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Latex-Particle-Stabilized Emulsions of Anti-Bancroft Type

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Here, we investigate water-in-oil (W/O) emulsions that are stabilized by polystyrene latex particles with sulfate surface groups. The particles, which play the role of emulsifier, are initially contained in the disperse (water) phase. The existence of such emulsions formally contradicts the empirical Bancroft rule. Theoretical considerations predict that the drop diameter has to be inversely proportional to the particle concentration, but should be independent of the volume fraction of water. In addition, there should be a second emulsification regime, in which the drop diameter is determined by the input mechanical energy during the homogenization. The existence of these two regimes has been experimentally confirmed, and the obtained data agree well with the theoretical model. Stable W/O emulsions have been produced with hexadecane and tetradecane, while, in the case of more viscous and polar oils (soybean and silicone oil), the particles enter into the oily phase, and Pickering emulsions cannot be obtained. The formation of stable emulsions demands the presence of a relatively high concentration of electrolyte that lowers the electrostatic barrier to particle adsorption at the oil−water interface. Because the attachment of particles at the drop surfaces represents a kind of coagulation, it turns out that the Schulze−Hardy rule for the critical concentration of coagulation is applicable also to emulsification, which has been confirmed with suspensions containing Na^+, Mg^{2+}, and Al^{3+} counterions. The increase of the particle and electrolyte concentrations and the decrease of the volume fraction of water are other factors that facilitate emulsification in the investigated system. To quantify the combined action of these factors, an experimental stability−instability diagram has been obtained.

1. Introduction

Particle-stabilized (Pickering) emulsions have attracted considerable attention because of their interesting properties as surfactant-free fluid dispersions[1,2] and their potential use for the development of novel materials.[3−5] The particle hydrophilicity/hydrophobicity plays a central role in the production of such emulsions. As a rule, hydrophilic particles (θ < 90°) stabilize oil-in-water (O/W) emulsions, while hydrophobic particles (θ > 90°) stabilize water-in-oil (W/O) emulsions.[1,2] (Here, θ denotes the three-phase contact angle, measured across the water phase.) In the produced emulsion, the continuous phase becomes this phase, in which the adsorbed particles exhibit greater protrusion. This rule is related to the fact that the steric stabilization is predominant for Pickering emulsions.[6−8]

Particles of inorganic materials, such as silica[9−16] and clay,[17−20] have been most frequently used as emulsion stabilizers. Nanocomposite microgel particles have been also used.[21] So far, organic latex particles, which are probably the most widespread type of monodisperse colloids, have found a relatively narrow application as emulsifiers.[22−28] The reason seems to be that, under normal conditions, the latex particles (initially dispersed in water) do not adsorb at the oil−water interface. The latex particles usually

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have a considerable negative surface electric charge, and, because of that, they are repelled from the like-charged oil−water interface.[29]

By addition of electrolyte (between 0.3 and 2.1 M NaCl in ref 24) the electrostatic barrier to particle adsorption could be suppressed. This facilitates the particle adsorption and the formation of stable emulsions. Binks and Rodrigues[24] used special polystyrene particles, whose surfaces are coated with ionizable carboxylic acid groups. The surface charge and surface hydrophilicity/hydrophobicity were controlled by the variation of pH. Inversion of the emulsion type was effected by a change in either the pH value or salt concentration.[24] In another series of experiments, specially synthesized latex particles were used, which were sterically stabilized by grafted cationic diblock copolymer.[25−28] At pH = 8, the surface charge is neutralized, and stable Pickering emulsions are formed, which could be either O/W or W/O depending on the type of oil used. On the other hand, at pH = 3, the particles become positively charged, and the formation of O/W emulsions only was observed with some oils.[27] In addition, temperature-induced phase inversion was established for the emulsions stabilized by these particles.[28]

In the case of common latex particles (like those with sulfate surface groups), the produced emulsions are of W/O type.[3,22] This system exhibits two intriguing properties. First, the particles are hydrophobic, but they are dispersed in water (thanks to the ionizable sulfate surface groups). Model experiments by Ashby et al.[30] and by Stancik and Fuller[31] showed that the contact angle of the latex particles at the oil−water interface is $\theta = 130−140°$. Having once adsorbed at the oil−water interface, such particles exhibit a predominant protrusion in the oil phase, and it is not surprising that they stabilize W/O emulsions.

Second, in the stable W/O emulsions, the emulsifier (the latex particles) is contained in the disperse phase (in the drops). This fact contradicts the empirical Bancroft rule, which states that "in order to have a stable emulsion, the emulsifier must be soluble in the continuous phase".[32] For brevity, emulsions that obey or disobey the latter rule are sometimes called *Bancroft* and *anti-Bancroft* emulsions, respectively.[33] To understand why anti-Bancroft emulsions could be stable, we have to address the physicochemical explanation of the Bancroft rule. According to the hydrodynamic theory by Ivanov and Traykov,[34] which has been experimentally confirmed,[35] when the surfactant is dissolved in the drop phase, it efficiently suppresses the surface (Gibbs) elasticity of the adsorption monolayer (the surface-tension gradients are damped by the supply of surfactant from the drop interior), and then the film between two colliding drops drains much faster than it does in the case when the surfactant is in the continuous phase. This effect tends to increase the rate of coalescence in the respective emulsion and leads to its destabilization (unless the drops are protected by a considerable repulsive surface force).[36,37] In the case of Pickering emulsions, the stability is ensured by the steric effect of dense (shell-like) particle adsorption layers, while the surface elasticity plays a secondary role (if any). In other words, the stability of the considered Pickering emulsions of "anti-Bancroft" type requires the formation of closely packed particle monolayers, which provide steric stabilization.

Stable Pickering emulsions have also been observed in the case when the particle adsorption monolayers are not closely packed.[9,12,38−40] In some experiments,[38,39] polystyrene particles were found to form small patches of local hexagonal order, separated by particle-free domains. The latter indicates the presence of predominant interparticle *attraction*, which would favor the formation of dense particle monolayers upon adsorption of additional particles. In other experiments,[40] the electrostatic *repulsion* between the adsorbed particles was predominant, which led to the formation of two-dimensional hexagonal lattices of great interparticle separation. In this case, the formation of stable emulsions is also possible because of the appearance of close-packed bridging monolayers of particles between the drops.[40]

The aim of the present study is to investigate in more detail the formation and properties of W/O emulsions stabilized by polystyrene latex particles with sulfate surface groups. We explore the effects of the type of oil, type and concentration of electrolyte, and the effect of the particle volume fraction on the mean drop size in the produced emulsions. The paper is organized as follows: Section 2 presents the physical background in relation to the expected dependence of the drop size on the particle concentration. Section 3 describes the experiment. Section 4 presents the results and their interpretation. Finally, in section 5 we consider the system's stability−instability diagram in terms of the concentrations of particles and electrolyte.

2. Physical Background

2.1. Case of Anti-Bancroft Emulsions. As mentioned above, here we consider Pickering emulsions in the case when the particles have been initially located in the drop phase. It is helpful to first discuss and analyze available experimental data for such system.

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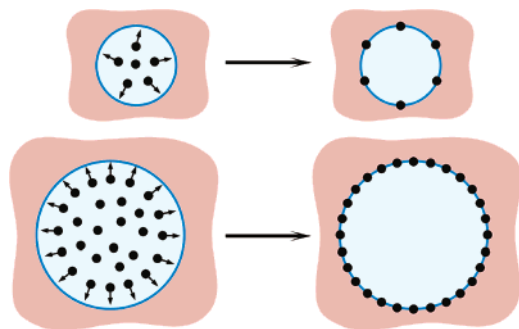
Figure 1. Sketch of emulsion drops, initially containing a given number of particles, which subsequently adsorb at the oil−water interface. At the same bulk concentration of particles, the surface coverage will be denser for the larger drop.

