

Creaming Stability of Flocculated Monodisperse Oil-in-Water Emulsions

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Received October 4, 1999; accepted February 3, 2000

The influence of droplet flocculation on the creaming stability of monodisperse *n*-hexadecane oil-in-water emulsions was studied. The creaming velocity of emulsions with different droplet radii (0.43 and 0.86 μm), droplet concentrations (1–67 vol%), and sodium dodecyl sulfate (SDS) concentrations (7–80 mM) were measured. Depletion flocculation was observed in the emulsions when the aqueous phase SDS concentration exceeded a particular level (~ 40 mM for 0.43- μm droplets and ~ 15 mM for 0.86- μm droplets). Creaming was monitored by measuring the back-scattered light from an emulsion as a function of its height. The creaming velocity increased with increasing flocculation and decreased with increasing droplet concentration. These results have important implications for the formulation of emulsion-based materials. © 2000 Academic Press

Key Words: emulsions; flocculation; monodisperse; creaming; SDS.

INTRODUCTION

Many natural and manufactured materials exist in emulsified forms, such as biological fluids, pharmaceuticals, agrochemicals, petrochemicals, foods, cosmetics, and explosives (1–4). The physicochemical characteristics of these materials are strongly influenced by droplet flocculation (5–7). The fraction of droplets that are flocculated, the spatial arrangement of the droplets within the flocs, and the strength of the attractive forces between the droplets ultimately determine the physical characteristics of a flocculated emulsion. Our ability to understand and predict the behavior of emulsified materials therefore depends on a good understanding of the relationship between colloidal interactions, floc structure, and bulk physicochemical properties (4).

Understanding of this area has improved considerably in recent years because of advances in theory, computational modeling, and analytical techniques. Theoretical equations have been developed to describe many of the interactions that exist between colloidal particles, e.g., van der Waals, electrostatic, steric, hydration, hydrophobic, depletion, and hydrodynamic (8). Theories have been developed to relate the bulk physical properties of emulsions to the characteristics of the droplets that they contain (5–7, 9). Computer modeling techniques are being used to investigate the relationship among colloidal interactions, collision

mechanisms, and floc structure (10–13). Analytical instruments are available to directly measure forces between the particles and surfaces (8, 14, 15). Imaging and scattering techniques can be used to provide information about the spatial arrangement of droplets in flocculated emulsions (16–19). A variety of sophisticated analytical instruments are now commercially available for characterizing the bulk physical properties of emulsions. Progress made in this area has been reviewed in a number of articles (5–7, 20–24).

The objective of the current study is to examine the influence of droplet flocculation on the creaming stability of monodisperse oil-in-water emulsions. Monodisperse droplets were used because this greatly facilitates the interpretation of the physical characteristics of colloidal dispersions. Depletion flocculation was induced in the emulsions by the addition of surfactant micelles (sodium dodecyl sulfate).

CREAMING OF FLOCCULATED EMULSIONS

The creaming rate of an isolated rigid spherical particle in an ideal liquid is given by Stoke's law (9),

$$U = -\frac{2gr^2(\rho_2 - \rho_1)}{9\eta_1}, \quad [1]$$

where U is the creaming velocity, η is the shear viscosity, r is the particle radius, g is the acceleration due to gravity, ρ is the density, and the subscripts 1 and 2 refer to the continuous and dispersed phases, respectively.

