

Effect of Degassing on the Formation and Stability of Surfactant-Free Emulsions and Fine Teflon Dispersions

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The results reported here demonstrate that the formation of surfactant-free, oil-in-water emulsions is significantly enhanced by the almost complete removal of dissolved gases. However, in an apparent contradiction, the reintroduction of dissolved gases does not destabilize already formed emulsions. Removal of dissolved gases enables the formation of much more turbid and stable hydrocarbon oil in water emulsions, which can be further studied without the effects of various additives, often needed as stabilizers. The observations reported here suggest that the dispersion of oil droplets in water is opposed by an attractive, hydrophobic force, which is dependent on the presence of dissolved gas. However, once formed, the stability of the emulsions appeared to be unaffected by any attractive hydrophobic force, in either gassed or degassed conditions. Degassing was also found to enhance the dispersion of fine Teflon particles in water.

Introduction

Everyday “common knowledge” tells us that oil and water do not mix. This fact is assumed to be related to the different properties of the two materials. Oil being nonpolar is “hydrophobic” and therefore water-hating. This view is certainly valid for molecular mixtures of oil and water. Simply put, the work required to force apart hydrogen-bonded water molecules to incorporate hydrocarbon solute molecules is too large and this work is not compensated by a strong solute–water bonding, which is the case for soluble solutes such as common salt, sugar and ethanol. Each of the latter solutes can form strong bonds with adjacent water molecules, which replace those between the water molecules themselves.

Another type of mixture, not molecular in nature, can be formed by the dispersion of microscopic droplets or particles, often in water, to form a “colloidal solution or dispersion”. However, hydrocarbon oils and finely divided hydrophobic particles will not readily disperse in water and will only remain stable for a short length of time, typically, for less than an hour, even after vigorous mechanical agitation. Thus, most industrial processes involving these mixtures require continuous agitation and fairly rapid reaction times. The efficiency of these processes is also reduced by the difficulty in maintaining small particle sizes and a high reaction surface area, because of the tendency to coalescence and coagulation. The stability of emulsions and dispersions can be much improved by the addition of surfactants and polymers, which can change the nature of the oil/water interface. However, these observations are, at first sight, not consistent with a simple application of the well-established DLVO theory of colloid stability.¹ This is because oil droplets and fine, hydrophobic particles, even without additives, are known to develop significant surface electrostatic potentials in water and, in addition, generally have weak van der Waals attractive forces. These conditions usually indicate that the colloidal dispersion will be stable.

It is, therefore, of some interest to consider in more detail why hydrophobic colloids, such as fine oil droplets, fail to

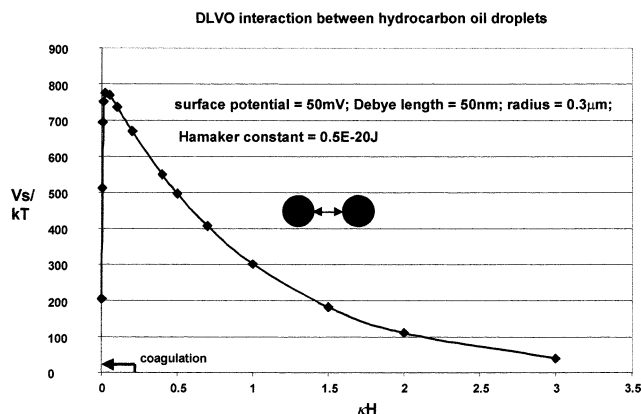


Figure 1. Calculated DLVO interaction between two similar spherical oil droplets.

maintain colloidal stability in water. The molecular force or bonding argument is not valid in this case (although it is directly related to the ultimate thermodynamic stability of the colloidal solution) because colloidal dispersions can be maintained in a meta-stable state by the operation of strong repulsion forces generated between the particles or droplets. The DLVO theory is based on the assumption that it is the charge on a colloidal particle (or droplet) surface which generates a repulsive electrostatic (double-layer) force between particles, which can be of sufficient strength to overcome the ubiquitous van der Waals attractive force. These combined forces can be estimated from the theory using the measured electrostatic potential on the surface of, for example, typical hydrocarbon oil droplets and their van der Waals attraction. The surface potential of dodecane droplets (as well as some other oils) was carefully measured in 1996,² and these values can be used to calculate the expected interaction energy between two oil droplets in water. Let us consider the static forces involved. Figure 1 gives the estimated DLVO interaction energies expected for 0.3 μm radius dodecane oil droplets in water, using the simplified, i.e., linear (low potential), Poisson–Boltzmann equation, combined with a nonretarded Hamaker attraction and using the Derjaguin approximation.¹ This radius was selected because

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smaller droplets will tend to coalesce through kinetic collisions and larger droplets have a greater buoyancy force and will rapidly coalesce with the upper oil phase. Droplets of 0.3 μm radius will rise at the rate of nearly 0.5 cm per day in water.

