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Review Article

Simple Ion Transfer at Liquid|Liquid Interfaces

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The main aspects related to the charge transfer reactions occurring at the interface between two immiscible electrolyte solutions (ITIES) are described. The particular topics to be discussed involve simple ion transfer. Focus is given on theoretical approaches, numerical simulations, and experimental methodologies. Concerning the theoretical procedures, different computational simulations related to simple ion transfer are reviewed. The main conclusions drawn from the most accepted models are described and analyzed in regard to their relevance for explaining different aspects of ion transfer. We describe numerical simulations implementing different approaches for solving the differential equations associated with the mass transport and charge transfer. These numerical simulations are correlated with selected experimental results; their usefulness in designing new experiments is summarized. Finally, many practical applications can be envisaged regarding the determination of physicochemical properties, electroanalysis, drug lipophilicity, and phase-transfer catalysis.

1. Introduction

Two solvents with low mutual miscibility define an interface between them with differentiated physicochemical properties. Studies covering electrochemical properties of the interface between two immiscible electrolyte solutions (ITIES) have acquired an enormous importance due to the biomimetic features of these processes [1–5] and their implication in practical applications like electroanalysis [6] ion extraction [7], phase-transfer catalysis, and electrocatalysis [8, 9]. Nowadays, however, interest in ITIES is mainly based on the latter aspects. The first electrochemical study of ITIES was carried out by Nernst and Riesenfeld in 1902 [10–12]. These authors were mainly interested in measuring the transport numbers in nonaqueous solvents. A summary of the main aspects of these works can be found in [13]. However, exhaustive electrochemical experiments were not performed until the 1970s, when several works started with studies of ion transfer reactions at ITIES using electrochemical methods [14–19]. These contributions and the theoretical considerations reported by Koryta and coworkers about the polarizability of ITIES [20, 21] triggered the undertaking of numerous studies on electrochemistry at ITIES and it gradually became a new independent research area [3, 4, 9, 13, 22–45].

After the pioneering works published during the 1970s, several research branches have evolved due to original papers devoted to different aspects of electrochemistry at ITIES. Heterogeneous charge transfer can be divided into ion transfer and electron transfer, while ion transfer can be either simple or assisted by a ligand dissolved in the system. The thermodynamic analysis of these two phase systems has also provided the main clues that we have nowadays about the interfacial structure. All the types of transfer mentioned depend on the microscopic features of the liquid|liquid interface, a topic which has shown a concomitant evolution.

To study the global ion transfer mechanisms at ITIES, several electrochemical methodologies have been employed, including potential-sweep voltammetry, chronopotentiometry, polarography with dropping electrolyte electrode, and electrochemical impedance spectroscopy. *In situ* spectroscopic techniques have also proven to be very useful as they can yield complementary information [9].

Theoretical calculations have provided valuable contributions to, and insights into, the interfacial structure and ion transfer mechanism across ITIES [46]. Several authors have used computer simulations to model the interface and the ion transfer processes [47–77] (vide infra, Section 4). Several reports using molecular dynamic simulations showed that ion transfer into the organic phase is accompanied by a hydration shell of water molecules [47, 57, 65, 70, 74–77].

Similarly, continuum models have also been employed to understand ion transfer between immiscible liquids [3, 78].

From the experimental viewpoint, it is well known that water molecules are coextracted into water|immiscible organic solvents when hydrophilic ions are transferred [79]. Accordingly, such phenomena can be elucidated in terms of selective hydration of ions in mixed solvents [80]. This concept has a fundamental significance for understanding the role of water in the transfer of hydrophilic ions between two immiscible liquids. To estimate theoretically the free energy transfer ($\Delta G_{\mathrm{tr},i}^{0,\alpha-\beta}$) values of hydrophilic ions, Osakai et al. [79, 81, 82] and Sánchez et al. [83] proposed a new model in which a strongly hydrophilic ion transfers across the oil|water interface as a hydrated ion.

This paper aims at compiling the literature on the different aspects of electrochemistry at ITIES with special emphasis on the simple ion transfer under diverse experimental conditions. Section 2 summarizes the main experimental aspects related to the study of charge transfer at ITIES involving electrochemical devices and other methodologies and includes, up to our knowledge, a complete bibliographic compilation of the experimental systems involving simple ion transfer. Section 3 deals with details about the different mathematical techniques that can be applied to simulate the charge transfer at ITIES. Section 4 summarizes the results obtained by computer simulations. Finally, Section 5 considers recent progress in the practical application of charge transfer at ITIES.

2. Experimental

2.1. Electrochemical Setup. To perform quantitative measurements of current or potential at the interface between two immiscible electrolyte solutions, a nonconventional electrochemical cell must be used [43]. In addition, a four-electrode setup instead of the usual two or three electrode systems can provide reliable results of electrochemical measurements of ion transfer at ITIES.

The first quantitative study of ion transfer at a liquid|liquid interface was the one carried out by Gavach and Henry [15]. In that work the authors perform measurements of the overpotential of a two-compartment cell defining a nonpolarizable liquid|liquid interface under galvanostatic conditions. The composition of the organic phase was tetrabutylammonium tetraphenylborate dissolved in nitrobenzene while the aqueous phase was tetrabutylammonium bromide solution. In a latter work, Koryta et al. [21] studied the same non-polarizable interface and a similar one containing tetraethylammonium bromide as the aqueous electrolyte by a polarographic method. In this case the cell design was almost identical to a drop mercury electrode, but containing an aqueous reference electrode close to tip of the capillary which reduces the resistance of the aqueous phase. In these works the potentials to which the interface is subjected contain a term due to the high resistance of the organic solution, known as solution or ohmic potential drop which can hinder any measurement at a polarizable liquid|liquid interface. In order to minimize this potential term to obtain feasible quantitative electrochemical measurements, Samec et al. [37, 84] reported the first use of a four-electrode potentiostat. In this system two counter electrodes and two reference electrodes were used, one for each phase. In this work, the authors obtained a cyclic voltammogram of tetramethylammonium transfer and quantified the diffusion coefficient at both phases and the heterogeneous standard transfer kinetic constant for this cation. When both reference electrodes are inserted into Luggin capillaries close to the interface, the ohmic potential drop decreases but is still not close to zero. The remaining ohmic potential drop value can be almost eliminated by an electronic correction. In this sense, Samec et al. [85] obtained feasible results for the transfer of Cs^{+} ion from water to nitrobenzene without ohmic potential drop interference, implementing a positive fedback loop in the experimental setup, often used for the elimination of the ohmic potential drop in the voltammetric measurements with three-electrode systems. Currently, this four-electrode system with a feedback correction of the ohmic potential drop is the experimental device most widely used to perform electrochemical experiments at ITIES.

It should be noted that ohmic potential drop correction, as described by Samec et al. [85], implies that the voltage that is feedback positively to the potentiostat must be adjusted manually until equalling the ohmic potential drop that needs to be compensated. This latter problem has been overcome by Baruzzi and Ühlken [86], who reported the use of a four-electrode potentiostat with the current interruption technique for the elimination of the ohmic potential drop by sampling the double layer voltage. The current is interrupted periodically during the electrochemical scan. While the current is interrupted, the voltage drop across the solution is zero, and thus the real interfacial voltage can be sampled. Thus, the ohmic potential drop is totally eliminated. This methodology can also correct variations in the ohmic potential drop during the heterogeneous ion transfer.

Micro-liquid|liquid interfaces are useful to study ion transfer reactions because the diffusion fields are controlled by the geometry of the system and because the ohmic potential drop is minimized. These are small-sized interfaces, with low charging current and high mass-transfer rate necessary for fast kinetic measurements. About thirty years ago, Taylor and Girault [87] and Ohkouchi and coworkers [88] introduced micrometer-sized liquid|liquid interface (μ-ITIES) supported at the tip of a glass micropipette or within a microhole made in a thin membrane (supporting film) using the ablation laser technique [89].

μ-ITIES supported at the tip of a micro-pipette can be used to provide spherical diffusion patterns similar to those observed at solid ultramicroelectrodes. This enhanced mass transport produces a steady-state current when the transferring species enters the pipette, whereas classical linear diffusion behaviour is observed when the ion exits the pipette. Simple ion transfer reactions at the micro-pipette are characterized by an asymmetric diffusion regime. The transfer of ions from the micro-pipette to the interface (egress transfer) is controlled by linear diffusion, whereas the transport of ions from outside the pipette to the surface (ingress transfer) is controlled by a cylindrical diffusion field. These two different processes can be easily distinguished during cyclic voltammetric experiments, as the egress and ingress transfers lead to a peak-shaped current response and to a steady-state current, respectively. This asymmetry can be used for the identification of the ion associated with the current observed, particularly when trying to determine which ionic species are responsible for limiting the potential differences range available, the so-called potential window [90, 91]. Studies of charge transfer processes at μ-ITIES have been reported by several authors during the last years [92–146].

2.2. Methodologies Based on Forced Hydrodynamic Conditions. The electrochemical study of ion transfer at ITIES has allowed determinating relevant thermodynamic and transport parameters, provided that the processes measured are limited by mass diffusion. For the study of kinetic parameters and mechanistic information, the mass transfer rate must be increased. Different experimental approaches have been employed in order to obtain a high mass-transport rate.

The imposition of a convective flow to increase the mass-transport has also been reported. An electrolyte dropping electrode, analogous to the dropping mercury electrode, has been developed by polarization of the ITIES [21, 147]. Other hydrodynamic liquid-liquid cells based on the wall-jet electrode configuration [148] and flow-injection have also been analyzed [149, 150]. Organic gels have been used to stabilize the ITIES in flow [151] and to channel configuration [152, 153] experiments.

An alternative approach to the study of liquid|liquid extraction processes involves the rotating diffusion cell (RDC), introduced by Albery and co-workers [154–156] and modified by Manzanares et al. [157] and Kralj and Dryfe [158, 159], to study the simple and facilitated ion transfer reactions by external polarization.

Manzanares et al. [157] employed an RDC to determine the rate constant of ion transfer kinetics across the interface between two immiscible electrolyte solutions. Tetrabutylammonium tetrakis-(4-fluorophenyl)-borate in 2-nitrophenyl octyl ether (NPOE) was used as the organic electrolyte solution supported in the porous membrane. This membrane was in contact with the aqueous electrolyte. The analysis of the experimental results was based on a comparison with the theoretical current-potential curves and on the Koutecky-Levich plots. These authors showed that some experimental limitations made the rotating diffusion cell suitable only for a limited range of values of standard rate constant to be determined. Particularly, the method requires an accurate evaluation of the different contributions of ion permeability.

Hydrodynamic voltammetry is reported at ITIES, using an RDC configuration. The voltammetry arises from laminar flow, induced separately in the organic and aqueous phases of the ITIES. The ITIES has been stabilized by a polyester track-etched membrane material. This methodology has been used to determine reaction mechanisms and kinetic parameters for reactions involving liquid|liquid interfaces [158]. This alternative procedure is extended to the study of facilitated ion transfer [159].

