

## Influence of Polysaccharides on the Rate of Coalescence in Oil-in-Water Emulsions Formed with Highly Hydrolyzed Whey Proteins

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The objective of this study was to examine the effects of added xanthan gum, guar gum, or  $\kappa$ -carrageenan on the formation and properties of emulsions (4 wt % corn oil) formed with an extensively hydrolyzed commercial whey protein (WPH) product under a range of conditions. The rate of coalescence was calculated on the basis of the changes in the droplet size of emulsions during storage of the emulsions at 20 °C. Compared with the emulsion made without the addition of polysaccharides, the rate of creaming and coalescence in emulsions containing xanthan gum, guar gum, or  $\kappa$ -carrageenan was markedly enhanced with increasing concentration of polysaccharides during storage for up to 7 days. At a given concentration, the rate of coalescence was highest in the emulsions containing guar gum, whereas it was lowest in the emulsions containing  $\kappa$ -carrageenan. All emulsions containing xanthan gum, guar gum, or  $\kappa$ -carrageenan showed flocculation of oil droplets by a depletion mechanism. This flocculation was considered to enhance the coalescence of oil droplets. The different rates of coalescence could be explained on the basis of the strength of the depletion potential, which was dependent on the molecular weight and the radius of gyration of the polysaccharides.

**KEYWORDS:** Emulsions; hydrolyzed whey protein (WPH); coalescence; xanthan gum; guar gum;  $\kappa$ -carrageenan; depletion flocculation

### INTRODUCTION

Whey proteins are widely used as emulsifiers in food systems. Whey proteins are sometimes hydrolyzed to produce small peptides and/or free amino acids, which are more easily digested. These hydrolyzed whey proteins have been used extensively in infant and specialized adult nutritional formulations (1). However, extensive hydrolysis of whey proteins, because of the production of many short peptides, has been found to be detrimental to their emulsifying and stabilizing properties (2–4). Because of the poor emulsifying properties of extensively hydrolyzed whey proteins, these formulations usually require the addition of emulsifiers and stabilizers to facilitate the formation of a stable emulsion.

Agboola et al. (3) showed that fairly stable oil-in-water emulsions could be formed with highly hydrolyzed whey protein (WPH) as the sole emulsifier when using appropriate WPH concentration and homogenization conditions. Emulsions (4% soy oil) prepared using 4 wt % WPH with two-stage homogenization, at pressures of 20.6 and 3.4 MPa in the first and second stages, respectively, were found to be stable to creaming and coalescence at 20 °C for more than a week. However, retorting (121 °C for 16 min) of these emulsions resulted in loss of stability (5). Addition of hydroxylated lecithin at 0.25

wt % was found to markedly improve the creaming stability after retorting and to prevent coalescence.

Polysaccharides are commonly added to food emulsions to prevent the dispersed droplets from creaming and to inhibit the rate of coalescence between the oil droplets because of the increased viscosity and yield stress. However, the presence of polysaccharides (e.g., xanthan gum, carrageenans, guar gum, gum arabic, and modified starch) at fairly low concentrations has been shown to enhance the rate of creaming of emulsion droplets due to depletion flocculation (6–13). Depletion flocculation is a phenomenon that arises from localized changes in osmotic pressure in mixed emulsion/polysaccharide systems. Because polysaccharide molecules have a large hydrodynamic radius, they tend to be excluded from the gap between two approaching droplets. The region between the droplets becomes depleted of polysaccharides and rich in solvent compared with the bulk aqueous phase. An osmotic pressure gradient results, which prompts the solvent to flow out of the region between the droplets. As a consequence, the volume of this region decreases and the droplets approach further (14).

Flocculation may also enhance coalescence because the droplets are brought into close proximity (15). However, little information on the coalescence of oil droplets in food emulsions that are stabilized by proteins and flocculated by the depletion mechanism has been reported in previous studies.

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The aim of this work was to investigate the properties of emulsions formed with WPH and hydroxylated lecithin and containing xanthan gum, guar gum, or  $\kappa$ -carrageenan at neutral pH. The stability of the emulsions with respect to coalescence, flocculation, and creaming was examined using time-dependent droplet size measurements, confocal laser scanning microscopy (CLSM), and viscometry.

## MATERIALS AND METHODS

**Materials.** Whey protein hydrolysate powder (WPH 931 with a 27% degree of hydrolysis, containing 90.5% protein, 4.5% moisture, 2.8% ash, 0.1% fat, and 0.2% lactose) was supplied by the Fonterra Co-operative Group. Hydroxylated lecithin (Precept 8120) was supplied by Central Soya Co. Inc., Fort Wayne, IN; the phospholipid content was 95% (as acetone insolubles). Commercial xanthan gum (Keltrol T, standard 80-mesh) was purchased from Germanotown International Ltd., Auckland, New Zealand. Commercial guar gum (Daviisco DG 74) was purchased from Swift and Co. Ltd., Melbourne, Australia. Commercial  $\kappa$ -carrageenan (Bengel KK-100) was purchased from Woods and Woods Pty Ltd., Sydney, Australia. Corn oil was purchased from Davis Trading Co., Palmerston North, New Zealand. All of the chemicals used were of analytical grade and were obtained from either BDH Chemicals (BDH Ltd., Poole, U.K.) or Sigma Chemical Co. (St. Louis, MO) unless specified otherwise.