The DLVO equation used here to calculate this interaction is given below:

$$V_s(kT) = \frac{a}{kT} \left[2\pi\epsilon_0 D \psi_0^2 \exp(-\kappa H) - \frac{A_{121}}{12H} \right]$$

where V_s is the interaction energy between spheres in kT units, " a " is the spherical radius, ψ_0 is the particle's electrostatic potential, κ^{-1} is the Debye length, A_{121} is the Hamaker constant for the system, and H is the interparticle separation distance. $\epsilon_0 D$ is the permittivity of water. In the dodecane/water system, the calculated barrier is almost 800 kT (see Figure 1), which would give long-term stability to emulsion droplets of this size.³ The significant surface potential reported,² of between -50 and -60 mV, is apparently caused by the specific adsorption of hydroxyl ions from the aqueous phase to the oil/water surface. The standard theory of coagulation of colloids³ indicates that coalescence or coagulation will become significant when the repulsive barrier approaches 10–20 kT or less. Clearly, these simple calculations indicate that fine droplets of hydrocarbon should be indefinitely stable against coalescence in water, because of a combination of surface charging via hydroxyl ion adsorption and a relatively weak van der Waals attraction, a result which is at complete variance with general observation.

Because the interparticle potential energy barrier is proportional to the droplet radius, smaller hydrocarbon oil droplets will readily coalesce, as observed for the fine droplets (less than 50 nm radius) produced by the sonication of oil and water mixtures.⁴ Larger droplets will feel a substantial buoyancy force and will readily combine with the upper phase of dodecane liquid, because it has a lower density than water. Droplets of intermediate (micron) sizes should be stable for longer periods, if only DLVO forces operate. Similar stability arguments can be applied to fine Teflon particles, which are known to be charged⁵ and have an even weaker van der Waals attraction in water (with a Hamaker constant of 0.3×10^{-20} J).¹ The failure of the DLVO theory to predict the behavior of oil in water emulsions raises the issue of whether there might be additional forces involved. About 20 years ago, a new long-range attractive force, called the "hydrophobic interaction",⁶ was discovered which acted over relatively large distances (> 10 nm) between hydrophobic surfaces in water. Subsequent workers have extended the range to over 100 nm in some systems (see, for example, ref 7).

In later work, it was also suggested that dissolved gases may play a significant role in this interaction,^{8,9} which has yet to be properly described by any theoretical model. At normal temperature and pressure, dissolved air in water has a concentration of around 1 mM, corresponding to about 20 mL of dissolved gas in a liter of water. In typical alkanes, gas solubility can be an order of magnitude higher. The role of dissolved gas in the properties of solutions has hardly been considered theoretically and, experimentally, only sporadically and often ignored (see, for example, refs 10 and 11).

In 1993, it was demonstrated that partial degassing, using a water jet pump aspirator to produce about 97% degassing for mixtures of dodecane/water, increased the stability of oil droplets on vigorous shaking.⁸ These initial observations stimulated an AFM study which attempted to address the issue of dissolved gas in the interaction of hydrophobic polypropylene surfaces.¹² The polypropylene surfaces used in that study, although very

hydrophobic as measured by the water contact angle, generated only a relatively short-ranged attraction measurable up to about 25 nm separations. The effect of degassing was only minor in this case. However, Horn et al.¹³ reported a significant decrease in the long-range attraction (20–400 nm) between two polystyrene latexes as the level of dissolved gas in solution was reduced. In further work on emulsion stability, using a water jet pump to degas to the 97% level, it was also demonstrated that dissolved gas plays a significant role in emulsion stability and emulsion polymerization⁹ and this led to the suggestion that dissolved gas may play a significant role in the balance of hydrophobic and hydrodynamic (drainage) forces responsible for the phase separation. By comparison, Zana et al. examined the effects of degassing on surfactant aggregation¹⁴ and microemulsions¹⁵ and reported no effect in either case. However, this is hardly surprising because the amount of dissolved gas present in the aqueous phase, at the mM level, could not possibly be sufficient to influence these high surface area systems. Recently, a study of the coagulation rates of solid paraffin wax mixed with carboxylic acid stabilizer has shown that partial degassing (to about 97% using a water aspirator) has a significant effect on reducing the initial coagulation rates.¹⁶ More recently, Ishida et al.¹⁷ have reported the complete absence of a long-range attraction (beyond 10 nm) from force measurements on systems that have never been exposed to dissolved gases.

Unfortunately, the literature produced over the last 20 years contains many reports of force measurements between hydrophobic surfaces with widely differing results, often depending on the preparation of the surfaces and the method used. In an attempt to overcome some of these difficulties, the present study was based on the simple and direct observation of the effect of almost complete degassing on the dispersion and stability of surfactant-free oil and water mixtures and powdered Teflon dispersions. The central hypothesis to be tested is that the electrostatic potential on an oil droplet or Teflon particle should be sufficient to stabilize fine droplets and particles and that their lack of stability might be related to the hydrophobic interaction generated between these surfaces.

Materials and Methods

The water used was produced from tap water purified via a Millipore unit. The permeate so obtained was used in a positive pressure, dust-free laminar flow cabinet. Glassware was thoroughly cleaned by first rinsing AR grade ethanol to remove any surface active material. It was then finally rinsed in Millipore water.