On the other hand, Wilke et al. [160] have proposed a new methodology consisting in alternatively stirring the aqueous or the organic phase during the potential sweep to elucidate ion transfer mechanisms across ITIES. The advantages and possibilities of controlling the convective flux of species towards the interface in either the organic or the aqueous phase were analyzed using two well-known transfer processes: the direct transfer of tetraethylammonium and the facilitated transfer of K^+ assisted by dibenzo-18-crown-6 (DB18C6). The convective flux in one phase produces asymmetry in the diffusion fields, that is, a selective decrease in the diffusion layer thickness on one side, which allows distinguishing the direction of the ion transfer. This methodology presents two advantages: the possibility of obtaining mechanistic information with a very simple experimental setup and of using a standard four-electrode configuration with almost no modification. Stirring the organic or the aqueous phase requires only a Teflon bar whose rotation frequency is controlled.

Figure 1 shows cyclic voltammograms corresponding to the transfer of tetraethylamonium (TEA^+) in quiescent and stirred aqueous phases. In this case, the cation mass transport rate in the aqueous phase is the current controlling process. When the shape of the current-potential profile is compared with the response in the unstirred solution, a stationary current in the forward sweep and a higher current peak in the backward sweep are observed. The rate of mass transfer of the ion in the aqueous phase is enhanced with stirring; a limiting current is reached if the stirring frequency is high enough. The shape of the backward peak is not affected; however, as the amount of substance transferred to the organic phase is higher than that in the absence of convection, the negative peak increases [160].

Fernández et al. [161] employed this methodology to elucidate the mechanism of the electrochemical transfer of a hydrophilic arenediazonium ion (Fast Red TR) followed by the azo-coupling reaction in the organic phase with 1-naphthylamine, a lipophilic reactant. Fujii et al. [162] performed measurements of ion transfer reaction at a rotating liquid membrane disk electrode (LMDE) and a rotating liquid membrane ring-liquid membrane disk electrode (LMRE-LMDE). The authors evaluated in this work the ion transfer kinetics and the analytical applications of this methodology. Finally, Fernández et al. [163, 164] characterized the transfer mechanism of antibiotics and their acid degraded products using the forced hydrodynamic conditions.

2.3. Other Techniques. In a heuristic way similar to that used for the studies in electrochemistry at solid electrodes, several techniques have been applied to analyze the charge transfer at ITIES.

Optical second harmonic generation (SHG) is a surface-sensitive and surface-selective technique that has been used to study photo-induced electron transfer and electrochemical adsorption processes of resonant molecules at

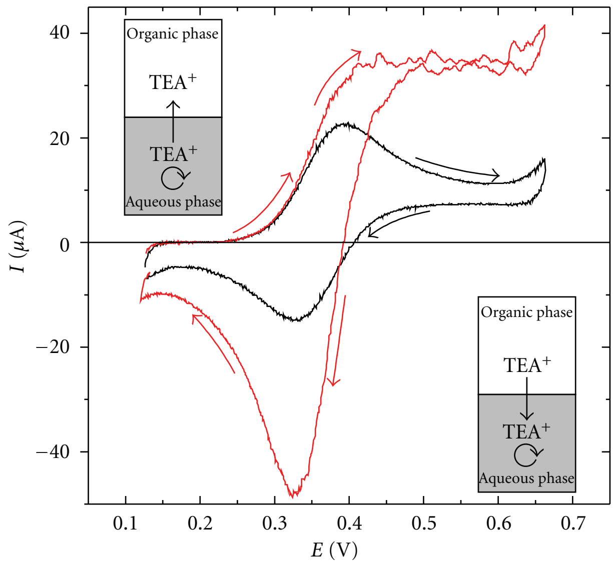

FIGURE 1: Cyclic voltammograms for the transfer of TEA^+. Quiescent solutions (black line) and aqueous phase agitated at 600 rpm (red line). Organic phase: 1.0×10^{-2} M TPADCC. Aqueous phase: KCl 1.0×10^{-2} M + 8.0×10^{-4} M TEABr. $\nu = 0.025\,V\,s^{-1}$.

liquid|liquid interfaces [165–167]. SHG requires a noncentrosymmetric medium. For this reason, at a liquid|liquid interface only the first few molecular monolayers that break the symmetry of the interface contribute to the SHG response. Enhanced sensitivity was obtained when these measurements were carried out in total internal reflection mode which allowed the direct optical measurements of the accumulation of base electrolytes at the ITIES upon externally applied potentials [168–170].

The application of scanning electrochemical microscopy (SECM) has been extended to studies of electron transfer across the ITIES [171–173]. The kinetics of electron transfer and ion transfer is determined directly by SECM.

In situ electron paramagnetic resonance (EPR) spectroscopy coupled to electrochemical measurements was employed by Compton and co-workers [174, 175] to study the charge transfer across ITIES. These authors analyzed the EPR adsorption data obtained from the different radical ions generated at the water|1,2-dichloroethane interface. Webster and Beaglehole [176] used *in situ* ellipsometry to characterize the properties of the water|1,2-dichloroethane interface during an electrochemical potential step experiment. By com-paring the polarization states of the beam before and after it is reflected off from the interface, many optical material properties can be determined, such as the interfacial thickness and refractive index. As the case with many other properties, the surface refractive index is often different from that of the bulk for sensitive studies. The ellipsometric responses provided spectroscopic evidence of ion transfer and accumulation processes by measuring changes in the refractive index and variation in the dielectric constant in the interface region. Webster and co-workers [177, 178] have developed the neutron reflection methodology for the investigation of the roughness of liquid|liquid interfaces. The authors presented an experimental setup for the generation of thin aqueous films in contact with 1,2-dichloroethane. These thin films were characterized using SECM.

Schlossman and co-workers [179–183] have pioneered the use of X-ray scattering techniques to understand the alkane|water and the nitrobenzene|water interfaces. Recently, Schlossman and coworkers [184–187] have used synchrotron X-ray reflectivity to study ion distribution at the liquid|liquid interface between a nitrobenzene solution of tetrabutylammonium tetraphenylborate and a water solution of tetrabutylammonium bromide. These structural measurements are well described by the ion distributions predicted by a version of the Poisson-Boltzmann equation that explicitly includes a free energy profile for ion transfer across the interface. This profile is described either by a simple analytic form or by a potential of mean force from molecular dynamics simulations. These X-ray measurements of the liquid|liquid interface indicate that the interfacial liquid structure is specifically important in determining interfacial ion distributions.

Quasi-elastic laser scattering (QELS) has been introduced as a suitable method for the study of the structure and dynamical properties of the ITIES, essentially of the time-resolved and equilibrium surface tension and viscoelastic properties [38, 188, 189].

Vibrational sum frequency (VSF) spectroscopy can be used to study the water structure and bonding characteristics at different liquid|liquid interfaces; the water|1,2-dichloroethane interface has proved to be the system with the most notable spectral differences in the OH stretch region. The VSF experimental spectrum of the H_2O-DCE interface gave a low signal in the OH stretch region with none of the distinct spectral features found in the other interfaces studied. It was thus concluded that the H_2O-DCE interfacial region was likely to become more diffuse than other liquid|liquid interfaces, with water molecules exhibiting a random orientation at this interface [190–193].

2.4. Representative Experimental Data. If two immiscible electrolyte solutions α and β are in contact with each other, the ions can partition between the two adjacent phases because of the difference in the ion energy in both phases. The simple ion transfer taking place at this interface can be represented as

$$I^{z_i}(\alpha) \rightleftarrows I^{z_i}(\beta), \tag{1}$$

where I^{z_i} is an ion that can be transferred from α-phase to β-phase and z_i is the charge of the species i.

For a given species i, at constant temperature and pressure, the thermodynamic equilibrium establishes equality between the electrochemical potentials $\tilde{\mu}$ in each phase:

$$\tilde{\mu}_i^{\alpha} = \tilde{\mu}_i^{\beta}. \tag{2}$$

The electrochemical potential involves a chemical and an electrical term:

$$\tilde{\mu}_i^{j} = \mu_i^{j} + z_i F \phi^{j}, \tag{3}$$

where z_i is the charge number of the ion, F is the Faraday constant, ϕ^j is the Galvani (or inner) potential of the phase j ($j = \alpha$ or β), and μ_i^j is the chemical potential defined as

$$\mu_i^j = \mu_i^{0,j} + RT\ln\left(a_i^j\right), \tag{4}$$

where $\mu_i^{0,j}$ represents the standard chemical potential, R and T are the universal gas constant and the absolute temperature, respectively, and a_i^j is the activity of i in the j-phase.

At the liquid|liquid interface, the equilibrium condition (2) is fulfilled and the following relationship can be obtained:

$$\mu_i^{0,\alpha} + z_iF\phi^\alpha + RT\ln(a_i^\alpha) = \mu_i^{0,\beta} + z_iF\phi^\beta + RT\ln\left(a_i^\beta\right). \tag{5}$$

From this expression, the Galvani potential difference, $\Delta_\beta^\alpha\phi$, between the phases α and β can be expressed as

$$\Delta_\beta^\alpha\phi = \frac{\Delta G_{\mathrm{tr},i}^{0,\alpha\to\beta}}{z_iF} + \frac{RT}{z_iF}\ln\left(\frac{a_i^\beta}{a_i^\alpha}\right), \tag{6}$$

where $\Delta_\beta^\alpha\phi = (\phi^\alpha - \phi^\beta)$ and $\Delta G_{\mathrm{tr},i}^{0,\alpha\to\beta} = (\mu_i^{0,\beta} - \mu_i^{0,\alpha})$ are the standard Gibbs energy of ion transfer from phase α to phase β. $\Delta G_{\mathrm{tr},i}^{0,\alpha\to\beta}$ is the difference standard Gibbs energies of solvation of the ion i in the phases β and α. If α corresponds to the aqueous phase, ions with a large positive or large negative $\Delta G_{\mathrm{tr},i}^{0,\alpha\to\beta}$ are denoted as hydrophilic or hydrophobic ions, respectively.

Rewriting (6), we obtained the following Nernst equation for ion transfer:

$$\Delta_\beta^\alpha\phi = \Delta_\beta^\alpha\phi_i^0 + \frac{RT}{z_iF}\ln\left(\frac{a_i^\beta}{a_i^\alpha}\right), \tag{7}$$

where $\Delta_\beta^\alpha\phi_i^0 = \Delta G_{\mathrm{tr},i}^{0,\alpha\to\beta}/z_iF$ is the standard Galvani potential difference of ion transfer for species i.

The standard molar Gibbs energy of ion transfer, $\Delta G_{\mathrm{tr},i}^{0,\alpha\to\beta}$, for an individual ion, contrary to the electrolyte as a whole, is not accessible to a direct measurement and, in order to be estimated, some kind of nonthermodynamic assumption must be made. Most frequently the "TATB assumption" [3, 9, 29, 40, 194–199] is made stating that the anion and the cation of tetraphenylarsonium tetraphenylborate have equal standard Gibbs transfer energies. On the basis of this assumption a scale for standard Gibbs transfer energies of ions from one solvent to another can be obtained using standard Gibbs transfer energies of salts calculated from partition coefficients.

During the last thirty years, the transfer of several ions through the ITIES was studied extensively using different electrochemical techniques. The transfer processes are fast so that, in most cases, they are reversible and diffusion controlled. Therefore, in the first place thermodynamic data on standard Gibbs transfer energies and on diffusion coefficients were obtained from the measurements. Standard Gibbs transfer energy values for a huge number of ions in different solvents have been compiled by Girault; this database is available on-line [200].

