Absence of Specific Cation or Anion Effects at Low Salt Concentrations on the Charge at the Oil/Water Interface

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Absence of Specific Cation or Anion Effects at Low Salt Concentrations on the Charge at the Oil/Water Interface

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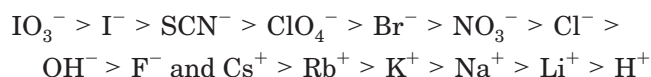*Received May 24, 2005. In Final Form: June 27, 2005*

Surfactant-free 2 vol % hexadecane-in-water emulsions have been prepared at pH 9 in the presence of various alkali-metal salts. The surface charge and zeta potential of these emulsions are independent of the identities of the monovalent cations and anions up to 0.01 M electrolyte concentrations. The surface charge density of -5 μC cm^{-2} is independent of the identity of the alkali-metal cation among Li, Na, and Cs. The zeta potentials decrease with the log of the salt concentration between 0.1 and 11 mM, independent of the identity of the anion of the sodium salts of iodide, bromide, chloride, fluoride, perchlorate, or iodate or of the identity of the cation of the chloride salts of Li, Na, or Cs. These results imply that neither hydration enthalpies nor ion dispersion potentials are significant in affecting the charge created by the hydroxide ion at the pristine oil/water interface at up to 0.01 M salt concentrations.

Introduction

Specific ion effects are well known in colloid science, beginning with the Hofmeister effect on the salting out of proteins[1] and extending to many other phenomena such as the surface tension of electrolyte solutions,[2] critical micelle concentrations,[3−5] critical coagulation concentrations,[6] and suspension rheology.[7,8] For monovalent ions the lyotropic series, arranged in order of increasing hydration enthalpy, are[9−11]

$$ClO_4^- < I^- < SCN^- \approx NO_3^- < Br^- < Cl^- < IO_3^- <$$
$$F^- < OH^- \text{ and } Cs^+ < Rb^+ < K^+ < Na^+ < Li^+ < H^+$$
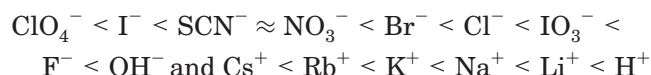
Similar, but slightly different, series are found when other criteria such as solution viscosity or conductivity are used to sequence the ions.[12] When ions are sequenced according to excess polarizability a different series emerges for anions. Arranged in order of decreasing excess polarizability, the ion series are[13,14]

$$IO_3^- > I^- > SCN^- > ClO_4^- > Br^- > NO_3^- > Cl^- >$$
$$OH^- > F^- \text{ and } Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ > H^+$$

In general, ion-specific effects become increasingly significant as electrolyte concentration increases above about 10 mM. We are interested in studying ion-specific effects at the oil/water interface, particularly as we strive to understand the mechanism for the preferential adsorption of the hydroxide anion at the interface, which is the cause of the negative charge associated with the interface.[15,16]

It is possible to prepare oil-in-water emulsions by high-pressure homogenization or sonication in the absence of conventional amphiphilic surfactants. These emulsions are negatively charged and stabilized by electrical double-layer repulsion. Although it now appears clear that the negative surface charge at the oil/water interface at pH > 3−4 is due to accumulation of OH$^-$ anions at the surface,[15] the mechanism for this accumulation is not well understood. In some previous work we observed that the pH dependence of the zeta potential of such hexadecane/water emulsions was independent of the identity of the anion of the sodium salts of chloride, iodide, and perchlorate at 0.4 mM concentration.[15] We also have results that indicate the zeta potential of hexadecane droplets is independent of anion type for the sodium salts of the dipolar anions thiocyanate, iodate, and acetate up to 10 mM concentration.[17] These initial studies suggest that ion polarizability is not a factor in the accumulation of hydroxide at the interface since ions with greater ion excess polarizability are not able to compete with hydroxide. Now we have extended these studies to other anions over a larger concentration range and to the monovalent cations lithium and cesium. Our aim is to elucidate the mechanism for hydroxide adsorption. The range of ions investigated allows us to determine conclusively if dispersion forces are significant in controlling the adsorption of ions to the oil/water interface (and zeta potentials) for 1:1 electrolytes