Dodecane (density, ρ , of 0.75 g/mL and refractive index, n_D , of 1.4216) and squalane, tetracosane, 2,6,10,15,19,23-hexamethyl-squalane, $C_{30}H_{62}$ (ρ of 0.81 g/mL and n_D of 1.4530) were chosen as the two hydrocarbon oils for study and were both obtained puriss from Fluka and were used as purchased. All mixtures were made up in a laminar flow cabinet. The surfactant-free Teflon powder was obtained as a sample from DuPont. The size range was on average around 4 microns, with a small proportion (about 10%) above 8 microns and below 0.3 microns. Teflon has a refractive index of 1.359¹ and a void-free polymer density of 2.2–2.3 g/mL. The nitrogen adsorption area for the Teflon powder was in the range 7–10 m²/g, which is an order of magnitude higher than the calculated value for smooth Teflon spheres. It is most likely, therefore, that the Teflon powder sample used here was porous.

The removal of dissolved gas from an oil and water mixture can be achieved by repeated freezing (in liquid nitrogen) and pumping using an efficient, clean mechanical pump connected

to the mixture via a liquid nitrogen trap, to maintain cleanliness. In the experiments reported here, the liquid mixture was always immersed slowly into the liquid nitrogen, to prevent ice expansion from cracking the glass tube. Once the space above the frozen liquid was outgassed, to typically better than a mTorr, a Teflon tap was closed and the liquid warmed to room temperature, so that remaining dissolved gases were pulled into the space above the liquid. For each sample, this process was repeated four times to ensure almost complete removal of the dissolved gas. When connected to a separate vacuum line, of substantially larger volume, the mechanical pump readily achieved pressures down to 20–40 μ Torr. Evacuation of the mixtures to lower than a mTorr corresponds to greater than 99.999% removal of dissolved gas.

To directly compare the effect of degassing, nitrogen gas was bubbled through the control or gassed samples to remove dissolved carbon dioxide and increase the pH value of the aqueous phase to 7, in agreement with that of the degassed samples. Otherwise, differences in pH values between the gassed and degassed samples might affect the surface charge on the oil droplets.

For the oil in water experiments, the glass tubes contained 2 mL of oil and 33 mL of water. For the Teflon study about 0.1 g of powder was placed in the bottom of the glass tube via a fine Teflon tube and about 35 mL of water added.

In some of the early experiments with dodecane and water mixtures, the outgassed tubes were sealed using a Teflon screw tap. However, it was discovered that these taps did not fully hold the vacuum (see Results section), and hence, all later studies were carried out via melt-sealing of the glass tube, using a propane/air flame, while the mixture was held frozen in liquid nitrogen and connected to the active pumping system.

The diameter of the outgassing tubes was selected to fit tightly inside the measuring cavity of a Micro 100 Turbidimeter (Nephelometer, from HF Scientific, Inc, USA). The device measured turbidity via detection of the amount of scattered light at right angles to an incident beam of white light. The turbidity of the aqueous phase of each sample was measured in Nephelometer Turbidity Units (NTU), where distilled water has a value of 0.02 and reservoir water typically 1–5.

In some of the experiments, the degassing tubes were shaken vigorously by hand for 10 s, to mechanically disperse the emulsion or dispersion. However, some samples spontaneously dispersed during degassing, without the need for additional shaking.

Results

It is interesting to note that even after only two cycles of freezing and pumping with a mixture of 33 mL water and 2 mL dodecane, the water phase became noticeably cloudy, without any mechanical shaking other than the mixing caused by gentle bubbling as the frozen (pumped) sample was allowed to warm to room temperature. After five cycles, the glass tube was sealed tightly using the Teflon screw tap. Without any external shaking, the water phase, on final melting of the outgassed solid, had an NTU value of over 50 and was completely opaque. The change in turbidity with time after this sample was vigorously shaken for 10 s is shown in Figure 2. Also, in this figure, for comparison, is the corresponding curve for a nitrogen-saturated mixture (in the same type of glass tube and with the same liquid volumes) which was also vigorously shaken by hand for 10 s. Prior to shaking, the water phase had an NTU value of about 0.06. The time plotted in Figure 2, in this case, was time after shaking. The nitrogen equilibrated