**Preparation of Emulsions.** Emulsions were prepared according to the procedure described by Agboola et al. (3) with some modifications. Appropriate quantities of WPH were dissolved in Milli-Q water at  $60 \pm 0.5$  °C with stirring for 15 min to give 4 wt % WPH in the final emulsion. Hydroxylated lecithin (0.1 wt %) was dispersed in corn oil at 60 °C for 15 min before mixing with the WPH solution. Appropriate amounts of xanthan gum, guar gum, or  $\kappa$ -carrageenan were dissolved in Milli-Q water at an appropriate temperature (60 °C for xanthan gum and  $\kappa$ -carrageenan, 85 °C for guar gum) with stirring for 1 h. The solutions of polysaccharides were then added to the WPH solution, with stirring for 1 h, to give a range of polysaccharide concentrations in the final emulsions. The pH of these solutions was adjusted in the range 6.8–7.0. The mixture of WPH, polysaccharide solution, and corn oil was then homogenized in a two-stage homogenizer (APV 2000, Albertslund, Denmark) at a first-stage pressure of 20 MPa and at a second-stage pressure of 4 MPa. The emulsions were homogenized twice for more effective mixing of the oil phase. Emulsions were prepared in duplicate.

**Determination of Average Particle Size.** A Malvern MasterSizer MSE (Malvern Instruments Ltd., Worcestershire, U.K.) was used to determine the average diameter ( $d_{32}$  and  $d_{43}$ ). The parameters that were used to analyze the particle size distribution were defined by the presentation code 2NAD. The relative refractive index ( $N$ ), that is, the ratio of the refractive index of the emulsion particle (1.456) to that of the dispersion medium (1.33), was 1.095. The absorbance value of the emulsion particle was 0.001.

**Calculation of the Rate of Coalescence in Emulsion Droplets.** The rate of coalescence largely follows first-order kinetics (16) and can be represented as

$$N_t/N_0 = e^{-K_c t} \quad (1)$$

where  $N_t$  is the number concentration of droplets at time  $t$ ,  $N_0$  is the number concentration of freshly formed droplets (time zero), and  $K_c$  is the rate constant, which is related to the probability of the interdroplet film (interfacial layer) rupturing in time  $t$  (17). The apparent rate of coalescence ( $K_c$ ) was estimated by plotting  $\ln(N_t/N_0)$  versus  $t$ . When the volume of emulsion droplets remains constant, that is, no oiling-off occurs in the emulsions, the relative droplet number ( $N_t/N_0$ ) can be estimated using the method described by Das and Chatteraj (18). The relationship between the emulsion droplet number,  $N$ , and the mean volume average droplet diameter,  $d_{30}$ , is

$$\frac{4}{3}\pi\left(\frac{d_{30}}{2}\right)^3 N = \text{constant} \quad (2)$$

with  $d_{30}$  obtained from the MasterSizer data. The relative number of emulsion droplets can then be obtained from

$$\frac{N_t}{N_0} = \left[\frac{(d_{30})_{t=0}}{(d_{30})_{t=t}}\right]^3 \quad (3)$$

Kinetic plots of  $\ln(N_t/N_0)$  versus storage time  $t$  for emulsions containing different concentrations of polysaccharides gave a straight line, with the slope being the apparent rate of coalescence ( $K_c$ ). All emulsions containing low polysaccharide concentrations and stored over relatively short times showed linear plots ( $R^2 > 0.95$ ).

**Determination of Creaming Stability.** Creaming stability was determined as described by Agboola et al. (3). About 15 mL of freshly prepared emulsion was poured into specially constructed “stability tubes”, and the samples were kept at 20 °C for 1 week. The tubes were graduated with 0.1 mL divisions. The separated cream layer was read after different times.

**Confocal Laser Scanning Microscopy.** A Leica (Heidelberg, Germany) confocal laser scanning microscope with a chosen objective lens and an Ar/Kr laser with an excitation line of 488 nm (in such a way that only the fluorescent wavelength band could reach the detector system) was used to determine the microstructure of the emulsions. Emulsions were made as described above, ~3 mL of sample was taken in a test tube, Nile Blue (fluorescent dye) was mixed through, and then the emulsion was placed on a microscope slide. The slide was then covered with a coverslip and observed under the microscope.

**Viscosity Measurements.** Viscosity was measured using a control stress Rheometrics S-5000 rheometer (Rheometrics Instruments, Piscataway, NJ) equipped with cone and plate geometry. The cone diameter was 40 mm, and the cone angle was 4°. All measurements were performed in a steady stress sweep mode at a temperature of  $25 \pm 0.1$  °C, 24 h after the emulsions were made.

**Statistical Analysis.** Results were analyzed statistically using the Minitab 12 for Windows package. Differences were considered to be significant at  $P \leq 0.05$ .

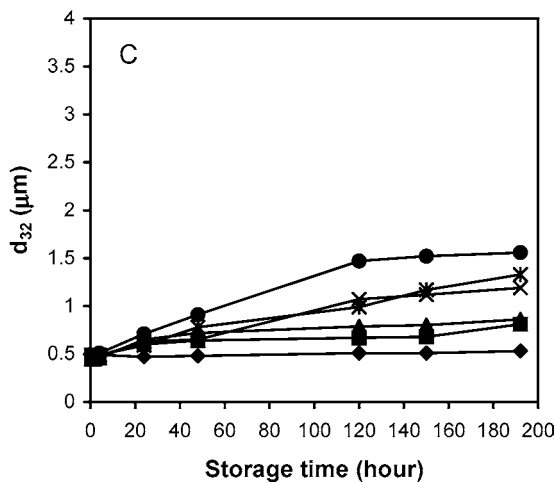
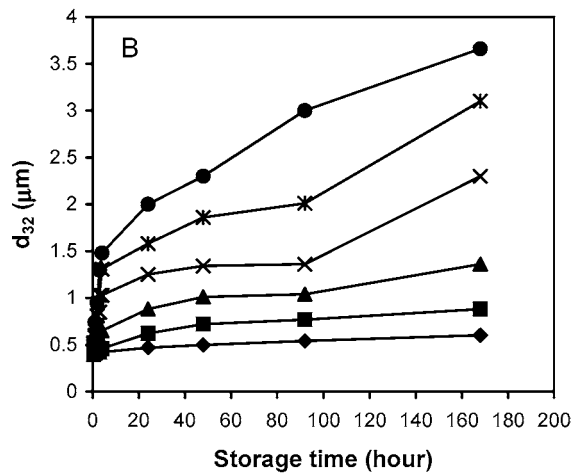
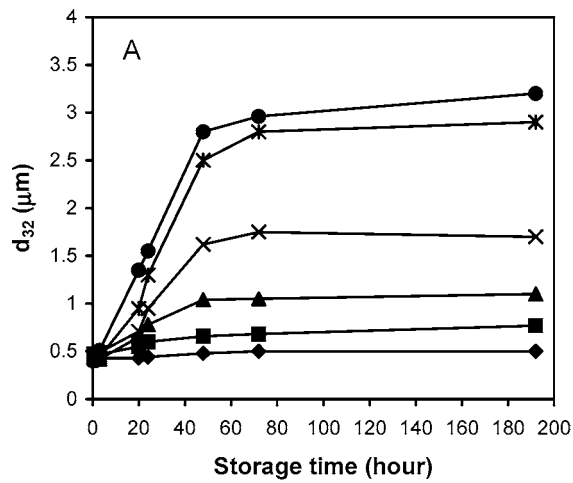
## RESULTS

