Coalescence of Charged Droplets in Agitated Liquid-Liquid Dispersions

T. Tobin and D. Ramkrishna
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907

Experimental studies have been performed to assess the effect of drop charge on turbulent drop coalescence. Although it is well known that surface charge can affect coalescence rates of Brownian particles in a quiescent medium, no studies have been found in the literature which explicitly examine charge effects on larger drops in turbulent media.

Results demonstate that drop charge can substantially inhibit coalescence between drops in agitated dispersions. Moreover, this effect can arise solely from latent drop charges, which are attributed to the preferential adsorption of hydroxide ions onto the water-organic phase interface. Ionic strength and pH thus are shown to play a major role in determining coalescence rates between agitated drops.

Results also demonstrate that reliance on measurement of average drop sizes for the purpose of determining coalescence rate dependencies is a precarious practice. Strong size-dependent effects such as obtained here have the potential to suggest erroneous conclusions when conclusions are based on measurements of average drop sizes rather than of drop-size distributions.

Introduction

The study of agitated liquid-liquid dispersions is an area of ongoing interest in engineering, for the simple reason that many engineering operations utilize or require multiphase mixing. For many of these operations, especially for two-stage liquid-liquid extractions, control of drop size distributions is essential in order to obtain optimal performance and productivity. The means to realize the goal of better control over drop-size distributions involves a development of detailed mechanistic models which account for the forces present in a turbulent dispersion, and the evaluation of these models against good experimental data.

In the literature on turbulent mixing of two-phase liquid systems, especially of experimental investigations performed in baffled mixing vessels, there are a fair number of studies to be found which investigate the effects of viscosity, turbulence intensity, and dispersed phase fraction on droplet coalescence. There is however a noticeable lack of studies dealing with the possible stabilizing effects of drop charge. This fact is somewhat perplexing, since it is well known that drop charge and ionic strength have a marked effect on the Brownian coagulation rates of organic-in-water emulsions. The current theory to describe these effects is known as DLVO theory, named after its four primary developers Deryaguin, Landau, Verwey, and Overbeek. The DLVO theory attempts to account for the stability of charged colloidal particles in a liquid medium by considering the electrostatic repulsion and Van der Waals attraction forces which the particles experience. Among other things the theory predicts that for spherical particles with a same-sign constant potential of small magnitude the repulsive potential energy is given by:

$$\Phi_r = 4\pi\epsilon \frac{R_1 R_2}{R_1 + R_2} \psi_o^2 \ln[1 + \exp(-\kappa h)] \tag{1}$$

for κR_i large ($> \sim 5$). In the above equation ϵ is the permittivity constant of the medium, R_i is the radius of a drop, ψ_o is the surface potential, h is the minimum separation between the drop pair, and κ is the "Debye parameter," a measure of the extent of the charged region known as the diffuse double layer which surrounds a charged particle. The value of κ is proportional to the square root of the ionic strength of the medium; thus, a large ionic strength clearly reduces the electrostatic

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Correspondence concerning this article should be addressed to D. Ramkrishna.