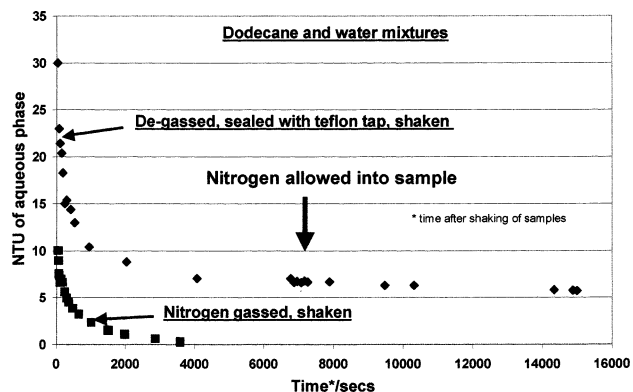


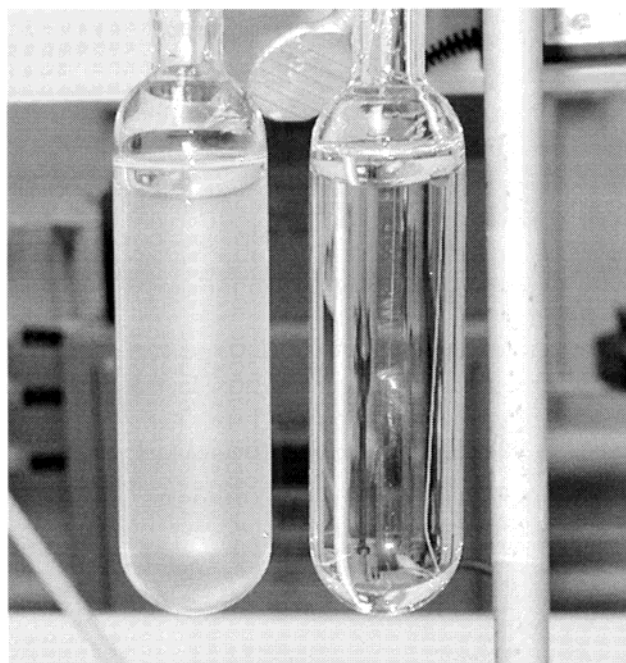
Figure 2. Comparison of the turbidity of dodecane and water mixtures with time after shaking, for degassed mixtures and after bubbling with nitrogen gas. In this case, the degassed mixture was sealed using a Teflon screw tap. Nitrogen gas was allowed into the degassed mixture halfway through the measurements.

mixture returned to the clear, two phase mixture within about an hour, whereas the degassed mixture was always much more turbid and maintained turbidity for a much longer period of time. After about 2 h, the degassed tube was opened and nitrogen gas let in. The results shown in Figure 2 clearly demonstrate that exposing the surfactant-free emulsion to dissolved gas *after* it has been formed has little or no effect on its stability. Forty-eight hours after shaking and exposure to gas, the aqueous phase still remained slightly turbid, with an NTU value of 2.3. Even after standing for 310 h, the NTU value of the aqueous phase was 0.35, significantly above the nitrogen blank value of 0.06.

Concerns about the ability of the Teflon screw taps to maintain a vacuum for long periods of time, led to repeat experiments with dodecane/water mixtures, in which the outgassed sample was melt-sealed under vacuum. This protocol was then followed in all of the subsequent experiments reported here. An example of the “spontaneous” turbidity of the aqueous phase of dodecane/water mixture, following five freezing/degassing cycles and after melt-sealing is shown in Figure 3, together with a nitrogen equilibrated sample, for comparison. Both tubes were exposed to similar, modest degrees of turbulence, because nitrogen gas was bubbled through the gassed mixture, for a similar time. The differences are visibly obvious, the degassed mixture had a uniform turbidity in its aqueous phase, whereas the aqueous phase of the gassed mixture remained optically clear.

Figure 4 gives a comparison of the turbidity of the aqueous phase of dodecane/water mixtures under various conditions: on degassing but without any additional shaking; on shaking of the degassed sample, after it has been left to settle for several days and the “blank” nitrogen equilibrated mixture, after shaking. Clearly, both the “spontaneous” emulsion, obtained by degassing, and the degassed sample, shaken after settling, were significantly more turbid and remained so for a much longer period of time, than the gassed mixture. Further, the spontaneously formed emulsion decayed much more slowly. For example, after 92 h its NTU value had fallen to 3.6 and after 262 h to 1.33, still much higher than the nitrogen (blank) value of 0.06. By comparison, the vigorously shaken sample, after only 50 h, had an NTU value of 2.6.

It is interesting to note that vigorous shaking seems to produce more turbid emulsions, initially, for the degassed samples compared with those degassed but not shaken. However, the latter were found to be much more stable with time, as shown in Figure 4 and in the squalane results later. It seems reasonable that shaking produces greater numbers of large oil droplets



Picture taken 12mins after the solid, in the LHS tube, had completely melted, following five stages of degassing (freeze/thaw process using liquid N₂) and final heat-sealing under vacuum.

LHS: de-gassed and sealed mixture (no-shaking) – NTU=53
RHS: nitrogen-equilibrated mixture (no-shaking) – NTU=0.06

[Mixture: 33ml water and 2ml dodecane]

Figure 3. Photograph of degassed and nitrogen gassed dodecane/water mixtures. Both samples were exposed to the same level of mild mechanical disturbance.

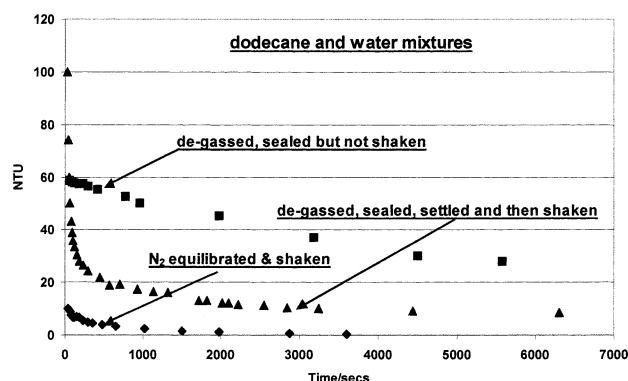


Figure 4. Comparison of the turbidity values for dodecane and water mixtures: degassed, sealed, and not shaken; degassed, sealed, and shaken; and nitrogen equilibrated and shaken.

which act as scavengers and “collect” many of the smaller droplets. The more gentle disturbance of the oil/water interface, inevitable during five cycles of freezing and degassing, seems to create a finer distribution of oil droplets (see Figure 3), which remains stable for much longer.

