Surfactant-Free Emulsions

The Pristine Oil/Water Interface: Surfactant-Free Hydroxide-Charged Emulsions**

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Oil and water do not mix spontaneously, so the formation of a stable oil-in-water emulsion is thought to require both the input of energy to create small oil drops and the presence of a surfactant to stabilize the newly formed surface of the otherwise metastable droplets.[1,2] Amphiphilic surfactants with a polar head group and a hydrophobic tail are typically used to create a charged surface around the oil drop for electrostatic stabilization. Yet it has long been known that the oil/water interface can acquire a negative charge in the absence of surfactants.[3,4] From the pH dependence of this

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charge it was inferred that hydroxide ions are responsible, but this inference was qualitative and tentative. The experiments involved only the small surface areas of dilute emulsions or plane interfaces, so the possibility of interference from trace contamination could not be excluded.[5–7] We have now used the new technique of electroacoustics to measure the increase in total surface area during homogenization of more concentrated oil-in-water emulsions and have found a linear relationship with the amount of hydroxide ion added to maintain a constant pH value. These pH-stat experiments quantitatively demonstrate that hydroxide ions do stabilize the oil/water interface; a fundamental reassessment of the perceived need for surfactants to obtain emulsion stability is thus required.

The electroacoustic technique can be used to measure the diameter d and the charge (zeta potential ζ) of emulsion droplets as they are being formed. An electroacoustic effect is created when an alternating megahertz electric field is applied to a concentrated (>1 vol%) colloidal suspension.[8] The charge on the particles causes them to "jiggle" in the field. Because of the difference between the density of the droplets and that of the surrounding fluid, this oscillatory motion creates a sound wave of the same megahertz frequency as the applied electric field. By measuring the phase and amplitude of this sound wave, the complex dynamic mobility spectrum is obtained, which can be analyzed to give the mean diameter of the emulsion droplets, their zeta potential, and the spread of a lognormal size distribution. The only input parameters required are the density and volume fraction of the oil. Because the droplets are spherical the total oil/water surface area can be immediately obtained from their diameter and the volume fraction of oil.

In a typical experiment a coarse emulsion was prepared by passing through a homogenizer a mixture of 2 vol% hexadecane in 0.2 mM NaCl solution prepared with freshly boiled water that had been cooled under a N_2 atmosphere. (The electrolyte was necessary for the electroacoustic measurements.) The pH value was then adjusted to pH 9 with NaOH solution, and the emulsion repeatedly passed through the homogenizer and the flow-through cell of a prototype of the AcoustoSizer-II, again under N_2. As the emulsification progressed the pH value would drop unless maintained at pH 9.0 ± 0.1 by the periodic addition of 20 mM NaOH solution. After each addition of alkali the dynamic mobility spectrum was measured and the droplet size d_{50}, lognormal size distribution d_{15} and d_{85}, and zeta potential were calculated (Table 1).

Table 1: Quantity of hydroxide ion required to maintain pH 9.0 during emulsification of 2 vol% hexadecane (4.9 mL) in 240 mL of 0.20 mM NaCl with calculated emulsion parameters: median droplet diameter d_{50}, the 15th and 85th percentiles of the lognormal distribution d_{15} and d_{85}, and the surface area (SA).

OH^- [μmol]	Q_{surf} [C]	d_{15}–d_{50}–d_{85}[a] [μm]	SA [10^5 cm^2]
2.4	0.23	0.90–2.5–6.9	1.95
5.0	0.48	0.90–1.55–2.7	2.50
8.4	0.81	0.80–1.1–1.5	3.12
11.0	1.06	0.69–0.82–0.97	3.89
14.4	1.39	0.63–0.73–0.85	4.33
17.0	1.64	0.59–0.65–0.72	4.75
19.6	1.89	0.54–0.58–0.62	5.24
22.4	2.16	0.49–0.51–0.53	5.88
25.8	2.49	0.42–0.46–0.50	6.66

[a] A large-particle correction was applied iteratively for the larger droplets to account for the effect these have on the observed phase lags in the dynamic mobility spectra.[22]