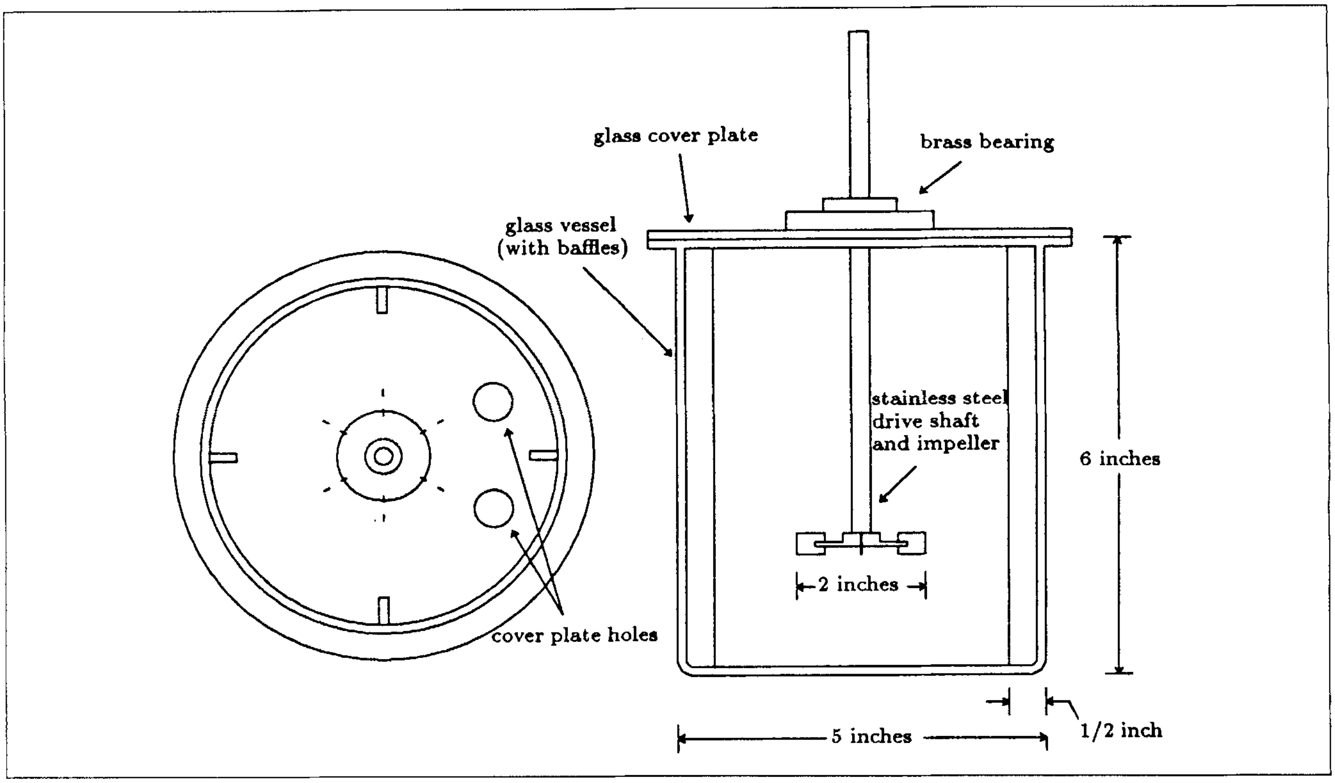

Figure 1. Mixing vessel used in coalescence rate studies.

repulsion between two like-charged particles. The reader is referred to Hiemenz (1986) for a more detailed description of DLVO theory and its application to dispersions of Brownian particles.

In one of the few reported works which attempted to measure the effect of electrolyte type and concentration on turbulent drop coalescence rates, Howarth (1967) was led to conclude that increasing ionic strength inhibits coalescence. The experiments were conducted on dispersions of benzene/carbon tetrachloride in water, and utilized a light probe to infer average drop coalescence rates in the dispersions. While Howarth's work clearly demonstrated the existence of some type of drop charge effect on turbulent coalescence, the experimental results showing enhanced coalescence at the lowest ionic strengths are most curious in light of the DLVO theory and therefore require further explanation.

In addition to the (albeit scant) evidence that drop charge can in some way influence turbulent coalescence, there is also evidence that drop charges are both pervasive and inherent to organic-in-water dispersions. Zeta potential measurements of various hydrocarbon droplets in water have revealed that such droplets can acquire a substantial negative charge which varies with the pH of the system. The source of the negative drop charge is generally attributed to a preferential adsorption of hydroxide ions onto the surface (Jordan and Taylor, 1952; Taylor and Wood, 1957; Stachurski and Michalek, 1985). Related to this, Reddy and Fogler (1980) have shown that organic-in-water emulsions can actually be substantially stabilized against Brownian coalescence merely by increasing the pH of the aqueous phase.

Given that a negative charge appears to be commonly present on the surfaces of pure organic droplets in water, one can appreciate the importance of fully determining the effect which drop charge may have on turbulent drop coalescence. If surface charge can contribute substantially to the coalescence stability of drops in an agitated system, then pH and ionic strength must certainly be added to the list of factors which affect drop-size distributions and droplet interaction rates in turbulent liquid-liquid dispersions. It is in light of the above that the present experimental investigation was undertaken. The objective of this work was to fully ascertain the nature of drop charge effects on coalescence of droplets in turbulent liquid-liquid dispersions. The following section describes the exact form of these experimental studies as well as the dispersions and conditions that were investigated. After this the results of the experiments are presented, followed by a discussion on the import and significance of these results to researchers as well as to engineers seeking to control drop-size distributions in agitated dispersions.