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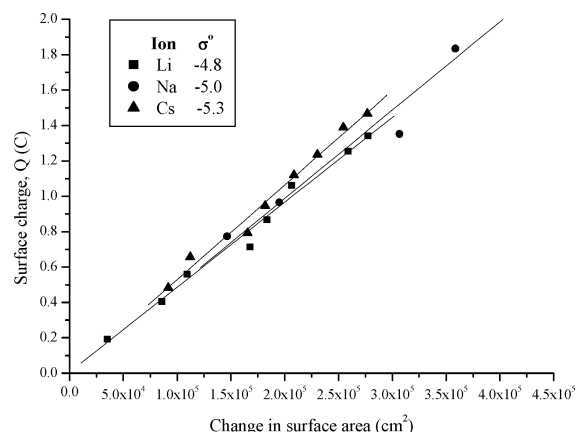
Figure 1. Surface charge density, σ° ($\mu C\ cm^{-2}$), from quantity of base MOH added as 250 mL of 2 vol % hexadecane was emulsified in 0.2 mM MCl at pH 9, where M is Li^+, Na^+, or Cs^+.

up to 0.01 M concentrations. We also consider if the adsorption of ions to the interface is controlled by a "like adsorbs like"[6-8,18] hydration mechanism.

Experimental Section

Three series of experiments were conducted. In the first pH stat experiments the alkali-metal cation was varied. We followed the protocol described previously:[15] Freshly boiled Milli-Q water was protected from CO_2 absorption with a guard tube containing soda lime. Solutions of 0.2 mM LiCl, NaCl, or CsCl were bubbled with N_2 for 30 min and then adjusted to pH 9 with LiOH, NaOH, or CsOH, respectively. Hexadecane was added to 2 vol %, and the mixture was circulated through the Milko-Tester homogenizer and AcoustoSizer-II cell and returned to a reservoir maintained at 25 °C equipped with pH and conductivity probes in a continuous loop. As the homogenization proceeded base was required to maintain pH 9; the quantity added was measured and dynamic mobility analyzed[19] to obtain the average droplet size.

In a second series of experiments the emulsion was prepared at pH 9 in the presence of 0.1 mM solutions of different sodium salts. The crudely mixed 2 vol % hexadecane emulsions were circulated through the Milko-Tester homogenizer for 1 h to reduce the droplet size to $1 \pm 0.15\ \mu m$. The zeta potentials were then measured from the dynamic mobility spectra as the salt concentration was increased to 11 mM while circulating the emulsion through both the homogenizer and the Acoustosizer cell. In a third series of experiments the zeta potentials of hexadecane emulsions were measured similarly with the chloride salts of Li, Na, and Cs between 0.1 and 11 mM.

Results

The results of the first series of measurements, in which the alkali-metal cation was changed and the amount of base required to maintain the pH at 9.0 while the emulsion was refined, are shown in Figure 1. The amount of hydroxide added (less the 10^{-5} M concentration maintaining the pH at 9.0) was deemed to have accumulated at the hexadecane surface. The amount of this charge is plotted against the surface area of the emulsion (which increases as the droplet size decreases during refinement) in Figure 1. The linear dependence on the surface area is inconsistent with the idea that the hydroxide ion is dissolved in the oil phase.[20] The slope of the charge versus surface area is a measure of the surface charge density. Within experimental error there is no difference among the three metal cations, Li^+, Na^+, or Cs^+. The surface

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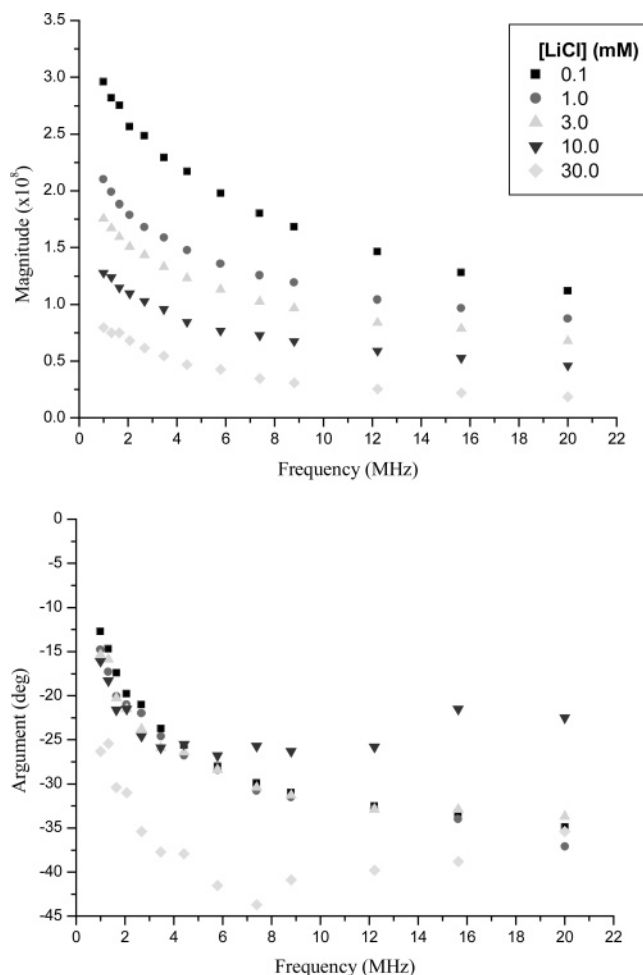(20) Chibowski, E.; Wiacek, A. *Surf. Sci. Ser.* **2002**, *106*, 893.