The surface area (SA) of a polydisperse distribution is $(6\Phi/d_{50})\exp(0.5\beta^2)$, where Φ is the volume fraction of the oil and $\beta = \ln(d_{85}/d_{15})$.[9] In this experiment, as homogenization proceeded, the droplet diameter decreased from 2.5 μm with a broad size distribution to 0.46 μm with a narrow distribution. This resulted in a threefold increase in surface area. The amount of hydroxide ion required to charge this newly formed surface is known directly from the quantity of base needed to maintain the constant pH value (Table 1). The amount of hydroxide ion added depends linearly on the new surface area created (Figure 1), which allows the surface charge density to be calculated from the slope as −4.9 μC cm^{-2} (0.31 unit charges per 100 Å^2). If the experiment is repeated at pH 7, the mixture requires more passes through the homogenizer to reduce the droplet size, but the amount of hydroxide ion added is again a linear function of the surface area created, with a slightly reduced surface charge density of −4.5 μC cm^{-2} (Figure 1).

Several alternative explanations of these results can be eliminated. For example, care was taken to eliminate carbon dioxide from the system, which otherwise would compromise the quantitative pH-stat experiments described above. Carbonate or hydrogencarbonate ions are not strongly adsorbed on the surface.[6] When 2 vol% hexadecane was homogenized in 1 mM Na_2CO_3 solution the droplet size (0.45 μm) and zeta potential (−45 mV) were found to be the same as those obtained in 1 mM NaOH solution. The purity of the hexadec-

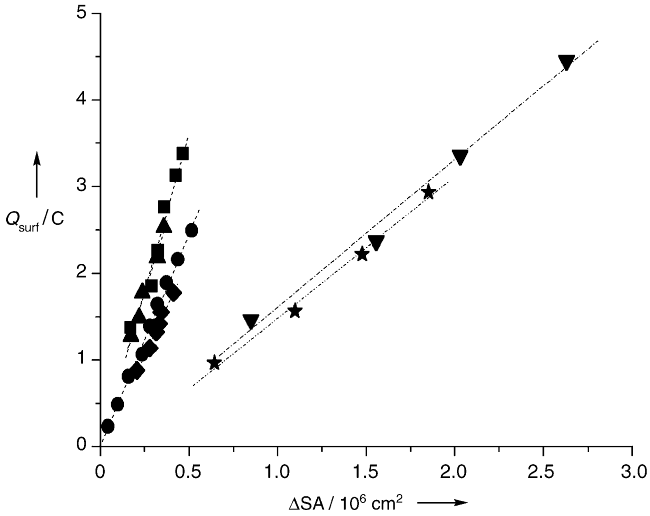

Figure 1. Surface charge density σ^o calculated from measured values of surface charge (Q_{surf}) and increase in surface area (ΔSA) for 2 vol% oils in 0.2 mM NaCl: perfluoromethyldecalin (■), pH 9.0, −7.3 μC cm^{-2}; squalene (▲), pH 9.0, −6.7 μC cm^{-2}; hexadecane (●), pH 9.0, −4.9 μC cm^{-2}; hexadecane (◆), pH 7.0, −4.6 μC cm^{-2}; hexadecane with 2 mM SDS (▼), pH 9.0; −1.7 μC cm^{-2}; squalene with 2 mM SDS (*), pH 9.0, −1.6 μC cm^{-2}.

ane was not critical. Hexadecane was purified by five passages through a column of basic alumina.[10] The use of unpurified hexadecane required about 20% more hydroxide to obtain the same droplet size and zeta potential. The method of homogenization of the oil also was not a factor; emulsions were obtained whether the hexadecane was homogenized by sonication or by passage through the multivalve homogenizer.

Most importantly, hydroxide-stabilized emulsions are not confined to hexadecane, but their formation occurs generally for oils with low solubility in water. The pH-stat experiment at pH 9 gives a surface charge density of $-7.3\,\mu\mathrm{C\,cm^{-2}}$ with perfluoromethyldecalin and $-6.7\,\mu\mathrm{C\,cm^{-2}}$ with squalene (Figure 1). We have also prepared stable emulsions with decane, dodecane, eicosane, and squalane.