**Effect of Polysaccharides on Coalescence Stability.** Changes in the average droplet size ( $d_{32}$ ) of emulsions containing different concentrations of polysaccharides as a function of storage time are shown in **Figure 1**. The  $d_{32}$  of all emulsions containing xanthan gum, guar gum, or  $\kappa$ -carrageenan increased during storage at 20 °C. The extent of increase in  $d_{32}$  was dependent on the type and concentration of polysaccharide. Emulsions containing  $\kappa$ -carrageenan showed much less increase in  $d_{32}$  during storage than emulsions containing guar gum or xanthan gum. At a given storage time, the emulsions containing higher polysaccharide concentration had a larger  $d_{32}$ . In contrast, the  $d_{32}$  of emulsions containing no polysaccharides did not change significantly during storage.

Droplet size distributions of emulsions after storage for 4 h are shown in **Figure 2**. All emulsions showed some large-sized droplets in the range of 10–100  $\mu\text{m}$ ; at a given concentration, the proportion of large droplets was highest in the emulsions containing guar gum followed by the emulsions containing xanthan gum and  $\kappa$ -carrageenan.

When the emulsions that showed an increase in droplet size after storage were dissolved in the sodium dodecyl sulfate (SDS) dissociating buffer, the bimodal size distribution did not change (data not shown), indicating that the increase in emulsion size was due to the coalescence of the emulsion droplets during storage.

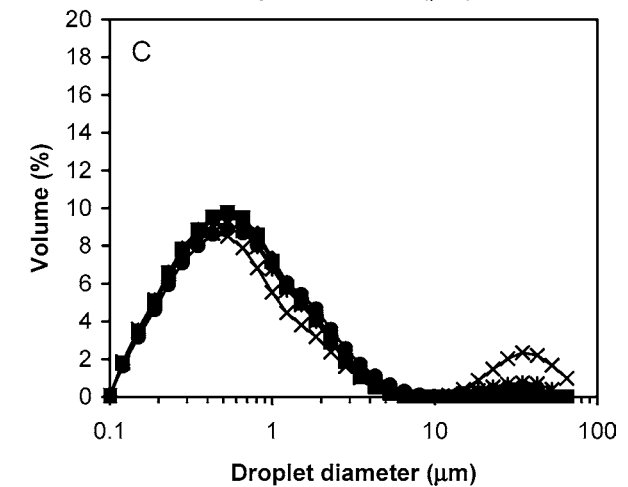
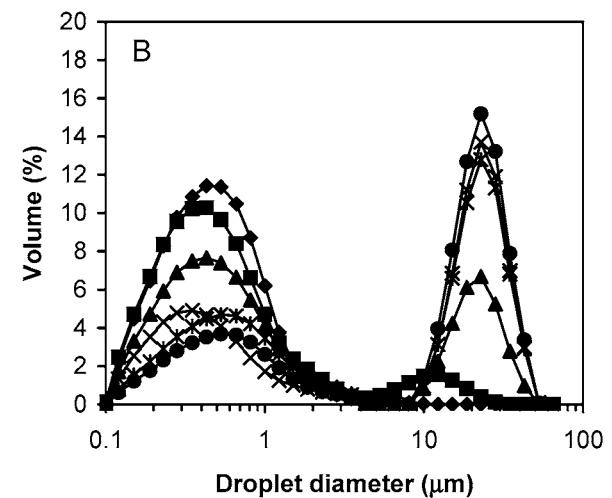
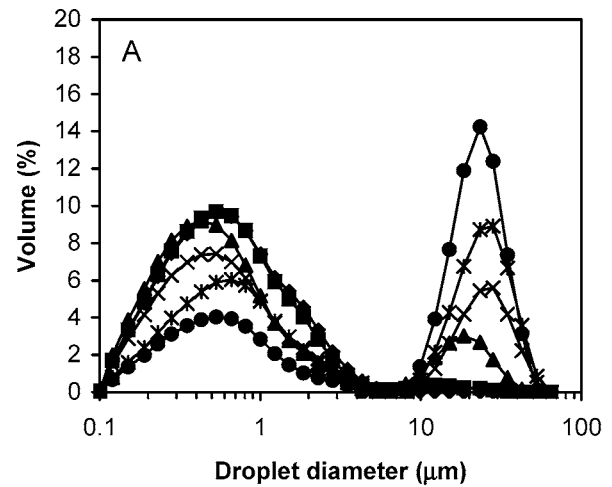
In **Figure 3**, the apparent rate of coalescence ( $K_c$ ) is plotted as a function of the polysaccharide concentration in the emulsions.  $K_c$  increased almost linearly as the xanthan gum or guar gum concentration increased from 0.01 to 0.12%. In emulsions containing  $\kappa$ -carrageenan,  $K_c$  increased with increas-



**Figure 1.** Influence of xanthan gum (A), guar gum (B), or  $\kappa$ -carrageenan (C) addition on the average droplet sizes ( $d_{32}$ ) of emulsions formed with WPH and hydroxylated lecithin as a function of storage time at 20 °C. Polysaccharides at different concentrations, 0% ( $\blacklozenge$ ), 0.01% ( $\blacksquare$ ), 0.025% ( $\blacktriangle$ ), 0.05% ( $\times$ ), 0.1% ( $*$ ), and 0.12% ( $\bullet$ ), were added before homogenization. The data represent averages of two determinations.

ing concentration up to 0.05%, but  $K_c$  decreased slightly as the concentration was increased further, probably because of the high viscosity or the formation of a gel at high  $\kappa$ -carrageenan concentrations.

