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Interfacial Charge

Why Are Hydrophobic/Water Interfaces Negatively Charged?**

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Interfaces between water and apolar media (gases, liquids, or solids) have a high cost in free energy. Therefore they tend to recombine to reduce the total interfacial area: in water, oil drops coalesce and air bubbles recombine following collision. The metastability of emulsions, foams, and polymer dispersions is achieved through adsorption of amphiphilic molecules (ionic or non-ionic), macromolecules, or particles, which block the recombination. The mechanisms of this stabilization are well understood.[1] Yet very fine emulsions made of pure oil droplets in pure water have also been found to be metastable in the absence of any added stabilizers.[2–4] According to sum frequency generation (SFG) spectroscopy [5] and electrophoretic mobility measurements,[2,3] the droplets of these surfactant-free emulsions are ionized and carry a negative electrical charge. Similar results have been reported for the water/air interface.[6–8] Moreover, this negative charge increases rapidly with pH value and therefore with the bulk concentration of hydroxide ions.[2,4,9]

The most frequent explanation given for these phenomena is that hydroxide ions adsorb at hydrophobic/water interfaces. While consistent with the pH signature of these phenomena, this explanation requires high adsorption energies, more than 20 times the thermal energy k_BT (about 50 kJ mol^{-}),[2,6] and an outstanding selectivity of hydroxide ions over other simple anions[2,6,10,11] that do not adsorb at such interfaces. On the theoretical side, some models attempt to account for this unexpected adsorption,[12–14] while others find no accumulation of hydroxide ions at hydrophobic interfaces;[15] still, other models look for another origin of the surface charge.[16] At present, there is no clear and straightforward understanding of this intriguing phenomenon.

The basic assumption of all previous experimental and theoretical studies has been that these systems have "pristine" oil/water interfaces, that is, oil molecules in contact with water molecules, although the possibility of contamination by anionic, surface-active impurities has been mentioned.[17] This assumption is supported by the use of pure components (99%) with additional purification, thoroughly cleaned glassware and equipment, inert atmospheres, and good reproducibility of the data. Moreover, the same variation with pH value of the surface charge has been found by different research groups with various experimental systems. However, the question remains whether these results leave no other choice but to accept a specific adsorption of hydroxide ions at hydrophobic interfaces? We propose that an alternative mechanism could be a reaction of hydroxide ions with species that are confined to the interface.

We conducted systematic experiments to find out whether such alternative explanations could account for all the published experimental results. We used emulsions obtained through a solvent-shifting method.[18–20] Solutions of hexadecane, of different purities, were prepared at a constant volume fraction of 10^{-3} in 99.9% pure acetone. They were then mixed with a much larger volume (×20) of Milli-Q water. The supersaturated solution separated spontaneously, yielding nanometer-sized hexadecane droplets (average diameter approximately 150–200 nm). This process is particularly well suited to the study of the stability of hydrophobic/water interfaces, because the droplets grow through a recombination mechanism that ends when their interfaces acquire a sufficient number of stabilizing ions. Hence, both final size and polydispersity of the nanometer-sized droplets decrease upon increasing the concentration of stabilizing ions. The final sizes of the droplets can also be controlled through the concentration of oil in acetone and the rate of addition of the acetone/oil solution into water.

We performed three types of experiments using these emulsions. First, we measured the electrophoretic mobility of oil droplets in emulsions made with different oils, as a function of the pH value of the aqueous phase (Figure 1). In these experiments, the emulsification process was adjusted so that the average droplet size was the same in each emulsion. The only difference between the three emulsions was the composition of the oil.

The first emulsion was made with 99% pure hexadecane in water at pH 6, ionic strength $I = 10^{-3}$ mol L^{-1} (sodium chloride), and with a mean droplet diameter was 170 nm. Then we varied the pH value and measured the electrophoretic mobility of the oil droplets, using a Malvern Zetasizer. We found that the pH variation (Figure 1), reproduced the signature of the surface-charging process described in previous studies.[2,4] The mobility was close to zero at pH 2–3, increased in magnitude until pH 8, and subsequently remained constant. If this variation was due to the adsorption of hydroxide ions, previously used models immediately show that their adsorption free energy would be above 20 k_BT.[2,6] We checked that the addition of other small anions (halides or carboxylates) did not produce any changes in the electrophoretic mobility, as had been reported.[6,11] Therefore the change in surface charge detected is specific to the concentration of hydroxide ions.