To test the generality of these observations, a significantly different hydrocarbon oil, squalane, was chosen for further study. Squalane is even less soluble in water than dodecane and is significantly more viscous. It is a clear liquid less dense than water. The results obtained with this hydrocarbon, shown in Figure 5, reflect precisely those obtained with dodecane. Once again the degassed state produced a much more turbid and stable emulsion in the aqueous phase, either spontaneously formed following the degassing procedure or after vigorous shaking. After 22 h, the “spontaneous” aqueous emulsion was still visibly

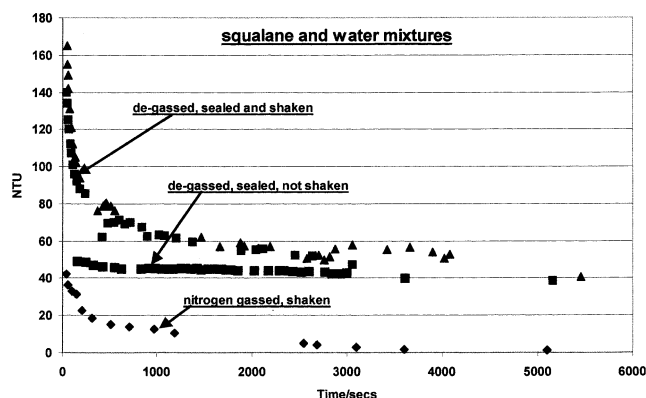


Figure 5. Comparison of the turbidity values for squalane and water mixtures: degassed, sealed, and not shaken; degassed, sealed, and shaken; and nitrogen equilibrated and shaken.

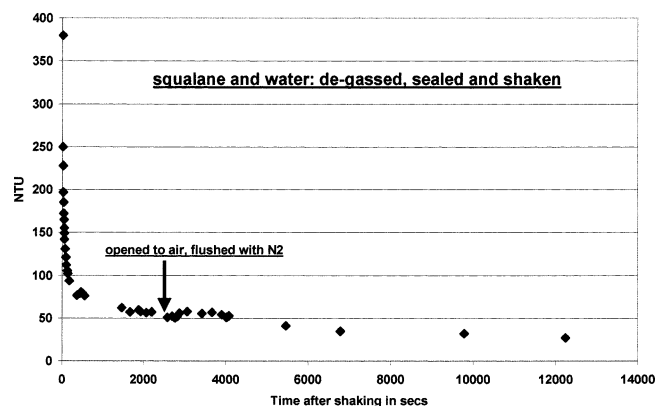


Figure 6. Turbidity values for squalane and water mixtures after degassing, sealing, and shaking. After 2400 s the mixture was opened to the air, the space above the liquid was flushed with nitrogen, and the tube was resealed with a rubber bung.

turbid, with an NTU value of 10.6. In comparison, the shaken sample decayed more rapidly initially, as for the dodecane mixture, and reached an NTU value after 46 h of 6.9.

In a repeat experiment, the degassed, melt-sealed and shaken mixture was opened in air about 2400 s after shaking. The sealed glass tube was cracked open in air, as carefully as possible, and immediately nitrogen gas was flushed into the air space above the mixture and the tube was then re-sealed with a rubber bung. The results obtained before and after exposure to gas are shown in Figure 6. Although initially, after opening, there was a slight increase in turbidity, probably because of the unintended disturbance to the mixture during the opening of the tube, the results clearly show, again, that once the surfactant-free emulsion is formed, exposure to dissolved gas does not destabilize the emulsion.

Figure 7 gives typical comparison curves for the decay in turbidity with time for squalane and dodecane mixtures, after shaking. The rates of decay are quite similar, although it is clear that squalane droplets produce much more turbid emulsions than dodecane. Figure 8 gives the corresponding comparison for the “spontaneous” emulsions, formed following the degassing process, without additional shaking. Again, the behavior is quite similar, with a greater turbidity, initially, for squalane.

The same type of degassing experiments were also carried out with hydrophobic Teflon powder. Unfortunately, these experiments were more difficult than those with the oil and water mixtures. Even when Teflon powder was physically placed in the base of the dry degassing tube, addition of water immediately floated the powder to the air surface and the material “climbed”

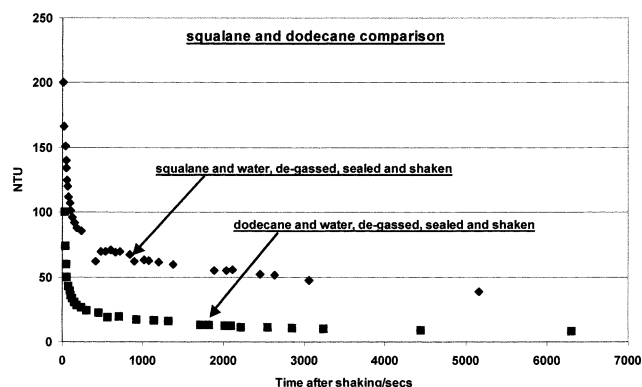


Figure 7. Comparison of dodecane and squalane after degassing, sealing, and shaking.