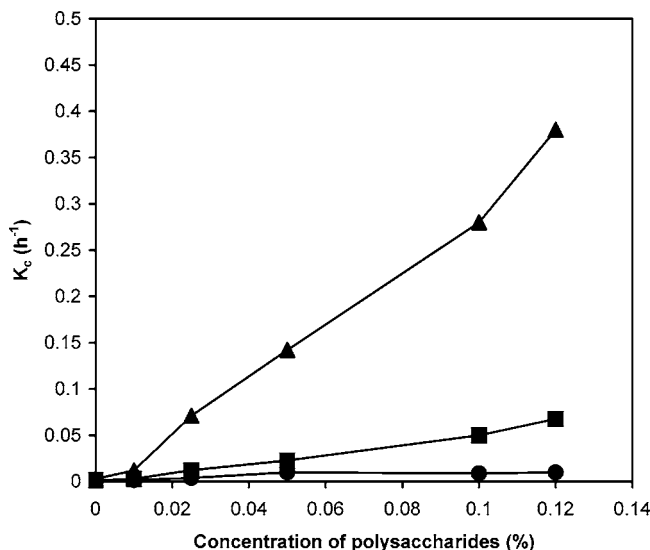
The increase in the  $K_c$  of the emulsions with an increase in the guar gum concentration was considerably larger than that for the emulsions containing xanthan gum or  $\kappa$ -carrageenan. This



**Figure 2.** Droplet size distributions of emulsions containing 0% ( $\blacklozenge$ ), 0.01% ( $\blacksquare$ ), 0.025% ( $\blacktriangle$ ), 0.05% ( $\times$ ), 0.1% ( $*$ ), and 0.12% ( $\bullet$ ) xanthan gum (A), guar gum (B), and  $\kappa$ -carrageenan (C). Emulsions were stored for 4 h at 20 °C.

result clearly indicates that the coalescence of droplets was strongly enhanced by the addition of xanthan gum or guar gum and to a limited extent by  $\kappa$ -carrageenan addition.

**Effect of Polysaccharides on the Creaming Stability of Emulsions.** Figure 4 shows the changes in the cream layer of emulsions containing different concentrations of polysaccharides as a function of storage time. In the emulsions containing low concentrations of polysaccharide (<0.05%), the changes in the



**Figure 3.** Apparent rate of coalescence ( $K_c$ ) of droplets in emulsions containing xanthan gum (■), guar gum (▲), or  $\kappa$ -carrageenan (●) as a function of polysaccharide concentration (percent).

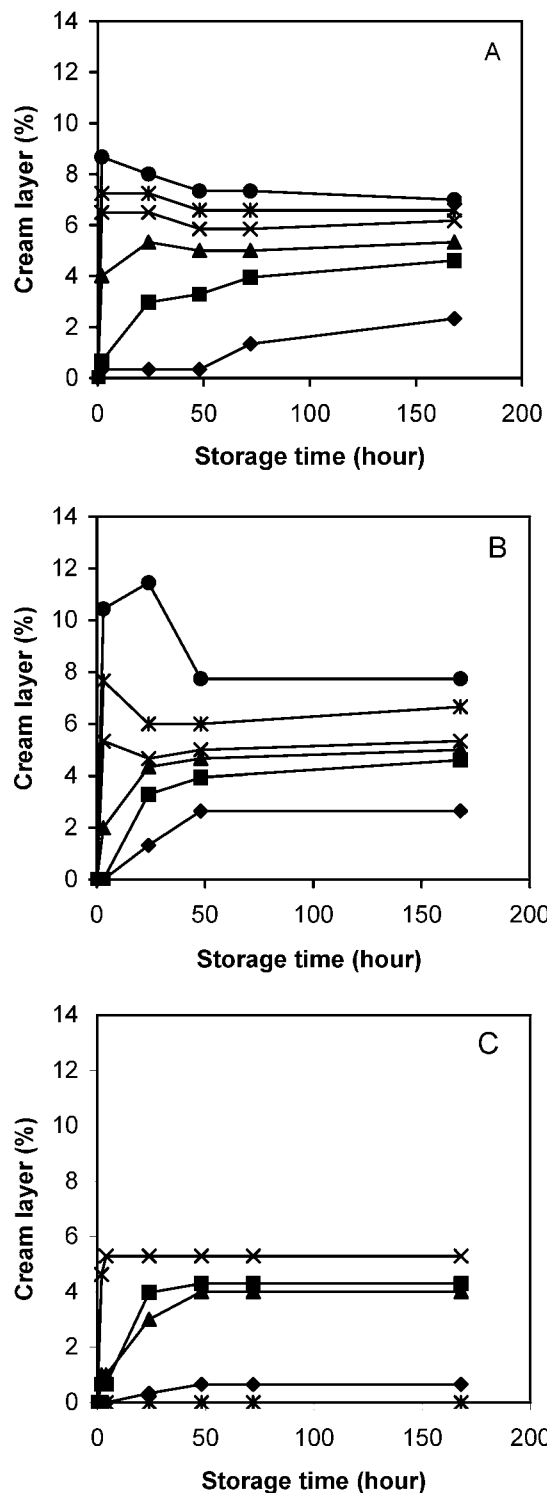
cream layer of the emulsions containing xanthan gum, guar gum, or  $\kappa$ -carrageenan were similar; the extent of cream layer formation increased gradually compared with the control (no added polysaccharide) up to  $\sim 24$  h and then remained essentially unchanged. In emulsions containing higher concentrations ( $\geq 0.05\%$ ) of xanthan gum or guar gum, the cream layer reached a maximum in the initial 24 h (2 h for xanthan gum, 24 h for guar gum), then slightly decreased until 50 h, and then remained unchanged during the observation time (7 days). This behavior was not observed in the emulsions containing high  $\kappa$ -carrageenan concentrations. No creaming was observed in the emulsions containing 0.1 or 0.12%  $\kappa$ -carrageenan during the storage time. A gel was formed in the emulsions containing  $>0.1\%$   $\kappa$ -carrageenan, which may have prevented creaming of the droplets. After  $\sim 48$  h of storage, the cream layer of all emulsions remained unchanged; the extent of cream layer formation followed the order emulsion containing guar gum  $>$  xanthan gum  $>$   $\kappa$ -carrageenan.

