Monitoring transient changes in the structure of water at a polarised liquid-liquid interface using electrocapillary curves

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ABSTRACT

The interface between two immiscible electrolyte solutions (ITIES) is a close approximation of an ideally polarisable interface, being non-equilibrated upon formation. Despite this, the formalism of equilibrium thermodynamics, e.g., electrocapillary equations, are universally applied to interpret electrochemical processes at the ITIES. This communication shows that interfacial energy measurements in real time during step potential experiments are a useful tool to detect transient changes in the structure of the electrolyte solutions at the ITIES, in particular in the presence of chaotropes or kosmotropes in the aqueous electrolyte. Molecular dynamics computer simulations substantiate our findings, quantifying the perturbation of the atomic-scale structure, dynamics and energetics of the interface in the presence of a kosmotrope.

1. Introduction

The physicochemical properties of immiscible liquid-liquid (L-L) interfaces impact several industrial applications, in particular liquid-liquid extraction and liquid chromatography [1], catalysis [2,3], drug delivery in pharmacology [4], artificial approaches to photosynthesis [5–8], and chemical reactions in micellar systems [9]. Therefore, understanding fundamental processes occurring at the Interface between two immiscible electrolyte solutions (ITIES) is a close approximation of an ideally polarisable interface, being non-equilibrated upon formation. Despite this, the formalism of equilibrium thermodynamics, e.g., electrocapillary equations, are universally applied to interpret electrochemical processes at the ITIES. This communication shows that interfacial energy measurements in real time during step potential experiments are a useful tool to detect transient changes in the structure of the electrolyte solutions at the ITIES, in particular in the presence of chaotropes or kosmotropes in the aqueous electrolyte. Molecular dynamics computer simulations substantiate our findings, quantifying the perturbation of the atomic-scale structure, dynamics and energetics of the interface in the presence of a kosmotrope.

The interfacial energy decreases with increasing surface electric charge, but this is not always the case. Ghosal et al. [12] reported an enhancement of anion concentration, with a concomitant increase of interfacial energy, at the water vapour interface of solutions of potassium halides. Such an enhancement is contrary to classical thermodynamic expectations. As a result, the assumptions implemented to deduce the relationship between surface tension and capacitance from classical thermodynamics are not universally valid.

Experimental measurements that provide information on interfacial water structure and hydrogen bonding at the ITIES are scarce because of the difficulty in selectively examining interfacial water molecules [13]. The primary experimental tool used is vibrational sum frequency spectroscopy (VSFS), a powerful surface-specific vibrational spectroscopic method for measuring the molecular structures of aqueous surfaces [14–16]. Herein, in proof-of-concept experiments, we demonstrate a purely electrochemical method, and therefore an easily accessible and cheap approach, to probe interfacial water structure and hydrogen bonding at the ITIES. By monitoring the interfacial energy in real time during potential steps, transient behaviours related to changes in the structure of water close to the interface are revealed in the presence of chaotropes or kosmotropes. To corroborate our findings, we use MD computer simulations to describe the atomic-scale changes in the interface in the presence of a well-known kosmotrope (methanesulfonate anions).

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2. Experimental methods

2.1. Electrocapillary curves at the ITIES

The materials used in this work are detailed in Section S1.1, Supplementary Information (SI). Electrochemical experiments were carried out at the water|α,α,α-trifluorotoluene (TFT) interface using a four-electrode configuration (the geometric area of the cell was 1.60 cm²), as described in Section S1.2, SI. The general configuration of the cell is outlined in Scheme 1.

The interfacial energy (γ) at the L-L interface was measured using an Attension Theta Optical Tensiometer (T200 from Biolin Scientific) by the pendant drop method. Pioneered by Girault et al. [17,18], this method records drop images and automatically analyses the drop shape by data fitting using the Laplace–Young equation [19]. The drop shape is a function of the interfacial energy between the liquids, gravity, density of both liquids and relative saturation of each liquid with the other liquid. The organic phase was inside a syringe provided with a counter and reference electrode, and the aqueous phase was inside an optical glass cell of 30 mL, which has another reference and counter electrode. This configuration was reported by Peljo et al. [20] and shown schematically therein. Experiments were performed at room temperature (20 ± 1 °C). The water and organic phase were not pre-saturated with each other prior to forming the interface to replicate the non-equilibrated experimental conditions employed by the vast majority of researchers when carrying out electrochemical experiments at the ITIES.