Experimental

Experimental measurements of steady-state and transient coalescing dispersions were conducted in a 2-L baffled mixing vessel of standard configuration, shown in Figure 1, with a Rushton-type turbine impeller to provide agitation. A nitrogen gas feed was attached to the system to enable the performance of experiments in the absence of carbon dioxide contamination from the air. (Since carbon dioxide is readily absorbed by fresh deionized water, altering the pH of the water, when performing controlled pH studies it is advantageous to prevent such absorption if at all possible.) All pH measurements were made with a Leeds Northrup model 501 pH meter, with a scale resolution of approximately 0.02 pH units.

The benzene and carbon tetrachloride used in this study were spectrophotometric grade (Malinckrodt) and the acetophenone was certified grade (Fisher). The water used was distilled and deionized, then filtered through a millipore water system. In further preparation for the experiments, the water was exposed to bubbling nitrogen gas for 24 hours immediately prior to its use. The ionic strength of the dispersions was modified with reagent-grade sodium chloride (Baker Analyzed), and the pH of the dispersions was adjusted with small quantities of dilute HCl and NaOH solutions.

Drop-size distributions were determined by removing small samples of dispersion with a micropipette to a microscope slide and stabilizing with sodium dodecyl sulfate (SDS) surfactant. Following this, images of the dispersions were captured from a microscope with a video camera and then processed using a Cambridge Instruments Q570 Image Analyzer. Typically 1,500–2,000 droplets were measured to construct each drop-size distribution. The sampling and analysis procedure is described in more detail by Tobin et al. (1990).

Both steady-state and transient drop-size distributions were measured, in order to assess the effect of pH and electrolytic strength on coalescence. The technique used to produce transient coalescing dispersions with minimal drop break-up involves subjecting a dispersion to a step-change in turbulence intensity, and is described in detail by Tobin et al. (1990). In this work the steady-state measurements of drop-size distributions were made after agitating a dispersion at 600 or 800 rpm for approximately two hours. The dispersions used in the transient studies were agitated at an initial impeller speed of 800 rpm for approximately 2 hours. Following this, at an experimental time $t=0$, the impeller speed was dropped to 200 rpm.

In order to ascertain whether CO_2 concentrations have any direct effect on drop charge (through adsorption onto the water-organic phase interface), additional steady-state experiments were conducted under conditions of both air- and nitrogen-equilibrium. The requirement that a steady stream of gas be maintained over the head-space of the mixing vessel for prolonged periods induced a large rate of evaporation from the benzene/carbon tetrachloride system, even when the gas was prewet in the dispersed phase by passing through a sparge tank. For this reason, a dispersed phase of acetophenone was chosen for this part of the study.

The experimental method involved first forming a dispersion in a nitrogen atmosphere at 600 rpm. After allowing sufficient time for steady-state to be reached, the drop-size distribution and pH were measured. Next, the pH of the system was raised to 7.0 with a few drops of 0.1 M NaOH. After this, the system was carefully monitored for a period of about 2 days, with periodic small adjustments to the pH being made until the system reached equilibrium with respect to both drop-size distribution and pH. At the end of this time, the dispersion was sampled and measured on a microscope slide as discussed previously. Thirdly, the gas line to the system was switched over from nitrogen to air, and the system was exposed to air for an extended period of time (about 2 days) in order to allow adsorption of CO_2 out of the air and the concomitant shift in the drop-size distribution. At the end of this period, a third dispersion sample was taken and the drop-size distribution and pH were measured. Finally, the pH of the system was raised to 7.0 and maintained (through periodic additions of NaOH) until the drift in pH subsided (about 3 days). After this time a fourth dispersion sample was obtained and the drops present were measured.

We report first on the results for neutrally buoyant dispersions of benzene/carbon tetrachloride in water, at a dispersed phase fraction of 0.05. These first two sets of experiments were undertaken in order to measure changes in dispersions with changes in pH and ionic strength. Following these are the results for the study of (CO_2) effects on a 5% dispersion of acetophenone.

Results

Steady-state with varying pH

The first series of studies were performed on steady-state dispersions at an agitation rate of 600 rpm. Figure 2 shows the volume fraction profiles for three different pH's at an ionic strength of approximately 0.0001 M. The uncertainty in the pH measurements was on the order of ±0.3 pH units, owing to the difficulty in measuring pH precisely at the very low ionic strength of the system. Nevertheless a very clear trend is evident in the data: increasing pH narrows the drop-size distributions, and causes them to shift to the left (smaller drops).