The creaming rate of a flocculated emulsion depends on the size, concentration, and structure of the flocs. If one assumes that the flocs are spherical and the system is dilute, then Stoke's Law can be used to predict the creaming velocity, except the characteristics of the individual droplets (r , ρ_2) are replaced by those of the flocs (r_{floc} , ρ_{floc}):

$$U_{\text{floc}} = -\frac{2gr_{\text{floc}}^2(\rho_{\text{floc}} - \rho_1)}{9\eta_1}. \quad [2]$$

The radius (r_{floc}) and density (ρ_{floc}) of flocs depend on the number of droplets per floc (n) and the internal packing (ϕ_i) of the droplets within the flocs. If it is assumed that the flocs are spherical, then their internal packing is given by the expression

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$\phi_i = V/V_{\text{floc}}$, where V is the volume of the droplets within the floc ($=4n\pi r^3/3$) and V_{floc} is the volume of the floc ($=4\pi r_{\text{floc}}^3/3$). The expressions for V and V_{floc} can be inserted into the expression for ϕ_i to give the following equation,

$$r_{\text{floc}} = r \cdot \sqrt[3]{\frac{n}{\phi_i}}, \quad [3]$$

where ϕ_i is independent of the floc size. This equation indicates that the floc size should increase as the number of droplets within it increases or the packing density decreases. If it is assumed that the droplets form fractal aggregates with a fractal dimension of D , then the floc size is related to the internal packing of the droplets within the floc by (25):

$$r_{\text{floc}} = r \cdot \phi_i^{1/(D-3)}. \quad [4]$$

This equation indicates that the size of a fractal floc increases as the fractal dimension decreases because the packing of the droplets within the flocs becomes more open. It should be noted that, for a constant fractal dimension, the internal packing of the droplets within the flocs decreases as the floc size increases (since $D < 3$).

The density of the flocs can be calculated from knowledge of the packing of the droplets within them:

$$\rho_{\text{floc}} = \phi_i \rho_2 + (1 - \phi_i) \rho_1. \quad [5]$$

Flocculation increases the effective size of the particles within the emulsion (which enhances creaming), while decreasing the density contrast between the particles and the surrounding fluid (which retards creaming). The overall influence of flocculation on the creaming velocity can be conveniently characterized by a creaming instability ratio: U_{floc}/U . For dilute emulsions this ratio can be calculated using Stoke's law (Eqs. [1] and [2]) and the density of the flocs (Eq. [5]):

$$\frac{U_{\text{floc}}}{U} = \frac{r_{\text{floc}}^2 \phi_i}{r^2} \quad [6]$$

As expected, this equation predicts that the creaming rate should increase as the size of the flocs increases or as the droplets become more densely packed within the flocs. For a fractal floc the creaming instability ratio is related to the fractal dimension:

$$\frac{U_{\text{floc}}}{U} = \left(\frac{r_{\text{floc}}}{r} \right)^{D-1}. \quad [7]$$

Since D ranges between 1 and 3, flocculation should always cause an increase in creaming velocity in dilute emulsions containing fractal flocs.

In a concentrated nonflocculated suspension the creaming velocity is reduced because of hydrodynamic interactions between the particles and can be described by a semiempirical

Eq. [9],

$$U_{\phi} = U \left(1 - \frac{\phi}{\phi_c} \right)^{k\phi_c}, \quad [8]$$

where ϕ is the disperse phase volume fraction and ϕ_c and k are parameters that depend on the nature of the spherical particles. Normally, ϕ_c is related to the disperse phase volume fraction at which the spherical particles become close packed. This equation predicts that the creaming velocity decreases as the droplet concentration increases until creaming is completely inhibited once a certain disperse phase volume fraction (ϕ_c) has been exceeded. In a first approximation, the creaming velocity of a concentrated suspension containing spherical flocs can be described by the same equation by replacing U with U_{floc} and ϕ with $\phi_{\text{floc}} (= \phi/\phi_i)$:

$$U_{\phi} = U_{\text{floc}} \left(1 - \frac{\phi}{\phi_c \phi_i} \right)^{k\phi_c}. \quad [9]$$

EXPERIMENTAL PROCEDURES

Materials

n-Hexadecane and sodium dodecyl sulfate (SDS) were purchased from the Sigma Chemical Co. (St. Louis, MO). Distilled and de-ionized water was used for the preparation of all solutions and emulsions.