#### Micrographs of Emulsions Containing Polysaccharides.

CLSM showed that the fresh emulsions made without polysaccharide had fine and uniform droplet distributions (Figure 5A). Flocculation of the emulsion droplets occurred in the emulsions formed with WPH containing 0.05% xanthan gum, guar gum, or  $\kappa$ -carrageenan (Figures 5C,E and 6A). After emulsions had been stored for 24 h at room temperature, some apparently large droplets were observed (Figures 5B,D,F and 6B). These large droplets were surrounded by many small droplets that had joined with the large droplets. The CLSM micrographs showed that, after storage, the emulsion containing guar gum had larger droplets than the emulsions containing xanthan gum or  $\kappa$ -carrageenan. This was consistent with the droplet size results obtained using light scattering (Figure 1).

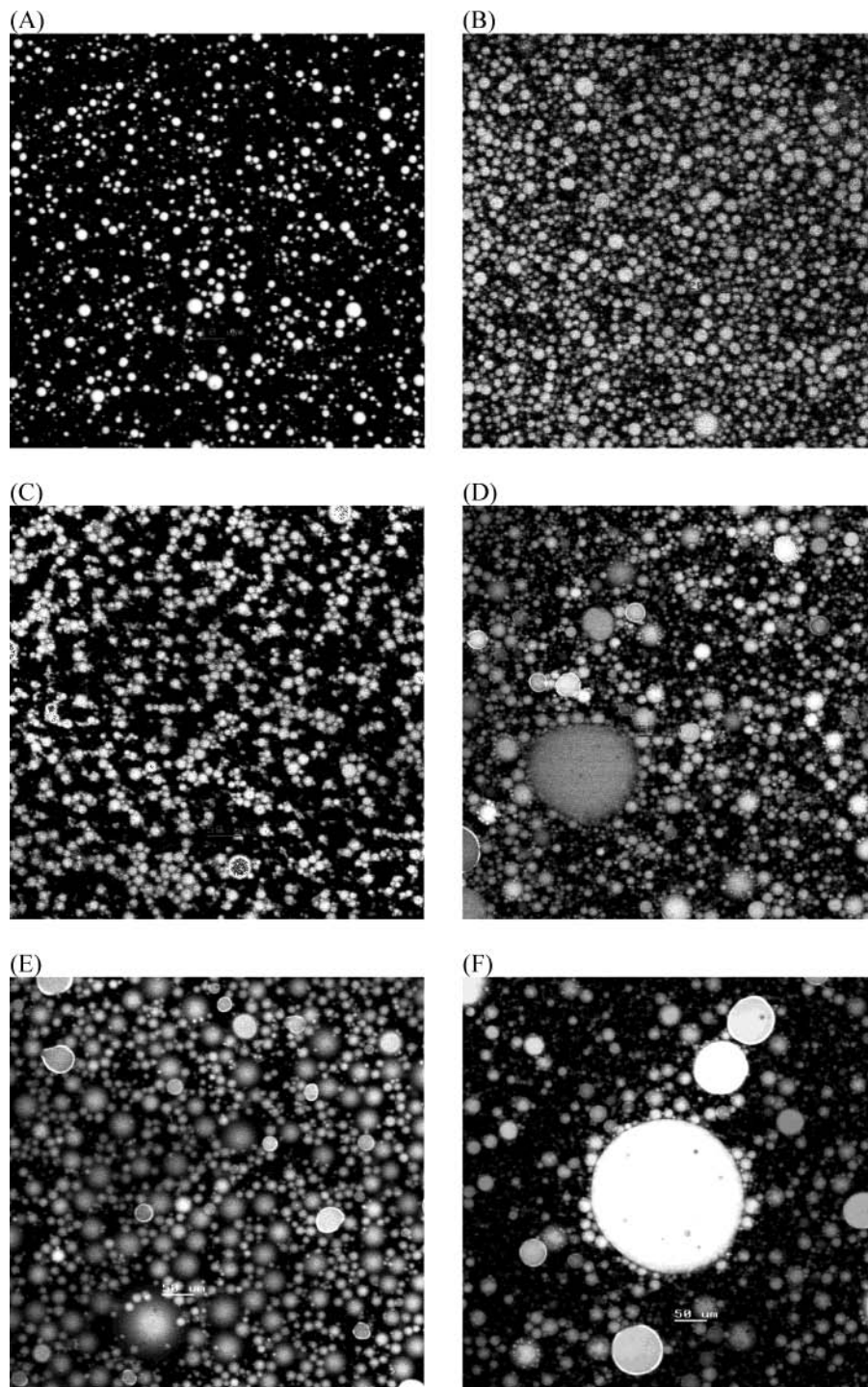
A gel was formed in the emulsion containing 0.12%  $\kappa$ -carrageenan after the emulsion was cooled to room temperature. The CLSM micrographs (Figure 6C,D) showed that a fine network structure of droplets had formed in this emulsion, in which the large droplets distributed randomly within the network formed by the small droplets.

