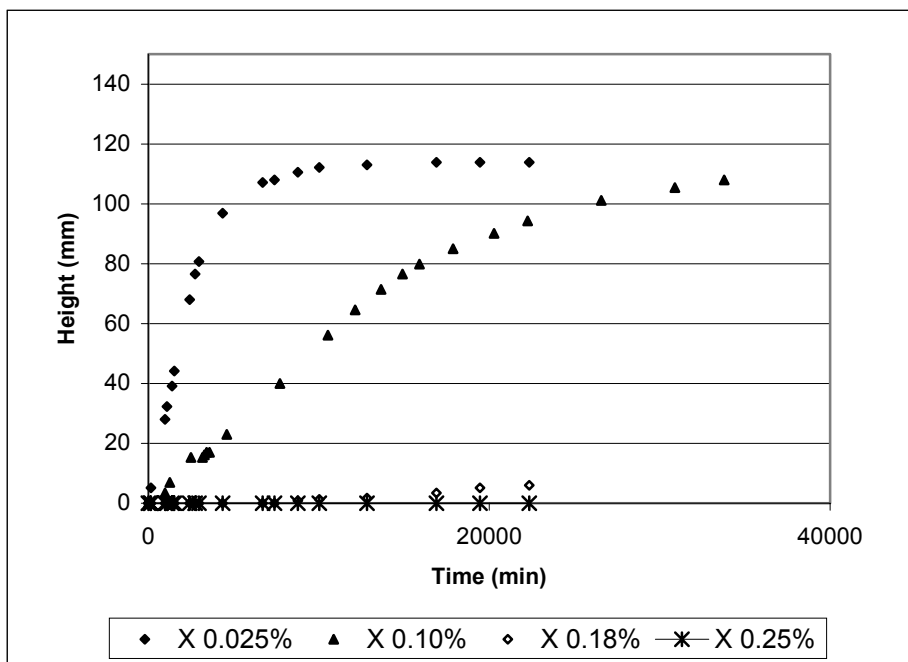


Figure 2: Specific viscosity and estimation of critical polymer concentration for λ -carrageenan and xanthan.



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Figure 3: Creaming behaviour of 5 mg/ml soy protein emulsions as a function of time for 20% corn oil and xanthan (0.025%, 0.10%, 0.18% and 0.25%).

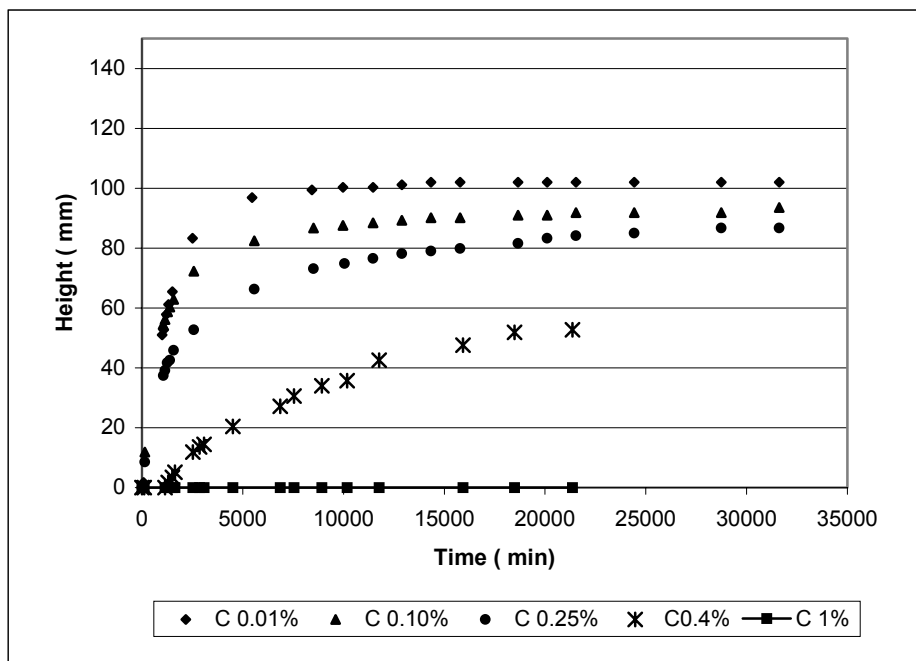


Figure 4: Creaming behaviour of 5 mg/ml soy protein emulsions as a function of time for 20% corn oil and λ -carrageenan (0.01%, 0.10%, 0.25% and 1%).