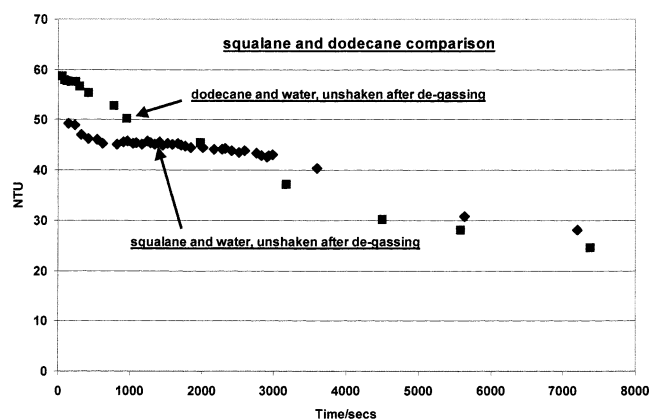


Figure 8. Comparison of dodecane and squalane after degassing but without shaking.

the glass walls, as shown in Figure 9. The process must involve flotation because void-free Teflon, at 2.2–2.3 g/mL, is much denser than water. Following, precisely, the same degassing procedure used for the oil/water experiments, the results shown in Figure 10 were obtained for Teflon dispersions. Once again, the degassed dispersion gave a much higher turbidity than the gassed case. However, these results need careful consideration because it was observed that for the nitrogen-gassed mixture, shaking produced a transient cloudy dispersion of clearly visible, large, white aggregates which generally rose in the tube after shaking. By comparison, for the degassed case, some of the clearly visible aggregates fell and some rose. In both cases, much of the Teflon powder remained at the top of the tube, at the surface and walls as shown in Figure 9, even after vigorous shaking. However, on degassing, more of the Teflon was forced into the aqueous phase. Degassing clearly had an effect on the buoyancy of the powder, which tends to dominate its dispersion properties.

Discussion

The discovery of the long-range hydrophobic interaction between surfactant coated surfaces⁶ initiated an extensive search for an explanation based on the effect of a nonpolar surface on adjacent water layers. The range and magnitude of this attraction is orders above that expected from van der Waals forces and has produced a major problem for theory. So far, no theory has been able to explain the range of interactions observed for the various surfaces and conditions reported over the last 20 years. The first observation of spontaneous cavitation of water held between two hydrophobic (surfactant-coated) surfaces was reported in 1985,¹⁸ where it was observed on separating two

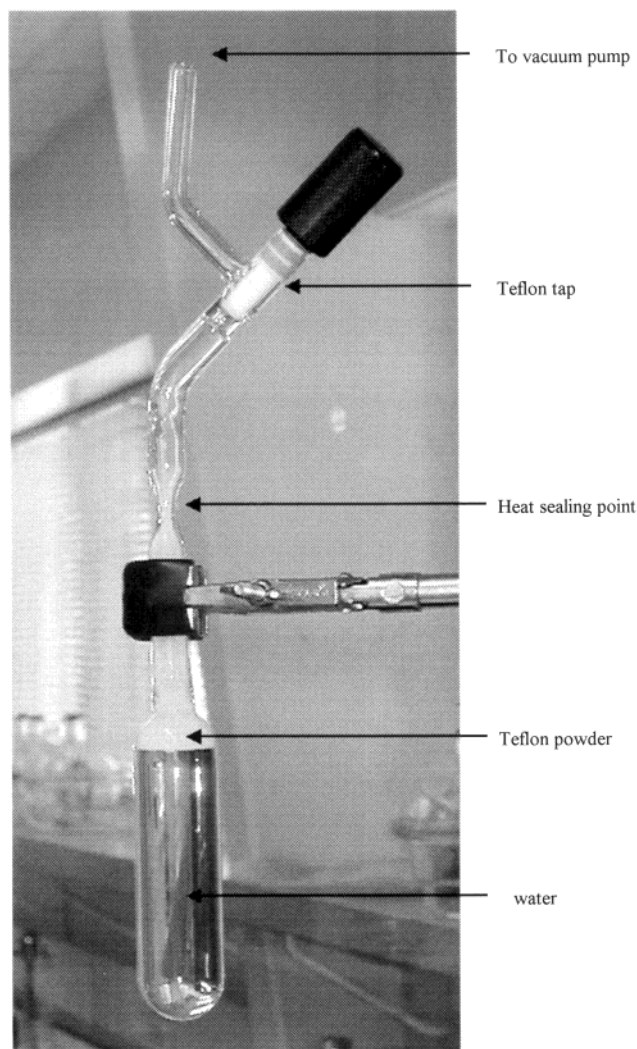


Figure 9. Photograph of the degassing tube containing water and Teflon powder prior to degassing.