2.2. Molecular modelling

In this study, we used atomistic molecular dynamics (MD) computer simulations to model the dynamics of the methanesulfonate ion (MS⁻) at the liquid-liquid interface between water and TFT. Two systems were considered, a system with only the two neat solvents forming the interface, which is used as reference (system A), and another which contained solutes, BA⁺ and TB⁻ in TFT, and MS⁻ and Na⁺ in water (system B). A detailed description of the procedure used to perform the MD computer simulations is provided in Section S1.3, SI.

3. Results and discussion

3.1. Electrocapillary curves at the ITIES

The change of interfacial energy at the ITIES upon potential cycling with an aqueous electrolyte of 10.6 mM LiCl in the L-L electrochemical cell is shown in Fig. 1. As expected, the surface energy decreases at potentials away from the potential of zero charge (PZC), which is approximately 0.08 V on the Galvani scale (see Fig. S1, SI). Additionally, the interfacial energy depends on the scanning direction (hollow arrow) and changes with time (solid arrow). The interfacial energy shifts to lower values as time progresses, showing that the interface is not in equilibrium during potential cycling. This change of interfacial energy with time can be due, at least in part, to mixing of the solvents to some extent in the inner region at both sides of the L-L interface. The maximum point of the electrocapillary curve shown in Fig. 1 is not at the PZC, irrespective of whether the potential was scanned positively or negatively.

Hou et al. [11] measured differential capacitances from electrocapillary experiments and fitted them to a model that uses a Poisson–Boltzmann potential of mean force analysis. Their conclusion was that differential capacitance determined using this method is more accurate than that obtained by AC voltammetry. However, as shown in Fig. 1, the interface can be dynamic, or non-equilibrated, during electrocapillary experiments. We observed that the interface required several hours to reach a stable surface tension. Moreover, in order to obtain the differential capacitance from electrocapillary experiments, either a numerical differentiation of the function surface energy vs. potential or a fitting of the experimental data to an appropriate model is required. Taking into account the instability of the signals and the need of many experimental points (at least one point per 5 mV) both methods are going to give a significant error. In this sense, we recommend the use of AC voltammetry to calculate the differential capacitance because it is a direct measurement and does not come from numerical analysis or complex fitting. Using a single frequency to calculate the capacitance where the real part is almost independent of the applied potential and where the contribution of faradic AC currents is negligible is a better option in our opinion. In any case, it is important to state that it is very difficult to measure the differential capacitance with high precision independently of the experimental approach because the measurements always proceed away from equilibrium. Consequently, the history and the time when the measurement is taken are important. Further in-depth discussion on the correlation between the interfacial energy and differential capacitance at the ITIES is provided in Section S2, SI.

3.2. Monitoring changes in the structure of water at a polarised L-L interface

In this section, we address the question: is it possible to detect changes in the structure of water close to the interface during potential step experiments? For example, the interaction of methanesulfonic acid (MSA) with water is known to be very strong since these two molecules can form strong hydrogen bonds [21–23]. On the other hand, MSA is highly soluble in both water and organic solvents. Thus, the balance of these two opposing trends with MSA will significantly influence the structure of water at the L-L interface.

The interfacial energy was measured during potential steps between the PZC and either positive or negative values from the PZC (Fig. 2). During these measurements, the externally polarised L-L interface is never at thermodynamic equilibrium and, in a best-case scenario,
reaches a steady-state. Nevertheless, we can measure properties in transient, steady-state and non-equilibrium conditions and this information can be rationalised using kinetics, mass transport laws and non-equilibrium thermodynamics. In the same way that thermometers measure a system’s temperature away from equilibrium (e.g., in non-equilibrium thermodynamics. In the same way that thermometers measure a system’s temperature away from equilibrium (e.g., during a chemical reaction), we measure interfacial energy in transient conditions. The latter measurements are highly reproducible, providing insights regarding the nature of the electrochemical double-layer during the adsorption of ions or molecules at the polarised liquid-liquid interface.