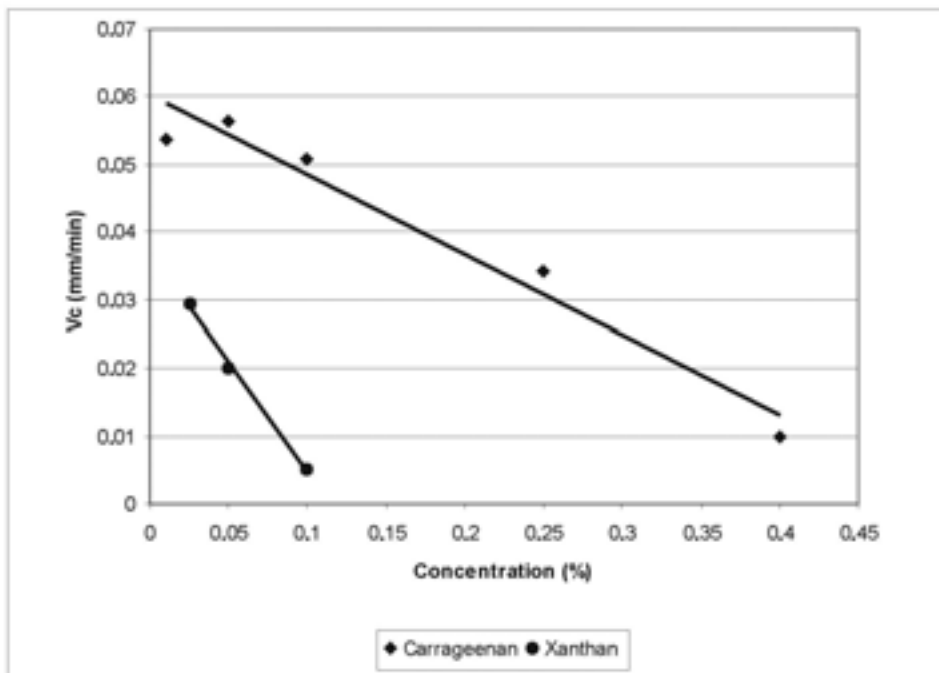


Figure 5: Creaming rate as a function of polymer concentration.

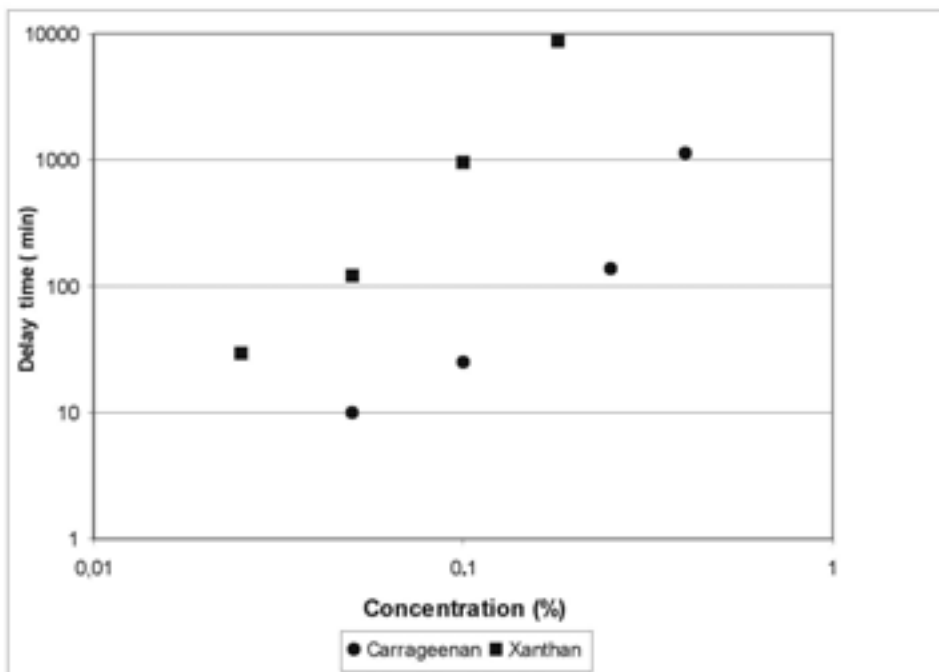


Figure 6: Delay time as a function of xanthan and λ -carrageenan concentration. Slope is 2.9 for xanthan and 2.1 for λ -carrageenan.

CONCLUSIONS

Addition of xanthan and λ -carrageenan to the soy protein emulsions produces flocculation by a depletion mechanism. The flocculated emulsions have a time-dependent yield stress, which is initially large enough to prevent creaming. The length of the delay phase shows a power law scaling with xanthan and λ -carrageenan concentrations. Xanthan reduced creaming of the emulsion to a lower concentration than λ -carrageenan. Nevertheless, more studies should be done to evaluate the behaviour of both polysaccharides with soy protein in the buffer solution. The creaming rate is faster for λ -carrageenan than for xanthan. This may be due to the lower molecular weight of λ -carrageenan.

This study can be useful for formulating dressings, taking into account that the delay phase exceeds the shelf-life.

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REFERENCES

- Dickinson, E., Golding, M. and Povey, M.J.W. (1997). Creaming and Flocculation of Oil-In-Water Emulsions Containing Sodium Caseinate. *J. of Colloids and Interface Sci.*, 185, 515-529.
- Fillery-Travis, A., Gunning, P.A., Hibberd, D.J. and Robins, M.M. (1993). Coexistent Phases in Concentrated Polydisperse Emulsions Flocculated by Non-Absorbing Polymer. *Journal of Food Colloid and Interface Sci.*, 159, 189-197.
- Manoj, P., Fillery-Travis, A.J., Watson, A.D., Hibberd, D.J. and Robins, M. (1998). Characterization of a Depletion-Flocculated Poly Disperse Emulsion. I Creaming Behaviour. *Journal of Colloids and Interface Sci.*, 207, 283-293.
- Parker, A., Gunning, P.A. and Robins, M.M. (1995). How does Xanthan Stabilize Salad Dressing? *Food Hydrocolloids*, 9, 333-342.
- Robins, M.M. (1991). Effect of Polysaccharide on Flocculation and Creaming in Oil-In-Water Emulsion Flocculation and Creaming. *ACS. Symp. Ser.*, 448, 230-246.