The measurements in this figure were all obtained from the same batch of liquid, the pH of the system being sequentially changed to 6, 7, and finally 8. After each change of pH, the dispersion was allowed two hours to come to a steady-state. Observations on transient (coalescing) dispersions and previous experimental results suggested that two hours should be more than sufficient to allow the distributions to equilibrate.

In order to verify that the above experimental results were not due to possible systematic errors or changes in ionic strength, the above experiment was repeated at an ionic strength of 0.01 M, well above the level of fluctuations in ionic strength which might take place due to a change in pH. The pH of the dispersion was changed to 6, 8, and finally 7, again allowing two hours between each change in pH for steady-state to be achieved. At this ionic strength, the uncertainty in the pH was ±0.1 pH units. The results of this experiment are displayed

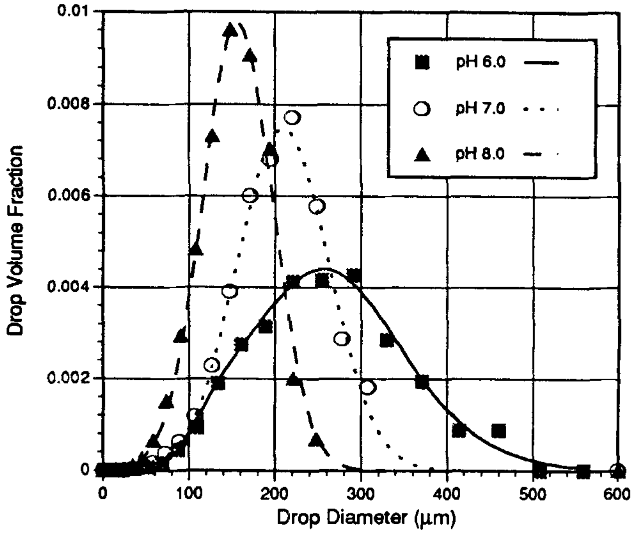

Figure 2. 600 RPM steady-state results for 5% benzene/ CCl_4 in water ($I \approx 10^{-4}$ M).

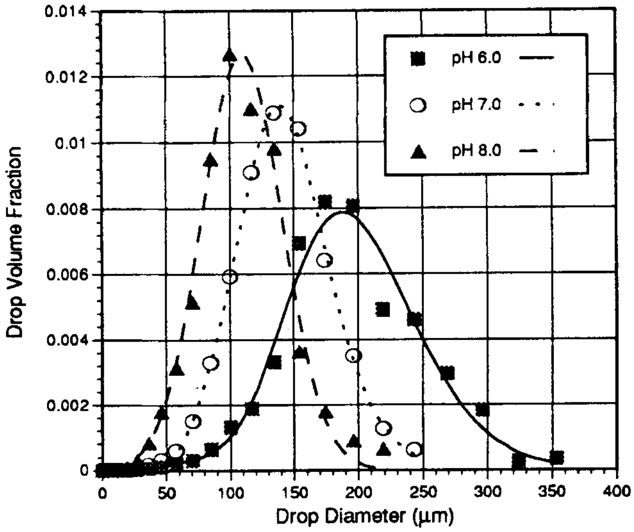

Figure 3. 600 RPM steady-state results for 5% benzene/CCl_4 in water ($I = 10^{-2}$ M).

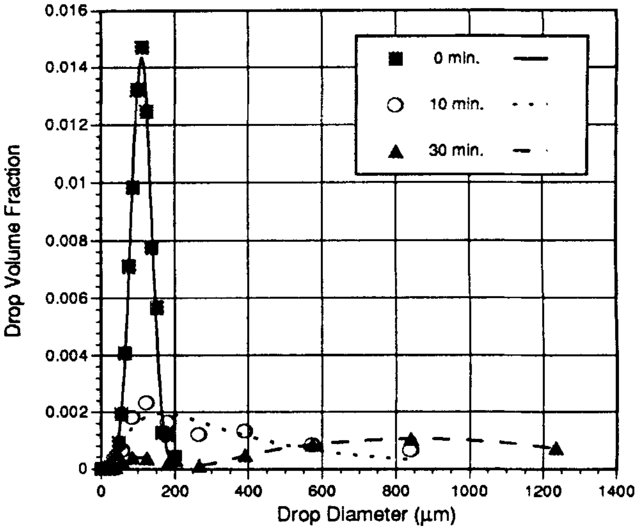

Figure 5. 800-200 RPM transient results for 5% benzene/CCl_4 in water ($I = 10^{-2}$ M).