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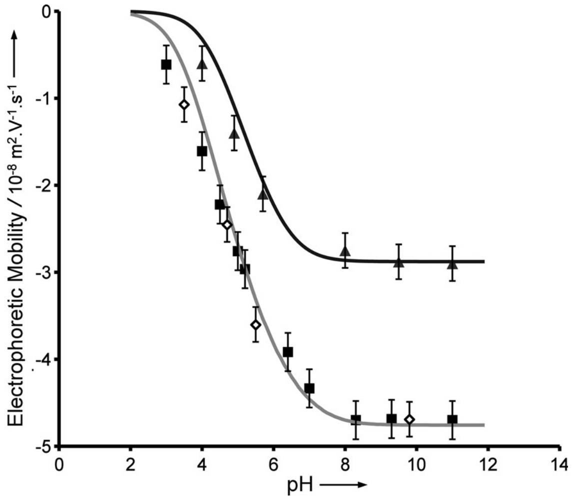

Figure 1. Variation of the electrophoretic mobility of hexadecane droplets with pH value, at a constant ionic strength of 1 mmol L^{-1} adjusted with NaCl. Emulsions were obtained though solvent-shifting using 99% pure hexadecane (■) or 99.8% pure hexadecane that was deliberately contaminated with oleic acid at a concentration of 5.8 mmol L^{-1} (◇) or also with fast mixing, using 99.8% pure hexadecane (▲). The mixing conditions were adjusted so that these three emulsions have the same mean diameter of 170 nm. Smooth lines are fit according to the model presented in the text, with a charging free energy of 20.7 k_BT or equivalently an acidity constant of $K_a = 10^{-5}$. The maximal surface densities of elementary charges are 0.25 nm^{-2} (■) and 0.034 nm^{-2} (▲), which correspond to stabilizer concentrations in the oil of 7.0 mmol L^{-1} (■) and 1.0 mmol L^{-1} (▲).

While the hydroxide ions are certainly important in the charging process, it is unlikely that they possess the amphiphilic behavior implied by high adsorption energies and ion specificity. To demonstrate that the surface charging is not caused by hydroxide ions alone, we performed solvent shifting using an oil with a different grade of purity: 99.8% pure hexadecane (also purchased from Sigma–Aldrich). The pH variation of the electrophoretic mobility of oil droplets in an emulsion made of 99.8% pure hexadecane is shown in Figure 1 (black triangles). With this oil, faster mixing conditions were needed to obtain the same mean droplet diameter of 170 nm. The curve is similar to the one obtained with 99% pure hexadecane, but the electrophoretic mobility has a smaller magnitude at each pH value. Since the ionic strength and the average droplet diameters are constant, this means that the surface charge density, and thus the concentration of stabilizing ions, was lower for the 99.8% pure hexadecane than for the 99% pure hexadecane.

In a second set of experiments, we compared the size distributions of emulsion droplets, using a Cordouan Vasco dynamic light scattering instrument (Figure 2). In this experiment, the emulsions were made using identical mixing conditions, and therefore in each emulsion the average droplet size was proportional to the amount of stabilizing ions available. While a low-polydispersity emulsion with nanometer-sized droplets was obtained using 99% pure hexadecane, a much coarser emulsion was obtained using 99.8% pure hexadecane. The respective interfacial areas are proportional to the amounts of stabilizing species available in either case, since the mixing conditions are the same. As the amount of hydroxide ions available was the same in both experiments, the difference shows immediately that another species was involved in the stabilization. Moreover, the mean diameter obtained with 99% pure hexadecane at pH 11 was smaller than that at pH 6. Accordingly, when a larger amount of hydroxide ions was available, more stabilizing molecules were also available. Therefore, the anionic stabilizers were not hydroxide ions but were produced by a reaction with hydroxide ions, which is a property of weak acids. Moreover, these weak acids are likely present as impurities in the oil and gradually removed during purification.