Preparation of Monodisperse Emulsions

A polydisperse emulsion was prepared by homogenizing 20 vol% *n*-hexadecane oil and 80 vol% surfactant solution (7 mM SDS) using a high-pressure valve homogenizer (APV-Gaulin, Model Mini-Lab 8.30H, Wilmington, MA). This emulsion was fractionated into a series of monodisperse emulsions by inducing depletion flocculation with different SDS concentrations (26). The polydisperse emulsion was placed in a separating funnel and sufficient SDS was added to cause droplets larger than some critical size (determined by the SDS concentration) to flocculate, leaving the smaller droplets nonflocculated. The flocculated droplets rapidly creamed to the top of the emulsion where they were separated from the remainder of the droplets by being decanted off the lower layer. This procedure was repeated either directly on the lower layer or on the creamed layer after re-dispersion of the droplets in aqueous phase. By using a range of different SDS concentrations, it was possible to fractionate the polydisperse emulsion into a number of differently sized monodisperse emulsions. Two different monodisperse emulsions were used in this study.

Creaming Measurements

The creaming stability of emulsions was monitored by measuring the backscattering of monochromatic light ($\lambda = 850 \text{ nm}$)

from an emulsion as a function of its height (Quickscan, Coulter Corp., Miami, FL). Emulsions were placed into flat-bottomed cylindrical glass tubes (100-mm height, 16-mm internal diameter) and stored at room temperature. The backscattering of light from emulsions was then measured with height at different times. The results are presented as the full creaming profile (backscattering versus height) or as the creaming velocity. The creaming velocity (U) was determined from a slope of a plot of the height of the lower layer (H_L) versus time (t) in the initial stages of creaming: $U = \Delta H_L / \Delta t$ (27). The height of the serum layer was defined as occurring at a position where the backscattering of light was halfway between the value in the lower and that in the middle layers of the emulsion.

Two monodisperse emulsions were used in this study. The radius of the droplets in these emulsions was determined from the measured creaming velocity in the 1% nonflocculated emulsions ($\phi = 1\%$) using Eqs. [1] and [2] and knowledge of the viscosity ($\eta_1 = 0.89$ mPa s) and densities ($\rho_1 = 997$ kg m⁻³, $\rho_2 = 773$ kg m⁻³) of the component phases. Values of $r = 0.43$ and 0.86 μm were determined for the emulsions with the smaller and larger droplets, respectively. These values were in reasonable agreement with the values of $r = 0.52$ and 1.08 μm determined for the small and large emulsions using a laser diffraction technique (LA 900, Horiba, Irvine, CA).

RESULTS AND DISCUSSIONS

Preparation of Flocculated and Nonflocculated Emulsions

Previous workers have shown that oil-in-water emulsions with different degrees of droplet flocculation can be created by adding excess surfactant micelles to the aqueous phase (26). The micelles are excluded from a narrow region (approximately equal to their radius) surrounding the droplets, which leads to an osmotic pressure that manifests itself as an attractive force between the droplets. Above a certain micelle concentration, referred to as the critical flocculation concentration (CFC), the attractive forces dominated the repulsive forces and the droplets flocculated. A preliminary experiment was therefore carried out to determine the surfactant concentrations required to produce flocculated and nonflocculated emulsions. In dilute emulsions flocculation leads to rapid creaming and an increase in viscosity. The creaming velocity of 0.43 and 0.86 μm of monodisperse emulsions were therefore measured (Fig. 1). The creaming velocity was relatively slow at low surfactant concentrations but increased rapidly once the CFC was exceeded (Fig. 1). These measurements indicated that the CFCs were approximately 15 and 40 mM for 0.86 - and 0.43 - μm monodisperse emulsions, respectively. The increase in CFC with decreasing droplet radius is well established in the literature (26) and is due to the fact that the magnitude of the depletion attraction increases with droplet size. In subsequent studies we used emulsions with aqueous phase concentrations of 7 and 80 mM SDS as representatives of nonflocculated systems and flocculated systems, respectively.

