

Interface between Two Polar Liquids: Neat and with Electrolytes

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Introduction

Understanding molecular ordering at the interface between two liquids is important in many chemical, biological, and condensed matter systems. Water/oil interfaces are a model for the interaction of water with a hydrophobic molecular environment and important for protein folding and the formation of structures in complex fluids. Recent x-ray studies of the interface between a nonpolar oil (alkanes) and water have improved our understanding of the neat water/oil interface and of surfactant ordering at this interface [1].

For the past several decades, electrochemical effects at the interface between two polar liquids have been studied. The structure of this interface has been debated in the electrochemical community because of its importance in understanding electrochemical measurements. For example, information on interfacial width (currently unmeasured) is necessary to determine association constants for ion-pairing from capacitance data [2]. Information on interfacial particle distributions (currently unmeasured) is necessary for determining molecular reaction rates or the rate of assisted ion transfer from electrochemical measurements [3].

The addition of electrolytes to the two polar liquids allows electrodes inserted into the two bulk phases to impose and control a large electric field across the interface. This field can be used to transfer electrolytes to or through the interface, control chemical reactions at the interface, and control electron transfer across the interface. These interfaces have not been previously studied with x-ray scattering because of the large x-ray absorption of the polar liquids. Here, we present our initial experiments in this area. These include x-ray reflectivity studies of the neat interface between nitrobenzene and water, 2-heptanone and water, and the influence of electrolytes added to the nitrobenzene and water.

Methods and Materials

X-ray reflectivity from the liquid/liquid interface was measured with 30-keV x-rays at sector 15-ID (ChemMatCARS) with instrumentation and techniques previously described [4-6]. Nitrobenzene and 2-heptanone (from Fluka) were purified with an

alumina column. Tetrabutylammonium tetraphenylborate (TBATPB) and tetrabutylammonium bromide (TBABr) were used as received from Fluka. The samples were contained in a stainless steel sample cell with Mylar[®] windows that is similar to a cell previously used for water/hexane interface studies [4].

Results and Discussion

X-ray reflectivity measurements from the neat nitrobenzene/water interface at 25°C and 55°C are illustrated in Fig. 1. These data can be interpreted by using the Born approximation to yield the interfacial width σ [7]. At 25°C, the measurements were repeated on three different samples and yield $\sigma = 4.1 \pm 0.1$ Å; at 55°C, $\sigma = 5.6 \pm 0.2$ Å. This can be compared with predictions of 5.1 and 5.7 Å, respectively, from the capillary wave theory. The value at 25°C indicates that the interface is smoother than expected. We are currently trying to understand if this can be a result of a bending rigidity of approximately 6 kT due to alignment of molecular dipoles at the interface.

Figure 2 illustrates data and a fit for x-ray reflectivity

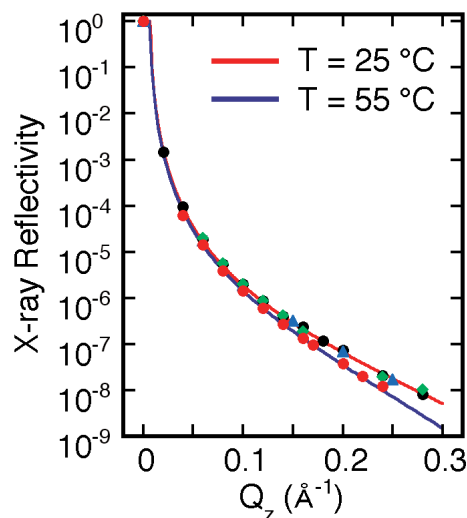


FIG. 1. X-ray reflectivity from the neat nitrobenzene/water interface at two temperatures. Results from three different samples are shown at 25°C.