The simple ion transfer of various ions in different solvents has been extensively studied. The rest of this section lists the transfer of ions in the most commonly used solvents to perform electrochemical measurements at ITIES in chronological order with their corresponding references.

2.4.1. Water|Nitrobenzene Interface. The transfer across the water|nitrobenzene interface has been studied in the following anions: octoate [201] dodecylsulfate [201, 202]; picrate [98, 201–215]; ClO_4^- [98, 147, 201, 205, 207–211, 214, 216–234]; I^- [98, 147, 213, 217–219, 222, 226, 233, 235]; Br^- [98, 147, 207, 213, 214, 218, 225–227, 232, 233, 235]; SCN^- [98, 207, 213, 214, 217, 218, 224–228, 232, 233, 235]; NO_3^- [98, 147, 207, 214, 216–219, 223, 225–228, 232–235]; IO_4^- [147, 217, 218, 236]; BF_4^- [147, 217, 218, 222, 224]; ClO_3^- [147, 218, 236]; BrO_3^- [147, 236]; SO_4^{2-} [231, 237]; $TClPB^-$, $TFPB^-$ [237]; carboxilate and sulphonate anions [238]; hetero- and isopolyanions [239–248]; MnO_4^- [209]; $Fe(CN)_6^{3-}$ [223]; PF_6^- [224, 232]; Cl^- [214, 225–228, 233, 249, 250]; acetate [214, 225, 233, 236]; hydrogenmalonate, hydrogenmaleate, hydrogensuccinate, hydrogencitraconate, hydrogenglutarate, phenolate, 2-nitrophenolate, 2-methylphenolate, benzoate, salicylate, acetylsalicilate, 2-clorophenolate [228]; formiate, propionate, butyrate, valeriate, capronate, oenanthate, caprylate, pelargonate, caprinate [228, 236, 251], IO_3^-, OCN^-, $SeCN^-$, CN^-, N_3^-, monofluoroacetate, difluoroacetate, trifluoroacetate, monochloroacetate, dichloroacetate, monobromoacetate, dibromoacetate, tribromoacetate, monoiodoacetate, cyclopropane carboxylate, cyclobutane carboxylate, cyclopentane carboxylate, cyclohexane carboxylate, cycloheptane carboxylate [236]; TPB^-, dipicrylaminate [213]; amino acid and peptide anions [252, 253]; 3-nitrophenolate, 4-nitrophenolate, 2,4-dinitrophenolate, 2,5-dinitrophenolate, naphtoate, 4-bromobenzoate, 4-chlorobenzoate, 3-chlorobenzoate, 4-iodobenzoate, ketoprofen, suprofen, naproxen, pirprofen, flurbiprofen, ibuprofen, carprofen, indomethacin, phenylbutazone, sulfinpyrazone, warfarin, phenobarbital, phenytoin [215]; $CF_3SO_3^-$ [231]; 4-octylbenzenesulfonate, p-toluenesulfonate [254]; F^- and $H_2PO_4^-$ [250].

A huge number of cations have also been measured in the water|nitrobenzene interface: tetrabutylammonium (TBA^+) [15, 19, 210, 212, 213, 217, 230, 255–260]; tetraethylammonium (TEA^+) [19–21, 98, 202, 208–214, 218, 222, 254, 256, 259–266]; tetrapropylammonium ($TPrA^+$) [19, 208, 211, 213, 218, 255, 256, 259, 263]; tetramethylammonium (TMA^+) [20, 37, 84, 98, 202, 208–214, 218, 222, 230, 257, 259, 260, 262, 263, 266–269]; tetrapentylammonium ($TPenA^+$) [224, 256]; Cs^+ [85, 98, 205, 213, 214, 216–218, 260, 262, 268, 270–272]; acetylcholine [151, 205, 266, 273–276]; choline [202, 211, 263, 274, 275]; tris(2, 2′-bipyridine) Ruthenium (II), 1,1′-dimethyl-4,4′-bipyridinium [205, 208, 275, 277]; 1,1′-diheptyl-4,4′-bipyridinium [275, 277]; tetraphenylarsonium ($TPAs^+$) [210, 217, 278]; tetracycline [279, 280]; 7-chlortetracycline, doxycycline, anhydrotetracycline [279]; aniline, o-phenylendiamine, p-aminophenol, 2-phenylethylamine, tyramine, 3-hydroxityramine, noradrenaline, methanephrine, phenylephrine, benzylamine [265]; oxytetracycline [280, 281]; ferricenium

[282]; 1,1′-dipentyl-4,4′-bipyridinium, 1,1′-dibenzyl-4,4′-bipyridinium [277]; 1,1′-dibutyl-4,4′-bipyridinium, 1,1′-diethyl-4,4′-bipyridinium, 1,1′-dipropyl-4,4′-bipyridinium, [208, 277]; tetrahexylammonium ($THexA^+$) [237, 260]; Li^+ [130, 214, 270]; Na^+ [130, 213, 214, 230, 270]; K^+ [130, 213, 214, 230, 260, 270, 271]; Rb^+ [213, 214, 260, 270]; rhodamine B [283]; ethyltrimethylphosphonium, trimethylpropylphosphonium, butyltrimethylphosphonium [208, 212]; ethylenediamine, N-methylethylenediamine, N-ethylethylenediamine, N-propylethylenediamine, N,N-dimethylethylenediamine [284]; trimethylammonium, ethyltrimethylammonium, diethyldimethylammonium, trimethylpropylammonium, triethylmethylammonium, butyltriethylammonium, triethylpropylammonium, ethyltripropylammonium [263]; butylammonium, pentylammonium, hexylammonium, heptylammonium, octylammonium, [222]; 1,10-phenantholinium [285]; tetramethylphosphonium (TMP^+) [212]; lidocaine [266, 286, 287]; acetyl-β-methylcholine, carbamylcholine, carbamyl-β-methylcholine, pilocarpine, homatropine, atropine, scopolamine, hezamethonium, succinylcholine, tubocurarine, epinephrine, norepinephrine, dopamine, phenylephrine, isoproterenol, tolazoline, yohimbine, ergotamine, phenoxybenzamine, oxyprenolol, alprenolol, propanolol, pindolol, benzocaine [266]; tetracaine, procaine, dibucaine [266, 286]; dicaine [287]; antipyrine, aminopyrine, 4-aminoantipyrine [244]; minocycline [288]; Tl^+ [130, 260], Ag^+, H^+ [130]; oxybuprocaine, prilocaine, mepivacaine, bupivacaine [286]; $NpO_2{}^+$, $UO_2{}^{2+}$, $NpO_2{}^{2+}$, $PuO_2{}^{2+}$ [289]; pyridinium [290]; alanine, valine, leucine, phenylalanine, tyrosine, lysine, histidine [252]; tetraheptylammonium ($THepA^+$), tetraoctylammomium (TOA^+) [260]; polyammonium ions [291]; tryptamine, serotonin and tryptophan [292].

2.4.2. Water|1,2-Dichloroethane Interface. The transfer across the water|1,2-dichloroethane interface has been studied in the anions that follow: I^- [217, 222, 226, 227, 293–295]; $ClO_4{}^-$ [210, 217, 222, 226, 227, 294–297]; $NO_3{}^-$ [217, 222, 227, 294] SCN^- [217, 226, 227, 294]; $IO_4{}^-$ [217]; $BF_4{}^-$ [217, 222]; picrate [210, 294, 298–300]; dodecylsulfate [301]; sulphonate anions ($RSO_3{}^-$) [222]; TPB^- [91, 294, 295, 297, 299, 302]; Cl^- [226, 227, 249, 293, 295]; Br^- [226, 227, 293–295]; rose bengal [303–305]; hetero- and isopolyanions [306]; trifluoroacetylacetone [307]; eosin B [305, 308, 309]; methyl-orange, ethyl-orange [310]; phenolate, 2-nitrophenolate, 3-nitrophenolate, 4-nitrophenolate, 2,5-dinitrophenolate [311]; lauric acid, diclofenac [312]; 2,4-dinitrophenolate [294, 300, 311]; anionic drugs [215, 313]; 1-pyrene sulfonate anion [314]; bromophenol blue [315]; erythosine B, eosin Y [316]; 4-octylbenzenesulfonate, p-toluenesulfonate [254]; sulforhodamine 101 [317]; $PF_6{}^-$ [297]; tetrakis(pentafluorophenyl)borate, HO^- [295], $AuCl_4{}^-$ and $AuBr_4{}^-$ [318].

Cations studied in this solvent are TBA^+ [210, 217, 218, 257, 259, 295, 299, 319–322]; TMA^+ [110, 139, 210, 218, 259, 320, 321, 323–325]; tris(2,2′-bipy-ridine) ruthenium (II) [275, 326–329]; 1,1′-dimethyl-4,4′-bipyridinium, 1,1′-diheptyl-4,4′-bipyridinium [275, 277]; Cs^+ [217, 270, 271, 295, 324, 330, 331]; tetraphenylarsonium ($TPAs^+$) [210, 217, 321, 324]; 1,10-phenanthrolinium [332–334]; 4,7-dimethyl-1,10-phenanthrolinium, 2,9-dimethyl-1,10-phenanthrolinium, 4,7-diphenyl-1,10-phenanthrolinium [332]; TEA^+ [160, 210, 218, 254, 259, 296, 321, 323, 325, 335–337]; H^+ [218, 293, 295, 322, 331]; $TPrA^+$ [218, 259, 321, 323, 325]; 1,1′-diethyl-4,4′-bipyridinium, 1,1′-dipropyl-4,4′-bipyridinium, 1,1′-dibutyl-4,4′-bipyridinium, 1,1′-dipentyl-4,4′-bipyridinium, 1,1′-dibenzyl-4,4′-bipyridinium, [277]; tris(2,2′-bipyridine) M (II) (M = Fe, Os, Ni, Co, Cu and Zn) [328]; Li^+ [270, 293, 295, 322, 324, 331]; Na^+ [270, 293, 299, 322, 324, 331]; K^+ [270, 271, 322, 324, 331]; Rb^+ [270, 324, 331, 338–340]; rhoda-mine B [283]; acetylcholine [341]; lidocaine, dicaine [287]; tris-(2,2′-bipyrimidine) ruthenium (II), tris-(2,2′-bipyrazine) ruthenium (II) [329]; carteolol, pilocarpine, clonidine, neostignine, papaverine [342]; metoprolol [342, 343]; sotalol [342, 344]; timolol, [342–344]; propanolol [342–345]; erythromycin [346, 347]; ferrocene, 1,1′-dimethylferrocene, decamethylferrocene [348]; quinidine [349, 350]; Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+} [351, 352]; amfepramone, N-methylephedrine, N,N-diethylaniline [353]; quinine [353–355], 3,5-N,N-tetramethylaniline [353, 356]; trimetazidine [353, 357]; acebutolol, alprenolol, atenolol, bisoprolol, carazolol, carvedilol, metipranolol, oxprenolol, penbutolol, pindolol [343]; pyridine [312, 358]; nicotine, hydralazine, N-(p-methylbenzyl)hexylamine, phenylalanine [312] arenediazonium ions [161, 359, 360]; phenosafranin [361]; sildenafil [362]; $NH_4{}^+$ [322, 325, 331]; polydiallyldimethylammonium, polyethylenimine [363]; cetirizine, hydroxyzine [364]; $TPenA^+$, S-butyrylthiocholine, carbamoylcholine, 1-ethylquinoline, homidium, N-methylderamciclane, methylhomatropine, methylquinidine, 14-methylrutecarpine, neostigmine, propantheline, pyridostigmine, trantheline, homatropine [321]; clonazepam, flunitrazepam, chlordiazepoxide, diazepam, alprazolam, bromazepam nitrazepam, oxazepam, lorazepam, midazolam [365]; dopamine [366]; thionine [367]; 7-chlortetracycline, oxytetracycline [368]; tetracycline, anhydrotetracycline [163, 368]; chlorpromazine, triflupromazin, methotrimeprazine, perphenazine, fluphenazine [369]; promazine [369, 370]; prometrine [371]; triazine herbicides (atrazine, simazine, ametryn, prometryn, atratone and terbutryn) [372]; dendrimers [373–375]; tylosin A, tylosin B [164]; $THexA^+$, TOA^+, bis(triphenylphosphoranylidine)ammonium (BA^+) [295]; boldine [376]; Co^{2+}, Mn^{2+}, Ni^{2+} [352] and dioxouranium ($UO_2{}^{2+}$) [377].