The changes in magnitude of the interfacial energy were greater for each aqueous electrolyte tested when the potential was stepped to negative values from the PZC (red lines), than when stepped to positive values (black lines). This is because the maximum point of the electrocapillary curve, as shown with 10.6 mM LiCl in Fig. 1, is not at the PZC. When the potential is stepped negatively away from the PZC, the slope of the decrease of the surface energy at this negative potential is larger than the slope when the potential is stepped positively away from the PZC.

With each aqueous electrolyte solution, the interfacial energy at the PZC increases upon consecutive potential steps between the PZC to more negative potentials (red lines). We consider this behaviour to be caused by the transfer of the organic electrolyte cation, BA⁺, to some degree to the aqueous phase during negative polarisation, and the ensuing slow recovery of the BA⁺ adsorption at the PZC. In other words, the diffusion of BA⁺ towards the bulk aqueous phase during negative polarisation leads to a depletion of BA⁺ at the interface. The latter causes an increase in the interfacial energy upon consecutive potential steps as the surface-active ion BA⁺ is depleted; the surface energy of a solution of 10 mM LiCl & 1 mM BACl (62 ± 2.9 mJ·m⁻²) is lower than the surface energy of pure water under otherwise identical experimental conditions (69.4 ± 2.9 mJ·m⁻²). However, in Fig. 2c, it seems that the adsorption of SO₄²⁻ inhibits the desorption and transfer of BA⁺ because the interfacial energy at the PZC is more stable upon potential steps.

The interfacial energy at the PZC is lower when an aqueous MSA solution is used (~19 mJ·m⁻²) in comparison to a LiCl solution (~28 mJ·m⁻²), see Fig. 2a and b, indicating strong adsorption of MS⁻ at the interface. The remarkable surfactant activity of MSA may be due as well to its solubility in both phases. Thus, MSA can generate a salt-in effect and reduce the interfacial energy. For MSA, when the potential is switched back to the PZC from −0.3 V, the curve of the surface energy vs. time plot has a well-defined peak (Fig. 2b, red line). One possibility is that during these potential steps the concentration of MS⁻ is much lower. Thus, Fig. 2 shows that the adsorption of MS⁻ to the bulk aqueous solution.

Furthermore, a slight peak and a well-defined peak can be observed in Fig. 2a and c (black lines), respectively, when the potential is switched back to the PZC from positive values. When the Li⁺ concentration increases in the aqueous solution close to the interface, the interfacial energy also increases. Ions with a high charge/radius ratio (e.g., Li⁺, Ca²⁺, and Al³⁺) or with the possibility of form hydrogen bonds, like MS⁻, are called structure making ions, since they increase the total number of hydrogen bonds and in this way the interfacial energy. Subsequently, the decrease of interfacial energy with time can result from the diffusion of MS⁻ to the bulk aqueous solution.

It has been reported that a large portion of interfacial water molecules at the organic solvent|water interface have weak or negligible hydrogen bonding interactions with other interfacial water molecules [13]. Therefore, it makes sense that kosmotropic ions increase the average number of hydrogen bonds or induce a more coherent water structure [24]. The peak of interfacial energy during the steps from +0.3 V to 0 V vs. PZC observed in Fig. 2c (black line) is higher than the one observed in Fig. 2a (black line) because the proportion of chaotropic ions (Cl⁻), in the former case decreases and kosmotropic ions increases (i.e., Li⁺ and SO₄²⁻). The reduction of interfacial energy at the PZC in Fig. 2c in comparison to Fig. 2a confirms that the adsorption of SO₄²⁻ is taking place.

Fig. 2. Change of the interfacial energy (γ/mJ·m⁻²) upon stepping the potential at the ITIES to positive (black lines) and negative (red lines) potentials relative to the PZC when the aqueous electrolyte in Scheme 1 was (a) 10.6 mM LiCl, (b) 10 mM MSA, and (c) 5.2 mM LiCl & 2.5 mM Li₂SO₄. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
interfacial energy in real time during potential steps reveal transient behaviours that can be correlated with the capability of ions to change the average number of hydrogen bonds of interfacial water molecules.