We can infer that the hydroxide ion is located at the surface of the droplet and not dispersed throughout the oil. There is insufficient water dissolved in the oil to hydrate the anion. The solubility of water in hexadecane is about $0.08\,\mathrm{g\,L^{-1}}$.[11] For the experiment described in Table 1 this corresponds to 2×10^{-5} mol, about the same magnitude as the amount of hydroxide adsorbed. It is also unlikely that the hydroxide ions are involved in hydrogen bonding to the water dissolved in the oil, as has been suggested,[12] for this would bring all of the water to the surface of the oil drop. Furthermore, the adsorption of hydroxide depends linearly on the surface area, as illustrated in Figure 1, and not on the volume of the droplet. Most of the hydroxide ion surface charge of $-4.9\,\mu\mathrm{C\,cm^{-2}}$ is compensated by Na^+ counterions in the Stern or stagnant layer inside the shear plane. The measured zeta potential of −105 mV at pH 9 in 0.2 mM NaCl corresponds to a diffuse layer charge of only $0.63\,\mu\mathrm{C\,cm^{-2}}$.[13,14]

Hydroxide ions are the specific charge-generating species at the hexadecane oil/water interface. When the 0.4 mM supporting electrolyte was changed from NaCl to NaI or $NaClO_4$, the same zeta potentials were observed with the same pH dependence (Figure 2). Hence dispersion forces are not significant at these low salt concentrations.[15] Extrapolation indicates an isoelectric point between pH 3 and 4.

Such surfactant-free emulsions are remarkably stable.[16] A hexadecane emulsion prepared at pH 10.5 in 1 mM NaCl solution was slowly titrated to pH 4.5 with HCl. After measurement at pH 4.5, reversal of the pH to 10 restores the original dynamic mobility spectrum, which indicates no irreversible change in the zeta potential or droplet size. At pH 9–10 the emulsions are stable for days. They do degrade, however, if the electrolyte concentration is increased to more than about 5 mM of salt. Hence these emulsions are stabilized electrostatically by a high zeta potential with a relatively thick double layer on the order of 10 nm or more. When the double layer shrinks to a few nanometers on addition of salt, the emulsions become unstable.

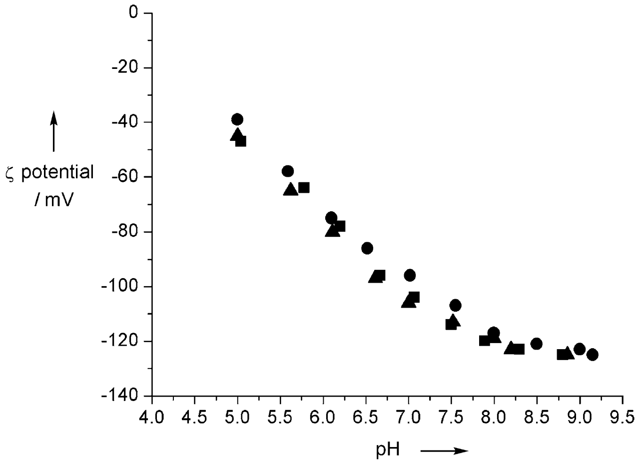

Figure 2. pH dependence of the zeta potential of 2 vol% hexadecane emulsions prepared at pH 9 in 0.4 mM $NaClO_4$ (■), NaI (●), or NaCl (▲) solutions.

When the surfactant sodium dodecylsulfate (SDS) is added to a hexadecane emulsion at pH 9 the pH rises, as SDS displaces the hydroxide ion from the surface, but the pH increase is not large enough to account for all of the adsorbed hydroxide ions. The implication is that some hydroxide ions remain on the surface in equilibrium with adsorbed SDS at pH 9–10. To test this hypothesis the pH-stat experiments were repeated in the presence of 2 mM SDS. In the presence of the surfactant the homogenization process is more efficient, and smaller droplets are produced with a consequently larger surface area (Figure 1). With both hexadecane and squalene a pH drop is still observed; the amount of base required to maintain the pH value amounts to a hydroxide surface charge density of −1.7 and $-1.6\,\mu\mathrm{C\,cm^{-2}}$, respectively, consistent with the adsorption of some hydroxide ion on the SDS-stabilized surface.

The pH-stat experiments in the absence of surfactant demonstrate quantitatively that hydroxide ions charge and stabilize these oil-in-water emulsion droplets. This conclusion previously could only be inferred from the pH dependence of the zeta potential[6,17] and has been disputed by some authors.[12] The large surface area created by the relatively concentrated emulsion produces a measurable pH effect, and the size of this effect eliminates the possibility of contamination from trace impurities.

A similar pH dependence of the charge of the air/water interface has been observed in a number of studies and also attributed to preferential adsorption of hydroxide ion.[7,18–20] The present results require that the many experimental and theoretical studies[21] of the air/water and oil/water interfaces that have ignored this charge on the surface be re-evaluated.

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