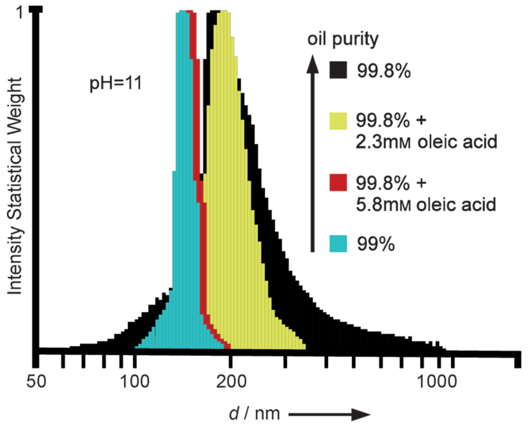

Figure 2. Normalized statistical size distributions obtained through dynamic light scattering measurements of emulsions at various oil purities and set hydroxide ion concentrations and mixing conditions.

To quantify the traces of weak acids in both oils, we performed a third set of experiments, using a standard chemical titration method. We titrated 99% pure hexadecane and 99.8% pure hexadecane using a standard method for quantification of fatty acids in an oil.[21] 10 mL of hexadecane were solubilized in 50 mL of a 1:1 mixture of 95% ethanol and diethylether and titrated by a 0.1 mol L^{-1} KOH solution in 95% ethanol. Phenolphthalein was used as a colorimetric indicator and the endpoint was obtained when the solution turned pink. The method was also checked against a hexadecane solution of known oleic acid concentrations and pure solvent. We obtained a weak acid concentration of 7.0 ± 1 mmol L^{-1} for 99% pure hexadecane and 1.0 ± 1 mmol L^{-1} for 99.8% pure hexadecane. This experiment therefore, provides a direct quantification of acid impurities in the oils. The value obtained for the 99% pure hexadecane compares well with the one that can be deduced from the electroacoustic titration experiment performed by Beattie and Djerdjev[4] (9.0 mmol L^{-1} versus our measurement of 7.0 mmol L^{-1}).

To determine if the stabilizing species could be fatty acid ions, that is, surfactant with a carboxylate ion as the hydrophilic head, we added a common fatty acid, 99% pure oleic acid, to the 99.8% hexadecane at a concentration of 5.8 mmol L^{-1} (which, together with the intrinsic impurities of the 99.8% hexadecane, equals the concentration of impurities in the 99% hexadecane), and produced an emulsion through solvent-shifting with a mean diameter of

170 nm. The mobility/pH value curve of this contaminated emulsion (empty diamonds in Figure 1) was identical to that of the emulsion obtained with 99 % hexadecane but different from the one obtained with the 99.8 % hexadecane. This result means that the addition of oleic acid increases the surface charge density, and thus stabilizes the droplet, but does not change the pH signature of the electrophoretic mobility. Therefore the weak acids that are present in the oil, according to the titration experiment, are fatty acids. Another way to visualize this is to follow the evolution of the size distribution of the emulsion, prepared under identical mixing conditions, upon contamination with oleic acid. As shown in Figure 2, adding increasing amounts of oleic acid to the 99.8 % hexadecane led to emulsions with progressively narrower distributions and smaller mean radii, matching the size distribution of the 99 % hexadecane when the concentration of oleic acid in hexadecane reached 5.8 mmol L^{-1}. These two experiments support the idea that fatty acids react with hydroxide ions to yield the anionic stabilizing species.

We can now consider whether this model accounts quantitatively for all observations, particularly the variation of mobility with pH value, using a single parameter, which is the pK_a value of fatty acids. For this purpose, we use the following relations: 1) pH to surface charge density, 2) surface charge density to surface potential, 3) surface potential to zeta potential, and 4) zeta potential to electrophoretic mobility.

To obtain relation 1, we must describe the acid–base equilibrium between fatty acids (RCOOH) and their anions ($RCOO^-$) at the oil/water interface. We use a mean field theory for calculating the activity of the fatty acid anions [Eq. (1)]

$$a_{\mathrm{RCOO^-}} = \frac{\sigma}{\sigma_{\max}} \exp\left(\frac{-e\psi_s}{k_B T}\right) \tag{1}$$

where σ is the surface density of elementary charges (m^{-2}), $\sigma_{\max}$ is the maximal surface density of elementary charges, ψ_s is the surface potential, k_B is the Boltzmann constant, T the temperature, and e the elementary charge. We define the acidity equilibrium constant, $K_a = (a_{\mathrm{RCOO^-}} a_{\mathrm{H_3O^+}})/a_{\mathrm{RCOOH}}$ with $a_{\mathrm{H_3O^+}} = 10^{-\mathrm{pH}}$. The total amount of stabilizer being constant, $a_{\mathrm{RCOOH}} = 1 - \sigma/\sigma_{\max}$. This leads to Eq. (2)

$$\sigma = \sigma_{\max} K_a / \left(K_a + 10^{-\mathrm{pH}} \exp\left(\frac{-e\psi_s}{k_B T}\right)\right) \tag{2}$$