3.3. Analysis of MD results

As discussed, MSA forms strong hydrogen bonds with water, decreases the interfacial tension and is highly soluble in both water and organic solvents. Based on these properties, sodium methanesulfonate salt (Na⁺ MS⁻) was selected as the model aqueous electrolyte to study the effect of a kosmotropic (order-making) ion on the structure of solvent at the ITIES. Using this salt instead of the acid form of MSA has the advantage of avoiding partition of MSA in both solvents, which reduces the required computational time, while capturing the effect of MS⁻ on the water structure.

Fig. 3a shows the density of water, TFT, MS⁻ and Na⁺ across the ITIES, with the density of water and TFT in control system A also plotted for reference. The intersection between water and TFT density allows the position of the interface to be mapped. The red line, which depicts the density of water in the presence of MS⁻ (system B), shows changes at the interface such as the formation of a small peak compared to the bulk density. MS⁻ density shows such a peak as well, followed by a pronounced depletion coincident with a peak in Na⁺ density. Comparing the density of water in systems A and B, the increase of water density at the interface appears to be correlated with the presence of a high local concentration of MS⁻. These results suggest that the interface induces a structuration of MS⁻ and its counter-ion Na⁺ as they both adopt a layering pattern, which in turn promotes restructuring of nearby water.

Fig. 3b shows the total dipole moment for water in system A (black), for water in system B (red) and for MS⁻ (green). In any bulk solution, the orientation of molecules is expected to be random, therefore the total dipole moment of a slice of a polar system is zero. A non-zero total dipole moment indicates a preferential orientation of the molecules and reveals the existence of a special electrostatic environment. Our data confirms the restructuring effect of MS⁻ on interfacial water. Indeed, although water at the interface in system A presents a very low dipole moment (black), the presence of MS⁻ at the interface considerably increases the magnitude (red). The total dipole moment at the interface is then at least five times larger than for pure water. Lastly, MS⁻ is also oriented in such a way at the interface that it results in a total dipole moment of 13.6 D.

Fig. 4 (upper panel) shows a typical representation of MS⁻ anions at the interface between TFT (cyan) and water (red). MS⁻ anions are represented with sticks and the solvents as continuous transparent surfaces. Some solute molecules appear broken as they are visualised protruding out of and sinking into the solvent clouds. (Lower panel) Representative structure of the H-bonding network that directs the localisation and orientation of the MS⁻ anions at the interface. The structure shows the solvents that form the liquid-liquid interface as transparent surfaces (once more coloured red for water and cyan for TFT). MS⁻ anions are shown as space-filling van der Waals’s spheres. Water molecules directly H-bonded to the anions in the first 3 Å solvation shell are shown as blue sticks and waters 3–6 Å out in the second solvation shell are shown as orange sticks. Dashed black lines illustrate inter-water H-bonds that connect up the extended water-mediated network. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. (a) Computed density of water, TFT, MS⁻ and Na⁺ sampled every 0.1 nm along the z-axis of the simulation cell, the direction normal to the plane of the ITIES. Black and red lines are water in neat and solute-containing interfaces (systems A and B, respectively), and gold and blue are TFT in systems A and B. The green and magenta lines are solutes MS⁻ and Na⁺. The data < 2 nm and > 18 nm may be ignored as artefacts arising from the presence of the boundary walls at the far edges of the simulation boxes. (b) Computed total dipole moment across the ITIES, averaged over 60+ ns of molecular dynamics. The black and red lines are water in system A and system B. The green line is MS⁻ (system B). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
increase of charge. It is then clear that under the appropriate experimental conditions, such as the use of an external field to increase the local concentration of MS− near the interface, MS− can spontaneously migrate at the contact between the two solvents and form a layer very much in the fashion of a surfactant. Finally, a representative snapshot of the H-bonding network that directs the localisation and orientation of the MS− anions at the interface is shown in Fig. 4 (lower panel).

4. Conclusions

Dynamically studying the change of interfacial energy during a potential step at the ITIES is introduced as a convenient method for testing the transient state of water and ions in the neighbourhood of an interface. In other words, the latter method can probe the effect of the nature and concentration of ions on the average number of hydrogen bonds of water in the interfacial region. The measured interfacial effects are substantiated using molecular dynamics computer simulations that show large increases in dipole moment localised at the ITIES. The experiments presented herein concerning the time-dependent nature of electrochemistry at the ITIES will facilitate a deeper analysis of electrochemical data generated by researchers in this emerging field.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2019.106564.

References