Binks and Lumsdon[41] reported interesting results for toluene−water emulsions stabilized by hydrophobic silica particles (see Figure 10 therein). The particles had been dispersed in the toluene at a fixed weight fraction, $\varphi_p = 0.02$. For a volume fraction of water $\Phi_w \leq 0.65$, the produced emulsions were of Bancroft type, that is, water-in-toluene, with particles in the continuous phase. For $\Phi_w > 0.65$, the produced emulsions were of anti-Bancroft type (toluene-in-water) with particles in the drops. It is interesting to note that the average drop diameter in the obtained Bancroft-type emulsions was $2R \approx 0.6$ μm, whereas, in the anti-Bancroft emulsions, $2R \approx 100$ μm, that is, much greater.[41]

A possible explanation of the drop size in the anti-Bancroft emulsion is the following. An emulsion drop initially contains a certain number of particles, which are expected to adsorb on the drop surface. A bigger drop contains more particles, which would form a denser monolayer upon adsorption (Figure 1). In other words, if the number of particles within a drop is $N \propto R^3$, while the drop surface area is $A \propto R^2$, then the surface coverage will increase proportionally to the drop radius: $\Gamma = N/A \propto R$.

For a more detailed description of this effect, we first express the number, N_p, of the spherical particles of radius a, which are contained on the surface of a drop of radius R, at surface coverage φ_a:

$$N_p = \frac{4\pi R^2 \varphi_a}{\pi a^2} = 4\varphi_a \frac{R^2}{a^2} \qquad (1)$$

Here, φ_a is the fraction of the surface area that is covered by adsorbed particles. At close packing, we have $\varphi_a = \pi/(12)^{1/2} \approx 0.907$. The bulk mass fraction, φ_p, of the solid particles in an oil drop of radius R is

$$\varphi_p = \frac{M_p}{M_p + M_s} =$$

$$\frac{(4/3)\pi a^3 N_p \rho_p}{(4/3)\pi a^3 N_p \rho_p + ((4/3)\pi R^3 - (4/3)\pi a^3 N_p)\rho_s} \qquad (2)$$

M_p and ρ_p are the total mass and mass density of the particles, respectively, while M_s and ρ_s are the mass and mass density of the solvent contained in the drop, respectively. Substituting eq 1 into eq 2, after some transformations, we obtain

$$\varphi_p = \frac{\rho_{ps}}{\rho_{ps} + R/(4\varphi_a a) - 1} \qquad (3)$$
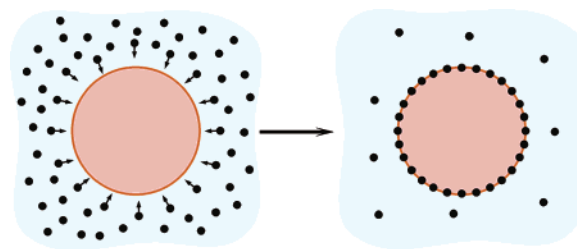
Figure 2. The inverted system (with respect to Figure 1): The drops are in contact with a large reservoir of particles dispersed in the continuous phase. Then, the density of the particle adsorption monolayer is not sensitive to the drop size.

where $\rho_{ps} \equiv \rho_p/\rho_s$. Solving eq 3 with respect to R, we obtain an expression for the diameter of the smallest *stable* drop:

$$d_S \equiv 2R = 8a\frac{\varphi_a}{\varphi_p}[\rho_{ps} - (\rho_{ps} - 1)\varphi_p] \qquad (4)$$

Equation 4 shows how large the mean drop diameter must be in order to have a stable drop, supposing that *all* particles (of bulk mass fraction φ_p) contained in the drop have been adsorbed on its surface, and that the surface coverage φ_a is high enough to protect the drops against coalescence during the collisions between them.

For the system in ref 41, we have $\varphi_p = 0.02$, $\rho_p = 2.7$ g/cm^3 (quartz), $\rho_s = 0.86$ g/cm^3 (toluene), and $d_S \approx 100$ μm. With the latter parameter values, assuming full coverage, $\varphi_a \approx 0.9$; from eq 4, we calculate $2a = 179$ nm. The latter value of the particle diameter is reasonable because the considered silica particles have been found to form aggregates having diameters on the order of 100 nm in toluene.[41] Hence, there is a good chance that eq 4 (and the underlying concept, Figure 1) provides the correct explanation of the drop size in the anti-Bancroft emulsions. In sections 2.3 and 4, this explanation is tested against our data for anti-Bancroft W/O emulsions stabilized by latex particles. (Note that, in ref 41, the anti-Bancroft emulsions are of O/W type.)

For small particle mass fractions ($\varphi_p \ll 1$), and/or for close densities of the particles and the solvent ($\rho_{ps} = \rho_p/\rho_s \approx 1$), we have ($\rho_{ps} - 1)\varphi_p \ll 1$, and then eq 4 reduces to

$$d_S \approx \frac{8a\varphi_a\rho_{ps}}{\varphi_p} \text{ (anti-Bancroft emulsion)} \qquad (5)$$

In other words, for stable anti-Bancroft emulsions, d_S should be a linear function of $1/\varphi_p$, with a slope equal to $8a\varphi_a\rho_{ps}$. In a given experiment, all parameters in the latter expression are known (or can be estimated), and one could directly check the adequacy of the theoretical model.

2.2. Case of Bancroft Emulsions. For the Bancroft emulsions (Figure 2), the drops are in contact with a large reservoir of particles dispersed in the continuous phase. In such a case, there are no limitations to achieve full coverage of the drop surface with particles. Then, the size of the drops in the direct emulsion is solely determined by the input of mechanical energy during homogenization (see section 2.3). (This seems to be the case for $\Phi_w \leq 0.65$ in ref 41, in which $2R \approx 0.6$ μm has been obtained.) In the turbulent regime, the Kolmogorov's theoretical approach[42] can be applied to estimate the average drop size (see also refs 43−50). The latter approach is applicable to both emulsions of Bancroft and anti-Bancroft type (see eq 15 below).

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However, the situation with the Bancroft emulsions is different when a large reservoir of particles is missing, and the particle bulk concentration essentially decreases during emulsification. For the limiting case, when all particles available in the continuous phase are adsorbed on the emulsion drops, Arditty et al.[14−16] obtained a dependence, $d_S \propto 1/\varphi_p$, which is similar, but not identical to eq 5.

For comparison with eq 5, here we derive the dependence of d_S on φ_p in the case of Bancroft emulsions in terms of the parameters present in eq 5. The total number of particles is

$$N = N_p N_d \quad (6)$$

N_d is the number of drops, while N_p is the number of adsorbed particles per drop; N_p is given by eq 1 again. For N_d we have

$$N_d = \frac{V_d}{(4/3)\pi R^3} = \frac{3\Phi_d V}{4\pi R^3} \quad (7)$$

where V_d and Φ_d are the volume and volume fraction of the disperse phase in the emulsion, respectively, and V is the total volume of the emulsion. Likewise, for N we obtain

$$N = \frac{\psi_p V_c}{(4/3)\pi a^3} = \frac{3\psi_p(1 - \Phi_d)V}{4\pi a^3} \quad (8)$$

where ψ_p is the volume fraction of the particles in the continuous phase, whose volume is V_c. Substituting eqs 1, 7, and 8 into eq 6, after some transformations, we derive an expression for the diameter of the smallest *stable* drop:

$$d_S \equiv 2R = 8a\varphi_a \frac{\Phi_d}{1 - \Phi_d} \frac{1}{\psi_p} \quad (9)$$

Equation 9 shows how large the mean drop diameter must be in order to have a stable drop, supposing that *all* particles (of bulk volume fraction ψ_p) contained in the continuous phase have been adsorbed on the drops, and that the surface coverage φ_a is high enough to protect the drops against coalescence during the collisions between them. To obtain a relation between the particle mass and the volume fractions, φ_p and ψ_p, we will use a counterpart of eq 2:

$$\varphi_p = \frac{\hat{M}_p}{\hat{M}_p + \hat{M}_s} = \frac{(4/3)\pi a^3 N\rho_p}{(4/3)\pi a^3 N\rho_p + (V_c - (4/3)\pi a^3 N)\rho_s} \quad (10)$$