in Figure 3, and demonstrate clearly that pH is indeed a major factor affecting the steady-state drop-size distribution. Not only is the effect of the pH extremely marked, but it is borne out even at an ionic strength of 0.01 M under which condition the extent of the electrical double layer surrounding each drop will have shrunk an order of magnitude over that of the previous case. One would expect from DLVO theory that for sufficiently large ionic strengths (large κ) the charge on the drops will no longer present a repulsive force. At such ionic stengths therefore, one should no longer see any change in the drop-size distribution with a change in pH.

Transient with varying ionic strengths

Figure 4 shows the transient coalescence results obtained for the system of benzene carbon tetrachloride in water at an ionic strength of approximately 10^{-4} M, Figure 5 for 10^{-2} M, and Figure 6 for 10^{-1} M. It seems clear that there is a marked acceleration of the drop coalescence rate with increasing ionic strength, especially for the larger drops of the system. This enhanced coalescence of the largest drops can be seen from the fact that the distributions become extremely broadened with time at the higher ionic strengths: small drops are tending to remain unchanged while large drops continue to grow through further coalescence.

Effect of CO_2 on coalescence

In any aqueous system that is exposed to air, an equilibrium is established betwen the free and dissolved CO_2. Three reactions are involved in this process:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (2)$$

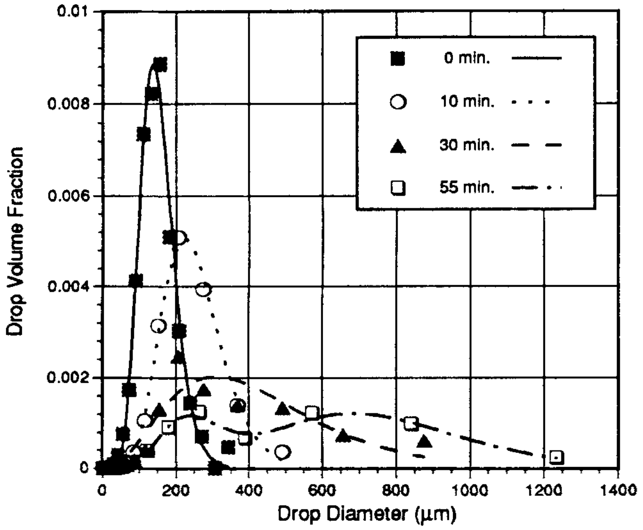

Figure 4. 800-200 RPM transient results for 5% benzene/CCl_4 in water ($I \approx 10^{-4}$ M).

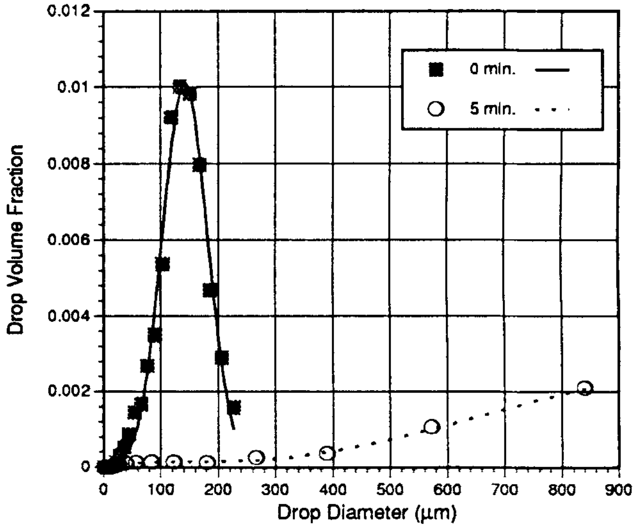

Figure 6. 800-200 RPM transient results for 5% benzene/CCl_4 in water ($I = 10^{-1}$ M).

