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Uncontaminated Hydrophobic/Water Interfaces Are Uncharged: A Reply

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In our communication „Why are hydrophobic/water interfaces negatively charged?“ we offer a simple explanation for the negative charge observed at hydrophobic interfaces with water.[1] We demonstrate that traces of carboxylic acid surfactant at these interfaces account qualitatively and quantitatively for the properties of „surfactant-free“ emulsions. This is a classic example of colloidal behavior where traces of surface-active substances can control the surface behavior and hence the macroscopic properties of the colloidal dispersion.[2]

Our demonstration rests on three simple but solid experimental observations:

1) Through straightforward acid–base titrations we detect trace amounts of acids at a concentration of 7 $\text{mmol}\,\text{L}^{-1}$ in 99 % pure hexadecane oil and 1 $\text{mmol}\,\text{L}^{-1}$ in 99.8 % pure hexadecane oil. For 100 nm diameter droplets in an aqueous phase, with 99 % pure oil, the concentration that we detect yields a surface charge of 0.065 $\text{e}\,\text{nm}^{-2}$ at pH 7.
2) We observe that these carboxylic acids accumulate at the interface of oil droplets in surfactant-free emulsions. Indeed, through electrophoretic mobility measurements we find a strong variation of the negative charge with pH, as reported by a large number of authors.[5,6] The free-energy associated with this variation is 20 times the thermal energy kT, which matches exactly the reaction free-energy between hydroxide ions and carboxylic acids.
3) The key observation was obtained by comparing different emulsions made with the same method, at constant pH, but with two oils of different purity (99 % hexadecane and 99.8 % hexadecane). All other parameters being kept constant, the concentration of impurities changed dramatically the surface properties of the droplets and particularly their colloidal stability.

Roke et al.[3] and Beattie et al.[4] challenge our assessment of the concentrations of impurities in hydrocarbon oils. They both state that their own samples were pure, free of ionic surfactant impurities. However, these two comments contradict each other since Roke et al. claim that they had no impurities in droplets made with 99 % hexadecane used as received, whereas Beattie et al. claim that their purification method is necessary to eliminate surfactant impurities from 99 % hexadecane.

At this stage the debate about hydrophobic/water interfaces has revolved mostly about the origin of surface charges carried by oil/water interfaces, with the assumption that these are „pristine“ oil/water interfaces. However a central tenet of the models proposed by Beattie et al. and Roke et al. is that they apply to all hydrophobic/water interfaces. For Roke et al. the surface charge density originates from asymmetric charge transfer between the water molecules next to a hydrophobic interface.[7] For Beattie et al. the surface charge originates from a Hamaker-like force driving the hydroxide ions to regions of low dielectric constant, such as hydrophobic interfaces.[8] Both models predict a negative surface charge in the molecular layers next to the hydrophobic interface, irrespective of the precise chemical nature of the hydrophobic phase.

Therefore, according to both models, it should be possible to obtain metastable colloidal dispersions in water with other hydrophobic materials besides the hydrocarbon oils in which we found traces of carboxylic acids. In response, we repeated our previous experiments with hydrophobic polymers instead of hydrophobic oils. This method is indeed routinely used for synthesizing polymer nanoparticles.[10] Polymethylmethacrylate (PMMA) was dissolved in acetone (good solvent), at a volume fraction of 10^{-3}, and then water (non-solvent) was added, which resulted in the formation of PMMA nanoparticles. We used two monodisperse PMMA: PMMA-COOH (weight average molecular weight $M_\text{w} = 9500\ \text{g}\,\text{mol}^{-1}$) where each endgroup of a macromolecule was a carboxylic moiety and PMMA-H ($M_\text{w} = 25\,000\ \text{g}\,\text{mol}^{-1}$) where each endgroup was a hydrogen atom. Through electrophoretic pH titrations we found that the nanoparticles of PMMA-COOH had surface charge densities in the order of 0.05 $\text{e}\,\text{nm}^{-2}$. This is far below what Beattie et al. predict for hydroxide ions at an interface (0.3 $\text{e}\,\text{nm}^{-2}$),[4,6] and below what we obtained for 99 % hexadecane droplets (order of 0.15 $\text{e}\,\text{nm}^{-2}$).[1]

The preparation method that we used[1,10] is particularly well-suited for the study of interactions of hydrophobic/water interfaces, because the droplets grow through a recombination