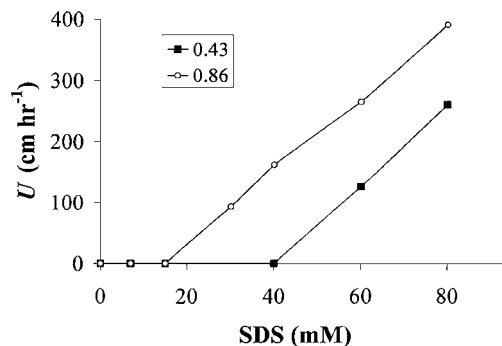


FIG. 1. Creaming velocities of 1% monodisperse *n*-hexadecane oil-in-water emulsions containing different concentrations of SDS in the aqueous phase. The droplet radii are given in the annotation box in μm .

Influence of Flocculation on Creaming Stability

The creaming stability of nonflocculated and flocculated 5% *n*-hexadecane emulsions with the same droplet radius ($r = 0.86$ μm) was monitored by measuring the backscattering of laser light as a function of height over 33 h (Figs. 2 and 3). For all of the emulsions the backscattering of light was fairly constant along their entire height at the beginning of the experiment because there was an even distribution of droplets throughout the system. Over time the droplets moved upward due to gravity which caused a decrease in the backscattering at the bottom of the emulsions (because the droplet concentration decreased) and an increase at the top (because the droplet concentration increased). It was convenient to divide the emulsion into three layers: (a) a lower layer, largely devoid of droplets; (b) a middle layer, with approximately the same droplet concentration as the original emulsion; and (c) an upper layer, where the droplets were closely packed (27). As the droplets moved upward, the thickness of the lower (H_L) and upper (H_U) layers increased, but the thickness of the middle layer (H_M) decreased (Figs. 2 and 3). In some of the emulsions, the middle layer completely disappeared after a certain time because all the droplets reached the upper layer and became closely packed together (Fig. 3). There

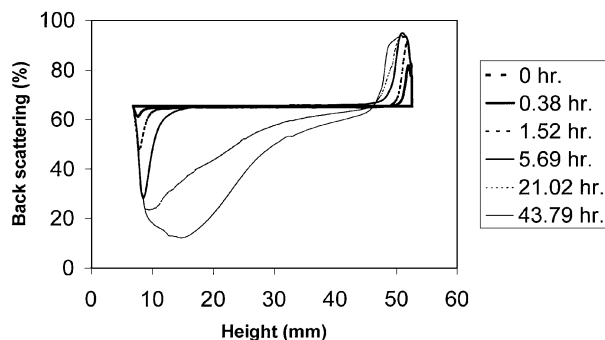


FIG. 2. Creaming profiles of nonflocculated 5% monodisperse *n*-hexadecane oil-in-water emulsions ($r = 0.86$ μm , SDS = 7 mM).

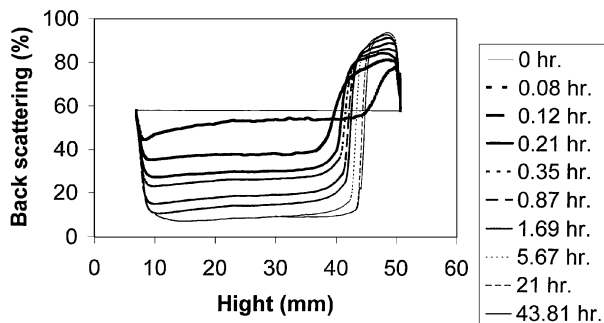


FIG. 3. Creaming profiles of flocculated 5% monodisperse *n*-hexadecane oil-in-water emulsions ($r = 0.86 \mu\text{m}$, SDS = 80 mM).

was also a decrease in the backscattering from the middle layer in the flocculated emulsions, presumably because flocculation reduced the extent of light scattering.