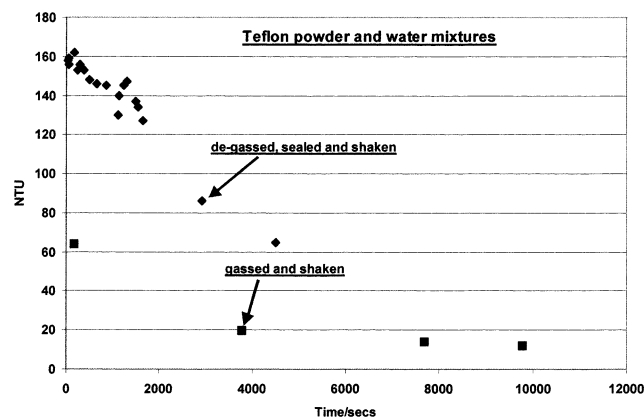


Figure 10. Comparison of turbidity values for Teflon dispersions after degassing and nitrogen equilibrated.

surfaces from adhesive contact. Later studies indicated that cavitation may actually occur prior to surface–surface contact of two hydrophobic surfaces.¹⁹ The possibility of dissolved air or vapor cavities, induced by hydrophobic surfaces in water, may offer a way forward in the search for an explanation of the range of the hydrophobic interaction. Hydrophobic surfaces in water should present a favorable adsorption surface for dissolved gases. One liter of water at room temperature and atmospheric pressure contains about 20 mL of dissolved gas,

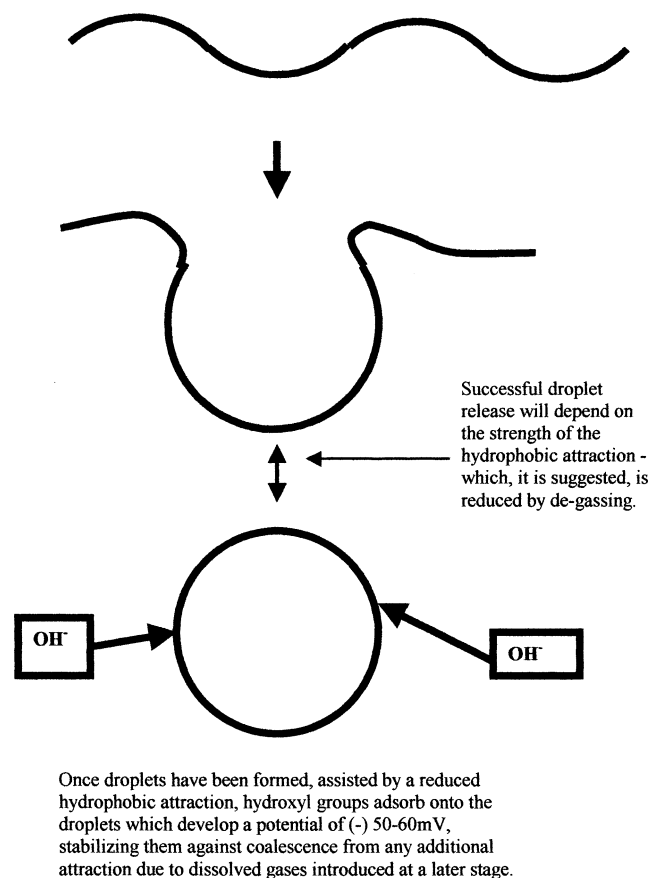


Figure 11. Schematic description of the break off of fine oil droplets from the water/oil interface.

close to its saturation level. The unfavorable interaction of water layers adjacent to a hydrophobic surface might act to concentrate dissolved gas and this could lead to cavitation when two such surfaces approach. The proximity of two hydrophobic surfaces might also induce spontaneous water vapor cavitation, but presumably the presence of nonpolar dissolved gas solutes would make the formation of these cavities more favorable. Unfortunately, at present, there is no theoretical framework to progress these ideas.

If dissolved gas is a central component of the hydrophobic interaction, the stability of oil droplets might be expected to change with the introduction of gas, into a degassed, oil in water, surfactant-free, emulsion. However, no effect was observed here. Instead, a strong effect was observed only at the formation stage of the emulsion. Thus, it appears that removal of dissolved gases enhances the ability of oil droplets to break away from the oil phase, even with modest mechanical disturbance, as illustrated in Figure 11. Once these droplets have been created, adsorption of hydroxyl ions will be expected (see ref 2) to produce a substantial electrostatic potential of at least -50 mV, which when combined with the relatively weak van der Waals force, should lead to emulsion stability (see Figure 1), with an expected barrier of nearly 800 kT. Although the results presented here clearly demonstrate a dramatic effect of degassing on the formation of emulsions, their long-term stability can be affected by droplet coalescence and Ostwald ripening, as well as by simple buoyancy effects. However, the similarity in turbidity behavior of dodecane and squalane degassed emulsions, even though the solubility of squalane in water is significantly lower than dodecane, suggests that Ostwald ripening is unlikely to be the main process for the observed change in turbidity. In addition, it appears from the estimated magnitude of the DLVO

barrier (see Figure 1) that droplet coalescence is also unlikely to occur. Also, the observation that exposing emulsions to dissolved gas has no effect on stability (see Figures 2 and 6) indicates that any hydrophobic attraction between equilibrated oil droplets, in either gassed or degassed conditions, is insignificant relative to the magnitude of the electrostatic repulsion. Thus, it seems likely that the observed slow reduction in turbidity may be simply due to the loss of droplets under the action of gravity.

The clear differences in formation of the emulsions in gassed and degassed conditions must be due to differences in their ease of formation. Thus, removal of dissolved gases apparently aids detachment of, presumably, weakly charged oil droplets, which would otherwise readily coalesce. However, once these droplets are formed, their charge increases and a significant barrier is formed against coalescence. Reintroduction of dissolved gases at this, later, stage then has little or no effect. The diffusion of hydroxyl ions to the rapidly formed, new droplet surface will be relatively slow, because of the low background concentration, of typically 10^{-7} – 10^{-8} M. Whether increasing the hydroxyl ion concentration would facilitate dispersion needs further study.