Here $\hat{M}_p$ and $\hat{M}_s$ are the masses of the particles and the solvent, respectively, which are contained in the continuous phase of volume V_c. With the help of eq 8, from eq 10 we derive

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$$\frac{1}{\varphi_p} = \frac{1}{\rho_{ps}\psi_p} + 1 \approx \frac{1}{\rho_{ps}\psi_p} \quad (11)$$

The neglecting of 1 (at the last step) is correct only for low particle concentrations. Finally, the combination of eqs 9 and 11 yields

$$d_S \approx \frac{8a\varphi_a\rho_{ps}}{\varphi_p} \frac{\Phi_d}{1 - \Phi_d} \text{ (Bancroft emulsion)} \quad (12)$$

The difference between the mean diameters of the smallest stable drops, d_S, given by eq 12 (Bancroft emulsion) and eq 5 (anti-Bancroft emulsion), is in the multiplier, $\Phi_d/(1 - \Phi_d)$. In other words, for the Bancroft emulsions, d_S strongly depends on the volume fraction of the disperse phase, Φ_d, while, for anti-Bancroft emulsions, such dependence is missing. In the special case when $\Phi_d = 0.5$, eqs 5 and 12 coincide.

Of course, the above conclusions are valid if the assumptions used to derive eqs 5 and 12 are fulfilled. Among them, the strongest assumption is that all available particles have been adsorbed at the oil−water interface. If the latter assumption is not fulfilled, deviations from eqs 5 and 12 should be expected. Experimentally, both situations can be observed: (i) practically all particles are adsorbed on the drops,[14−16] or (ii) not all particles have been adsorbed.[51]

An expression equivalent to eq 12 was successfully applied in refs 47−49 to describe the relation between the mean drop size and the emulsifier concentration for emulsions stabilized by globular protein molecules (acting as nanoparticles) or by the nonionic surfactant Brij 58, which were prepared at various oil volume fractions and hydrodynamic conditions (intensity of stirring).

2.3. Kolmogorov Diameter of the Drops. The physical picture of the emulsification in turbulent flow (e.g., rotor−stator homogenizer) is as follows. The turbulent eddies interact with the emulsion drops and cause their breakage into smaller drops. Two different regimes have been identified:[42] (i) In the turbulent-*viscous* regime, the eddies are bigger than the drops and act like a mill. (ii) In the turbulent-*inertial* regime, the eddies are comparable in size or smaller than the drops and could break them upon collision. As a rule, the drops produced in the viscous regime are smaller than those produced in the inertial regime. The Kolmogorov expressions for the mean diameter of the drops produced in the two regimes are[42−46]

$$d_K \approx \epsilon^{-1/2}\sigma_{ow}\eta_c^{-1/2} \text{ (viscous regime)} \quad (13)$$

$$d_K \approx \epsilon^{-2/5}\sigma_{ow}^{3/5}\rho_c^{-1/5} \text{ (inertial regime)} \quad (14)$$

where ϵ is the input mechanical energy per unit time and per unit volume, σ_{ow} is the oil−water interfacial tension, and η_c and ρ_c are the viscosity and mass density of the continuous phase, respectively. It is important to note that eqs 13 and 14 are derived under the assumption that there is no coalescence in the emulsion, that is, all formed drops survive.

The mean drop diameter cannot be smaller than d_K because the input mechanical energy, ϵ, is insufficient to produce smaller drops. However, the mean drop diameter can be greater than d_K if the produced drops can coalesce. In other words, d_K, defined by eq 13 or 14, gives the mean diameter of the drops in noncoalescing emulsions, whereas d_S, defined by eq 5 or 12,

(51) Saleh, N.; Sarbu, T.; Sirk, K.; Lowry, G. V.; Matyjaszewski, K.; Tilton, R. D. Oil-in-water emulsions stabilized by highly charged polyelectrolyte-grafted silica nanoparticles. *Langmuir* **2005**, *21*, 9873−9878.
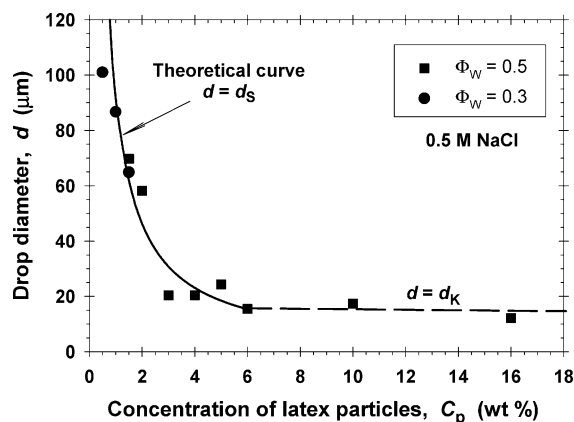
Figure 3. Plot of the drop diameter, d, vs the concentration of latex particles in the water phase, $C_p = \varphi_p \times 100$. The experimental points are for water-in-hexadecane emulsions stabilized by D-latex at two volume fractions of water, $\Phi_w = 0.3$ and 0.5, as denoted in the figure. The theoretical curve is drawn by means of eq 15, along with eqs 5 and 14.

gives the smallest *stable* drops in coalescing emulsions. Hence, for $d_S < d_K$, all produced drops will be stable and will have a mean diameter d_K.

For $d_S > d_K$, the produced drops will again have a mean diameter $d \approx d_K$, but they will be unstable. After ceasing the agitation, such drops will coalesce until reaching diameter $d \approx d_S$, which corresponds to the smallest stable drops (such a process was called limited coalescence in ref 14). Thus, the opposite-acting tendencies (coalescence and breakage of drops) lead to the formation of emulsion drops whose diameter is $d \approx d_S$. (The smaller unstable drops would coalesce, while the bigger drops would be broken by the eddies.)

In this way, we arrive at the following expression for the mean drop diameter:

$$d = \begin{cases} d_S & \text{for } d_S > d_K \\ d_K & \text{for } d_S < d_K \end{cases} \qquad (15)$$

where d_S is given by eq 5 or 12, and d_K is given by eq 13 or 14 (see also refs 47–50).

As an illustration, in Figure 3 we show results for the mean drop diameter in water-in-hexadecane emulsions stabilized by latex particles (details in sections 3 and 4). In our experiments, we have $\epsilon = 2 \times 10^8$ J·m^{-3}·s^{-1} (determined independently in ref 47), $\sigma_{ow} \approx 30$ mN/m, and $\rho_c = 0.773$ g/cm^3. The substitution of the latter values in eq 14 yields $d_K = 15.4$ μm (the horizontal line in Figure 3). In addition, in eq 5, we substitute $\rho_s = 0.998$ g/cm^3 (water), $\rho_p = 1.05$ g/cm^3 (polystyrene latex), $a = 109$ nm, and $\varphi_a = 0.9$. With these parameter values, from eqs 5 and 15, we calculate the theoretical curve $d = d(\varphi_p)$, which is compared with the experimental data in Figure 3. As seen in the figure, the theory and experiment are in a good agreement (no adjustable parameters). The results indicate that, for $\varphi_p < 0.06$, we have a regime of limited coalescence in an anti-Bancroft emulsion (see eq 5 and Figure 4a), while, for $\varphi_p > 0.06$, we are dealing with the Kolmogorov turbulent-inertial regime (see eq 14 and Figure 4b).