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mechanism that ends when their interfaces acquire a sufficient number of charges. Hence both final size and polydispersity of the nanoparticles decrease upon increasing the number of surface charges. We display in Figure 1 the variation of the PMMA particle diameter upon gradually replacing PMMA-COOH with PMMA-H, that is, decreasing the number of charged endgroups. The pH was set at 10 and the ionic strength was kept constant at 10^{-3} mol L^{-1}. First a regular increase of the diameter is observed, which follows from the decrease of the number of charged endgroups that stabilized the nanoparticles. A dramatic change occurs at higher fractions of PMMA-H where we observed the formation of macroscopic aggregates coexisting with smaller particles. If we used PMMA-H alone, the same method yielded only a macroscopic precipitate. Therefore the colloidal stability of the PMMA particles originated solely from the endgroups. This was confirmed by a colloidal stability calculation using the DLVO theory:[2] the loss of colloidal stability with PMMA without charged endgroups was reproduced if the surface charge was below 0.005 e nm^{-2}. Therefore the surface charge of the PMMA-H/water interface is far below the surface charge of the hexadecane/water interface. This is incompatible with both models by Beattie et al. and Roke et al., each of which predicts similar surface charges for any type of hydrophobic interfaces.

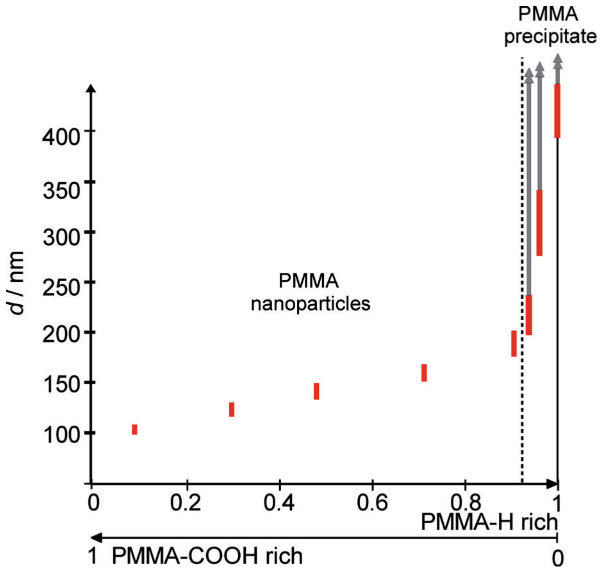

Figure 1. Diameter of nanoparticles prepared through solvent-shifting from solutions containing both PMMA with ionizable endgroups and PMMA with nonionizable endgroups. The pH was set at 10 and the ionic strength at 10^{-3} mol L^{-1} with NaCl. At high fractions of the nonionizable PMMA-H, macroscopic aggregates coexisting with smaller particles were observed. If only PMMA-H was used, the nanoparticles formed macroscopic aggregates, indicating that their interfaces were not charged enough to provide colloidal stability.

We will now address separately the remaining points of the comments by Roke et al. and Beattie et al.

Roke et al.[3] propose an explanation for the charging of the interface, caused by the orientation of water molecules at the interface. We disagree on the following grounds:

1) Through modeling of the charge transfer between water molecules near the interface, they estimate a surface charge density of −0.00014 to −0.0028 e nm^{-2}. For 100 nm diameter droplets, this corresponds to (at the most) 9 charges per droplet, which is far too low to account for the colloidal stability of surfactant-free emulsions. On the contrary the traces of carboxylic acid we titrated in the oils correlate with the observed colloidal stabilities. Indeed, for 100 nm droplets of the 99 % oil we find 2200 surface charges per droplet, which insures colloidal stability, as observed. Conversely, for 100 nm droplets of the 99.8 % oil we find 315 surface charges per droplet, which yields marginal metastability, as observed.
2) They estimate quite different charge densities from electrophoretic mobility measurements, in the range of −0.008 to −0.42 e nm^{-2}. According to their theory, these surface charge densities should not depend upon the nature of the hydrophobe, and therefore the PMMA-H/water interface should carry the same surface charge, but it does not, as discussed above.
3) The spectroscopic observations of Roke et al. do not show any pH dependence. This is clearly stated in their comment:[3] „Figure 1 A shows there is no change in the chemical surface structure at different pH values. We observe no additional interference, no new vibrational modes and no change in the water structure that would be reminiscent of the presence of ions upon changing the pH. Furthermore, spectra recorded with 99 % and 99.8 % pure oil showed the same results“. This is in conflict with numerous reported electrokinetic measurements that show a strong pH dependence.[5,6] We demonstrate that this pH dependence is the signature of the traces of carboxylic acids that we also find through acid–base titrations.
4) As cited above, Roke et al. did not find any difference between emulsions made with 99 % pure oil or with 99.8 % pure oil. This demonstrates that their method is not sensitive to traces of impurities adsorbed at the interface. They show that they can detect hexadecanoic acid at a concentration of 0.005 mol L^{-1} in water. With their oil volume fraction of 1 %, the concentration of hexadecanoic acid in the oil must have been 0.5 mol L^{-1}. This concentration is enormous and much beyond the detection limit that they indicated.

