



Interfacial distribution of ions and the surface tension of electrolytes

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Report:

Ion specificity, i.e. effects of ions in solution which cannot be explained by Coulombic interactions only, is known since the work of Hofmeister on protein crystallization (1888). Since then, the so-called Hofmeister series, essentially related to the interfacial behavior of ions in aqueous solutions, have been found in a large variety of fields from biology to environmental and atmospheric science. According to the Gibbs adsorption rule, the surface tension of salted water should always be larger than the surface tension of pure water, since ions are repelled by their image charges, as predicted in the 1934 Onsager-Samaras theory [1]. However, this theory is sometimes wrong by orders-of-magnitude and sign, as it is for the surface potentials. For example, with sodium as a cation, the order from negative to positive surface potentials is unexplained and follows the so-called Hofmeister series in reverse order. Recently, a theory based on dispersion forces has been proposed by Ninham and Yaminsky[2]. It postulates that any ion at an interface distribution is not only sensitive to the electric potential, but also to the dispersion forces. Molecular dynamics calculations have more recently demonstrated that the heavier halogen ions have a propensity for the interface which is proportional to their polarizability[3].

The aim of the experiment was to measure the adsorption of ions using grazing incidence x-ray fluorescence. The experiment consists in recording the fluorescence from the ions (chemical sensitivity) as a function of the grazing angle of incidence (depth sensitivity) with a penetration depth varying from 4nm below the critical angle for total external reflection to microns above it (providing a reference for bulk concentration). The fluorescence from Cl^- , Br^- , I^- , ClO_4^- , K^+ , Cs^+ , Ni^{2+} , La^{3+} could be measured and their salts with H^+ , Li^+ , and Na^+ were also considered.

The main results are the following.

- There is a good qualitative agreement between our results and the expectations from surface tension measurements, for example $ClO_4^- > Cl^-$
- Quantitative measurements are possible. For the simple cases like KCl , our measurements are in good agreement with a phenomenological theory only assuming an ion-free layer at the interface [4] (Fig.1).
- In a monovalent salt like KCl , different profiles are expected for K^+ and Cl^- but when integrated over the 4nm of our penetration depth, the difference is very small due to electroneutrality. A way to circumvent this problem is to use mixtures. An example is given in Fig. 2 for a mixture of $CsCl$ and CsI . Obviously, I^- is much less repelled from the interface than Cl^- .
- A first theoretical analysis (L. Belloni) using Coulombic interactions and dispersion forces predicts an effect opposite to the experimentally observed one as dispersion forces lead to a larger repulsion for more polarisable ions.
- We are now adding a short range attraction in the potential in order to take the static polarisation of partly dehydrated ions by water molecules at the interface into account. This is expected to be the main effect [3] and a quantitative measurement of the potential strength will be possible.

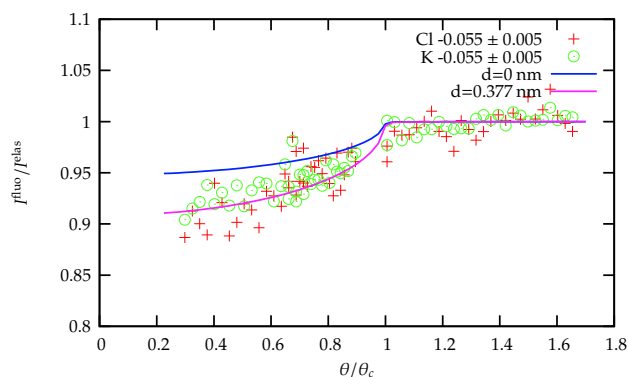


Fig. 1: Fluorescence signal normalised to the elastic scattering for a 0.1 mol/l solution of KCl . The adsorptions of K^+ and Cl^- are approximately the same and well described by the phenomenological theory [4] with an ion-free layer of 0.377nm.

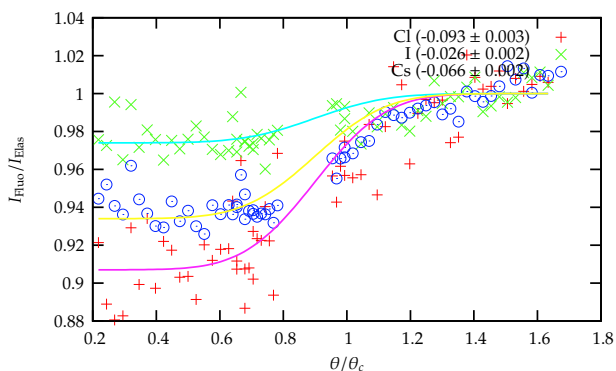


Fig. 2: Fluorescence signal normalised to the elastic scattering for a mixture of $CsCl$ 0.1 mol/l and CsI 0.1 mol/l. Obviously, I^- is much less repelled from the interface than Cl^- .

References

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