Figure 2. Dynamic mobility spectra of 2 vol % hexadecane emulsions in LiCl solutions as a function of increasing salt concentration as indicated.

charge density is $-5.0 \pm 0.3\ \mu C\ cm^{-2}$, and the zeta potentials measured for similar size droplets are -80 mV.

Typical dynamic mobility spectra as a function of increasing salt concentration are shown in Figure 2. The AcoustoSizer software finds the best fit of a size and zeta potential to the dynamic mobility spectra.[19] The resulting fits to the data have errors of less than 2–6% for salt concentrations less than or equal to 11 mM. Measurements at 33 mM and greater concentrations produced poor fits (errors greater than 10%) and are not presented in this work. The example presented in Figure 2 shows how the argument (phase lag) begins to deviate with frequency at higher salt concentrations. Other emulsions showed mobility magnitudes that increased with frequency. This behavior indicated that the emulsions became unstable and the spectra could not be fit to the model. Several factors make it difficult to obtain reliable dynamic mobility spectra at high salt concentrations. First the magnitude of the zeta potential decreases to below the level needed to produce electrostatic stabilization, so that the droplets tend to coalesce. Also, the electrolyte produces a signal that must be subtracted from the colloid signal. As the signal from the electrolyte increases (as concentration increases) relative to the signal from the colloid, the error associated with this correction increases. The evidence shown in Figure 2 illustrates how the dynamic mobility spectra, particularly the phase angles, are acutely sensitive to the stability of the emulsion samples.

The reproducibility of the zeta potential measurements, in which the emulsions were prepared at pH 9 in the
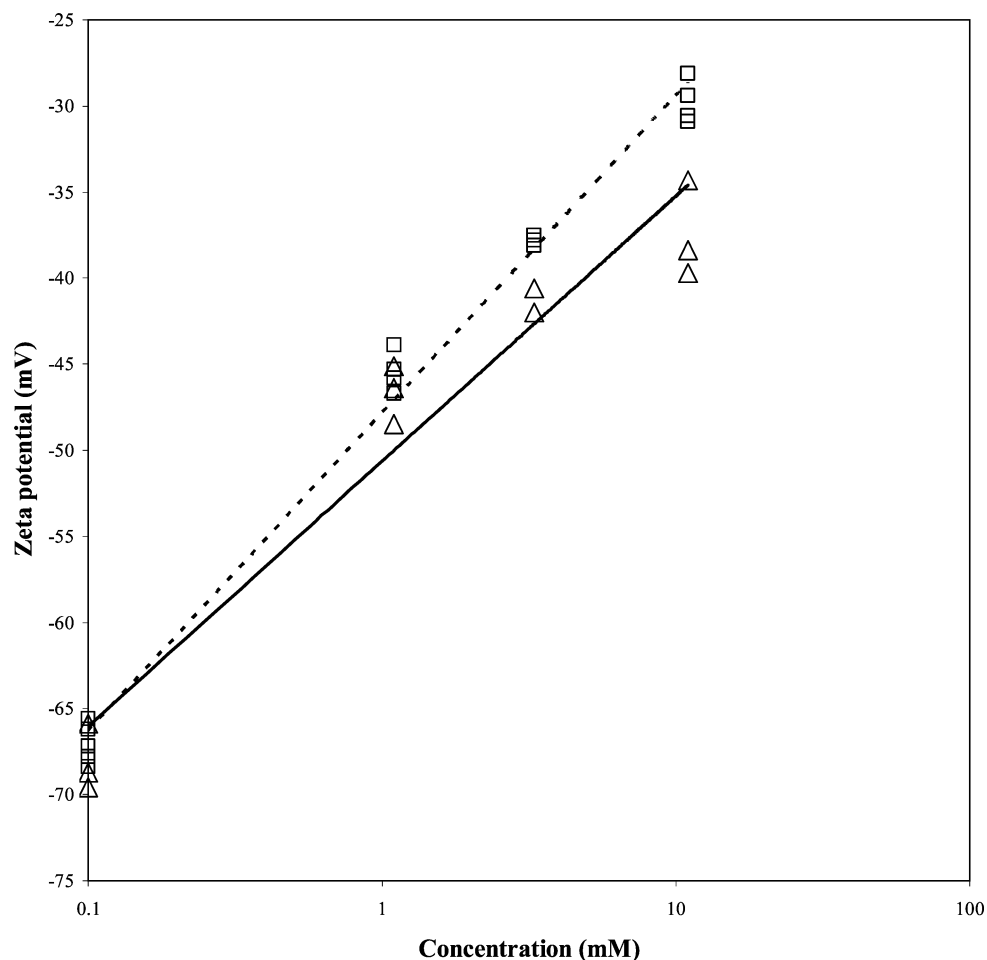
Figure 3. Zeta potential measurements of 2 vol % hexadecane emulsions in NaCl. Three measurements at each concentration were measured for two different emulsions (emulsion 1, triangles and solid line; emulsion 2, squares and dotted line). The lines are the best logarithmic fit.