**Apparent Viscosity of Emulsions Containing Polysaccharides.** Viscosity versus shear rate plots for WPH-stabilized emulsions containing different concentrations of xanthan gum, guar gum, or  $\kappa$ -carrageenan from 0 to 0.12% are shown in



**Figure 4.** Changes in the cream layer (percent) as a function of storage time (hours) for emulsions containing 0% (◆), 0.01% (■), 0.025% (▲), 0.05% (×), 0.1% (\*), and 0.12% (●) xanthan gum (A), guar gum (B), and  $\kappa$ -carrageenan (C). The data represent averages of two determinations.

**Figure 7.** The viscosities of the emulsions containing xanthan gum were higher than those of the emulsions containing guar gum at all concentrations and also higher than those of the emulsions containing  $\kappa$ -carrageenan at concentrations  $<0.1\%$ , particularly at low shear rates. The very high viscosity shown in the emulsions containing 0.1 or 0.12%  $\kappa$ -carrageenan indicated gel formation in these emulsions.



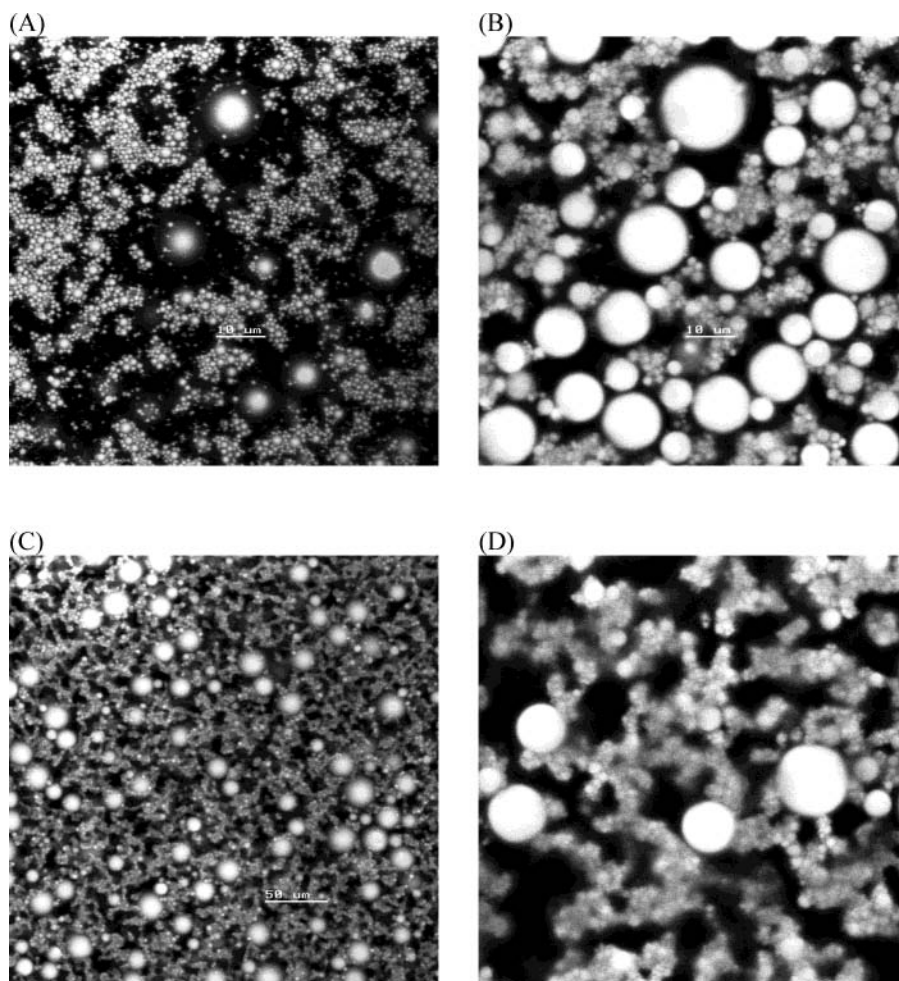
**Figure 5.** Confocal micrographs of emulsions containing no polysaccharide (A, B), 0.05% xanthan gum (C, D), and 0.05% guar gum (E, F). Emulsions were stored for 0.5 h (A, C, E) and 24 h (B, D, F) at 20 °C.

## DISCUSSION

Coalescence is determined mainly by the properties of the interface. It requires rupture of the stabilizing film at the oil–water interface, but this occurs only when the layer of continuous phase between the droplets has thinned to a certain critical thickness. Factors that influence the drainage kinetics include the viscosities of the dispersed and continuous phases, the droplet deformability, the droplet size, the interdroplet forces, the interfacial tension, and the mobility of the adsorbed film (15). Protein-stabilized emulsions, in which protein molecules form a dense viscoelastic interfacial layer at the droplet surface,

are stable to both drainage and rupture and hence to coalescence (15). Peptides adsorbed at the droplet surface in WPH emulsions would almost certainly have a reduced surface viscosity compared with intact whey protein, and this could lead to reduced stability to drainage and film rupture.

Film thinning is enhanced by increasing the attractive forces between the droplets and reducing the continuous phase viscosity (15). The viscosity of the continuous phase increases by the addition of polysaccharides to the continuous phase of emulsions, which results in reduced mobility of the droplets and a reduced collision frequency. However, the results of the present study were in contrast to those expected. The stability of the



**Figure 6.** Confocal micrographs of emulsions containing 0.05% (A, B) and 0.12% (C, D)  $\kappa$ -carrageenan stored for 0.5 h (A, C) and 24 h (B, D) at 20 °C.

emulsions decreased with the addition of polysaccharides in the range of concentration used.