3. Experimental Section

3.1. Materials. Two types of polystyrene latex particles (with sulfate surface groups), supplied by Dow Chemical Co. and Lukoil-Neftochim (Bourgas), were used in our experiments. For brevity, here they are cited as D-latex and L-latex, respectively. They were in the form of water suspensions having concentrations of 32 and
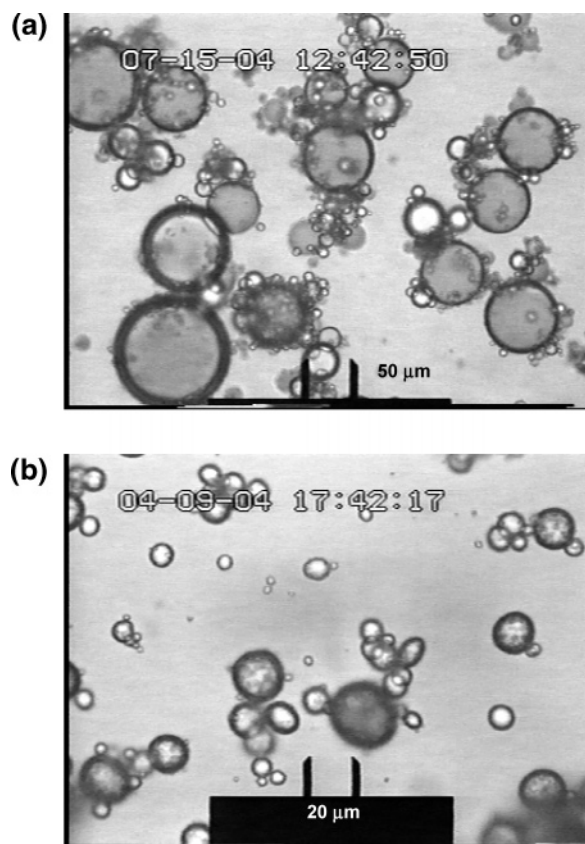

Figure 4. Photographs of water-in-hexadecane emulsions stabilized by D-latex in the presence of 0.5 m NaCl at $\Phi_w = 0.5$. (a) $C_p = 2$ wt %: larger drops of mean diameter $d_S = 58.2$ μm produced in the regime of limited coalescence. (b) $C_p = 10$ wt %: smaller drops of mean diameter $d_K = 17.4$ μm produced in the Kolmogorov regime (see Figure 3).

38 wt %, respectively. The particle size distribution was obtained by dynamic light scattering. The measurements were performed at 27 °C by means of a Malvern Instrument 4700C (UK) with an argon laser (488 nm). We determined the number average particle diameter to be $d_p = 218 \pm 21$ nm for the D-latex (Figure 5a), and $d_p = 193 \pm 31$ nm for the L-latex (Figure 5b).

Four different oil phases were used: tetradecane (dynamic viscosity $\eta = 2.1$ mPa·s, Merck), hexadecane (viscosity $\eta = 3.1$ mPa·s, Merck), silicone oil SO-50 of viscosity $\eta = 50$ mPa·s (Rhodia Silicones), and soybean oil (viscosity $\eta = 50$ mPa·s, commercial vegetable oil). The latter was purified from polar contaminants by passing through a glass column filled with absorbent Silica Gel 60. The interfacial tension of the purified soybean oil against water was 30.0 ± 0.5 mN/m. The other oils were used as received.

The aqueous solutions were prepared with deionized water (Milli-Q Organex system, Millipore). Sodium chloride (NaCl, product of Merck) was used for adjusting the ionic strength of the latex suspension in most of the experiments. In a special series of experiments, we also used other electrolytes: magnesium chloride (MgCl$_2$) and aluminum chloride (AlCl$_3$) (products of Sigma), tetraethylammonium bromide (TEAB) (product of Merck), and sodium citrate (Na$_3$Citrate) (product of Himsnab). To remove any possible organic contaminants, the used NaCl was heated to 500 °C for 3 h. The other electrolytes were used as received.

We measured the air–water and oil–water interfacial tensions, σ_{aw}, and σ_{ow}. The oil phase was hexadecane, and the water phase was latex suspension diluted with pure water to particle weight fraction $\varphi_p = 0.02$. The results are shown in Table 1. The electrical conductivity of the suspension (at $\varphi_p = 0.02$) was measured by a conductivity meter, model 30 (Denver Instrument Co.). The results are given in Table 1 in terms of the concentration of NaCl solution with the same conductivity. Samples of the L-latex were subjected
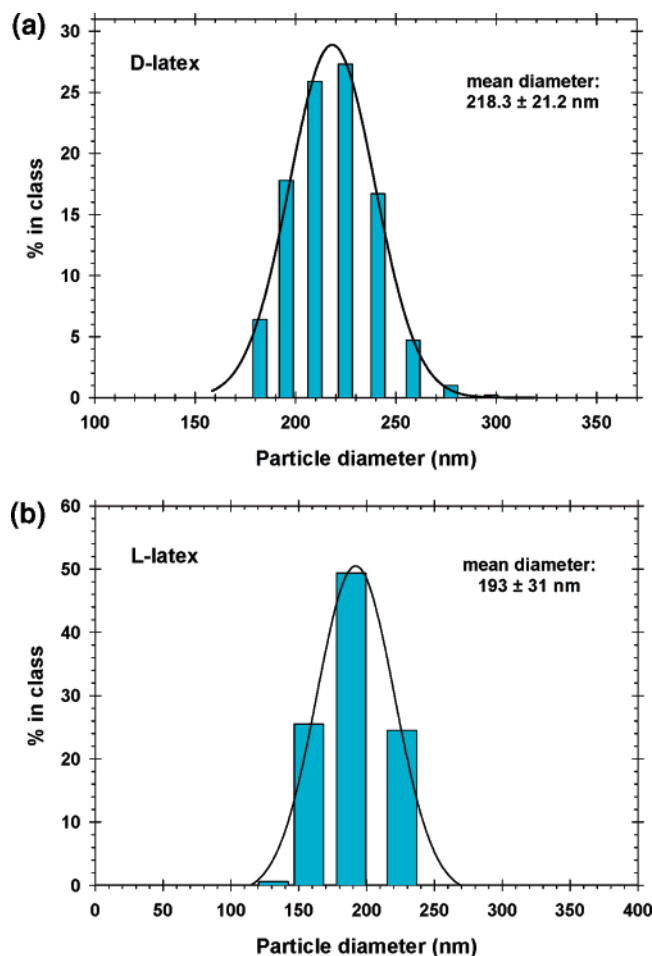
Figure 5. Size distribution of the latex particles determined by dynamic light scattering. (a) D-latex; (b) L-latex.

to dialysis for 30 days. For this purpose, cellulose tubing from Viskasa Co. was used. The values of σ_{aw}, σ_{ow}, and the conductivity in Table 1 indicate that the dialysis partially removes admixtures of surfactant and electrolyte (or ionic surfactant) from the L-latex suspension. As seen in Table 1, the interfacial tensions of the dialyzed L-latex against air and oil are close to those for the D-latex, and for this reason the D-latex was not subjected to dialysis.

3.2. Emulsions. The emulsions were prepared by a rotor–stator homogenizer Ultra Turrax T25 (Janke & Kunkel GmbH) operating at 13 500 rpm. The duration of stirring was 5 min for all emulsions. The drop size distribution in the formed emulsions was determined by optical microscopy. The drops were observed in transmitted light with an Axioplan microscope (Zeiss, Germany), equipped with Epiplan objectives 10×, 20×, and 50×, and connected to a CCD camera (Sony) and video recorder (Samsung SV-4000). The diameters of the recorded drops were measured (one by one, semiautomatically) by using custom-made, image analysis software operating with Targa+ graphic board (Truevision, Indianapolis, IN). For each emulsion, the diameters of at least 1000 drops (all drops on the photographs of several different samples of the same emulsion) were measured to ensure good statistics. The mean volume–surface diameter, d_{32}, was calculated from the size-distribution histogram by using the standard relation

$$d_{32} = \frac{\sum_i N_i d_i^3}{\sum_i N_i d_i^2} \qquad (16)$$

where N_i is the number of drops with diameter d_i.