presence of 0.1 mM NaCl and then the NaCl concentration was increased up to 11 mM, is shown in Figure 3. Three measurements were taken at each concentration for each of two different emulsions. The range of the measurements increased as the concentration was increased. The zeta potentials are linear in the log of the added salt concentration. At 11 mM the typical range of three measurements from any single emulsion was ± 3 mV. The typical difference between two different emulsions with 11 mM salt concentration is ± 5 mV. One reason the experimental error increases as the salt concentration increases is because the magnitude of the zeta potential decreases to below about -30 mV and the emulsions approach instability.

Figure 4 shows a comparison of the zeta potentials as a function of salt concentration for a series of anions of sodium salts. Within the experimental reproducibility (described above) there is no difference among the anions I^-, Br^-, Cl^-, F^-, IO_3^-, or ClO_4^-. Finally, in the third series shown in Figure 5 increasing the salt concentration of the chloride salts revealed no differences up to 11 mM among the three alkali-metal cations Li^+, Na^+, and Cs^+.

Discussion

The results imply that the hydroxide ion is the potential-determining species responsible for the charge and the electrical double-layer stabilization of these surfactant-free oil-in-water emulsions. The addition of other anions in up to 11 mM concentrations reduces the zeta potential through the normal double-layer compression. Even

though the concentration of salt ions is 10^3 times greater than the hydroxide concentration at pH 9, there is no selective adsorption of specific anions, i.e., no Hofmeister effects. Neither hydration enthalpy nor ion excess polarizability seems to have any influence on the zeta potential of the hexadecane surface in aqueous solutions of monovalent salts up to at least 11 mM salt concentration. It is remarkable that there is no discrimination among the alkali-metal cations for the surface charge of $-5\,\mu C\,cm^{-2}$ (Figure 1) is largely compensated by condensation of the cations in the stagnant layer. The zeta potentials of -75 to -80 mV at 0.2 mM salt concentrations require a charge of only $0.5\,\mu C\,cm^{-2}$ at the shear plane, implying that $\sim 90\%$ of the cations are involved in 'ion pairs' within the stagnant layer but without any significant discrimination among Li^+, Na^+, and Cs^+.

The hydroxide ion at 10^{-5} M (pH 9) is preferentially adsorbed at the interface in competition with up to 10^{-2} M of other anions, some highly polarizable. Thus, it appears that ion polarizability is not a significant factor in the accumulation of hydroxide (or other ions) at the oil/water interface. This is in accord with the calculations of, for example, Boström, Williams, and Ninham, who show that the DLVO model is reasonably accurate for the low salt concentrations used in the present work, where electrostatics dominate, but fails at higher salt concentrations (>50 mM), where electrostatic forces are screened and dispersion forces are increasingly important.[21]