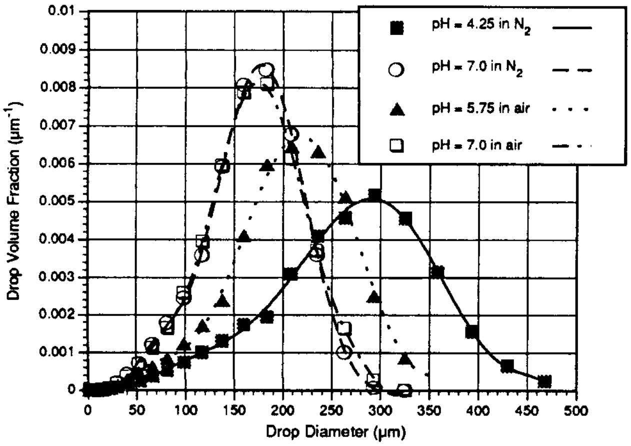

Figure 7. CO_2/N_2 study for 5% acetophenone in water: volume fraction vs. drop diameter ($I = 2 \cdot 10^{-3}$ M).

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \quad (3)$$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^= + H_3O^+ \quad (4)$$

Because absorption of CO_2 from air by an aqueous solution can substantially reduce its pH (from 7.0 to approximately 5.5 for pure water, for example) it is certain in light of the above results that such absorption can at least indirectly alter the drop coalescence rates in a dispersion. In addition however, it is important to determine whether OH^- is the only species in such a system which adsorbs onto the drop surface, or if perhaps another (such as HCO_3^- or $CO_3^=$) is also adsorbed onto the water-organic phase interface. If the latter is the case, then it is not sufficient to know only the pH and ionic strength in order to characterize the magnitude of charge repulsion between drops; one must also determine CO_2 levels through the above equilibrium equations.

Figures 7 and 8 show the steady-state results obtained from the experiment on CO_2 effects in terms of both volume fractions and drop number densities. The initial pH of the system in a nitrogen atmosphere (after an agitation time of approximately 20 hours) was in the neighborhood of 4.25 (not 7.0), which is probably due to the very strong adsorption of OH^- onto the water-organic phase interface. The final pH in the system exposed to air is approximately 5.75, which is very close to the equilibrium pH of approximately 5.5 for pure water exposed to air.

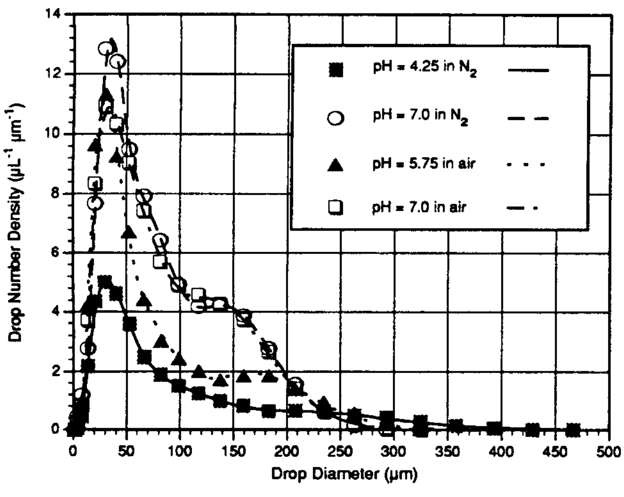

Figure 8. CO_2/N_2 study for 5% acetophenone in water: number density vs. drop diameter ($I = 2 \cdot 10^{-3}$ M).

Both Figures 7 and 8 reveal that the two distributions at pH 7.0 are virtually the same, except for perhaps the very smallest drops. In terms of volume fraction, the two distributions are completely coincident to within the range of experimental error. On the number density plot, which effectively amplifies the contribution of the smallest drops, the very slight deviation in the lowest region is likely due to incomplete equilibrium. It is possible that even after several days of agitation, the small droplets having extremely low coalescence and breakup rates have still not fully achieved equilibrium.

In addition to showing that there is no significant effect of CO_2 on the drop-size distributions, apart from the effect which CO_2 has on the pH of the system, Figures 7 and 8 also show the same trends as the steady-state experiments with benzene/carbon tetrachloride in water. Increasing pH causes a marked increase in the number of smaller drops, suggesting that the drops have become substantially more stable against coalescence.