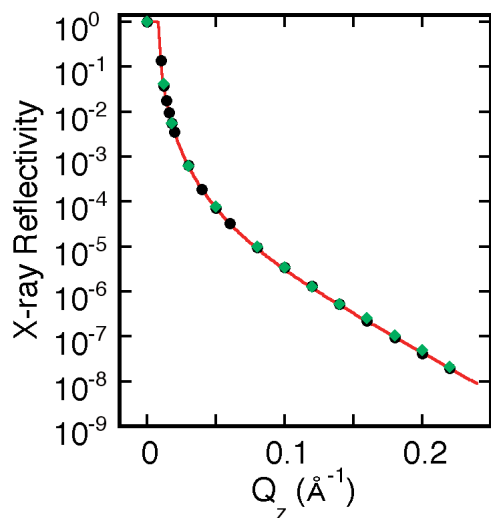


FIG. 2. X-ray reflectivity from the 2-heptanone/water interface at 25°C. Results from two different samples are shown.

from the 2-heptanone/water interface at 25°C. The measured interfacial width is $6.9 \pm 0.2 \text{ \AA}$ and can be compared to the value of 7.3 \AA calculated from capillary wave theory. Again, the interfacial width is smaller than the capillary wave value, although the discrepancy is only a 2-sigma effect.

Figure 3 shows reflectivity data and fits from a nitrobenzene/water interface for which the interfacial electrical potential has been adjusted by dissolving the electrolytes TBATPB and TBABr. TPB^- is preferentially soluble in the nitrobenzene, Br^- is preferentially soluble in water, and TBA^+ is soluble in both. Varying the TBABr concentration while keeping the TBATPB concentration fixed at 0.01 M alters the interfacial electrical potential [8]. This, in turn, alters the interfacial tension. By directly measuring the tension, we can calculate a prediction from the capillary wave theory for the interfacial width as measured by x-ray reflectivity. If the tension is lower, then the interface fluctuates more easily, and the interfacial width predicted from capillary wave theory will be larger.

As anticipated, the x-ray measurements demonstrate that the interfacial width varies with the electrical potential determined by the electrolyte concentration. At a TBABr concentration of 0.05 M, the measured interfacial width is $\sigma = 7.4 \pm 0.2 \text{ \AA}$ (calculated capillary wave value for the width is $\sigma_{\text{cap}} = 6.9 \text{ \AA}$); for 0.01 M, $\sigma = 6.1 \pm 0.2 \text{ \AA}$ ($\sigma_{\text{cap}} = 5.8 \text{ \AA}$); and for 0.0001 M, $\sigma = 4.8 \pm 0.2 \text{ \AA}$ ($\sigma_{\text{cap}} = 5.3 \text{ \AA}$). The increase in width with TBABr concentration is qualitatively consistent with the predicted capillary wave value. However, there are discrepancies with the predicted values. Part of the

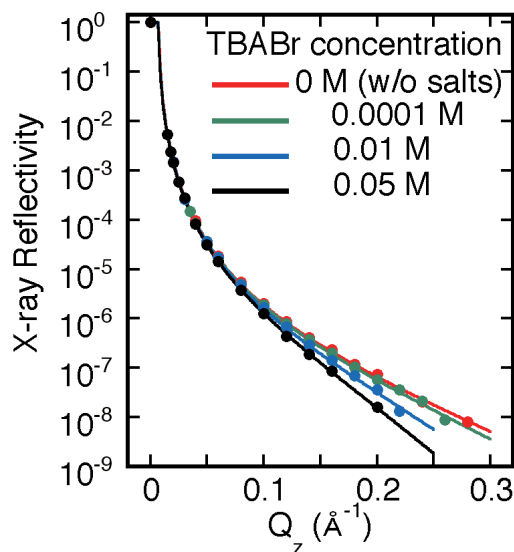


FIG. 3. X-ray reflectivity from the interface between an aqueous solution of TBABr and a nitrobenzene solution of TBATPB at 25°C.

discrepancy may be due to the need to include a bending rigidity that will reduce the width. In addition, the two highest concentrations have an interfacial width larger than the capillary wave width. This larger width is most likely due to an ionic double layer at the interface. Further analysis is required to confirm this expectation.

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