To conclude, we think that the surface charge mechanism that is proposed by Roke et al. does not produce a charge of sufficient magnitude to account for the colloidal metastability of surfactant-free emulsions and does not reproduce the pH variation of this surface charge. Moreover, it is not consistent with the large surface charge differences between different hydrophobic interfaces such as PMMA and hydrocarbon oil. It may be that this surface charge mechanism exists, but in surfactant-free emulsions the corresponding surface charge is small compared with that from trace amounts of fatty acids, and in polymer nanoparticles it is small compared to that from the endgroups of the macromolecules.

Beattie et al. argue that our results describe the effects of both carboxylic surfactant impurities and hydroxide ions adsorption. We disagree with their analysis on the following grounds:

1) Beattie et al. are „puzzled“ that we did not try to purify our compounds, since they are confident in the purification method they use. We think that any purification method such as the exchange with an alumina column used by Beattie et al. reaches a limit in terms of the concentration of remaining impurities. In the first part of our response, we provided an example of uncontaminated hydrophobic/water interface, using hydrophobic polymer nanoparticles. As discussed above these uncontaminated interfaces must have surface charge densities at least two orders of magnitudes lower than those predicted by Beattie et al. for hydroxide ion adsorption.
2) Beattie et al. are concerned about the values of the surface charges we use. This is directed to our calculations of the number of surface charges from the concentration of impurities in the oil. The surface charge can be estimated through three different methods: titration, electrophoretic mobility, and colloidal stability. We agree with Beattie et al. that the determination of surface charges from electrophoretic mobility is imprecise. What matters is the relative magnitude of the surface charges for oils of different purity. We find a 7/1 ratio in the surfaces charges required to model the electrophoretic mobility of the two oils, which corresponds to a 7/1 ratio in the carboxylic acid concentration of these two oils. However we thank Beattie et al. for pointing out an imprecision in our communication: regarding electrophoretic mobility, the position of the slip-plane is unknown and thus the precise absolute value of the surface charge cannot be deduced from electrophoretic mobility measurements. Therefore the absolute surface charge values were not directly deduced from the titration experiment, only their relative values and an order of magnitude.
3) Beattie et al. state that for the 99 % pure hexadecane, the surface charge density is 0.25 nm^{-2}, of which half (0.12 nm^{-2}) originates from fatty acids ionization and the other half (0.13 nm^{-2}) from hydroxide ions adsorption. This is based on an argument in which they compare the electrophoretic mobility of the 99 % hexadecane with that of the 99.8 % hexadecane. They argue that, since the former contains 7 $\text{mmol}\,\text{L}^{-1}$ of fatty acid, and the latter only 1 $\text{mmol}\,\text{L}^{-1}$ fatty acid, the mobility ratio ought to be equal to the ratio of concentrations, that is, 7:1. This is of course wrong, since it is well-known that both the relation of mobility to surface charge density[8] and the relation of the surface potential to the surface charge density[2] are highly nonlinear. Their additional conclusion that the surface charge density of the 99.8 % hexadecane originates mostly from hydroxide ions is then also in error.

To conclude, we believe that we provide a mechanism, which explains quantitatively the otherwise puzzling adsorption of hydroxide ions at hydrocarbon oil/water interfaces. Hydroxides ions react with fatty acids adsorbed on the interface. We also provide an example of uncontaminated hydrophobic/water interfaces, namely those of hydrophobic polymer particles, which are then uncharged.

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