Discussion

The above results of pH and ionic strength effects in the absence of charged surfactants are consistent with the drop mobility studies of Taylor and Wood (1957), in which it was concluded that hydroxide ions are preferentially adsorbed onto the surface of an organic drop in water. Thus an increase in pH would favor hydroxide adsorption, by increasing the bulk phase concentration of hydroxide. The resulting higher potential on the surface of the drops would strongly stabilize the drops against coalescence. In contrast to the effect of increased pH, increased ionic strength reduces repulsion between particles by reducing the size of the electrical double layer surrounding each charged drop. In fact at very large ionic strengths, the effect of surface potential can be completely negated, as was likely seen in the transient experimental results of Figure 6.

Of further interest to the above qualitative observations is the fact that it is the larger drops which seem the most sensitive to the level of electrostatic repulsion. Thus, when electrostatic repulsion is lowered, either by reducing the pH of the system or by elevating the ionic strength (or both) one observes from transient experiments that the distributions do not simply "shift" to the right, but rather they "stretch". Quantitatively, this phenomenon can be seen from the changes in various moments of the distributions. Table 1 presents the number-average diameter and Sauter mean drop diameter of the drop-size distributions presented in Figures 4–6. The number-average diameter is defined as:

$$<d> = 2 \times \int_0^\infty r n(r, t) dr \quad (5)$$

where r is the radius of a drop and $n(r, t)$ is the number density

Table 1. Drop Diameter Moments from Transient Experiments

Figure No.	Time (min)	$<d>$ (μm)	d_{32} (μm)
4	0	90	136
4	10	138	223
4	30	160	334
4	55	158	446
5	0	81	103
5	10	83	241
5	30	72	560
6	0	71	125
6	5	56	592

of drops of size r at time t. The Sauter mean drop diameter, which is inversely proportional to the surface area per unit volume of dispersion, is defined as:

$$d_{32}=2\times\frac{\int_0^\infty r^3 n(r,\,t)dr}{\int_0^\infty r^2 n(r,\,t)dr} \tag{6}$$

As seen in Table 1, the Sauter diameter increases monotonically with time in each transient experiment although the number-average diameter does not. In fact, as ionic strength increases, the skewing of the distributions becomes so severe that the number-average diameter actually decreases with time.

From the above result it is clear that the measurement of one or even of several distribution moments is not at all adequate to characterize the process of drop coalescence. The behavior of the number-average diameters in these experiments demonstrates that one might actually reach erroneous conclusions (for example, that increasing ionic strength inhibits drop coalescence) by relying too heavily on the measurement of distribution moments.

The observed effect of drop charge on coalescence can be understood at least qualitatively by considering the magnitude of forces directed upon a drop pair undergoing coalescence. It is typically assumed that the turbulent force acting on a drop pair has a net negative value (in favor of coalescence) owing to the dampening of force fluctuations in the fluid between the drop pair. Muralidhar et al. (1988) have estimated this force to be proportional to $\overline{R}^{8/3}$, where $\overline{R}$ is the mean radius of the drop pair.

In contrast, the DLVO theory predicts that in accordance with Eq. 1 the force of electrostatic repulsion between two charged bodies should, for a given separation distance, scale according to $\overline{R}$; that is, $F_r \propto \overline{R}$. Thus, considering only these two main deterministic forces of attraction and repulsion applied to a drop pair one may write:

$$F_{net}=(F_r-F_a)\propto(a\overline{R}-\overline{R}^{8/3}) \tag{7}$$

where a represents the relative strength of the electrostatic repulsion force over the average attraction force from the turbulence. Figure 9 then plots the expected net force on a drop pair for different relative magnitudes of the electrostatic force component. It is apparent from this figure that electrostatic forces will be effective in preventing coalescence only for the drops below some critical size. In addition, as the magnitude of the electrostatic force is reduced (as, for example, by lowering the pH or by raising the ionic strength) the coalescence rate of large drops will be promoted more and more, while coalescence of the smallest drops remains inhibited.

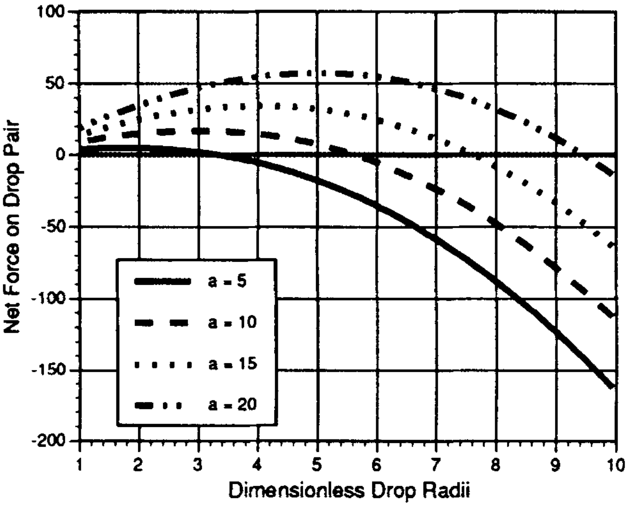

Figure 9. Effect of electrostatic repulsion on the net force between two droplets in an agitated medium ($F_{net}=a\overline{R}-\overline{R}^{8/3}$).

