Angewandte Chemie

Oil/Water Interface (2)

DOI: 10.1002/ange.201205927

Oil/Water Interface Charged by Hydroxide Ions and Deprotonated Fatty Acids: A Comment**

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emulsions · interfaces · oil · water · zeta potentials

The surface charge of hydrophobic droplets at water interfaces is of fundamental importance across a range of disciplines and applications. The correct understanding of the observable phenomena has been a hotly debated issue for over a century and has only recently been resolved.[1] However, in their recent communication[2] Roger and Cabane argue wrongly that the negative charge observed on hexadecane oil drops in aqueous emulsions arises solely from deprotonated fatty acid impurities in the oil, and not from the adsorption of hydroxide ions. They claim that their results „demonstrate that hydroxide ions in water do not adsorb to hydrophobic interfaces, but rather react with traces of fatty acids…“.

There is no doubt that long-chain fatty acids are surface active and would contribute to the negative zeta potential when deprotonated by reaction with hydroxide ions. In our original article with hexadecane emulsions we guarded against this possibility by purifying the oil by five passages through an alumina column,[3] as recommended in the literature.[4] It is a puzzle why Roger and Cabane did not report any results with similarly purified oil. We found that emulsions prepared with unpurified oil required about 20 % more hydroxide ion than those with the purified oil.[3] The significance of this observation will be described below.

Roger and Cabane titrated their 99 % purity oil and found a fatty acid concentration of (7 ± 1) mmol L^{-1}. They then calculated that their emulsion drops with an average diameter of 170 nm would have a maximum surface charge density of 0.25 nm^{-2} if all of the fatty acid were surface active. But they appear to have made an error by a factor of two, presumably confusing the diameter with the radius of the drops. A 170 nm diameter drop with a volume of 2.6×10^{-18} L with a fatty acid concentration of 7 mmol L^{-1} could generate a maximum surface charge density of only 0.12 nm^{-2} over the surface area of 9.1×10^{4} nm^{2}, not 0.25 nm^{-2} as given in their communication. (If the drops had a radius of 170 nm then their volume would be eight times larger and their surface area four times larger, which would increase the surface charge density by a factor of two to the value given in their communication. But the authors consistently give the size of the drops as the diameter, in several instances in this article and in other publications, and following the usual convention. It is very unlikely that 170 nm is the radius.)

In Figure 1 of their communication (reproduced below) the authors successfully fit the pH dependence of the electrophoretic mobility of emulsion drops prepared with their 99 % purity hexadecane with a maximum surface charge density of 0.25 nm^{-2}. Yet the actual maximum surface charge density is apparently only 0.12 nm^{-2}. We submit that the difference is the charge of adsorbed hydroxide ions.

Two pieces of experimental evidence support this interpretation. First, if the mobility of −4.8 as shown in Figure 1 is entirely due to the 7 mmol L^{-1} of fatty acid, then the upper curve of the mobility of the 99.8 % hexadecane which contains 1 mmol L^{-1} should have a maximum mobility of about −0.7 units and not the observed value of −2.8. But their

