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Structure and reactivity of the polarised liquid-liquid interface: what we know and what we do not.

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Abstract

Charge transfer phenomena at the interface between two immiscible electrolyte solutions (ITIES) are electrochemical reactions taking place in soft media. Owing to their liquid nature, ITIES show a large panel of electrochemical reactions including electron transfer reactions, ion transfer reactions, coupled electron-ion transfer reactions or biomimetic redox reactions. Nevertheless, the mechanisms by which these reactions proceed are yet to be fully understood. The goal of this short review is to summarise the work accomplished over the past decades towards the elucidation of the structure and reactivity at the ITIES highlighting the main questions still to be answered.

Introduction

The particularity of liquid-liquid interfaces (LLI), in comparison to other interfaces, is that the two condensed phases they separate are fluid. In this respect, they can be continuously deformed to allow matter motion. One of the difficulties in studying liquid phases is that unlike solids, they do not have a crystal order, and unlike vapour phases, intermolecular interactions are of critical importance. Thus, no assumption of periodicity or homogeneity of their structure can be made. For these reasons, the molecular structure of the water-organic solvent interface has remained controversial. However, using different experimental approaches like neutron reflectivity¹, X-ray reflectivity² or molecular mechanics simulations³, their structure could be elucidated and it is now established that these interfaces are molecularly sharp but roughened by capillary waves, with an amplitude of approximatively one nanometre¹⁻³.

The relevance of the interface between two immiscible electrolyte solutions (ITIES) to electrochemistry was shown in 1968 by Gavach *et al.* who demonstrated that potential dependent ion transfer currents could be observed at these interfaces⁴. Later, Samec *et al.* reported the observation of currents associated to an electron transfer reactions at the polarised ITIES⁵. These two fundamental studies show that electrochemistry at the ITIES was actually more diverse than that at the Electrode-Electrolyte Interface (EEI) since they allow both ionic and electronic currents. Since then, many other charge transfer phenomena have been reported. The work accomplished by the pioneers of ITIES has answered some of the fundamental questions regarding soft polarised interfaces. However, it also brought new interrogations that still need to be addressed.

Structure of the polarised ITIES: beyond mean-field theories?

In the early years of the study of the ITIES, their structure was deduced from surface tension measurements and was found to be well described by two back-to-back diffuse ionic layers separated by oriented solvent molecules ⁶⁻⁹. This model, the so-called Modified Verwey-Niessen model (MVN), was also able to qualitatively describe the trends of the capacitance curves of the polarised ITIES ^{10,11}. However, these studies were limited mainly to the water/nitrobenzene interface and to a restrained choice of organic supporting electrolytes, typically tetraalkylammonium / tetraphenylborate. Such systems offer a relatively narrow potential window, which does not allow testing the validity of the MVN in various experimental conditions or at large polarisations. The limitations of the MVN model appeared when the capacitance of the ITIES was systematically studied with different organic solvents and various aqueous and organic supporting electrolytes at different concentrations. In particular, several authors questioned the relevance of an ion-free layer of oriented solvent molecules and it became clear that ion penetration inside the solvent layer was necessary to match the experimental results ¹²⁻¹⁶. Indeed, they showed that the surface tension of a non-polarised ITIES was dependent on the aqueous electrolyte composition and concentration ¹³, implying that ions are present at the interface as they change its physical properties, but also that the capacitance of the ITIES could not be decomposed in the sum of diffuse and compact layer contributions ^{14,15}.

Later, computer simulations of the polarised ITIES highlighted the importance of the ion-solvent interaction. This was first observed using a lattice gas model that showed that the capacitance of the ITIES was dependent on the ion Gibbs energy of transfer, but also that there was an overlap of the aqueous and organic ionic layers at the interface ^{17,18}, in agreement with the experimental results. A limitation of the lattice gas models is their reliance on a crude description of the intermolecular interactions. On the opposite, molecular mechanics simulations provide a more accurate representation of these interactions, but at a higher