It is interesting to observe that the use of charged surfactants to stabilize emulsions, via adsorption at the oil/water interface, might well be effective more because of the consequent reduction in hydrophobicity of the interface, via rapid surface diffusion, rather than to any enhancement of the surface charge. Nonionic surfactants must also stabilize emulsions by reducing the hydrophobic attraction between droplets. Of course, both types of surfactant will also substantially reduce the interfacial energy and change the thermodynamic stability of the emulsion.

Further work needs to be carried out on these degassed emulsions, possibly using light scattering techniques, to establish the precise details of droplet size and distribution. For example, the magnitude and range of the double-layer repulsion could be widely varied by controlling electrolyte levels and hence cause droplet coalescence. It might also be interesting to look at the effect of different dissolved gases. Fluorocarbon liquid emulsions could also be studied. Oils with densities close to water would also be interesting with regards to their long-term stability.

The initial results reported here for the effect of degassing on Teflon dispersions are difficult to interpret because of the strong hydrophobicity of Teflon and its effect on the buoyancy of the particles. The observation that the larger Teflon aggregates were easy to see dispersed in water for both the gassed and the degassed samples suggests that in both cases the particles contained significant air or vapor cavities. The refractive index of the polymer (1.359) is close to that of water (1.33), and yet the aggregates, when immersed in water, were clearly white. Also, the particles, after dispersion, mostly rose upward, even though the polymer density is between 2.2 and 2.3 g/mL. The Teflon particles are most likely quite porous, and it is reasonable to expect that the high water contact angle, of 110° , would produce air or vapor cavitation around clumps of particles and within the porous particles themselves, as illustrated in Figure 12. Degassing did enhance dispersion, but this could have been, in part, because of a buoyancy effect keeping the gassed particles at the water surface (for example, see Figure 9). Unlike oil emulsions, Teflon dispersions seem to be dominated by buoyancy effects. It was clear that, even for degassed Teflon dispersions, the particles often floated and must therefore contain more than their own volume of attached vapor bubbles and cavities. Thus, the interaction between these particles and their stability must be dominated by the attached gas and vapor

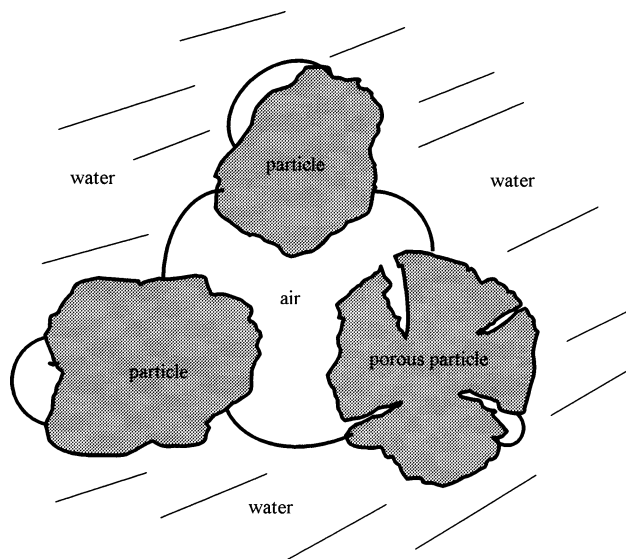


Figure 12. Schematic description of the air and vapor entrapment and attachment apparent from the results obtained with hydrophobic Teflon dispersions in water.

bubbles. The presence of dissolved gas appears not to be so important for these systems because of their ability to form vapor cavities, even in the absence of dissolved gases. Hydrophobic particles with contact angles less than 90° should be easier to study and should be more dependent on dissolved gas.

The discovery that removal of dissolved gases strongly enhances the formation of surfactant-free emulsions and hydrophobic dispersions should be applicable to any hydrocarbon or fluorocarbon water-insoluble oil and water mixture and to any finely divided solid hydrophobic powder, such as talc or carbon black. These surfactant and polymer free emulsions and dispersions can be stored, indefinitely, under vacuum or can be used for some time, within hours to days, after exposure to air. Using this process, it is possible to form oil in water emulsions without the use of additives, which will enable further study of the properties of the "natural" oil/water interface. There may also be some potential industrial applications for this process, for the formation of emulsions without the use of surfactants and polymer stabilizers.

Conclusions

This study has demonstrated that degassing enhances the formation of oil in water emulsions and the dispersion of fine (hydrophobic) Teflon particles in water, without the use of stabilizers, such as surfactants and polymers. Once dispersed, hydrocarbon emulsion droplets apparently become charged and

are not then destabilized by exposure to dissolved gases. These results suggest that the reduction in the hydrophobic attraction between oil droplets in degassed water enhances droplet release and emulsion formation. Emulsions formed by this process could be used for the study of the oil/water interface, without the presence of surface active additives. Initial studies of powdered Teflon dispersions indicate that vapor cavitation can occur in the absence of dissolved gas for these very hydrophobic systems and that these effects will dominate their dispersion properties. There may be some useful industrial applications of the degassing process, whereby stable mixtures and dispersions of hydrophobic materials might be formed without the use of additives.

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