2.4.3. Water|o-Nitrophenyloctylether Interface. The transfer across the water|o-nitrophenyloctylether interface has been studied in the following anions: $ClO_4{}^-$ [378–382]; picrate [215, 378, 380, 381, 383, 384]; TPB^- [322, 379, 382, 383]; Cl^- [380–382]; Br^- [380, 382]; I^- [380, 381], $NO_3{}^-$, SCN^- [380–382]; sulphonate anions ($R\text{-}SO_3{}^-$) [380]; 2,4-dinitrophenolate [215, 385, 386], phenolate, 2-nitrophenolate, 3-nitrophenolate, 4-nitrophenolate, 2,5-dinitrophenolate, benzoate, naphtoate, 4-bromobenzoate, 4-chlorobenzoate, 3-chlorobenzoate, 4-iodobenzoate, ketoprofen, suprofen, naproxen, pirprofen, flurbiprofen, ibuprofen, carprofen, indomethacin, phenylbutazone, sulfinpyrazone, warfarin, phenobarbital, phenytoin, maleate [215], $SbCl_6^-$ and $AuCl_4^-$ [384].

Several cations have also been measured in the water|o-nitrophenyloctylether interface: TMA^+ [378–380, 382–384, 387]; TEA^+ [116, 378–380, 382–384, 387–389]; Cs^+ [379, 380]; TBA^+ [322, 379, 382–384, 387]; $TPenA^+$ [379, 382, 383]; $TPAs^+$ [379, 380, 382, 383]; $TPrA^+$ [379, 380, 382–384, 387]; procaine, prilocaine, bupivacaine, lidocaine, dibucaine [390]; tetracaine [390, 391]; Li^+ [322, 383]; K^+ [322, 380, 382]; hexadimethrine [380]; NH_4^+, H^+ [322]; Na^+ [322, 382]; 3,5-N,N-tetramethylaniline [385]; pyridine [386]; $THexA^+$ [382], verapamil, clomipramine, tacrine, imipramine [392]; and BA^+ [387].

2.4.4. Other Water|Oil Interfaces. Water|dichloromethane interface: tris(2,2′-bipyridine) Ruthenium (II) and 1,1′-dimethyl-4,4′-bipyridinium, 1,1′-diheptyl-4,4′-bipyridinium [275].

Water|isobutylmethylketone (hexone) interface: picrate, Cl^-, TBA^+, TEA^+ and Li^+ [393].

Water|acetophenone interface: I^-, SCN^-, IO_4^-, ClO_4^-, NO_3^- [218, 394], ClO_3^-, TPB^-, $TPAs^+$ [394] and TBA^+ [218, 394].

Water|chlorobenzene + nitrobenzene interface: I^-, SCN^-, IO_4^-, ClO_4^-, NO_3^-, TPB^-, TMA^+, TEA^+, TBA^+ and $TPAs^+$ [395].

Water|chloroform interface Cl^-, ClO_2^-, $Cr_2O_7^{2-}$, BrO_3^- [147], I^-, Br^-, IO_4^-, BF_4^-, ClO_4^-, ClO_3^-, NO_3^-, NO_2^-, [147, 218], SCN^- [218], carboxilate, sulphonate anions [238], Cs^+, TMA^+, TEA^+, $TPrA^+$ and TBA^+ [218].

Water|aniline interface: Br^-, SCN^-, ClO_4^-, TMA^+, TEA^+ and TBA^+ [218].

Water|o-chloroaniline interface: Br^-, SCN^-, ClO_4^-, H^+, Cs^+, TMA^+, TEA^+, $TPrA^+$ and TBA^+ [218].

Water|m-chloroaniline interface: Br^-, SCN^-, ClO_4^-, Cs^+, TMA^+, TEA^+, $TPrA^+$ and TBA^+ [218].

Water|bis(2-chloroethyl)ether interface: SCN^-, ClO_4^-, H^+, Cs^+, TMA^+, TEA^+, $TPrA^+$ and TBA^+ [218].

Water|1-nitropropane interface: SCN^-, ClO_4^-, Cs^+, TMA^+, TEA^+, $TPrA^+$ and TBA^+ [218].

Water|2-nitropropane interface: Br^-, SCN^-, ClO_4^-, H^+, Cs^+, TMA^+, TEA^+, $TPrA^+$ and TBA^+ [218].

Water|benzonitrile interface: SCN^- [218], ClO_4^- [218, 396], IO_4^-, picrate, TPB^- [396], TMA^+, TEA^+, TBA^+ [218, 396], $TPrA^+$ [218] and $TPAs^+$ [396].

Water|o-dichlorobenzene interface: SCN^-, ClO_4^- [218, 397], I^-, MnO_4^-, BF_4^-, PF_6^-, ClO_3^-, NO_3^-, picrate, TPB^- [397], H^+, Cs^+ [218], TMA^+, TEA^+, $TPrA^+$, TBA^+ [218, 397] and $TPAs^+$ [397].

Water|o-nitrotoluene interface: SCN^-, IO_4^-, ClO_4^-, TPB^-, TMA^+, TEA^+, TBA^+, $TPAs^+$ [398].

Water|nitroethane interface: Cl^-, Br^-, picrate, dodecyltrimethylammonium, cetyltrimethylammonium, TBA^+, TEA^+, H^+ [399].

Water|methyl n-pentyl ketone (2-heptanone) interface: I^-, ClO_4^- [400], $TPrA^+$, TBA^+ [400, 401], TMA^+ and TEA^+ [401].

Water|methyl n-hexyl ketone (2-octanone) interface: I^-, ClO_4^-, $TPrA^+$ and TBA^+ [400].

Water|1,6-dichlorohexane interface: Cl^-, NO_2^- [402], Br^-, I^-, NO_3^-, SCN^-, [294, 402], picrate, TPB^-, ClO_4^- [294, 402, 403], 2,4-dinitrophenolate [294], PF_6^- [403], choline, acetylcholine, $TPenA^+$ [294, 402], TMA^+, $TPrA^+$, TBA^+ [259, 294, 402, 403], TEA^+ [259, 294, 402–404], $TPAs^+$ [294, 402, 403], mono-, di-, tributylammonium, Cs^+ [294] and propanolol [345].

Water|chiral menthol interface: D-tryptophan and L-tryptophan [405].

Water|n-octanol interface: Br^-, I^-, SCN^-, BF_4^-, TPB^- [406], Cl^-, NO_3^-, ClO_4^- [406, 407], phenolate, 2-nitrophenolate, 3-nitrophenolate, 4-nitrophenolate, 2,4-dinitrophenolate, 2,5-dinitrophenolate, benzoate, naphtoate, 4-bromobenzoate, 4-chlorobenzoate, 3-chlorobenzoate, 4-iodobenzoate, ketoprofen, suprofen, naproxen, pirprofen, flurbiprofen, ibuprofen, carprofen, indomethacin, phenylbutazone, sulfinpyrazone, warfarin, phenobarbital, phenytoin, maleate [408], perfluoroalkyl carboxylate, sulfonate [409], TBA^+, $TPAs^+$ [105], Li^+, Na^+, K^+, Rb^+, Cs^+, TMA^+ and TEA^+ [407].

Water|1,4-dichlorobutane interface: TPB^-, Br^-, I^-, NO_3^-, SCN^-, ClO_4^-, picrate, 2,4-dinitrophenolate, Cs^+, choline, acetylcholine, mono-, di-, tributylammonium, TMA^+, TEA^+, $TPrA^+$, TBA^+, $TPenA^+$ and $TPAs^+$ [294].

Water|4-(3-phenylpropyl)-pyridine interface: F^-, HO^-, IO_3^-, N_3^- [410], SCN^- [410, 411], Cl^- [410–412], ClO_4^-, NO_3^- [410, 411, 413, 414], OCN^-, CN^-, Br^-, I^- [411], PF_6^- [411–415], SO_3^{2-} [413] and carboxilates [412], NO_2^- [414], Li^+, Na^+, K^+, TMA^+ and TEA^+ [410].

Water|chiral 2-octanol interface: D-lysine, L-lysine, D-tyrosine, L-tyrosine, D-phenylalanine, L-phenylalanine, D-2-chloropropionate, L-2-chloropropionate [416]; R-lactate, R-2-chloropropionate and R-2-bromopropionate [417].

Water|N-octyl-pyrrolidone interface: PF_6^- [415].

2.4.5. Water|Room-Temperature Ionic Liquid Interfaces. Room-temperature ionic liquids (RTILs) have recently gained increasing attention as environmentally benign alternatives to conventional organic solvents in a variety of synthetic, catalytic, and electrochemical applications, as a result of their unique physical and chemical properties and the relative ease with which these properties can be tuned by altering the cationic or anionic moieties in the RTIL [418]. Their physical and chemical properties include high thermal stability, negligible vapour pressure, low toxicity, low melting temperature, and good electrochemical stability. It has been recently demonstrated that the interface between a hydrophobic RTIL and an aqueous electrolyte solution can be electrochemically polarizable [419–422]. The state of the art can be revised in specific reviews recently published [423–426]. The simple ion transfer across the water|RTIL interface has been studied electrochemically in the following cases.

Water|tetrahexylammonium bis(perfluoroethylsulfonyl) imide interface: PF_6^-; 1-octyl-3-methylimidazolium (C_8-mim$^+$), $TPrA^+$ and TBA^+ [422].

Water|tetraoctylammonium 2,4,6-trinitrophenolate interface: SCN^- [420].

Water|(1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide interface: F^-, Cl^-, Br^-, SCN^-, BF_4^-, PF_6^-, NO_3^- and ClO_4^- [427–429].

Water|1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide interface: F^-, Cl^-, Br^-, SCN^-, BF_4^-, PF_6^-, NO_3^- and ClO_4^- [427] and ferrocenium cation [430].

Water|1-butyl-3-methylimidazolium hexafluorophosphate interface: F^-, Cl^-, Br^-, SCN^-, BF_4^-, PF_6^-, NO_3^- and ClO_4^- [427].