computational cost. An interesting way to benefit from the fine description of ion-solvent interaction at a low computational cost was to include the results of the molecular mechanics simulations in a mean-field approach, yielding the Poisson-Boltzmann Potential of Mean Force (PB-PMF) model²¹. This approach described successfully the electron density at the polarised ITIES measured by X-ray reflectivity. Compared to the previous theories based on the basic MVN model, the PB-PMF predicts sharp ion densities on both sides of the interface and, similarly to the lattice gas models, an overlap of the ionic densities^{21–25}. Despite its success for some systems, this model sometimes predicts unrealistic ionic profiles at zero or negative polarisations²⁶. More importantly, mean-field theories assume that the interface can be described as two bulk phases in contact. Thus, the solvents are treated as continuum media of constant permittivity, usually that of the bulk phases. However, the molecularly sharp structure of the interface, extending over roughly one nanometre, questions the relevance of using a macroscopic quantity like the dielectric constant. In fact, comparison of finite element simulations and differential capacitance data show that a relative permittivity profile can account for the variation of ion solvation in the interfacial region, and therefore upon the diffuse double layer itself²⁷. In this respect, non-linear optical spectroscopy has shown that water and solvent molecules were oriented at the interface^{28–30}, which implies a different dielectric constant at the interface. In the case of polarised interfaces, the reorientation of the solvent molecules effectively screens the surface potential, which affects the distribution of ions at lipid membranes³¹. However, the orientation of the dipoles of the solvent molecules induces a potential difference that is not accounted for in the mean field approaches and whose magnitude estimations vary over hundreds of millivolts^{32–34}. Thus, it appears that mean-field approaches might miss some important molecular aspects of the ITIES. A challenge for the years to come would therefore be to understand, at the molecular level, the influence not only of the electrolytes but also of the solvents in the potential profile of the

interface. In this respect, Suárez-Herrera *et al.* recently suggested that anions adsorption at the ITIES could weaken the water hydrogen bond network at the interface and affect both ion transfer and capacitance^{35,36}. This was explained by the kosmotropic effect of these anions. Such conclusions are in agreement with the observation that urea, a chaotropic agent, also affected the energetic of ion transfer by modifying the ion solvation in the aqueous phase³⁷.

Ion transfer at the ITIES: water fingers or ion shuttles?

Before the advent of molecular representations of the ITIES, ion transfer was studied mainly from the point of view of electrochemical kinetics, based on the observed potential dependent currents through the interface^{38–40}. It was suggested that the ion transfer was an activated process, although the nature of the activated step was debated. Indeed, some authors would envisage the ion transfer as an electrochemical reaction^{41–44}, while others considered it as a mass transport phenomenon^{38,45}. The difference between these two approaches is that in the former case, the activation step is treated in a framework similar to the Marcus theory of electron transfer, while in the latter case it relies on the diffusion kinetic theory of Stearn and Eyring.⁴⁰ This topic has been reviewed recently in more detail⁴⁶.

Figure 1: (a) Illustration of a “water finger” at a water-dichloroethane interface, only the ion

and the water molecules are shown. W_d represents the “water finger” coordinate as defined by Kikkawa *et al.*¹⁹. (b) Illustration of the “ion shuttle” mechanism as defined by Laforge *et al.*²⁰ (right).

Similarly to the studies of the structure of the ITIES, the study of ion transfer benefited from the progress of computational chemistry. Interestingly, in some molecular mechanics simulations, the transfer of charged species at the ITIES appeared as a non-activated process, *i.e.* the energy of the ion rose monotonically from one phase to the other^{47–50}. These conclusions were in contradiction with the electrochemical measurements, but also with the lattice gas models, that indeed showed a potential dependent activation barrier at the polarised ITIES^{51,52}. Although the intermolecular interactions in the lattice gas models are more approximate than molecular mechanics simulations, the conclusions they draw are more general because they take into account the whole ITIES structure (solvents, supporting electrolytes and counter-ions) and not only a single ion. Improvements of the molecular mechanics models, in particular simulations using polarisable force fields⁵³ or carried out in an external electric field¹⁹, showed non-monotonic energy profiles, with minima at the interface, or even activation barriers, given a redefinition of the transfer reaction coordinates in terms of “water fingers”^{19,54} as shown in Figure 1a.

One of the limits of the molecular mechanics simulations is that they did not take account of the presence of other ions in the system because of the large computational requirements. However, several experimental results demonstrated later that supporting electrolytes are necessary to explain the mechanism of ion transfer reactions. Indeed, using nanometre-sized interfaces - an experimental configuration that allows to work without supporting electrolytes⁵⁵ - Laforge *et al.* showed that organic phase electrolytes were necessary to “shuttle” the transfer of alkali metal ions from the aqueous phase to the organic phase²⁰ (Figure 1b). Using the same method, Sun *et al.* suggested that the transfer of strongly hydrophilic ions did not take place from the aqueous to the organic phase, but rather to

aqueous clusters in the organic phase⁵⁶. These conclusions are supported by the recent work of Mareček and co-workers who, using open circuit potential measurements in a novel experimental configuration⁵⁷, showed that during ITIES equilibration the transfer of organic ions induced the formation of water clusters in the organic phase⁵⁸.

