X-ray studies of the interface between two polar liquids: Neat and with electrolytes

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We demonstrate the use of x-ray reflectivity to probe the electron density profile normal to the interface between two polar liquids. Measurements of the interfacial width at the neat nitrobenzene/water and the neat water/2-heptanone interfaces are presented. These widths are consistent with predictions from capillary wave that describe thermal interfacial fluctuations determined by the tension and bending rigidity of the interface. Variation of the temperature of the water/nitrobenzene interface from 25°C to 55°C indicates that the role of the bending rigidity decreases with increasing temperature. X-ray reflectivity measurements of the electrified interface between an aqueous solution of BaCl$_2$ and a nitrobenzene solution of TBATPB demonstrate the sensitivity of these measurements to the electrolyte distribution at the interface. A preliminary analysis of these data illustrates the inadequacy of the simplest, classical Gouy-Chapman theory of the electrolyte distribution.

The kinematics of reflectivity is illustrated in Fig. 1. The incident and outgoing angles are equal for specular reflection, therefore, the wave vector transfer,

$Q = k_{scat} - k_{in}$, is only in the z-direction normal to the interface. X-ray reflectivity probes the electron density in the z-direction, averaged over the interfacial plane.
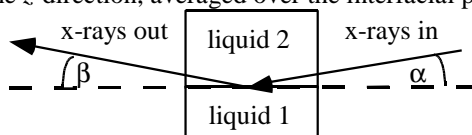

Figure 1 Experimental geometry. Liquid 2 is either water or 2-heptanone for studies of the nitrobenzene/water or water/2-heptanone interface, respectively.

X-ray reflectivity from the liquid/liquid interface was measured at the ChemMatCARS' sector 15-ID (Advanced Photon Source, Argonne National Laboratory, USA) with instrumentation and techniques previously described.[6,11,21] scattering. The reflectivity is given by subtracting the background from the reflected intensity, then normalizing by the incident flux.

The x-ray reflectivity measurements and analysis shown later in Figure 2 are typical of those presented in this paper. The theory of capillary waves predicts certain thickness of the interfacial region, for which the Q_z vs. reflectivity can be predicted. However, fitting to this equation alone does not quite fit the experimental values. We have included a term for bending rigidity, expressing a degree of stiffness in the system. Figure 2 illustrates x-ray reflectivity data for four different values of $\Delta\phi^{w-o}$

along with fits from a simple interface model given by the electron density profile.
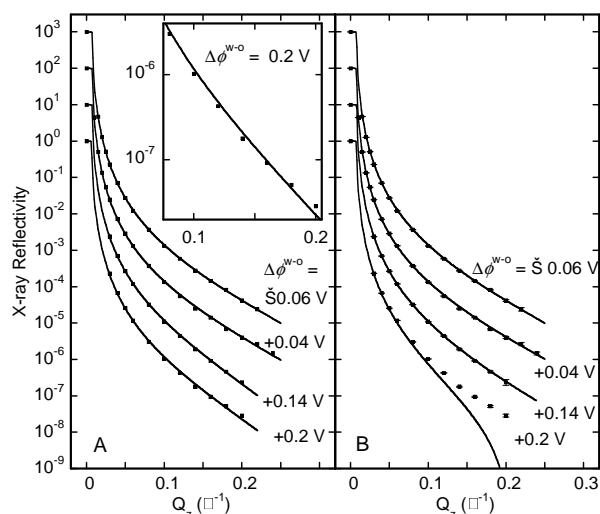

Figure 2 X-ray reflectivity data for four different values of $\Delta\phi^{w-o}$ from the interface between a 0.1 M solution of BaCl$_2$ in water and a 0.01 M solution of TBATPB in nitrobenzene (data offset by factors of ten for viewing purposes). (A) The lines are fits from a simple interface model given by the electron density profile. The inset illustrates the high Q_z data from $\Delta\phi^{w-o}$ = 0.2V to show the difference in the curvature of the data and the fit. (B) The lines are fits from the simplest Gouy-Chapman double layer.

Our preliminary analysis of the data from Fig. 2 indicate that the simplest Gouy-Chapman model for the interfacial electrolyte distribution cannot adequately explain our structural measurements. The future research will require additional equation terms that will be deduced from the experimental data and additional structural considerations. The discrepancy in the experiment is not entirely surprising as more traditional electrochemical measurements have also found discrepancies with the classical Gouy-Chapman model.

Kakiuchi and Senda used interfacial tension measurements to suggest the existence of a sharp boundary between the two solvents that contains an ion-free solvent layer.[1] For the second view, also using interfacial tension measurements, Girault and Schiffrin disputed the existence of the compact inner layer and suggested that the boundary is a region of diffuse mixed solvent.[2-5] Different views of the interface also appear in the theoretical literature. Marcus calculated rate constants for an electron transfer for two redox species in opposite phases, using both the sharp and the diffuse boundary layer model.[6-7] The two results differ by two orders of magnitude. The current debate on the interfacial structure is partially due to a lack of techniques that directly probe the structure. The x-ray interrogation should prove to be the required tool.

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