Table 1. Interfacial Tensions and Conductivity of the Used Suspensions at $\varphi_p = 0.02'$

type of latex suspension	σ_{aw} (mN/m)	σ_{ow} (mN/m)	conductivity NaCl (mM)
D-latex	65.0	35.5	1.595
L-latex (nondialyzed)	55.0	26.0	1.667
L-latex (dialyzed)	60.2	36.7	0.376

The emulsion type was determined by dilution of the emulsion in pure water or oil. (An O/W emulsion disperses in water, while a W/O emulsion disperses in oil.)

4. Experimental Results and Discussion

4.1. Effects of NaCl and the Type of Oil. As known, above a given critical concentration of coagulation, electrolytes suppress the double-layer repulsion and cause aggregation in various colloids.[52–55] In our experiments, we used NaCl to lower the electrostatic barrier to particle adsorption at the oil–water interface. However, the addition of NaCl to the aqueous phase also produces an undesired effect: aggregation of the latex particles.

Our experiments indicate that the two types of aggregation, particle–particle and particle–drop, happen (approximately) at the same threshold concentration, which is $C_{NaCl} = 0.5$ M for the D-latex and the nondialyzed L-latex, and $C_{NaCl} = 0.3$ M for the dialyzed L-latex. It seems that the dialysis removes admixtures of anionic surfactant from the L-latex. This surfactant could adsorb (by its hydrocarbon tail) at hydrophobic portions of the particle surface, thus increasing the surface charge of the nondialyzed L-latex and its stability to coagulation.

An additional fact showed the presence of an admixture of ionic surfactant in the nondialyzed L-latex. With this latex, O/W emulsions were formed at $C_{NaCl} = 0$ and 0.01 M ($\Phi_w = 0.5$, oil phase = hexadecane). Closer inspection (microscopic observations of emulsion films and measurement of their thickness; see, e.g., refs 35 and 36) indicated that these emulsions were surfactant-stabilized, rather than particle-stabilized. At greater electrolyte concentrations, $0.05 < C_{NaCl} < 0.5$ (M), no stable emulsions were produced. For $C_{NaCl} \geq 0.5$ M, the nondialyzed L-latex stabilizes W/O emulsions.

The scanning for various NaCl concentrations showed that the dialyzed L-latex and the D-latex never stabilize O/W emulsions. As mentioned above, W/O emulsions are stabilized by these latexes only for $C_{NaCl} \geq 0.3$ and 0.5 M, respectively (oil = hexadecane and tetradecane). The lower critical concentration of coagulation for the dialyzed L-latex indicates that this latex is more hydrophobic than the D-latex (i.e., it has a lower surface density of sulfate groups). This conclusion is supported by the measured ζ-potentials of the two types of latex particles (Zetasizer 2C, Malvern Instruments, UK). As seen in Table 2, the magnitude of the ζ-potential of the L-latex is markedly lower than that of the D-latex.

Further, we studied the effect of the oily phase on the emulsification. In these experiments, a D-latex suspension of particle weight fraction $\varphi_p = 0.02$ was used. The volume fraction of the water phase in the emulsion was $\Phi_w = 0.5$. The

(52) Schulze, H. Schwefelarsen im wässeriger Losung. *J. Prakt. Chem.* **1882**, 25, 431–452.

(53) Hardy, W. B. A preliminary investigation of the conditions, which determine the stability of irreversible hydrosols. *Proc. R. Soc. London* **1900**, 66, 110–125.

(54) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1992.

(55) Tcholakova, S.; Denkov, N. D.; Sidzhakova, D.; Ivanov, I. B. Campbell, B. Effects of electrolyte concentration and pH on the coalescence stability of β-lactoglobulin emulsions. *Langmuir* **2005**, 21, 4842–4855.

Table 2. ζ-Potentials of the Used Latex Particles

	ζ-potential (mV)[a]	
C_{NaCl} (mM)	L-latex	D-latex
10	−57.6 ± 0.8	−87.3 ± 0.3
50	−53.7 ± 0.6	−88.7 ± 0.8

[a] Average of five measurements.

concentration of NaCl was varied from 0.01 to 1 M. The emulsification performance of the polar oils (soybean and silicone oils) was compared with that of the nonpolar oils (hexadecane and tetradecane). The experimental results are illustrated in Figure 6.

When *soybean* or *silicone* oil (both of viscosity 50 mPa·s) is used, complete emulsification of the two phases is never observed. At C_{NaCl} < 0.1 M, there is no formation of emulsion, and the latex particles remain dispersed in the aqueous phase. At $0.2 \leq C_{NaCl} \leq 0.4$, the presence of water drops in the oily phase is observed after stirring. Transfer of latex particles from the aqueous to the oily phase takes place. The particles, which remain in the aqueous phase, are nonaggregated, while those transferred into the oil are strongly aggregated. The addition of 0.5 M NaCl in the latex suspension, prior to emulsification, leads to aggregation of the particles in the water. All of them are transferred into the oily phase after stirring (see Figure 6). The amount of water, which is dispersed as drops in the oily phase, is about 20%. The separated water phase is clear, that is, it does not contain dispersed particles. In other words, the used soybean and silicone oils wet well the latex particles, which enter the oily phase (upon agitation) instead of adsorbing at the oil−water interface.

We also tried experiments with a less viscous silicon oil, SO-5 (Rhodia Silicones), of dynamic viscosity $\eta = 5$ mPa·s. With this oil, we obtained stable emulsions such as those obtained with hexadecane and tetradecane (see below). This fact indicates that not only the polarity of the oil, but also its viscosity plays a role in emulsification. When the particle contact angle is close to 180°, it is possible that the particles are detached from the drops during the stirring if the oil has a greater viscosity, but the particles cannot be detached if the oil is not so viscous.

When *hexadecane* or *tetradecane* is used, stable W/O emulsions are formed at $C_{NaCl} \geq 0.5$ M. Under these conditions, the oily phase is clear, with no indication for the presence of latex particles in it. The formed W/O emulsions are stable: they were observed for more than 20 days, and no coalescence or phase separation was detected. The size of the water drops (between 10 and 50 μm) remained the same during the whole period of observation. Only a slow, gravity-driven sedimentation of the water drops was observed. However, the microscopic observations showed that the water drops coalesce easily when the emulsion is subjected to shear. In our next experiments (the results are discussed in the rest of this paper), we worked only with hexadecane as the oil phase. Illustrative photographs of the studied emulsions are shown in Figure 4.

We recall that the investigated latex suspensions are able to form stable W/O emulsions when the latex particles have been initially *aggregated* in the aqueous suspension. During emulsification, the latex aggregates serve as sources of latex to cover the drop surfaces. In the produced emulsions, large latex aggregates are not seen, as in the water phase before the stirring.
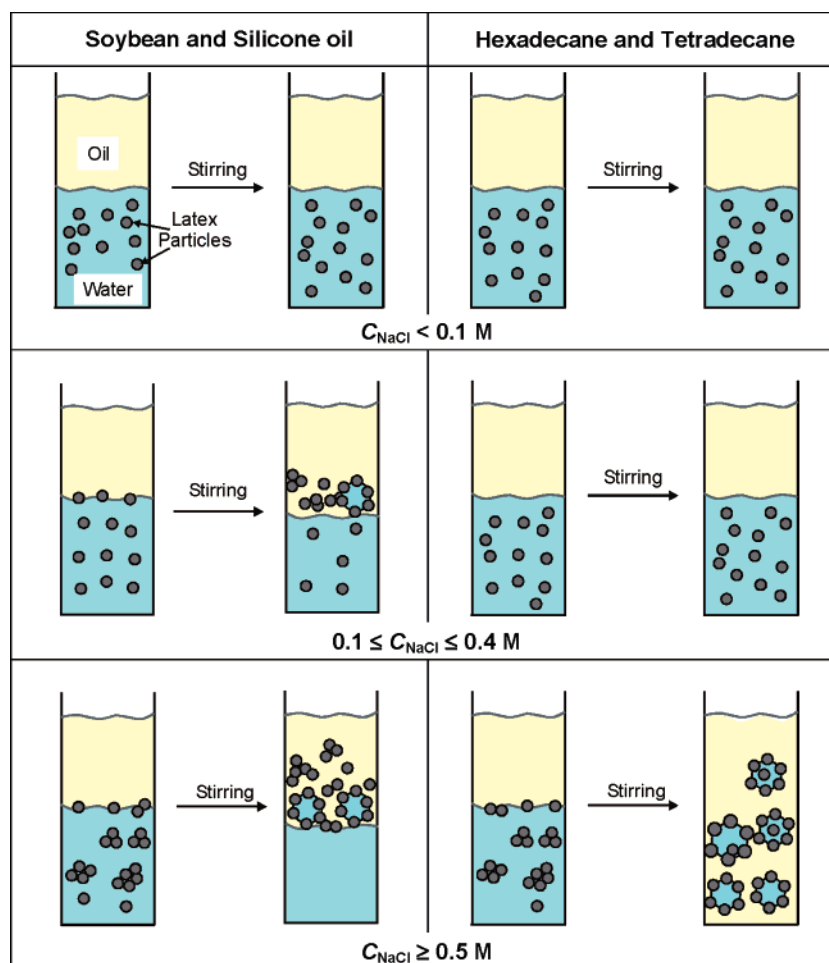