Water|tetrahexylammonium bis(trifluoromethylsulfonyl)imide interface: BF_4^-, IO_4^-, ClO_4^-, $TPrA^+$, TBA^+ and tetrabutylphosphonium (TBP^+) [431].

Water|N-octadecylisoquinolinium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate interface: bis(trifluoromethylsulfonyl)imide ($C_1C_1N^-$), bis(perfluoroethylsulfonyl)imide ($C_2C_2N^-$), TMA^+, TEA^+, $TPrA^+$, choline and acetylcholine [421].

Water|1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate interface: Cl^-, SCN^-, ClO_4^-, Li^+ and K^+ [432].

Water|tridodecylmethylammonium tetrakis(pentafluorophenyl)borate interface: tetrakis(pentafluorophenyl)borate ($TPFPB^-$), TPB^-, PF_6^-, picrate, TMA^+, TEA^+, $TPrA^+$, TBA^+, $TPenA^+$, tetrahexylammonium (THA^+) and $TPAs^+$ [433].

Water|tri(hexyl)decylammonium tetrakis(pentafluorophenyl)borate interface: TMA^+ [434].

Water|trihexyltetradecylphosphonium bis(1,1,2,2,3,3,4,4,4-nonafluoro-1-butanesulfo-nyl)imide interface: ClO_4^-, TMA^+ and C_8mim^+ [435].

Water|trioctylmethylammonium bis(nonafluorobutanesulfonyl)amide interface: pentadecafluorooctanoate and $TPrA^+$ [436].

Water|trihexyltetradecylphosphonium tris(pentafluoroethyl)trifluorophosphate interface: BF_4^-, TPB^-, PF_6^-, TEA^+, $TPrA^+$ and TBA^+ [437].

Water|trioctylmethylammonium bis(nona-fluorobutanesulfonyl)amide interface: tridecafluoroheptanoate and $TPrA^+$ [438].

Water|1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide interface: ferrocenium cation [430].

Water|1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide interface: ferrocenium cation [430].

Water|N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide interface: ferrocenium cation [430].

Water|tetraoctylphosphonium bromide interface: Br^-, Cl^-, HSO_4^-, ClO_4^- and NO_3^- [439].

2.4.6. Water|Redox Liquid Interfaces. In the last years, investigations involving immobilized microdroplets of redoxactive liquids have been developed exhaustively. The immobilization of droplets was meant to provide a controlled environment to separately elucidate processes involving the direct and simultaneous contact of immiscible liquids, redox liquid and water, to an electrode surface. Since then, a wealth of information regarding electron and ion transfer processes as well as chemical reactions of the deposited redox liquids has been gathered. The state of the art can be revised in specific reviews [440, 441] and book [442] recently published. The simple ion transfer across the water|redox liquid interface has been studied electrochemically in the following cases.

Water|*N,N,N′,N′*-tetrahexylphenylenediamine (THPD) interface: Cl^- [443–446], I^- [443–445], HO^- [443], ClO_4^- [443–448], PF_6^- [443, 445–447], NO_3^- [445–447], SCN^- [445–447, 449], Br^- [444, 445], acetate, OCN^- [445, 450], F^- [445, 446, 450], SO_4^{2-} [444–446, 450], AsF_6^- [445, 446], N_3^-, IO_3^-, tartrate and oxalate [445] and H^+ [448].

Water|N^1-[4-(dihexylamino)phenyl]-N^1,N^4,N^4-trihexyl-1, 4-phenylenediamine (DPTPD) interface: sulfide [451].

Water|*N,N,N′,N′*-tetrahexylphenylenediamine (THPD) interface: SCN^- [452].

Water|*N,N,N′*-trihexyl-*para*-phenylenediamine (p-TriHPD) interface: ClO_4^- and H^+ [448].

Water|*N,N,N′,N′*-tetrakis(6-methoxylhexyl)phenylenediamine (TMHPD) interface: ClO_4^-, F^-, Cl^-, Br^-, I^- and SO_4^{2-} [444].

Water|*N,N,N′,N′*-tetraoctylphenylenediamine (TOPD) interface: AsF_6^-, PF_6^-, F^-, Cl^-, SCN^-, NO_3^- [446], $CrO4_2^{2-}$, $Cr_2O_7^{2-}$ [453], SO_4^{2-} [446, 453], ClO_4^-, [446, 453, 454], phosphate and arsenate [453].

Water|n-butylferrocene interface: acetate, N_3^-, SCN^- [450], Cl^-, Br^- [450, 455] and F^- [455].

Water|t-butylferrocene interface: Br^-, F^- [455], Cl^- [454, 455].

Water|*N,N,N′,N′*-tetrabutylphenylenediamine (TBPD) interface: PF_6^-, ClO_4^-, SCN^- [445, 446], F^-, Cl^-, Br^-, I^-, N_3^-, OCN^-, NO_3^-, IO_3^-, AsF_6^-, acetate, tartrate, oxalate and SO_4^{2-} [445].

Water|*N,N,N′,N′*-tetraheptylphenylenediamine (THePD) interface: PF_6^-, ClO_4^-, F^-, Cl^-, SCN^-, NO_3^-, SO_4^{2-} [445, 446], Br^-, I^-, N_3^-, OCN^-, IO_3^-, AsF_6^-, acetate, tartrate and oxalate [445].

Water|*N,N,N′,N′*-tetranonylphenylenediamine (TNPD) interface: PF_6^-, ClO_4^-, F^-, Cl^-, SCN^-, NO_3^-, SO_4^{2-} [445, 446], Br^-, I^-, N_3^-, OCN^-, IO_3^-, AsF_6^-, acetate, tartrate and oxalate [445].

Water|4-nitrophenyl nonyl ether interface: H^+, Li^+ and Na^+ [456].

Water|*N,N*-Diethyl-*N′,N′*-dibutyl-*para*-phenylenediamine (p-DEDBPD) interface: ClO_4^-, F^-, Cl^-, Br^-, SCN^-, NO_3^-, IO_3^-, PF_6^- and SO_4^{2-} [457].

Water|*N,N*-Diethyl-*N′,N′*-dihexyl-*para*-phenylenediamine (p-DEDHPD) interface: ClO_4^-, F^-, Cl^-, Br^-, SCN^-, NO_3^-, IO_3^-, PF_6^- and SO_4^{2-} [457].

Water|*N,N*-Diethyl-*N′,N′*-diheptyl-*para*-phenylenediamine (p-DEDHePD) interface: ClO_4^-, F^-, Cl^-, Br^-, SCN^-, NO_3^-, IO_3^-, PF_6^- and SO_4^{2-} [457].

3. Digital Simulations

Several numerical methods have been applied to solve the differential equations involved in electrochemical systems at liquid|liquid interfaces. The main equations to be solved include mass transport processes with different initial and boundary conditions depending on the system studied. The numerical tools most frequently used to solve these equations are Laplace transforms [458–460], finite differences [458, 459, 461–464], and finite element method [462, 464–466].

After the pioneering work by Homolka et al. [467], where the authors performed digital simulation of the current-potential curves for the formation of complexes of different stoichiometry (1 : 1, 1 : 2 or 1 : 3), numerical simulations of the voltammetric response for diverse mechanisms have been successfully carried out. Kakiuchi and Senda [468] solved the theoretical voltammograms, using explicit finite differences, for the formation of successive complexes in the organic phase. They demonstrated that the shape of the voltammograms is determined by the ratio of the association constants and that the peak-to-peak potential value in the voltammograms depends on the cation and ligand concentration ratio. In addition, Kakiuchi [469] solved the theoretical current-potential profiles, using explicit finite differences, for the formation of a 1 : 1 complex in the organic phase and included explicitly the interfacial ligand adsorption. Matsuda and co-workers [470, 471] derived the theoretical equations for assisted ion transfer without restrictions on the concentration values and with the species present in both phases. On the basis of this, Girault and co-workers solved diverse kinds of mechanisms. These authors described for the first time the effect of mixed diffusion control of the cation and the ligand on the shape of the voltammograms for the facilitated transfer by formation of a single 1 : 1 complex [472], complex formation of different stoichiometries (1 : 1· · · 1 : 4) that allow the competition between them [473, 474], and formation of neutral complexes [475]. Kudo et al. [476] started working on the competitive transfer of a two-cation mixture assisted by a neutral ligand. Iglesias and Dassie [477] generalized this mechanism for all the experimental conditions. In this paper, the results were analysed as different zones determined by the ratio between cation and ligand concentrations. Similarly, Garcia et al. [478] presented the general equations for facilitated ion transfer reactions across oil|water interfaces based on different competitive ligands. This work has shown that, under given conditions, the ion transfer occurs through a mechanism that involves ligand exchange. Recently, Gulaboski et al. [479] presented some mathematical models for cyclic staircase voltammetry and electrochemical impedance spectroscopy considering kinetic effects due to the complexation reaction by the facilitated transfer of metal ions at polarized interfaces.

A theoretical approach for the proton facilitated transfer or protonable species transfer was studied by Reymond et al. [480] and they developed a theory of reversible transfer reactions for molecules containing an unlimited number of protonation-deprotonation sites that can cross the interface in all their ionic forms. Sawada and Osakai [481, 482] deduced a theoretical equation for the polarographic current potential profiles corresponding to the transfer of an oligopeptide or an amino acid at the oil|water interface, facilitated by a neutral ionophore. Dassie [483, 484] derived the general equations for ion transfer reactions across oil|water interface assisted by a protonatable neutral ligand. This model was solved using Laplace transforms; the explicit consideration of the water autoprotolysis was analyzed. Finally, the latter model was solved by Garcia et al. [354] using explicit finite difference to account for the different diffusion coefficients of each species in each phase. This model was corroborated by the experimental results for the quinine transfer across the water|1,2-dichloroethane interface under different conditions [354]. Finally, Garcia et al. [355] performed a model that describes ion transfer reactions across the oil|water interface assisted by a neutral protonatable ligand in the presence of a buffer solution. Effect of the concentration of the buffered solution and its identity on the voltammetric signal, the pH profile, and the buffer capacity of the system was analyzed.

Digital simulations of anion transfer reactions across the oil|water interface assisted by a neutral ligand were performed by Dassie [485]. Analysis was mainly focused on the effect of water autoprotolysis on the shape of the current-potential profiles. Formation of complex with $j : k$ anion-to-ligand stoichiometry is analyzed.

On the other hand, the electron transfer at ITIES was performed in a variety of works. Stewart et al. [486] proposed a mathematical model to describe electron transfer at ITIES and showed how the cyclic voltammograms vary when different ratios of reactants and products are used. Later, Osakai and co-workers [487] elucidated the mechanism of interfacial electron transfer reaction between ferrocene and hexacyanoferrate (III) by digital simulation applying explicit finite difference.

Additionally, homogeneous reactions coupled to the heterogeneous charge transfer, treated in a general way, have been reported in few cases. Ion transfer processes across a liquid|liquid interface coupled to different kinds of chemical reactions taking place in the organic phase were simulated by Iglesias et al. [488] using the explicit difference method. The interfacial absorbance at a given wavelength in a total internal reflection mode and the electrochemical responses were simulated in order to extract kinetic and thermodynamics parameters. Holub et al. [489] performed a digital simulation of reversible ion transfer followed by an irreversible homogeneous reaction and the possible ion transfer of the products of the latter reaction.