In the absence of polysaccharides, the rate of coalescence of the emulsion formed by the WPH and hydroxylated lecithin was low. This is attributed to the adsorption of high molecular weight peptides in the WPH and hydroxylated lecithin at the oil droplet interface of emulsion (3). In emulsions containing polysaccharides (above a certain critical concentration), the droplets were flocculated (Figures 5 and 6), resulting in enhanced creaming (Figure 4). In the flocculated emulsions, the rupture of the interfacial film was largely dependent on the properties of interfacial layers. No coalescence was observed in the emulsion stabilized by whey protein isolate (WPI) (intact protein molecules) in the presence of polysaccharides during storage (data not shown), although flocculation had occurred in these emulsions. In these emulsions, whey protein molecules probably formed a dense viscoelastic interfacial layer at the droplet surface, which was stable to drainage and rupture. However, in the WPH emulsion, peptide fragments obtained from whey protein hydrolysis formed a weaker and looser mobile structure than that of intact whey protein, and this resulted in the coalescence of flocculated droplets.

Xanthan gum, guar gum, and  $\kappa$ -carrageenan show little surface activity (19) and very weak ability of adsorption (20) at neutral pH. Thus, the nonadsorbing molecules of xanthan gum, guar gum, and  $\kappa$ -carrageenan in the continuous phase can induce flocculation in emulsions when they exceed a certain critical concentration because of an osmotic effect (depletion

flocculation) (4, 6–8, 13, 21–23). The osmotic driving force that favors droplet aggregation increases as the concentration of polysaccharides in the aqueous phase increases (24). The different rates of coalescence in emulsions containing xanthan gum, guar gum, or  $\kappa$ -carrageenan may be attributed to different physicochemical characteristics of these polysaccharides. Depletion flocculation theories state that the attraction force is dependent on the radius of gyration and the molecular weight of the polysaccharide molecules (24, 25).

When the attraction force is the strongest, that is, droplets come into contact, the droplet–droplet interaction potential,  $-w_{\text{dep}}(0)$ , is given by the expression (24)

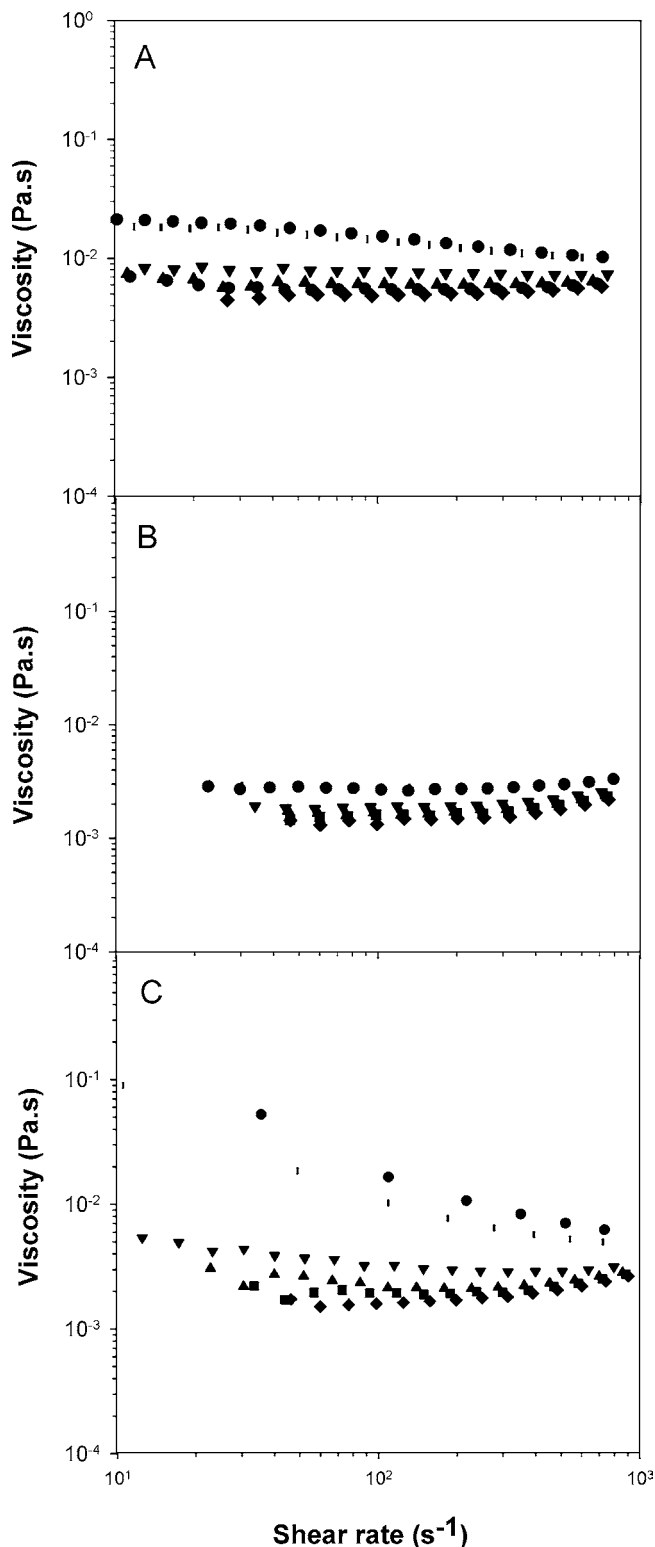
$$w_{\text{dep}}(0) = -\frac{3kT}{2} \frac{cR_v}{\rho} \left( 1 + \frac{1}{2} \frac{cR_v}{\rho} \right) \left( \frac{\gamma_d}{\gamma_g} + \frac{2}{3} \right) \quad (4)$$

where  $c$  is the polysaccharide concentration (in  $\text{kg m}^{-3}$ ),  $\rho$  is the polysaccharide density (in  $\text{kg m}^{-3}$ ),  $\gamma_d$  is the radius of the emulsion droplets,  $\gamma_g$  is the radius of gyration of the molecule, and  $R_v$  is given by

$$R_v = 4\pi\gamma_g^3 \rho N_A / 3M \quad (5)$$

$N_A$  is Avogadro's number and  $M$  is the molecular weight of the polysaccharide.