Significance

Although we have only presented here results for 5% dispersions of benzene/carbon tetrachloride and acetophenone in water, we have observed to varying degrees these same behaviors in other dispersion systems as well. In addition, transient experiments performed at different values of pH have confirmed that coalescence rates decrease with increasing pH. Thus the shift in the steady-state distributions with a change in pH is certainly due primarily if not wholely to the effect which pH has on coalescence (and not on breakup).

These results, together with the organic drop charge measurements of previous investigators lead us to conclude that the presence of substantial drop charges in organic-in-water dispersions is quite common. In addition, these charges seem fully able to retard coalescence in such dispersions.

The results of this work are seen to be important in three regards. First is that the experimental studies presented here clearly show that electrostatic effects due to OH^- adsorption onto organic-water interfaces can present a substantial degree of stabilization for agitated dispersions. Moreover such stabilization against drop coalescence occurs in the absence of added surfactants. This is an extremely important point because not only have the possible contributions of drop charge to stabilization in turbulent dispersions been neglected in the literature, but there do not appear to be any studies which have sought to address the role of latent drop charges in O/W dispersions. It is acknowledged that studies of charged and uncharged droplets in electrical fields, including coalescence rates in electrostatic coalescers have been reported; however, these studies deal with a phenomenon (namely, the motion of droplets in the presence of an applied electric field) which is quite different than that of the present study.

With regard to modelling the coalescence rate of droplets in an agitated dispersion, it can be seen that consideration of electrostatic repulsion is important for systems of low to medium ($\approx 10^{-1}$ M) ionic strength. Previous work by one of us (see for example Muralidhar and Ramkrishna (1988)) has gone toward the development of several fundamental models, based upon a stochastic analysis of the film drainage process between colliding drops. These models did not seek to incorporate electrostatic effects, but they provide a basis for our current work in the study of such effects. We are in the process of generalizing our previous analyses to take account of factors such as ionic strength and drop charge in the modelling of agitated drop coalescence, with the intention of publishing this work shortly.

The second significant point to be made from the results presented in this paper is that they offer a possible explanation for the experimental "reproducibility problem" encountered by many experimentalists in this field. Contamination of deionized water by carbon dioxide is both variable (depending on the time length of air exposure) and pervasive (especially when its effects go unappreciated). Since even slight changes in pH have been demonstrated to produce marked changes in drop interaction rates, it is entirely possible that variable pH is the primary factor responsible for the variability of experimental results.

Moreover, the common solution employed for eliminating such variability (namely, raising the electrolyte concentration, typically to a value of 0.1 molar or thereabouts) is fully explained by the fact that such high ionic strengths are able to completely negate any charge repulsion between drops.

Thirdly, the fact that the charge effects observed in this study appear to affect large and small droplets to different degrees demonstrates that full distributions (not average values or distribution moments) must be measured in order to properly understand the true effects on coalescence. Howarth (1967) performed experiments on a system of 5% benzene/CCl_4 in water in which he calculated average values of coalescence based upon rate changes of the Sauter mean drop diameter. His investigations on the effect of ionic strength led him to conclude that high ionic strengths inhibit drop coalescence. It is clear from the experiments in this present study that such a conclusion was wholly erroneous, and likely arose at least in part out of the uncertainties in assessing dispersion changes from single distribution moments cited above.

In summary, it is imperative that drop charge effects due to hydroxide adsorption be seriously considered when performing experimental studies, and when theorizing models of drop coalescence in turbulent dispersions. Future work must be based firmly upon an accurate understanding of the forces at work in turbulent dispersion systems, and must employ detailed experimental data showing the drop-size distributions in such systems. Only with such data may one be able to fully and confidently evaluate mechanistic models of the turbulent coalescence process.

Acknowledgment

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