Conventionally, voltammetry at the ITIES is performed under diffusion-only conditions where steady-state currents are only reached at micrometer-scale interfaces. Stewart et al. [90], performed an approximate solution for cyclic voltammetry of ion transfer at a micropipette assuming that the diffusion of the ions for ingress transfer takes place in a hemispherical way and the egress transfer in a planar diffusion way. Murtomäki and Konturri [97] combined a microhole ITIES with ac impedance and developed a simple model for calculating the faradaic impedance at the equilibrium and at the formal potential. Girault and co-workers [99] applied finite element method to study the influence of the properties of the hole (depth, interfacial position) and diffusion coefficient ratio on the electrochemical response of ion transfer reaction at a polarized micro-liquid|liquid interface. On the other hand, Murtomäki and co-workers [490] simulated the simultaneous ion transfer across microhole ITIES in the absence of the supporting electrolyte. Then, Wilke [130] proved that voltammetric measurements without any supporting electrolyte in the aqueous phase can be useful for studying the transfer of hydrophilic ions across the microhole-supported water|nitrobenzene microinterface provided that ternary electrodiffusion is negligible due to the polarity of the organic phase. Josserand et al. [491] analyzed the contact diffusion potential in microsystems and proposed a practical application of this phenomenon to quantify the mixing efficiency in microchannels using finite element method. Amemiya and co-workers [137] demonstrated that chronoamperometry at liquid|liquid microinterfaces can be used to determine diffusion coefficients directly. Simulations of microinterfaces were performed by Nishi et al. [492]. They demonstrated the relationship between the form of the orifice of a micropipette and the limiting current and the half-wave potential of the voltammogram. Recently, Strutwolf and Arrigan [493] analyzed the influence of different micropores array designs on cyclic voltammograms through finite element method.

On the other hand, to reach steady-state fluxes at ITIES, hydrodynamics techniques were applied to impose a flow of solution phases. Rotating diffusion cell and wall jet electrodes are performed in order to generate different flow regimes. The advances in simulations of the last technique are described below.

Stevens and Fisher [494] used finite element technique to simulate the steady-state current flowing in a channel cell to describe the one electron-transfer reaction. Cooper and Compton [495] reported the studies that simulate the flow of single phase in electrochemical channel cells. Manzanares and co-workers [152] simulated the channel flow at immobilised liquid|liquid interface to describe the transfer of a monovalent cation using explicit finite difference method. By comparison with two-dimensional simulations, the authors demonstrated that a simple one-dimensional theory can be used to describe the cyclic voltammetry response of the channel flow cell.

Jones and Dryfe [496] simulated voltammetry in liquid|liquid interface with implicit finite-difference approach, where both phases flow at different rates, showing how the shape of the current-potential profiles at forward sweep was affected.

The next section focuses attention on describing a model which represents voltammetric response for a simple ion transfer across a liquid|liquid interface controlled by diffusion and which accounts for a solution provided by explicit difference method. Finally, Section 3.2 is devoted to showing the effect of forced hydrodynamic conditions on the electrochemical signal.

3.1. Charge Transfer Processes Controlled by Diffusion

3.1.1. Model. The simple ion transfer taking place at ITIES can be represented as

$$I^{z_i}(w) \rightleftarrows I^{z_i}(o), \tag{8}$$

where I^{z_i} is an ion that can be transferred from aqueous phase (w) to organic phase (o) and z_i is the charge of the species i.

In order to simulate the cyclic voltammetric response for a reversible heterogeneous charge transfer with semi-infinite linear diffusion, Fick's second law of diffusion with specified boundary and initial conditions must be solved for I^{z_i} at each phase, that is,

$$\frac{\partial c^{\alpha}_{I^{z_i}}(x,t)}{\partial t} = D^{\alpha}_{I^{z_i}} \frac{\partial^2 c^{\alpha}_{I^{z_i}}(x,t)}{\partial x^2}, \tag{9}$$

where $c^{\alpha}_{I^{z_i}}(x,t)$ denotes the ion concentration in the α-phase (w or o) at a given distance (x) from the interface and time (t), and $D^{\alpha}_{I^{z_i}}$ is the ion diffusion coefficient in the α-phase. The distance from the interface is defined as positive in the aqueous phase and negative in the organic phase while the interface lies at $x = 0$.

The initial conditions can be defined as

$$\begin{aligned} c^{w}_{I^{z_i}}(x,0) &= c^{w*}_{I^{z_i}}, \\ c^{o}_{I^{z_i}}(x,0) &= c^{w*}_{I^{z_i}} \theta_{I^{z_i}} S_\lambda(0), \end{aligned} \tag{10}$$

where $S_\lambda(0) = 1$, being

$$\begin{aligned} \theta_{I^{z_i}} &= \exp\left[\frac{zF}{RT}\left(\Delta^w_o \phi_{\text{init}} - \Delta^w_o \phi^{o'}_{I^{z_i}}\right)\right], \\ S_\lambda(t) &= \begin{cases} \exp\left[\dfrac{zF\nu t}{RT}\right] & 0 \le t < \lambda \\ \exp\left[\dfrac{zF\nu(2\lambda - t)}{RT}\right] & t \ge \lambda, \end{cases} \end{aligned} \tag{11}$$

where $c^{w,*}_{I^{z_i}}$ denotes the bulk concentration in the aqueous phase, $\Delta^w_o \phi^{o'}_{I^{z_i}}$ is the formal transfer potential, $\Delta^w_o \phi_{\text{init}}$ is the starting potential, ν is the scan rate, λ is the switching time, and the rest of the symbols have their usual meaning.

The boundary conditions for semi-infinite linear diffusion can be written as

$$x \longrightarrow \infty : \quad c^{w}_{I^{z_i}}(x,t) = c^{w}_{I^{z_i}}(x,0), \tag{12}$$

$$x \longrightarrow -\infty : \quad c^{o}_{I^{z_i}}(x,t) = c^{o}_{I^{z_i}}(x,0), \tag{13}$$

$$x = 0 : \quad D^{w}_{I^{z_i}} \left.\frac{\partial c^{w}_{I^{z_i}}(x,t)}{\partial x}\right|_{x=0} = D^{o}_{I^{z_i}} \left.\frac{\partial c^{o}_{I^{z_i}}(x,t)}{\partial x}\right|_{x=0}, \tag{14}$$

where the last equation is the flux continuity at the interface.

3.1.2. Solution with the Explicit Finite Difference Method. The finite difference method [458, 462, 497] applied to the previous equations involves the discretization of time and distance into small intervals, δt and δx, respectively. The expressions for these parameters can be obtained as follows:

$$\delta t = \frac{t_{\exp}}{M}, \tag{15}$$

where $t_{\exp}$ is the total experimental time and M is the number of time intervals, and

$$\delta x = \left(\frac{D_{\max}}{D_M}\delta t\right)^{1/2}, \tag{16}$$

where $D_{\max}$ represents the highest value of the diffusion coefficients. D_M is the model diffusion coefficient, whose optimized value is 0.45, to ensure that the mean free path of particles in the system does not exceed δx.

Using these simulation parameters, the differential equations that appear in Fick's second law are redefined as

$$\begin{aligned}
\frac{\partial c_{I^{z_i}}^{\alpha}(x,t)}{\partial t} &= \lim_{\delta t\to 0}\frac{c_{I^{z_i}}^{\alpha}(x,t+\delta t)-c_{I^{z_i}}^{\alpha}(x,t)}{\delta t},\\
\frac{\partial^2 c_{I^{z_i}}^{\alpha}(x,t)}{\partial x^2} &= \lim_{\delta x\to 0}\left[\frac{c_{I^{z_i}}^{\alpha}(x+\delta x,t)-c_{I^{z_i}}^{\alpha}(x,t)}{\delta x^2}\right]\\
&\quad - \lim_{\delta x\to 0}\left[\frac{u\left[c_{I^{z_i}}^{\alpha}(x,t)-c_{I^{z_i}}^{\alpha}(x-\delta x,t)\right]}{\delta x^2}\right]
\end{aligned} \tag{17}$$

with $u = 2$ for the first box and $u = 1$ for the rest.

Using this discretization, the Fick's second law (9) is rewritten as

$$\begin{aligned}
&\lim_{\delta t\to 0}\frac{c_{I^{z_i}}^{\alpha}(x,t+\delta t)-c_{I^{z_i}}^{\alpha}(x,t)}{\delta t}\\
&\quad = \lim_{\delta x\to 0}\left[\frac{c_{I^{z_i}}^{\alpha}(x+\delta x,t)-c_{I^{z_i}}^{\alpha}(x,t)}{\delta x^2}\right]\\
&\qquad - \lim_{\delta x\to 0}\left[\frac{u\left[c_{I^{z_i}}^{\alpha}(x,t)-c_{I^{z_i}}^{\alpha}(x-\delta x,t)\right]}{\delta x^2}\right].
\end{aligned} \tag{18}$$

Using these equations and considering that $x = i\delta x$ and $t = j\delta t$, the diffusion of I^{z_i} in both phases can be calculated through the following iterative equations:

$$\begin{aligned}
c_{I^{z_i}}^{\alpha}(1,j+1) &= c_{I^{z_i}}^{\alpha}(1,j)\\
&\quad + \frac{D_{I^{z_i}}^{\alpha}\delta t}{\delta x^2}\left[2c_{I^{z_i}}^{\alpha}(0,j)-3c_{I^{z_i}}^{\alpha}(1,j)+c_{I^{z_i}}^{\alpha}(2,j)\right]
\end{aligned} \tag{19}$$

for the first box and

$$\begin{aligned}
c_{I^{z_i}}^{\alpha}(i,j+1) &= c_{I^{z_i}}^{\alpha}(i,j)\\
&\quad + \frac{D_{I^{z_i}}^{\alpha}\delta t}{\delta x^2}\left[c_{I^{z_i}}^{\alpha}(i-1,j)-2c_{I^{z_i}}^{\alpha}(i,j)\right.\\
&\qquad \left.+c_{I^{z_i}}^{\alpha}(i+1,j)\right]
\end{aligned} \tag{20}$$

for the rest of the boxes.

The flux continuity (14) can be similarly treated to obtain the interfacial concentration of I^{z_i} at each phase:

$$\begin{aligned}
c_{I^{z_i}}^{w}(0,j) &= \frac{D_{I^{z_i}}^{o}c_{I^{z_i}}^{o}(1,j)+D_{I^{z_i}}^{w}c_{I^{z_i}}^{w}(1,j)}{D_{I^{z_i}}^{o}\theta_{I^{z_i}}S_\lambda(j)+D_{I^{z_i}}^{w}},\\
c_{I^{z_i}}^{o}(0,j) &= \theta_{I^{z_i}}S_\lambda(j)c_{I^{z_i}}^{w}(0,j).
\end{aligned} \tag{21}$$

Therefore, the concentration of I^{z_i} at any distance can be calculated at each time.