Thus, if it seems now accepted that the activation step of the ion transfer is the breaking of the “water finger”⁵⁹, the “shuttle mechanism” has, to the best of our knowledge, never been observed in simulations. This would be nevertheless of particular interest since these two mechanisms appear as antithetical. In this respect, Liang *et al.* reported an experimental and computational study of strontium ion extraction at the water-dodecane interface where they suggest that the ion was extracted in the organic phase by reverse micelle “budding”⁶⁰. This mechanism would therefore support the “shuttle” mechanism.

Electron transfer at the ITIES: homogeneous or heterogeneous?

Figure 2: Schematic representation of the heterogeneous (left) vs. homogeneous (right) current generation mechanisms. The phenomena responsible for the interfacial current are represented with green arrows. In the homogeneous mechanism, the low solubility of the donor in the acceptor phase is compensated by a larger reaction volume.

The evolution of the understanding of the electron transfer at the polarised ITIES has followed, to some extent, the same path than that of the ion transfer. Indeed, the first publication dedicated to this subject attempted to apply the theories of the electrode/electrolyte interfaces to the ITIES in order to understand the potential dependence of the kinetics of the reaction^{61–64}. Nevertheless, the lack of understanding of the ITIES at the molecular level brought several questions regarding the mechanism of the electron transfer. In particular, the role of the Galvani potential difference on the kinetics was debated. Indeed, some authors reported that the rise of the interfacial current with the polarisation was due to an increase of the reaction driving force^{65,66}, while other claimed that this could be explained by a concentration change of the reagents^{67,68}. Fortunately, compared to ion transfer, electron transfer can be studied with a larger range of experimental tools. Thus, the question of the role played by the polarisation on the kinetics of the electron transfer reaction could be tackled by SECM⁶⁹, *in situ* UV-vis spectroscopy⁷⁰, fluorescence spectroscopy⁷¹ or time-resolved UV-vis spectroscopy⁷². Nevertheless, contradictory results concerning the dependence of the current on the polarisation were published, with claims of a potential dependent^{73,74} and potential independent^{75,76} electron transfer reaction. In addition to the question raised by the potential dependence of the electron transfer, the mechanism of the current generation was also debated. Thus, comparing experimental results to finite elements simulations⁷⁷, some authors suggested that the observed charge transfer was not a true electron transfer but actually an interfacial ion transfer following a redox reaction in one of the phases^{78,79}. This mechanism was called “homogeneous” electron transfer as opposed to the “heterogeneous” electron transfer, *i.e.* a truly interfacial electron transfer (Figure 2). The possibility of a homogeneous mechanism was actually envisaged earlier but without a dedicated study⁸⁰.

The necessity of carefully defining the experimental conditions to study electron transfer reactions is illustrated in the publications of Hotta *et al.*⁷⁸ and Osakai *et al.*⁸¹. Indeed, using identical experimental methods, they draw different conclusions on the electron transfer mechanism at the ITIES, because they worked with different reagents^{78,81}, whose partial solubility in the opposite phase varied. In this respect, as a recommendation to avoid confusion, authors should always specify whether they measured an interfacial current, which can be homogeneous or heterogeneous, or directly an electron transfer, which by definition can only be heterogeneous at the ITIES.

Conclusion

Significant progress has been made over the past decades in the understanding of electrochemistry at the ITIES. Nevertheless, our representations of these reactions remain imperfect. One of the reasons for this incertitude is that we still lack a complete knowledge of the molecular structure of the polarised ITIES. Thus, ion transfer and electron transfer reactions could only be studied by indirect methods, which explains to some extent why their mechanisms are still debated.

In the case of electron transfer, the main question regarding its dependence on the potential difference at the interface still remains. In the case of ion transfer, the kinetic aspects and the role played by the supporting electrolytes continues to be controversial. Molecular mechanics simulations have been shown to be a valuable tool to understand the ITIES at the molecular level but, unfortunately, previously published results using this method did not take account of the whole complexity of these systems, which somehow limited the range of their conclusions.

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