Figure 6. Schematic presentation of the effect of NaCl on emulsification for the cases of more viscous and polar oils (soybean and silicone oil, $\eta = 50$ mPa·s) and less viscous nonpolar oils (hexadecane and tetradecane); the water phase is a 2 wt % D-latex suspension.

It seems that during the homogenization, the bulk aggregates adsorb, release particles, and considerably diminish their size. Observations about the disassembly of aggregates at an interface have been recently reported: aggregates present at the air—water interface decompose to the constituent particles when the air is replaced by oil.[56]

We checked whether the stable W/O emulsions, formed at φ_p = 0.02, C_{NaCl} = 0.5 and 1 M, and Φ_w = 0.5, can be inverted into O/W emulsions upon increase of the volume fraction of water, Φ_w. Phase inversion was not observed. Instead, the addition of water, up to Φ_w = 0.9, resulted in the formation of a W/O emulsion with residual, nonemulsified water.

4.2. Effect of the Type of Electrolyte. As discussed above, to produce W/O emulsions stabilized by charged latex particles, it is necessary to suppress the barrier to particle adsorption at the oil—water interface by the addition of electrolyte. Because the particle-to-drop attachment represents a kind of coagulation, one can expect that the known Schulze—Hardy rule[52-54] should be applicable. According to this rule, the critical concentration of coagulation is $C_{cr} \propto 1/Z^6$, where Z is the valence of the counterion. We checked whether the Schulze—Hardy rule is applicable also to emulsification. In all experiments described in the present subsection, the aqueous phase was a 2 wt % water suspension of D-latex at Φ_w = 0.5; the oil was hexadecane.

For our latexes, 1 M NaCl is above the critical concentration of emulsification (i.e., for C_{NaCl} = 1 M, stable emulsions are produced). Then, we could expect that stable W/O emulsions should also be produced if the water phase contains 1/3 = 0.333 M Na₃Citrate, $1/2^6$ = 0.0156 M MgCl₂, or $1/3^6$ = 0.00137 M AlCl₃. (For MgCl₂ and AlCl₃, the concentrations are according to the Schulze—Hardy rule; 0.333 M Na₃Citrate contains 1 M Na⁺ counterions, just as 1 M NaCl.) This expectation was confirmed by our experiments: for the aforementioned concentrations of Na₃Citrate, MgCl₂, and AlCl₃, we obtained stable W/O Pickering emulsions.

The Na⁺, Mg²⁺ and Al³⁺ counterions lower the barrier to adsorption mostly by suppressing the diffuse electric double layer (reducing the Debye screening length). The barrier could be also affected by reducing the surface charge density of the latex particles by binding counterions that exhibit a pronounced specific adsorption. Such a counterion, tetraethylammonium (TEA⁺), is provided by the TEAB. Our experiments with D-latex showed that the critical emulsification concentration was 0.01 M for TEAB, versus 0.50 M for NaCl. This considerable decrease in the critical concentration could be attributed to the adsorption of TEABs ethyl groups on the hydrophobic portions of the latex-particle surface.

4.3. Effect of Particle Concentration on the Drop Size. Here, we present results from our experiments with D-latex and dialyzed L-latex.

D-Latex + 0.5 M NaCl. Experimental data for the mean diameter of the emulsion drops, $d = d_{32}$, are plotted versus $C_p = \varphi_p \times 100$ in Figure 3. The left-hand branch of the experimental curve corresponds to the regime of limited coalescence in anti-Bancroft emulsions (eq 5), while the horizontal right-hand branch corresponds to the Kolmogorov diameter of the drops in the turbulent-inertial regime (eq 14). Note that (unlike eq 12) eq 5 does not contain the volume fraction of the disperse phase, Φ_d. Therefore, experimental points obtained for different Φ_d (in Figure 3, for $\Phi_d \equiv \Phi_w$ = 0.3 and 0.5) should comply with the same theoretical curve.

(56) Horozov, T. S.; Binks, B. P. Particle behaviour at horizontal and vertical fluid interfaces. *Colloids Surf., A* **2005**, *267*, 64—73.
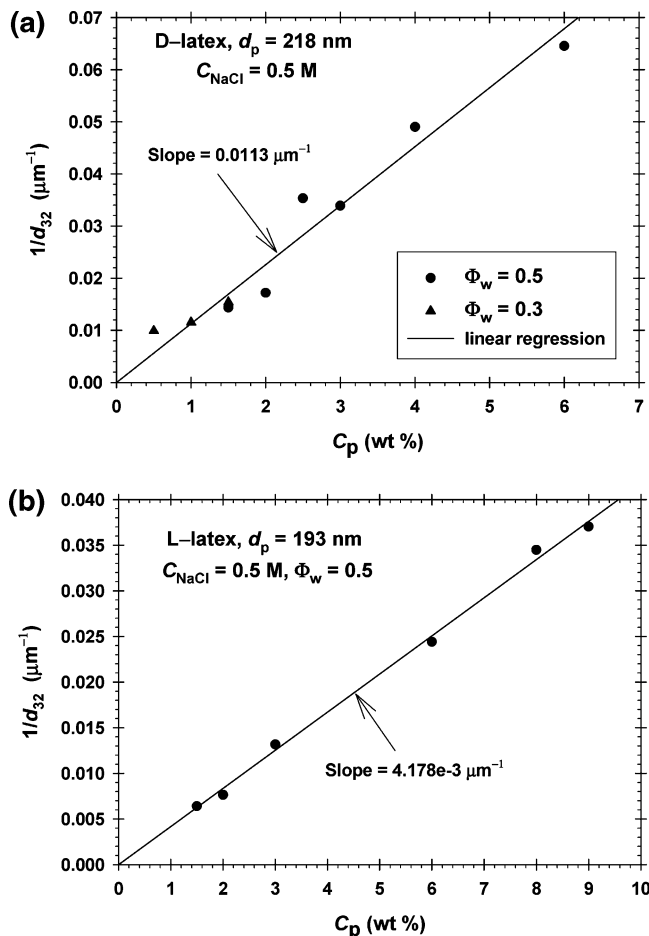

Figure 7. Plots of $1/d_{32}$ vs the particle concentration, $C_p = \varphi_p \times 100$, for water-in-hexadecane Pickering emulsions. The linear regression is drawn in accordance with eq 5. (a) Data for D-latex with 0.5 M NaCl. (b) Data for L-latex with 0.5 M NaCl. The volume fraction of water in the emulsions, Φ_w, is denoted in the figure.