The ion transfer current can be obtained with the discrete form of the ion flux at the interface:

$$I(j) = zFAD_{I^{z_i}}^{\alpha}\frac{2}{\delta x}\left[c_{I^{z_i}}^{\alpha}(1,j)-c_{I^{z_i}}^{\alpha}(0,j)\right], \tag{22}$$

where A is the interfacial area.

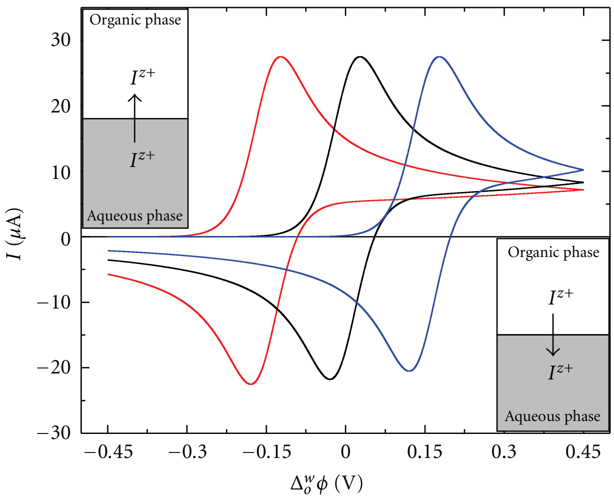

FIGURE 2: Simulated voltammograms corresponding to the transfer of I^{z+} for different formal transfer potential values, $\Delta_o^w\phi_{I^{z+}}^{o'}\cdot\Delta_o^w\phi_{I^{z+}}^{o'}$ = −0.15 V (red line), 0.00 V (black line) and +0.15 V (blue line). Simulation parameters: $z = 1$, $A = 0.18\,\text{cm}^2$, $\nu = 0.050\,\text{V s}^{-1}$, $D_{I^+}^{W} = 1\times10^{-5}\,\text{cm}^2\,\text{s}^{-1}$, $\xi = \sqrt{D_{I^{z+}}^{0}/D_{I^{z+}}^{W}} = 1.12$ (water|1,2-dichloroethane system) and $c_{I^{z+}}^{\text{initial}} = 1\times10^{-3}$ M.

Figure 2 compares simulated cyclic voltammograms of three different cations. In all the cases, the initial potential will be taken as negative, that is, the voltammetric scans will always start from the negative side of the potential window. By convention, the transfer of a positive (negative) charge from the aqueous (organic) phase to the organic (aqueous) phase will produce a net positive (negative) current. Thus, in the forward scan the cation is transferred from the aqueous to the organic phase and vice versa in the backward scan. When the cation is more hydrophilic, more energy needs to be transferred from the aqueous to the organic phase. For cations, the more positive the value of $\Delta_o^w\phi_{I^{z_i}}^{o'}$ is, the more hydrophilic the ion is, and vice versa for anions (see (7)). All the voltammograms present a peak-to-peak separation of $59\,\text{mV}/z_i$ characteristic of reversible charge transfer processes controlled by diffusion.

3.2. Charge Transfer Processes Controlled by Diffusion-Convection. Forced convection can be used to enhance the mass transport, thus the second Fick's diffusion law is modified to incorporate forced hydrodynamic conditions as an extra term. In this way, (9) is replaced by

$$\frac{\partial c_{I^{z_i}}^{\alpha}(x,t)}{\partial t} = D_{I^{z_i}}^{\alpha}\frac{\partial^2 c_{I^{z_i}}^{\alpha}(x,t)}{\partial x^2} - v_x^{\alpha}\frac{\partial c_{I^{z_i}}^{\alpha}(x,t)}{\partial x}, \tag{23}$$

where v_x^{α} is the convection velocity of species in α-phase, that is, the rate with which a volume element moves in solution and is responsible for the flow of species from and toward the interface.

The second term on the right side of (23), convection term, is self-regulated because the concentration gradient forms part of it; therefore, when no net flux is found,

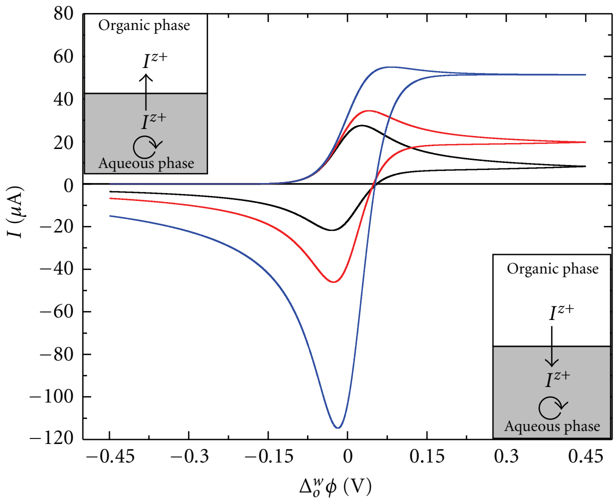

FIGURE 3: Simulated voltammograms in different conditions of mass transport. Quiescent solution (black line) with forced hydrodynamic condition applied in aqueous phases: $\nu_x^W = 1\times10^{-3}$ cm s^{-1} (red line) and $\nu_x^W = 3\times10^{-3}$ cm s^{-1} (blue line). $\Delta_o^w\phi_{I^{z+}}^{o'} = 0.00$ V. Other parameters are as in Figure 2.

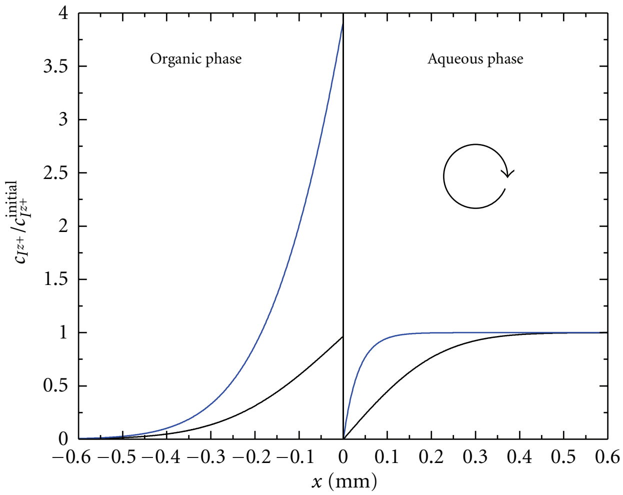

FIGURE 4: Concentration profiles obtained at switching time, λ. Quiescent solution (black line) with forced hydrodynamic condition applied in aqueous phase, $\nu_x^W = 3\times10^{-3}$ cm s^{-1} (blue line). Other parameters are as in Figure 3.

the contribution of the convection term to the mass transport is negligible.

When the explicit finite difference method is applied to (23), concentrations of each species can be calculated from the following expressions:

$$c_{I^{z_i}}^{\alpha}(1, j+1) = c_{I^{z_i}}^{\alpha}(1, j) + \frac{D_{I^{z_i}}^{\alpha}\delta t}{\delta x^2}\left[2c_{I^{z_i}}^{\alpha}(0, j) - 3c_{I^{z_i}}^{\alpha}(1, j) + c_{I^{z_i}}^{\alpha}(2, j)\right] - \nu_x^{\alpha}\left[c_{I^{z_i}}^{\alpha}(0, j) - c_{I^{z_i}}^{\alpha}(1, j)\right] \quad (24)$$

for the first box and

$$c_{I^{z_i}}^{\alpha}(i, j+1) = c_{I^{z_i}}^{\alpha}(i, j) + \frac{D_{I^{z_i}}^{\alpha}\delta t}{\delta x^2}\left[c_{I^{z_i}}^{\alpha}(i-1, j) - 2c_{I^{z_i}}^{\alpha}(i, j) + c_{I^{z_i}}^{\alpha}(i+1, j)\right] - \nu_x^{\alpha}\left[c_{I^{z_i}}^{\alpha}(i-1, j) - c_{I^{z_i}}^{\alpha}(i, j)\right] \quad (25)$$

for the rest of the boxes.

The effect of convection-diffusion is evident in simulated voltammograms (Figure 3); it can be observed that when forced hydrodynamic conditions (stirring) are applied to aqueous phase in forward and backward scans, current peaks increase as the convection velocity increases. For large convection velocity values in forward scan, a limit current is established. These simulated voltammograms can be compared with the experimental results shown in Figure 1 for the TEA^+ transfer.

This effect is caused by the narrowing of the diffusional layer as it can be in the concentration profiles (Figure 4).

Concentration profiles in both phases obtained under forced hydrodynamic conditions differ from unstirred solution. It should also be noted that the concentration of I^{z_i} in the aqueous side of the interface overcomes the analytical concentration when the aqueous phase is stirred.

4. Computer Simulations

Molecular simulation methods, like Monte Carlo or molecular dynamics, have contributed considerably to our current view of the interfacial structure. These methods can provide the potential of mean force (PMF) governing the ion transfer and the means to investigate the exchange of the ion solvation shell: key step in the transfer process.

To calculate the free energies associated with the transfer of an ion across the liquid|liquid interface, a constrained molecular dynamics technique can be employed [64, 498]. The reaction coordinate for ion transfer can be considered as the z_s position of the ion. The Helmholtz free energy difference, $\Delta F(z_s)$, between a state where the ion is located at z_s, $F(z_s)$, and a reference state where the ion is at z_0, F_0, is simply

$$\Delta F(z_s) = F(z_s) - F_0 = \int_{z_0}^{z_s} \langle F_z(z_s') \rangle \, dz_s', \quad (26)$$

where $F_z(z_s')$ is the z-component of the total force exerted on the center of mass of the solute at a given z-position, $z_s's$, averaged over the canonical ensemble. In general, F_0 was chosen as the free energy of the system with the solute located in the bulk liquid region. During the simulation, the z-coordinate of the solute was reset to its original value after each step and the average force acting on the solute was evaluated. The average forces are subsequently integrated to yield the free energy profile.

Exchange of the ion solvation shell during the charge transfer process at the liquid|liquid interface can be analyzed using the radial distribution function (RDF). This study aims at describing the ion solvation environment at the interface analyzing the ion tendency to preserve its solvation shell

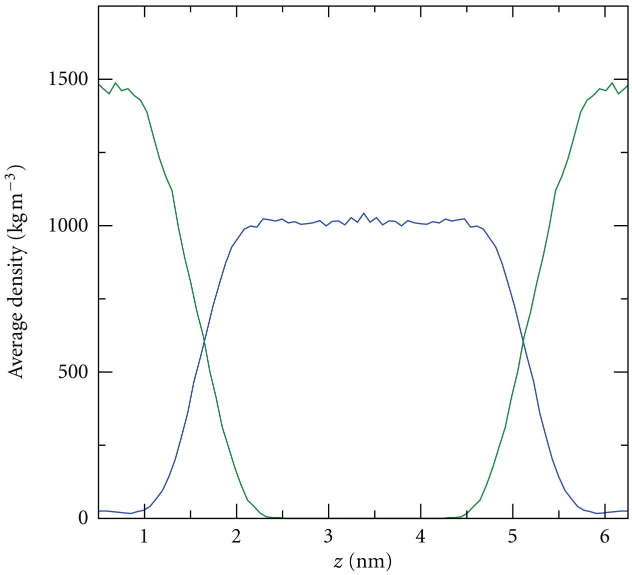

Figure 5: Average density profiles from the H_2O-$CHCl_3$ system. Average density profile of water (blue line) and of chloroform (green line). The liquid|liquid interfacial system consists of two adjacent liquid slabs of 616 water molecules and 246 molecules arranged in a rectangular box of size 3.3 nm × 3.3 nm × 3.3 nm. All simulations were performed using the Gromacs package in the NpT ensemble at 298 K and 1.00 atm. Periodic boundary conditions were applied in all three directions of the Verlet Leapfrog algorithm which was used to integrate the equations of motion, with a time step of 2 fs.