Although hydroxide is the most well hydrated (largest hydration enthalpy) of the anions investigated, we do not
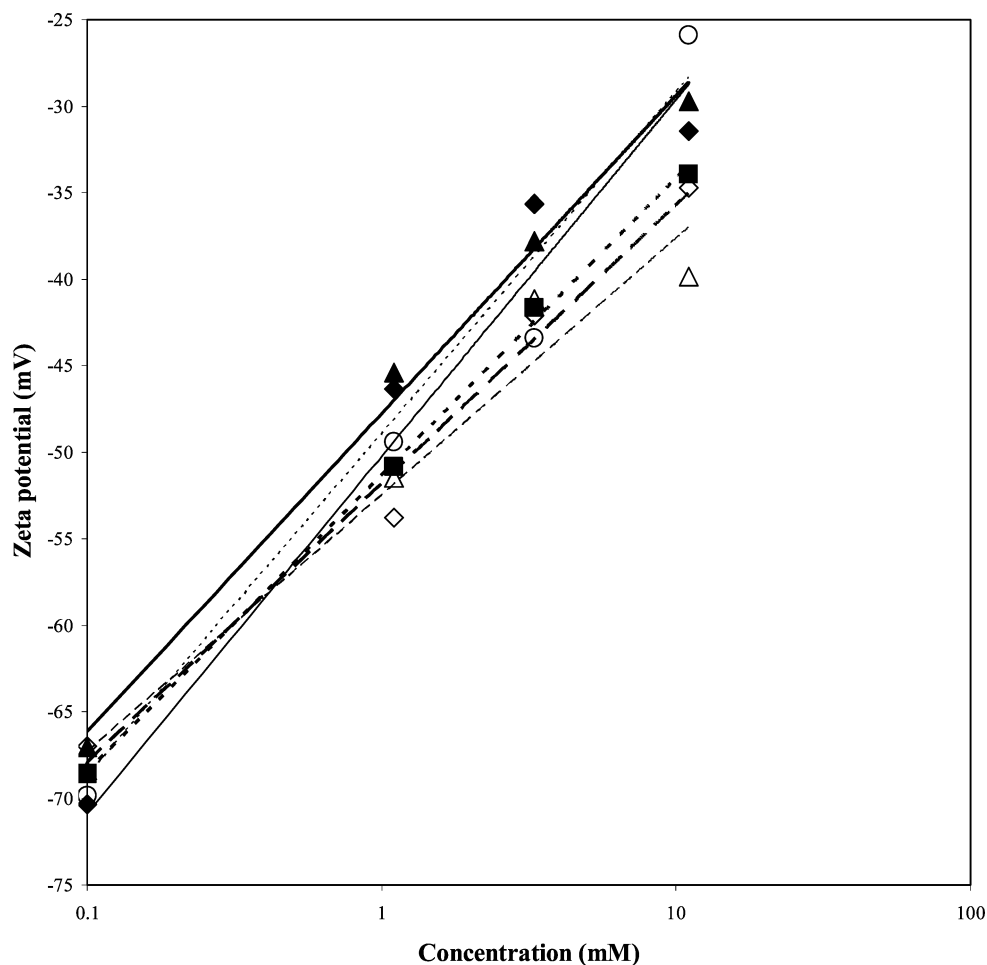
Figure 4. Zeta potentials of 2 vol % hexadecane emulsion droplets at pH 9 as a function of sodium salt concentration of various anions. Each point represents the average of three measurements: (▲) NaCl; (◇) NaBr; (○) NaI; (■) NaF; (△) NaClO₄; (◆) NaIO₃. The lines are the best logarithmic fit for each anion.

believe that the "like adsorbs like" approach can be used to justify the preferential adsorption of hydroxide relative to the other anions and cations, including the hydronium ion. Most evidence points to macroscopic oil/water interfaces that have vicinal water that is less well hydrogen bonded than bulk water. This picture is in contrast to the hydrophobic solvation of small alkane molecules that are surrounded by strongly hydrogen-bonded clathrate-like structures.[22,23] Assuming the region of water near the oil is similar to water near poorly hydrated ions, the "like adsorbs like" mechanism correctly predicts that the hydroxide anion would adsorb in preference to the proton in pure water since the proton is much more hydrated than hydroxide (about double the hydration enthalpy). If ion hydration were the only factor influencing adsorption to the hexadecane interface, however, one would expect other anions (which are less well hydrated than hydroxide) to adsorb in preference to hydroxide. Our results with the more poorly hydrated anions indicate that they do not adsorb in preference to hydroxide. The "like adsorbs like" concept is not successful in explaining the mechanism for strong hydroxide adsorption to the oil/water interface.