This expression contains only two parameters, the maximum surface charge density, $\sigma_{\max}$, and a free energy $-k_B T \ln(K_a)$

In order to obtain relation 2, we use the Poisson–Boltzmann theory, as expressed in the Grahame Equation [Eq. (3)]:[1]

$$\frac{\sigma}{e} = \sqrt{8\varepsilon\varepsilon_0 k_B T I} sh\left(\frac{e\psi_s}{2k_B T}\right) \tag{3}$$

where $\varepsilon\varepsilon_0$ is the local dielectric constant and I is the ionic strength (number of ions per unit volume). There are no free parameters in this Equation, that is, the value of the surface charge uniquely determines the surface potential.

Obtaining relation 3 is more difficult since the zeta potential is defined at the shear plane, which is at a short distance, d, from the surface. The electrical potential at the shear plane is attenuated with respect to the surface potential by a factor that increases with the distance d between the surface and the shear plane. We calculate this factor using the Gouy–Chapman theory.[1]

For relation 4, we did not use the simple linear Smoluchowski[22] relation, since it holds only when the product of the Debye length and the droplet radius is much higher than unity, which is not the case in our experiments. Instead we used the analytical expression developed by O'Brien and Hunter,[23] which is more accurate. There are no free parameters, and the mobility is uniquely determined by the zeta potential (note that the reverse is not true, and for this reason we present our results as mobility values rather than zeta potential values).

At this point, it is possible to calculate the electrophoretic mobility as a function of pH value, using all four relations. The free parameters are K_a, $\sigma_{\max}$, and the distance between the surface and the shear-plane, d. Two fits were performed for the two hexadecane purities (99 % and 99.8 %). In both cases, we used $K_a = 10^{-5}$, which is the acidity constant for fatty acids and $d = 1$ nm.[24] Maximal surface densities of elementary charges were chosen according to the impurity concentrations determined through the titration experiments, $\sigma_{\max} = 0.25\ \mathrm{nm^{-2}}$ for 99 % pure hexadecane and $\sigma_{\max} = 0.034\ \mathrm{nm^{-2}}$ for 99.8 % (smooth lines in Figure 1). With these values of the parameters, this model provides a very good fit to the experimental data. However, it should be mentioned that only K_a is determined with excellent accuracy through this fitting procedure, whereas other acceptable fits are produced with simultaneously smaller values of d and larger values of $\sigma_{\max}$. We therefore conclude that the variations in the surface charge with the hydroxide ion concentrations, as shown in Figure 1, can be explained by considering the acid–base reaction between hydroxide ions and fatty acids with an equilibrium constant $K = 10^9$, which corresponds to acids with an acidity constant of $K_a = 10^{-5}$. The free energy extracted from this curve is 20.7 $k_B T$, which matches the free energy of a chemical reaction rather than that of an adsorption process.

These results demonstrate that hydroxide ions in water do not adsorb to hydrophobic interfaces, but rather react with traces of fatty acids, which have been dissolved in the oil and delivered to the interfaces. The accumulation of fatty acid anions through this acid–base reaction is at the origin of the negative charging of the hydrophobic/water interface and the cause of the metastability of surfactant-free emulsions.

The pH signature of this charging process is the acid–base titration curve of a carboxylic acid functional group, hence the similar pH value dependence observed for water/air interfaces may also be explained by the presence of fatty acid impurities. As those experiments were performed on large single bubbles, the available surface area was much smaller compared to our collection of nanometer-sized droplets.[7] Consequently, the concentrations of trace carboxylic acids to produce a similar effect are much lower, and they are likely introduced from the glassware, water, and air. Moreover, if other surface-active species that possess ionized or ionizable functional groups are also available, the charging will have a different origin, which will be displayed by a different pH signature. The procedures described in this work are thus an instructive way to examine any kind of hydrophobic/water interfaces to gain information on the origin of their surface charge.

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