[57, 499]. The small ions tend to keep its hydration shell unaltered, while the first hydration shells of the large ions were found to be significantly reduced as they moved from the aqueous to the organic phase. The ability of the ions to keep part or all of their hydration shell depends on their size and polarizability. This stability of the first solvation shell as the ion approaches the interface plays an important role in many other systems [55, 500].

Using molecular simulation methods, several liquid|liquid interfaces are studied considering neat interfaces: water|1,2-dichloroethane [47, 501], water|octanol [502], water|tetrachloromethane [503] water|nitrobenzene [504, 505], water|dichloromethane [506–508] water|2-heptanone [509], and water|chloroform [506]. Generally, all studies conclude that the structure of liquid|liquid interface is molecularly sharp and very rough. In order to represent these results, characteristic average density profiles for a water|chloroform interface, calculated in our group by molecular dynamics, is depicted in Figure 5. The liquid|liquid interfacial system consists of two adjacent liquid slabs of 616 water molecules and 246 chloroform molecules arranged in a rectangular box of size 3.3 nm × 3.3 nm × 3.3 nm. All simulations were performed using the Gromacs package in the NpT ensamble at 298 K and 1 atm.

Due to the dynamical nature of the interfacial region, the definition of the interfacial structure is dependent on the calculation time scale. In the time scale of few picoseconds, molecular dynamics simulations showed that the liquid| liquid interfaces are molecularly sharp but particularly rough. On longer time scales, the picture of the interface is more diffuse than sharp. This picture is confirmed by methods not involving dynamics (i.e., Monte Carlo).

The incorporation of polarization effects into potential models provides insight into the adaptability of the monomer dipole moment in clusters and interfacial environments. The incorporation of many-body interactions into the potential model [498, 503, 510–516] is also expected to be especially critical for the study of ionic interactions. One advantage of using polarizable potential models [514, 517–520] is that they can, more realistically, account for the electrostatic properties of molecules in the inhomogeneous environments. For example, the polarizable potential is able to describe the increase of the dipole moments of H_2O molecules in bulk liquid as compared to the gas-phase value [521, 522], while the nonpolarizable model [523] only gives a constant dipole moment. It is well known that these dipolar interactions can contribute significantly to interpreting the interfacial transport processes. Thus, to understand the effect of polarization on the electrical properties of the H_2O molecules, we calculated the total dipole moments of the water molecules as a function of the z-axis of liquid| liquid interface. A few simulations with nonpolarizable models included the TIP4P water model [522, 524] and OPLS CCl_4 model [190] and simulations with polarizable models used the Dang and Chang water model [521], a polarizable CCl_4 model, and a polarizable iodide [525]. One recent study of the transfer of iodide across the CCl_4|water interface compared the free energy profile with polarizable and nonpolarizable models [74].

More advanced studies have concentrated on simple ion transfer at liquid|liquid interfaces. In the last years, the transfer of several inorganic and organic ions was analyzed extensively using different molecular simulation methods. The processes of ion transfer studied include Cl^- [48, 49, 70, 75], Cs^+ [70, 75], Li^+, Na^+, K^+, F^-, Br^-, I^- [70], and SCN^- [77] at water|1,2-dichloroethane; Cl^-, Cs^+ [56], and I^- [74] at water|carbon tetrachloride; Na^+, K^+, Rb^+, Sr^{2+}, TMA^+ [62], and I^- [57] at water|2-heptanone; I^- [57] at water|isooctane; Ca^{2+} [526] and TMA^+ [58] at water|nitrobenzene; Cl^- [64] at water|dichloromethane; Na^+ and Cl^- [527, 528] at water|hexanol interfaces. Simulation results showed that small, hydrophilic ions keep their solvation shells at least partly going from water to the organic phase. On the other hand, as the ion transfer occurs, few hydrophilic ions lose the solvation gradually and fully [49, 56–58, 62].

Further details of the liquid|liquid interfaces most widely studied in electrochemical research are specifically discussed in the subsequent sections.

4.1. Water|1,2-Dichloroethane Interface. In the transfer process for SCN^- ion, from the aqueous to organic phase the free energy minimum is followed by a strictly monotonically increasing of the free energy in the subsurface region of water phase. This behaviour is a consequence of the ability of SCN^- ion to be adsorbed in the close vicinity of the interface. The SCN^- ion coextraction of the water molecules of its first hydration shell occurs in the organic phase [77].

For Cl^- and Cs^+ ions the free energy profile across the water|1,2-dichloroethane interface shows no minimum in the free energy profile for Cl^- ion in the interface [48, 49], because of the Cl^- ion unfavorable interaction with 1,2-DCE. Otherwise, cesium present a free energy minimum near the interface, showing a propensity for the aqueous region near the water|1,2-dichloroethane interface. The authors showed that 1,2-dichloroethane presents an average interfacial orientation resulting in unfavourable interactions with anions but favourable ones with cations [75]. Recently, Rose and Benjamin [70] calculated the free transfer energies of hydrated alkali and halide ion clusters from bulk water to bulk 1,2-dichloroethane using molecular dynamics simulations. For each ion, the free transfer energy decreased as the number of water molecules in the cluster increased. This dependence is more often found in small than in large ions.

4.2. Water|Nitrobenzene Interface. The transfer process across the water|nitrobenzene interface was studied for Ca^{2+} [526] and TMA^+ [58]. Dos Santos and Gomes [526] showed that calcium ion transfer process occurs with the formation of a water cone that perturbs the interface. When the ion crosses the interface, the first hydration shell remains intact and part of the second hydration shell is lost; a substitution of water by nitrobenzene molecules occurs. This three-stage substitution process begins as the ion approaches the interface, increases as the ion crosses the interface with the water cone formation, and stops with the water cone breaking. The authors also found that the withdrawal of water molecules occurs with a replacement with nitrobenzene molecules and that the substitution process is concerted. The most notable change in the increase of the free energy occurs while the ion is in the organic phase moving away from the interface. The PMF calculated by Dos Santos and Gomes [526] for this process is a monotonic increasing function of the distance to the interface, hence, no energy barriers were found. The transfer process was found to be nonactivated, as shown for the transfer of other ions in other interfaces [57, 62]. Tetraethylammonium ion transfer process was studied by Schweighofer and Benjamin [58]. The authors showed that the transfer of tetramethylammonium across the water|nitrobenzene interface involves only a small change in the solvation free energy, compared with a much larger free energy of transfer which accompanies the transfer of small inorganic ions [48, 49]. Unlike the transfer of small inorganic ions, TMA^+ does not keep a hydration shell when going into the organic phase [58]. This is chiefly attributed to the fact that the water-ion interaction varies less markedly along the interface. This delay in the "shedding off" of the hydration shell during the nonequilibrium transfer is accompanied by a significant increase in the surface roughness in the form of "fingering." It is similar to the case of the transfer of small ions [58].

It is remarkable that simple ion transfer processes at liquid|liquid interfaces are one-step reactions. According to representative experimental data shown in Section 2.4, this large group includes important transfers of various inorganic and organic ions. Among several contentious points in the theory of simple ion transfer is the nature of its rate-limiting step. One model attributes the finite ion transfer rate to slow diffusion of the species transferred through the interfacial layer [529, 530], while another treatment considers activation-controlled changes in ion solvation [50, 72, 531, 532].

5. Practical Applications

Studies on polarized ITIES are relevant to different fields, such as deposition of metallic nanoparticles [533–549] and polymerization [550–556] at liquid|liquid interfaces, ion and neutral species partition [342, 349, 557–560] and electro-assisted extraction [561, 562]. Particular cases related to electroanalysis are discussed in this section. It should be noticed that these electroanalytical procedures are based on different global mechanisms of charge transfer, that is, simple and facilitated ion transfer [5, 9, 32].

In the last three decades, the interfaces between two immiscible electrolyte solutions were applied exhaustively in analytical chemistry. These interfaces can be used for understanding and developing practical electroanalytical processes and devices [9, 32, 36, 563, 564]. The electrochemical methods applied to liquid|liquid interfaces have proved a useful tool for the determination of ionic analytes not easily oxidized or reduced [36, 45, 119, 121, 136, 141, 149, 153, 254, 273, 336, 496, 562, 564–580].

The ITIES may also be employed for detection in ion chromatography [119] and has also been incorporated into capillary electrophoresis systems to allow the separation of species before their detection at the interface [581, 582]. Recently, Arrigan and co-workers have used the ion transfer at ITIES as a detection method in a capillary electrophoresis separation system. The authors reported the optimal experimental conditions for the separation of different substances of practical interest [583]. Capillary electrophoresis system with the ITIES-based detector provides a platform for the detection of cationic or anionic analytes.

Kihara and coworkers have proposed the use of a flow cell for the coulometric determination of redox inert ions based on the electrochemical ion transfer at the aqueous-organic solution interface [571, 584–586]. Osakai and co-workers used a microflow cell with a stationary organic phase stabilised below a hydrophilic dialysis membrane, to detect ions using pulsed amperometry [587]. Later, Kihara and co-workers constructed a two-step flow-cell system in view of applications to clinical samples [584], and Gohara and Osakai applied a similar two-step flow-cell system to the on-line electrochemical separation of acetylcholine and choline and their simultaneous determination [588].

Finally, the application of charge transfer reaction at liquid|liquid interfaces in bioassays has been reported recently by Shao and co-workers [141]. In this paper, the authors highlighted the advantage of ITIES in the study of biologically and pharmaceutically interesting molecules.

6. Conclusion and Outlook

The main aspects of simple ion transfer at liquid|liquid interfaces have been summarized in this paper. Complete and up-to-date bibliography has been compiled for each topic, based not only on the latest reports, but also on the history and development of this novel research area. Special emphasis was placed on numerical simulations of simple ion transfer at ITIES, as we believe this tool can provide important clues to the future development in electroanalysis.

The extensive compilation of electrochemical studies, given in Section 2.4, for the simple ion transfer at different water|organic solvent interfaces, constitutes a useful database for future experimental studies. Due to a historical evolution in the field, the most studied interfaces are probably water|nitrobenzene and water|1,2-dicholoroethane, where the ion transfer of almost all the alkaline, alkaline earth and transition cations and several anions have been measured. Yet, other environment-friendly solvents have been studied. The latter aspect must receive special attention if we intend ion transfer at ITIES to be extended to practical applications. As regards this, ion transfer at novel polarizable interfaces between water and room-temperature ionic liquids is being studied.

Electrochemistry at ITIES is a relatively new research area with less than forty years of evolution. During this time, different practical applications have been developed as metallic nanoparticles synthesis and polymerization. However, several other promising aspects need to be explored, mainly related to electrocatalysis, electroanalysis of pharmaceutically and biologically related systems and to the possibility of charge separation between phases.

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