Grunze and co-workers[24,25] suggested that the asymmetric adsorption of the products of water autodissociation

are responsible for the preferential adsorption of hydroxide anion, although they do not clearly explain the mechanism. Zimmerman et al.[26] suggest a mechanism that is related to ion hydration. Their concept is that less stable hydration shell of hydroxide (compared to the hydronium ion) allows it to "escape" its hydration shell and form hydrogen bonds with the interfacial water molecules. Thus, the concentration of hydroxide ion at the interface is greater than the concentration of hydronium ion. This is in direct contrast to a recently expressed view that hydronium ions are preferentially attracted to the water/vapor interface.[27] The lack of a Hofmeister series in the surface charge and zeta potential measurements implies that something special about hydroxide is responsible for its accumulation at the oil/water interface. Presumably, this involves its hydrogen-bonding interactions with the altered water structure at the interface.

These surfactant-free emulsions become unstable to coalescence at higher salt concentrations as the zeta potential decreases with increasing electrolyte concentration. This makes measurement of zeta potentials with the procedure used in this paper unreliable at salt concentrations above about 0.01 M (see Figure 2). Hence, to examine

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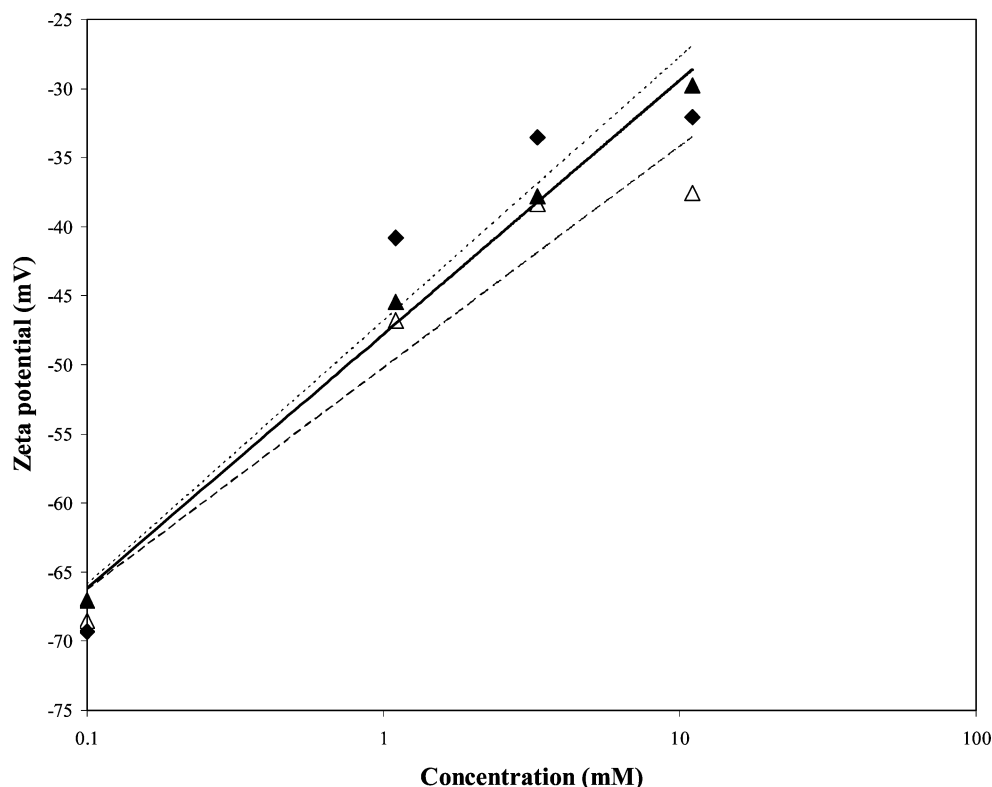
Figure 5. Zeta potentials of 2 vol % hexadecane emulsion droplets at pH 9 as a function of the Li$^+$, Na$^+$, or Cs$^+$ chloride salt concentrations. Each point represents the average of three measurements: (▲) NaCl; (△) LiCl; (◆) CsCl. The lines are the best logarithmic fit.

Hofmeister effects at pristine hydrophobic surfaces at higher salt concentrations, other techniques will be required, such as streaming potential measurements on stable plane surfaces.[26]

Conclusions

Surface charge density and zeta potential measurements of hexadecane emulsions in monovalent electrolyte solutions indicate that hydroxide anions preferentially adsorb relative to all other ions. Neither the ion's polarizability nor its hydration have any significant influence on the surface charge density or zeta potential up to 0.01 M concentration. The reason for the preferential adsorption of the hydroxide anion remains elusive but is likely to have to do with the hydration environment (particularly hydrogen bonding) of the interfacial water and the hydroxide ion.