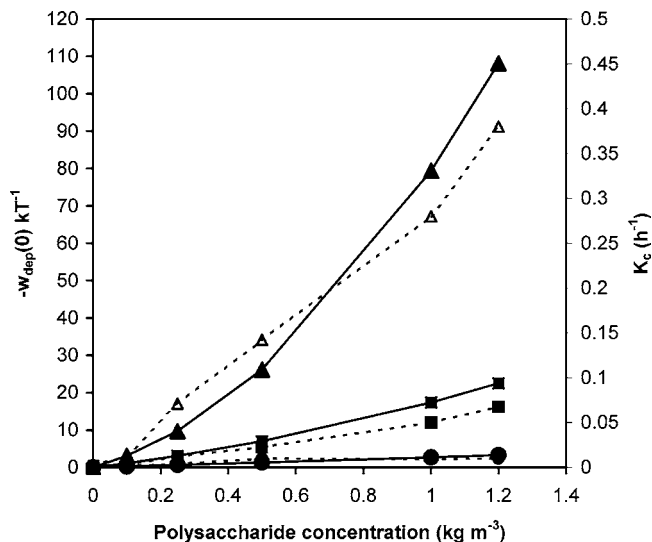
From this theoretical prediction, the droplet–droplet interaction potential,  $-w_{\text{dep}}(0)$ , increases with an increase in the polysaccharide concentration. Also, the depletion attraction will



**Figure 7.** Apparent viscosity (Pa s) at 20 °C as a function of shear rate for emulsions containing 0% (◆), 0.01% (■), 0.025% (▲), 0.05% (▼), 0.1% (■), and 0.12% (●) xanthan gum (A), guar gum (B), and  $\kappa$ -carrageenan (C). The data represent averages of two determinations.

largely increase with an increase in the radius of gyration of the polysaccharide molecules and decrease with an increase in the polysaccharide molecular weight, when the radii of the emulsion droplets are similar.

The molecular masses of xanthan gum, guar gum, and  $\kappa$ -carrageenan have been reported to be  $\sim 2.0 \times 10^6$ ,  $\sim 2.0 \times 10^6$ , and  $\sim 3.1 \times 10^5$  Da at 50 °C, respectively (26, 27). The



**Figure 8.** Changes in the calculated depletion interaction potential  $[-w_{\text{dep}}(0)]$  (solid line) and the rate of coalescence ( $K_c$ ) (dotted line) of emulsions containing xanthan gum (■), guar gum (▲), or  $\kappa$ -carrageenan (●) versus concentration added (percent).

average radii of gyration are  $\sim 100$ ,  $\sim 150$ , and  $\sim 50$  nm for xanthan gum, guar gum, and  $\kappa$ -carrageenan, respectively (26, 27). Using the above theory, the droplet–droplet interaction potential,  $-w_{\text{dep}}(0)$ , in the emulsions ( $r_d$  was  $\sim 0.5 \mu\text{m}$ ) induced by polysaccharides was calculated, and the changes in  $-w_{\text{dep}}(0)/kT$  with varying xanthan gum, guar gum, or  $\kappa$ -carrageenan concentrations are shown in **Figure 8**. The  $-w_{\text{dep}}(0)$  increased with increasing concentration of polysaccharides; the increase in  $-w_{\text{dep}}(0)$  in the emulsions containing guar gum was considerably larger than that in the emulsions containing xanthan gum or  $\kappa$ -carrageenan, and the emulsions containing  $\kappa$ -carrageenan had the lowest increase in  $-w_{\text{dep}}(0)$ . At 0.05%, the interaction potentials,  $-w_{\text{dep}}(0)$ , of emulsions containing xanthan gum, guar gum, or  $\kappa$ -carrageenan were  $12.8kT$ ,  $5.5kT$ , or  $1.3kT$ , respectively. The results of this calculation indicate that the extent of flocculation in the emulsions containing polysaccharides followed the order guar gum > xanthan gum >  $\kappa$ -carrageenan, which is consistent with the results of the rate of coalescence and creaming in these emulsions (**Figure 3**). The trends of changes in the rate of coalescence in the emulsions were similar to the trends of changes in  $-w_{\text{dep}}(0)$  (**Figure 8**). This indicates that the coalescence of emulsions is driven by the depletion interaction force between the droplets and that the rates of coalescence in emulsions containing different polysaccharides largely depend on the strength of depletion force, which in turn depends on the radius of gyration and the molecular weight of the polysaccharide.

It was also noted that, in the emulsions containing high concentrations ( $\geq 0.1\%$ ) of polysaccharide, the increase in  $K_c$  with concentration was slower than the increase in  $-w_{\text{dep}}(0)$  with concentration (**Figure 8**). This may suggest that other factors, that is, increased viscosity because of the presence of polysaccharides, would also influence the coalescence of emulsion droplets. Higher viscosity as a result of the presence of polysaccharides could slow the rate of drainage. It is interesting to note that the viscosity of emulsions containing xanthan gum was higher than that of emulsions containing guar gum at the same concentration (**Figure 7**). Therefore, the higher rate of coalescence in the emulsions containing guar gum was probably a result of a higher droplet–droplet interaction potential,  $-w_{\text{dep}}(0)$ , and a lower viscosity.

In the emulsions containing  $\kappa$ -carrageenan, a gel was formed at concentrations  $\geq 0.1\%$ . Creaming did not occur, and the rate of coalescence was lower in the gelled emulsions. However, CLSM micrographs showed that flocculation of droplets had occurred in these emulsions (**Figure 6**); this flocculation may have occurred before the emulsion gel was formed, because the emulsions were homogenized at 60 °C. At this temperature,  $\kappa$ -carrageenan has a coil (disordered state) structure; the coil structure could induce depletion flocculation, which would subsequently enhance the coalescence of droplets. When  $\kappa$ -carrageenan undergoes a coil to helix (ordered state) transition to form a gel at temperatures  $< 25$  °C, coalescence is markedly reduced.

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