The creaming behavior of nonfloculated and flocculated emulsions was clearly different (Figs. 2 and 3). Creaming was much more rapid in the flocculated emulsion than in the nonfloculated emulsion, as would be expected because of the increase in the size of the particles in the system (Eq. [6]). The creaming velocity of nonfloculated and flocculated emulsions with different droplet concentrations was also measured (Figs. 4 and 5). The creaming velocity of dilute (3%) flocculated emulsions was over 3 orders of magnitude faster than that of the nonfloculated emulsions, i.e., $U_{\text{floc}}/U \sim 1600$. If we assumed that the droplets were close packed ($\phi_i = 0.63$) and approximately spherical, then this ratio corresponds to a floc radius of about $43 \mu\text{m}$ (Eq. [6]). The measured floc size would be greater if the droplets were more openly packed (Eq. [6]) or had a fractal structure ($D < 3$) (Eq. [7]).

As the droplet concentration increased, the creaming velocity of both emulsions decreased (Fig. 6) because of hydrodynamic effects and particle–particle interactions (9). At sufficiently high droplet concentrations the creaming became extremely slow ($U < 0.01 \text{ cm h}^{-1}$), presumably because the droplets were so closely packed together that their movement was severely restricted. Examination of the full creaming profile clearly shows the retardation of creaming when the droplet concentration is

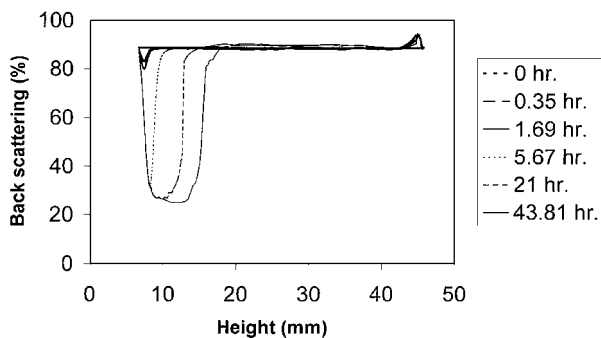


FIG. 4. Creaming profiles of flocculated 33% monodisperse *n*-hexadecane oil-in-water emulsions ($r = 0.86 \mu\text{m}$, SDS = 80 mM).

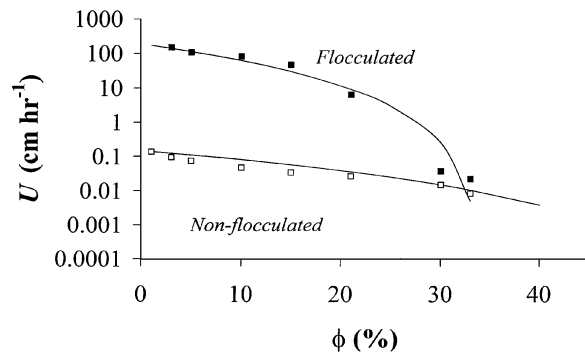


FIG. 5. Concentration dependence of the creaming velocity of flocculated (SDS = 80 mM) and nonfloculated (SDS = 7 mM) *n*-hexadecane emulsions ($r = 0.86 \mu\text{m}$).

increased from 5% to 33% (Fig. 4). The dependence of the creaming velocity on droplet concentration for the nonfloculated emulsions was calculated using Eq. 8 and the values of $k = 5.4$ and $\phi_c = 0.585$ were determined for spherical hard spheres in a previous study (9). For the flocculated emulsions we used Eq. [9] and assumed that the droplets within the flocs were packed closely so that $\phi_i = \phi_c = 0.585$. There was very good agreement between the experimental measurements and the predictions made using this approach for both emulsions (Fig. 6). This suggests that the creaming behavior of the flocculated emulsions used in this study could be described using existing semiempirical equations, provided the increase in effective volume fraction of the particles due to flocculation was taken into account. It is possible that the previous approach would not be applicable for emulsions where flocculation was induced by a different mechanism (e.g., electrostatic screening or hydrophobic attraction) than the one used in this study (i.e., depletion).

