

Dipolar Anions Are Not Preferentially Attracted to the Oil/Water Interface

James K. Beattie,^{*,†} Alex M. Djerdjev,[†] George V. Franks,[‡] and Gregory G. Warr[†]

School of Chemistry, University of Sydney, NSW 2006, Australia, and Department of Chemical Engineering, University of Newcastle, Callaghan NSW 2308, Australia

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Homogenization of hexadecane in water at pH 9 gives the same surface charge density in the presence of 0.2 mM thiocyanate or acetate anions as in the presence of chloride, indicating that these dipolar anions are not preferentially adsorbed at the oil/water interface. The decrease in the zeta potential of the emulsion droplets as the sodium salts of iodate, thiocyanate, or acetate are added from 0.1 to 10 mM is the same as that when sodium chloride is added, leading to the same conclusion. Increasing the sodium hydroxide concentration from pH 9 to 11.5 has a different effect on the zeta potential, consistent with the specific adsorption of hydroxide ion at the oil/water interface.

The properties of water at hydrophobic surfaces are of considerable significance in physics, chemistry, and biology.^{1–3} There have been many experimental and theoretical studies on water at interfaces with low dielectric constant media, either vapor or oil or hydrophobic molecules or solids. It is obvious that the hydrogen bonding structure of bulk water must be interrupted at the interface. Most recent theoretical calculations find that the water molecules at the interface are oriented with their dipole moments parallel to the surface, with a slight tilt on average pointing the hydrogens (and the dipole moment) away from the bulk water.^{4–9} Some find alternation of the orientation of the dipole moment across the interface,^{10,11} while others describe results with the dipole moment pointed toward the bulk water phase.^{12,13} There is general agreement that the orientations of the dipole moments of the interfacial water are not isotropic.

It has been known for decades that the oil/water interface is negatively charged at neutral pH.¹⁴ We have recently shown quantitatively that this negative charge arises from the adsorption of hydroxide ions at the interface.¹⁵ The reasons for this preferential adsorption of hydroxide ions are not clear.¹³ One possibility is the existence of a strong electric field gradient created by the orientation of the interfacial water dipoles, which has been estimated to be as large as ~ 0.5 V.⁹ Another is the possible dipole–dipole interaction between the oriented water molecules and the dipolar hydroxide ion. Here, we subject this latter explanation to an experimental test, which is to examine whether other dipolar anions are similarly adsorbed. We measured the dependence of the zeta potential of a hexadecane-in-water emulsion at pH 9 on the concentration of added sodium salts of different anions. In our previous work,¹⁵ none of the anions (X^-) used (Cl^- , I^- , and ClO_4^-) were dipolar and the zeta potential of the emulsion drops was found to be independent of the identity of the anion. In the present work, the dipolar anions SCN^- , CH_3COO^- , and IO_3^- were used and compared

with hydroxide ion. The calculated dipole moments of OH^- , NCS^- , IO_3^- , and CH_3COO^- are 1.39, 1.44, 4.85, and 3.5 D, respectively.^{16–19}

We followed the protocol described in previous work;¹⁵ that is, a 2 vol % hexadecane/water mixture in 0.2 mM NaX solution is homogenized at an initial pH of 9 under surfactant-free conditions. As the emulsion is formed, the pH decreases due to the adsorption of hydroxide ion from the solution onto the new surface. Maintaining the pH at 9 in a pH-stat experiment by the addition of NaOH allows the hydroxide surface charge to be measured from the amount of base required. Measurement of the droplet size then gives the surface area of the emulsion. From these two measurements, the surface charge density due to the hydroxide ion can be calculated.

In the first experiments, the dipolar anions SCN^- and CH_3COO^- were used as sodium salts, initially in 0.2 mM concentration. The first important observation is that the pH falls during emulsification in the presence of the dipolar anions, just as it does in the presence of the nondipolar anions. Maintenance of the pH at 9 gives surface charge densities of -5.3 and $-5.0 \mu C cm^{-2}$, respectively, in comparison with $-4.9 \mu C cm^{-2}$ measured previously with NaCl. This implies that hydroxide ion (at 10^{-5} M) is still preferentially adsorbed in competition with other dipolar anions present at 20 times higher concentrations.

Dipolar anions are not adsorbed even at higher concentrations. After preparation of the emulsion at pH 9 in 0.1 mM NaX solutions, the zeta potential was measured with the electroacoustic technique as further NaX was added to the dispersion up to 10 mM, where X^- was Cl^- , NCS^- , IO_3^- , CH_3COO^- , or OH^- . For all of the anions except hydroxide, the zeta potential decreased, from ~ -80 to ~ -30 mV, due to the usual double layer compression with an increase in ionic strength, but the decrease was the same for the dipolar anions as for chloride (Figure 1).

In contrast, an emulsion was prepared in 0.2 mM NaOH and homogenized until the pH dropped to 9. The addition of more

* Corresponding author. E-mail: j.beattie@chem.usyd.edu.au.

[†] University of Sydney.

[‡] University of Newcastle.

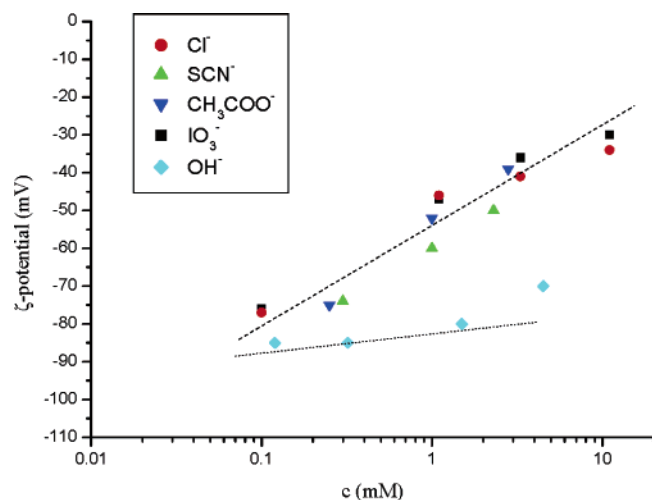


Figure 1. Zeta potentials of hexadecane-in-water emulsions from pH 9 as a function of added sodium salts of the anions shown.

NaOH resulted in no significant decrease in the zeta potential until about 5 mM was added. Presumably, up to this concentration, more hydroxide is being adsorbed at the interface, compensating for the increase in ionic strength. It is clear that hydroxide ion behaves differently from the other dipolar anions (Figure 1). (The common intersection of the two curves reflects the zeta potential at pH 9 at an initial salt concentration of 10^{-4} M.)

These results imply that the preferential adsorption of hydroxide ion at this hydrophobic surface is not due to dipole–dipole forces nor due to simple electrostatic attraction, but it is specific to hydroxide ion. This suggests that it is a feature of the hydrogen bonding structure of the interfacial water, perhaps a consequence of the different hydration structures of hydroxide and hydronium ions.^{20,21} Streaming potential measurements on solid hydrophobic surfaces suggest that hydronium ions can be adsorbed, but 10^6 more weakly than hydroxide ions.²²

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