The theoretical model behind eq 5 implicitly assumes that the particle adsorption is fast, that is, $\tau_c > \tau_a$, where τ_c is the characteristic drop collision time, while τ_a is the characteristic particle adsorption time. To be sure that the drop size is not affected by undesirable kinetic effects ($\tau_c < \tau_a$), for the lowest particle concentrations, we carried out measurements at a smaller drop volume fraction, Φ_w = 0.3 instead of Φ_w = 0.5. (At a smaller Φ_w, the characteristic drop collision time increases, which facilitates the fulfillment of the requirement $\tau_c > \tau_a$.)

In Figure 7a, we plotted the data from the left-hand branch in Figure 3 as $1/d_{32}$ versus C_p. In accordance with eq 5, the data points comply with a straight line through the coordinate origin. From the fit, we determine a single adjustable parameter: the slope of the line. Next, from the slope, one can calculate the particle radius:

$$a = \{8\varphi_a \times (\text{slope}) \times 100\}^{-1} \, (\mu m) \qquad (17)$$

In our estimates, we assume that φ_a = 0.907, that is, the particle adsorption monolayer is closely packed. Using eq 17, from the slope of the linear regression in Figure 7a, we calculate particle radius a = 116 ± 5 nm. The latter value is close to the particle radius a = 109 ± 11 nm determined by dynamic light scattering (Figure 5a).

L-Latex + 0.5 M NaCl. The experimental data for d_{32} versus C_p are shown in Table 3. The experiments are carried out at Φ_w = 0.5. For $C_p \geq 9$ wt %, the particle diameter levels at $d_{32} \approx$

Table 3. L-latex + 0.5 M NaCl: d_{32} vs C_p at $\Phi_w = 0.5$

C_p (wt %)	d_{32} (μm) ($\Phi_w = 0.5$)	C_p (wt %)	d_{32} (μm) ($\Phi_w = 0.5$)
1.5	156	8.0	29
2.0	131	9.0	28
3.0	76	10.0	27
6.0	41	16.0	27

27 μm, which seems to be the Kolmogorov diameter (d_K) for these emulsion drops. In Figure 7b, we have plotted the data for $C_p \leq 9$ wt % as $1/d_{32}$ versus C_p to check whether they agree with eq 5 (regime of limited coalescence in anti-Bancroft emulsions). As seen in Figure 7b, the data points comply very well with a straight line through the coordinate origin. From the slope of this line, using eq 17 (with $\varphi_a = 0.907$), we determine the effective radius of the adsorbed particles to be $a = 313 \pm 4$ nm, which is 3.2 times greater than the mean radius of the separate particles, $a = 96.5 \pm 15.5$ nm (Figure 7b). The simplest possible interpretation of this result could be that the adsorbed particles are in the form of aggregates with a mean aggregation number of about 4, which corresponds to a surface coverage of $\varphi_a = 0.726$. Indeed, a floc comprising four particles will tend to form a tetrahedron shape and hence have a spherical-average diameter of two particle diameters.[57] This hypothesis is in qualitative agreement with the microscopic observations of the L-latex suspension with 0.5 M NaCl, where many aggregates are seen (see section 4.1). Another hypothesis for the explanation of the same result could be that not all particles have been adsorbed at the drop surfaces, and that some particles remain in the bulk. However, this hypothesis is less probable insofar as the L-latex is more hydrophobic than the D-latex and should adsorb easier (see section 4.1).

5. Stability−Instability Diagram

As mentioned above, the production of stable W/O Pickering emulsions is favored by the rise of C_{NaCl} and C_p, and by the decrease of Φ_w. We scanned the conditions for obtaining stable W/O emulsions by varying electrolyte concentration, C_{NaCl}, and particle concentration, C_p, at two fixed volume fractions of water, $\Phi_w = 0.3$ and 0.5. In these experiments, a D-latex suspension and hexadecane were used. The results are shown in Figure 8 in the form of a stability−instability diagram. In this figure, the data points represent the minimum C_p (at a given C_{NaCl}) that can provide the formation of a stable W/O emulsion with the whole amount of water emulsified. The two lines in Figure 8 separate the regions of stable and unstable emulsions for the two different volume fractions of water ($\Phi_w = 0.5$ and 0.3). For the unstable emulsions, separation of water phase is observed very soon after ceasing the agitation; some big water drops could remain in the oil phase (Figure 9b). The decrease of the volume fraction of water from $\Phi_w = 0.5$ to $\Phi_w = 0.3$ leads to expansion of the stability region and shrinking of the instability region (Figure 8). This could be explained by the fact that, at lower Φ_w, the period between two consecutive drop collisions is longer ($\tau_c \propto 1/\Phi_w$), so there is sufficient time for particle adsorption on the oil−water interface, which ensures effective drop protection against coalescence. The increase of Φ_w above 0.5, at values of C_p and C_{NaCl} corresponding to stable emulsions ($C_p = 2$ wt % and $C_{NaCl} = 0.5$ M for $\Phi_w = 0.5$) resulted in the formation of a W/O emulsion with residual, nonemulsified water. The existence of

(57) Zerrouki, D.; Rotenberg, B.; Abramson, S.; Baudry, J.; Goubault, C.; Leal-Calderon, F.; Pine, D. J.; Bibette, J. Preparation of doublet, triangular, and tetrahedral colloidal clusters by controlled emulsification. *Langmuir* **2006**, *22*, 57−62.
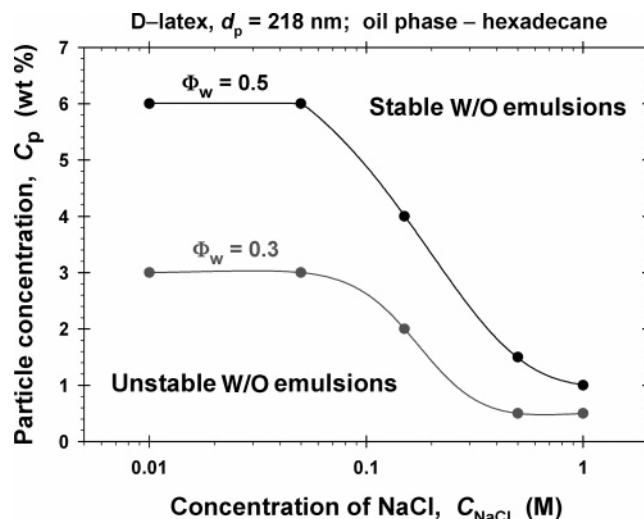

Figure 8. Stability−instability diagram for W/O Pickering emulsions stabilized by polystyrene latex particles at various NaCl concentrations. The experimental points represent the minimum values of C_p (at given C_{NaCl}), for which the formation of stable emulsion is observed. The lines are guides to the eye.
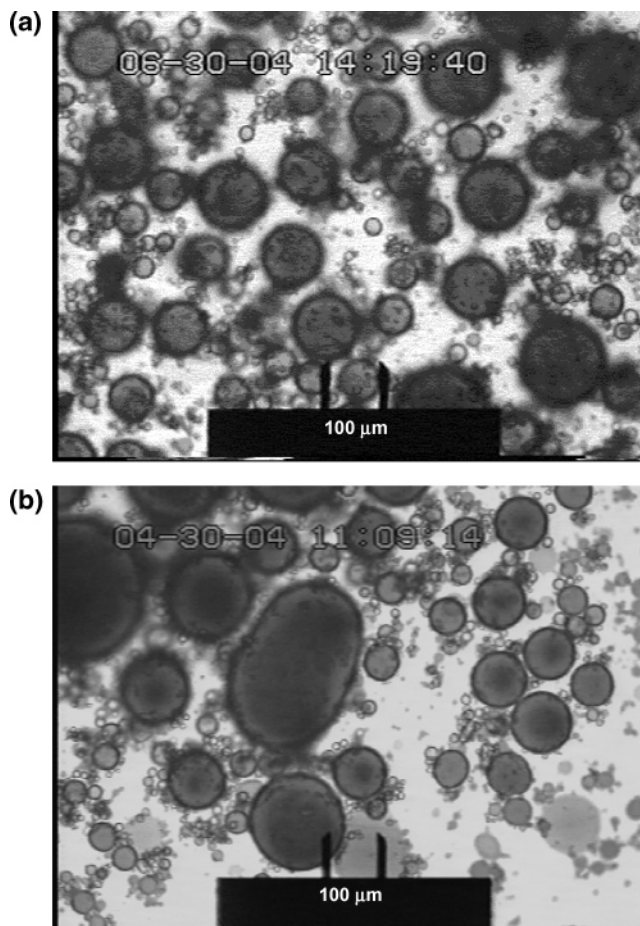