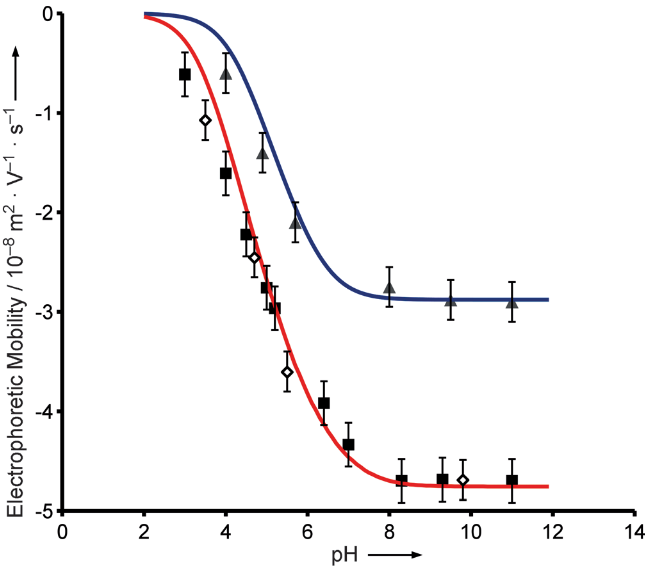

Figure 1. Reproduced from Ref. [2]: Variation of the electrophoretic mobility of hexadecane droplets with pH value, at a constant ionic strength of 1 mmol L^{-1} adjusted with NaCl. Emulsions were obtained though solvent-shifting using 99 % pure hexadecane (■) or 99.8 % pure hexadecane that was deliberately contaminated with oleic acid at a concentration of 5.8 mmol L^{-1} (◇) or also with fast mixing, using 99.8 % pure hexadecane (▲).

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[**] This work was supported by the Australian Research Council.

results are just what would be expected if the mobility of the 99 % hexadecane is in equal parts due to the fatty acids and hydroxide ions. Then the mobility of the 99.8 % hexadecane is predicted to comprise 2.4 units from the hydroxide and 0.4 units from the fatty acid, a total of 2.8 units, just as observed.

The second piece of experimental evidence is more qualitative and comes from our earlier work on the surface charge density of pristine hexadecane emulsions.[3] There we found the hydroxide ions contribute by 0.3 charges nm^{-2}. If the oil we used had the same level of impurity as that found by Roger and Cabane (0.12 nm^{-2}) then after purification the hydroxide ions required to charge the surface would drop by 29 % (0.12/(0.3+0.12)). This is in reasonable agreement with our report of a 20 % decrease, given the many assumptions made in this comparison. We note that these charge densities are not the same as the equal contributions made by the hydroxide and the fatty acid inferred from Figure 1. This presumably reflects a smaller hydroxide surface charge when it is in competition with fatty acid adsorption.

There is other evidence in the literature that is inconsistent with the authors' fatty acid hypothesis. Two examples from our own work should suffice. One comes from our original titration experiments.[3] It would not be expected that widely different oils would have the same level of contaminating acidic impurities, but we found that hexadecane, squalene and perfluoromethyldecalin each produced a surface charge density of (6 ± 1) $\mu C\,cm^{-2}$, consistent with a common hydroxide charging mechanism, but requiring a coincidental equimolar impurity level in these disparate oils.

A similar argument can be made about the acidity of different oils: it would not be expected that different oils would have the same acid dissociation constant (pK_a). But with Creux et al. we showed that benzene, nitrobenzene, octane, decane, and dodecane all have almost the same zeta potential/pH titration curves.[5] While similar pK_a values occur for the aliphatic carboxylic acids, different values would be anticipated for aromatic acids; for example (octanoic acid, $pK_a = 4.89$; benzoic acid, $pK_a = 4.19$; 2-, 3-, or 4-nitrobenzoic acids, pK_a values of 2.16, 3.47, and 3.41). The hydroxide explanation, however, predicts similar energies for the hydroxide adsorption at each of these interfaces as all have similar low dielectric constants.

At these oil/water interfaces the surfactant impurity is assumed to be contained in the oil. At the air/water or solid/water interfaces, however, it is more likely contained in the water. The fatty acid explanation requires that the same identity and concentration of impurity has occurred in different laboratories at different times, an improbable coincidence. The authors also contend that the high energy of 20 $k_b T$ for the hydroxide adsorption is not characteristic of a physical adsorption process but of a chemical reaction. They overlook our fluctuation correlation explanation for the phenomenon that accounts for an adsorption energy of 16–20 $k_b T$.[1]

In summary the authors have not presented evidence for an alternative explanation of the negative charge at hydrophobic/aqueous interfaces. Instead they have described the expected behavior of a fatty acid surfactant and provided additional evidence for the presence of hydroxide ions at such interfaces. Their results do not exclude the role of hydroxide ions but instead support that interpretation of the observations.

Eingegangen am 25. Juli 2012

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