The final thickness of the upper layer provides some insight into the packing of the droplets within the flocs. The thickness of the creamed (upper) layer of nonfloculated and flocculated emulsions containing different initial droplet concentrations was measured after 48 h (Table 1). The packing of the droplets within the upper layer (ϕ_U) was calculated from the following

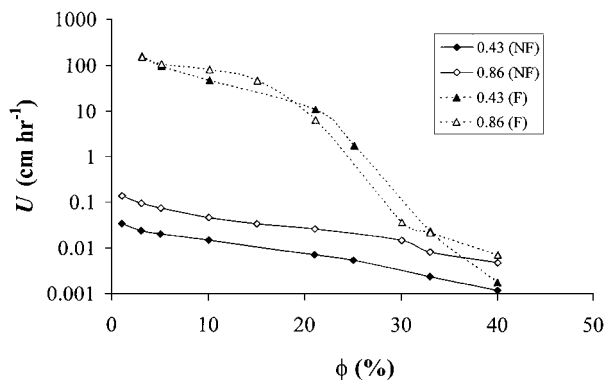


FIG. 6. Influence of droplet size on the creaming velocity of *n*-hexadecane emulsions.

TABLE 1

Thickness of Creamed Layer and Calculated Packing Parameter ($\phi_c = 100\phi/[\% \text{ Thickness}]$) of Droplets within the Creamed Layer of Nonfloculated and Floculated *n*-Hexadecane Emulsions ($d = 0.86 \mu\text{m}$) after 48 h of Storage

ϕ (%)	Nonfloculated		Floculated	
	Thickness (%)	ϕ_c (%)	Thickness (%)	ϕ_c (%)
10	20	50	24	41
15	29	51	34	44
21	40	53	43	49
30	61	49	61	49
33	74	45	74	45
40	90	45	81	50
	Mean: $48.8 \pm 3.2\%$		Mean: $46.3 \pm 2.5\%$	

relationship: $\phi_U = \phi H_E/H_U$. The droplet packing was relatively insensitive to the initial droplet concentration and was approximately the same for nonfloculated and floculated emulsions, being about 47%. This value is significantly less than the value expected for close packing, $\phi_c = 58.5\%$, which may be because of electrostatic repulsion between the droplets or because the droplets are not able to adopt their most densely packed arrangement within the creamed layer. The fact that the droplets in both emulsions had fairly similar packing densities suggests that the droplets were not strongly aggregated in the floculated emulsions. The depletion attraction is a relatively weak type of droplet–droplet interaction (4), and so the droplets within the flocs are able to change their configurations and pack relatively efficiently within the creamed layer.

Influence of Droplet Size

The creaming stability of nonfloculated and floculated emulsions containing monodisperse droplets of different radii (0.43 and 0.86 μm) were measured (Fig. 6). The creaming velocity of droplets in the nonfloculated emulsions increased with increasing droplet size as expected; however, that in the floculated emulsions was relatively insensitive to droplet size. This suggests that the size of the flocs in both emulsions was fairly similar.

CONCLUSIONS

The creaming stability of monodisperse oil-in-water emulsions is strongly influenced by droplet flocculation. The creaming velocity increased with droplet flocculation because of the increase in particle size and decreased with droplet concentration because of hydrodynamic effects and particle–particle interactions. The creaming velocity of floculated emulsions could be approximately modeled using equations developed to describe creaming in nonfloculated systems, provided the increase in the effective volume fraction due to flocculation was taken into account. These results have important implications for the formu-

lation of many types of commercially important emulsion-based products.

ACKNOWLEDGMENTS

This material is based upon work supported by the Cooperative State Research, Education and Extension Service, U.S. Department of Agriculture, under Agreement 97-35503-4371. We also thank Coulter Corp. for providing the Quicksan instrument used in these experiments.

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