Figure 9. Photographs of water-in-hexadecane emulsions stabilized by D-latex particles at $C_{NaCl} = 0.15$ M and $C_p = 3$ wt %. (a) $\Phi_w = 0.3$: the produced emulsion is stable, and the whole amount of water is emulsified. (b) $\Phi_w = 0.5$: the water phase is partially separated, and the oil phase contains the large water drops seen in the photograph.

nonemulsified water is due to drop−drop coalescence because the collision time becomes shorter than the particle adsorption time.
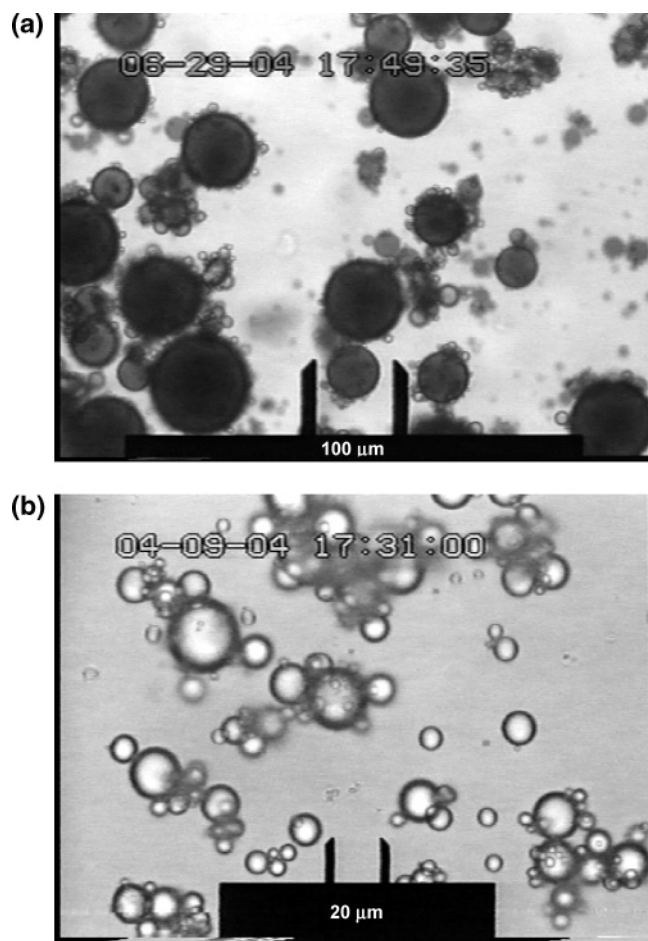
Figure 10. Photographs of water-in-hexadecane emulsions stabilized by D-latex particles at $C_p = 6$ wt % and $\Phi_w = 0.5$. (a) $C_{NaCl} = 0.05$ M. (b) $C_{NaCl} = 0.5$ M.

Figure 9 shows photographs of W/O emulsions produced at $C_{NaCl} = 0.15$ M and $C_p = 3$ wt %. These concentrations correspond to a point that is located between the two curves in Figure 8. Thus, for $\Phi_w = 0.3$, the point is in the region of stable emulsions (Figure 9a), while, for $\Phi_w = 0.5$, the point is in the region of unstable emulsions (Figure 9b).

Figure 8 indicates that, for $C_{NaCl} > 0.5$ M, the effect of NaCl on the emulsification exhibits a saturation. Probably, at these high electrolyte concentrations, the electrostatic barrier to particle adsorption has completely disappeared. In the intermediate concentration range, $0.05 < C_{NaCl} < 0.5$ (M), the addition of electrolyte favors the formation of stable emulsions, which could be explained by a decrease in the barrier to particle entry at the oil−water interface.

Most intriguing is the tendency of the curves in Figure 8 to level off at $C_{NaCl} < 0.05$ M. In accordance with the Derjaguin−Landau−Verwey−Overbeek (DLVO) theory, the height of the barrier to particle adsorption is expected to grow exponentially with the decrease in C_{NaCl}.[54,55] In contrast, in this concentration region, the boundary between the stable and unstable emulsions becomes insensitive to C_{NaCl} (Figure 8). The latter fact indicates the presence of a "nonbarrier" way of adsorption, which is effective at sufficiently high values of the particle concentration, C_p. We could hypothesize that this type of adsorption is driven by the hydrodynamic flows accompanying the acts of drop breakage and coalescence. At not-too-high particle adsorptions, the drop surfaces are expected to be tangentially mobile. The expansion of these surfaces (during drop deformation) drives a hydrodynamic flux from the bulk toward the surface, which carries along particles and displaces the surface charges. This is a hydrodynamic mechanism of nonbarrier adsorption, which is insensitive to C_{NaCl}. In such a case, greater surface concentrations of particles can be obtained by subsequent drop coalescence.

Indications for such coalescence are seen in Figure 10a, which shows a stable emulsion corresponding to a point on the boundary curve in Figure 8: $\Phi_w = 0.5$, $C_p = 6$ wt %, and $C_{NaCl} = 0.05$ M. For comparison, in Figure 10b, we show a photograph of an emulsion with the same Φ_w and C_p, but with $C_{NaCl} = 0.5$ M; the point corresponding to this emulsion is deep in the stability region in Figure 8. The drops in Figure 10b are much smaller than those in Figure 10a. In particular, the experimental mean drop diameter in Figure 10b, $d_{32} = 15.5$ μm, corresponds to the Kolmogorov turbulent-inertial regime, eq 14 (see section 2.3).

6. Summary and Conclusions

Here, we investigate W/O emulsions that are stabilized by polystyrene latex particles with sulfate surface groups. The particles, which play the role of emulsifier in this system, are initially contained in the disperse (water) phase. The existence of such emulsions formally contradicts the empirical Bancroft rule, and, because of that, they are termed anti-Bancroft emulsions. Theoretical considerations predict that the drop diameter in these emulsions is inversely proportional to the particle concentration, but is independent of the volume fraction of water (section 2.1, eq 5). In addition, a second emulsification regime exists, in which the drop diameter is determined by the input mechanical energy during the homogenization in the turbulent regime (section 2.3, eq 15). The existence of these two regimes is experimentally confirmed (Figure 3). The experimental data agree well with the theoretical model. From the fits of the data, the size of the adsorbed particles or aggregates is determined (Figure 7 and section 4.3).

Stable W/O emulsions were produced with nonpolar and less viscous oils (hexadecane and tetradecane), while, for polar and viscous oils (soybean and silicone oil), the particles enter into the oily phase, and Pickering emulsions are not obtained (section 4.1, Figure 6). In addition, the formation of stable Pickering emulsions demands the presence of a relatively high concentration of electrolyte in the aqueous phase. Its role is to lower the electrostatic barrier to particle adsorption at the oil−water interface. Since the attachment of particles at the drop surfaces represents a kind of coagulation, it turns out that the Schulze−Hardy rule for the critical concentration of coagulation is applicable also to emulsification. This is experimentally confirmed with latex suspensions containing Na^+, Mg^{2+}, and Al^{3+} counterions (section 4.2). TEAB also promotes the emulsification because of the specific adsorption of its counterions on the latex particles. The increase in the particle and electrolyte concentrations and the decrease in the volume fraction of water are other factors that facilitate the emulsification. To quantify the combined action of these factors, an experimental stability−instability diagram is obtained (Figure 8).