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Studying the Thermodynamics and Kinetics of Ion Transfers Across Water-2-nitrophenyloctyl Ether Interface by Means of Organic-solution-modified Electrodes

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Transfer reactions across a water-2-nitrophenyloctyl ether (WINPOE) interface for a series of monovalent inorganic ions and tetraalkylammonium cations are studied by means of square-wave (SWV) and cyclic voltammetry at thin organic-film-modified (TFE) and three-phase electrodes (TPE). Both electrode configurations are assembled using lutetium bis(tetra-*tert*-butylphthalocyaninato) as the redox probe, whose properties enable assessment of both anion and cation transfer reactions in a single voltammetric experiment. It is demonstrated that TFE can be effectively applied to measure the Gibbs energy of ion transfer reactions when the transferring ion is common to both liquid phases, controlling the Galvani potential difference at the WINPOE interface. A comparative study of the thermodynamics of ion transfer reactions performed with TFE and TPE reveals that both electrode configurations provide a consistent set of data. Kinetic measurements referring to the transfers of ClO_4^- , and a series of tetraalkylammonium cations have been conducted by combining TFE and SWV according to the method known as “quasireversible maximum” in thin-film voltammetry (Mirčeski, V. J. Phys. Chem. B 2004, 108, 13719).

1. Introduction

The ion transfer across an interface between two immiscible liquids is a process of exceptional importance that has been intensively studied over decades. The charge transfer across an aqueous/organic solution (W/O) interface is regarded as a simplified model that provides information about the energetics and kinetics of complex charge transfer phenomena across biomembranes, which play a key role in living cells of all organisms. In the past few years, solid electrodes modified with redox-active water immiscible organic liquids or solution of organic solvents emerged as a versatile tool to assess the ion and electron transfer reactions across liquid/liquid (L/L) interfaces. Bard et al.¹ conducted the first experiment in which a microelectrode was covered with a film of an organic solvent. Later on, Anson et al.^{2,3} developed an electrode configuration consisting of pyrolytic graphite, the surface of which was completely covered with a thin film of a water-immiscible organic solvent in order to study the electrochemistry of lipophilic redox probes dissolved in the film. Moreover, Anson et al. developed a simple but valuable methodology for assessment of electron transfer processes across L/L interface by virtue of TFE.^{4–9} Recently, combining TFE and a fast and sensitive voltammetric method such as square-wave voltammetry (SWV), a novel methodology for estimation of the kinetics of ion transfer reactions across nonpolarizable liquid interface was developed.^{10–13} Such thin-organic-film-modified electrodes (TFE), where a thin organic film membrane is sandwiched between the electrode and an aqueous electrolyte, are proven to be a valuable biomimetic experimental system that provides insight into complex coupled electron–ion transfer reactions relevant

to biomembrane electrochemistry.¹⁴ Following the advance of thin-film electrodes, a three-phase electrode (TPE) system has been developed, which appears in a variety of configurations, such as electrodes modified with randomly distributed microdroplets of redox active organic liquids^{15–19} or a paraffin-impregnated graphite electrode partly covered with a single macroscopic droplet of an organic solvent containing a neutral lipophilic redox probe.^{20,21} Three-phase electrodes are extensively applied to inspect the ion transfer reactions across the interface between water and a variety of solvents, with a particular emphasis put on the measurements of energy of ion transfer reactions.^{20,22} The unique characteristic of the TPE configuration is the three-phase boundary line, that is, electrode/organic liquid/aqueous electrolyte triple interface, which plays a critical role in the functioning of the electrode.^{16–18,21,23} The three-phase and thin-film electrodes paved the way to study the ion transfers across L/L interfaces by means of a conventional three-electrode configuration, as well as to analyze the transfers of strongly hydrophilic ions that otherwise are difficult to be assessed by other electrochemical techniques.

The present communication concerns the thermodynamics and kinetics of ion transfer reactions across water/2-nitrophenyloctyl ether (WINPOE) interface studied by means of thin-organic-film and three-phase electrodes. Both electrode configurations are assembled using lutetium bis(tetra-*tert*-butylphthalocyaninato) ($\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$) as a redox probe, which was recently proven to exhibit superior properties compared to all other redox probes used for preparation of both thin-film and three-phase electrodes,^{23,24} in different solvents (NB,²⁴ n-octanol²⁵) or ionic liquid.²⁶ Among various organic solvents, NPOE is the most suited for the design of electrochemical sensors for ionic or ionizable species because it has poor solubility in water, as well as a low water content, a low vapor pressure, and a medium permittivity ($\epsilon_{\text{rel}} = 24.2$). In comparison with most of the

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solvents such as NB, DCE or DCH, NPOE possess the highest kinetic viscosity η . This solvent is a good compromise for the modification of solid electrodes and preparation of potentiometric and voltammetric sensors. Hence, significant efforts have been done to assess the mechanism^{27,28} and thermodynamics of ion transfer reactions across the WINPOE interface,²⁹ including various ionizable drugs,^{30,31} as well as to estimate the kinetics of tetraalkylammonium cations transfers.^{32–34} Due to the lack of appropriate electrochemical methods, the kinetics of the transfer of most inorganic monovalent ions is yet unknown.

2. Experimental Section

$\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ is synthesized and purified according to the procedure already described.^{35,36} All other chemicals, including 2-nitrophenyloctyl ether (Aldrich), were of high purity and were used as received. Tetrakis(4-chlorophenyl)-borate (TPBCl) of tetramethyl- (Me_4N^+), tetraethyl- (Et_4N^+), tetrapropyl- (Pr_4N^+), tetrabutyl- (Bu_4N^+), tetrapentyl- (Pen_4N^+), tetrahexylammonium (Hex_4N^+) and tetraphenylarsenium (TPAs^+) were prepared by metathesis and purified by two recrystallizations in acetone/ethanol mixtures. Potassium tetrakis(4-chlorophenyl)-borate and sodium tetrakis(4-fluorophenyl)-borate (NaTPBF) were Fluka products. Aqueous solutions (W) were prepared with redistilled water (Millipore Q). Both solvents, water and NPOE, are mutually saturated.

A disk electrode (0.32 cm²) of highly oriented pyrolytic graphite, perpendicular to the graphitic planes (EPGE) was used. The preparation and pretreatment of the electrode is describe elsewhere.¹⁰ For experiments with thin-film electrodes, 1.5 μL of the organic solution was layered on the electrode surface, completely covering the graphite surface. Both aqueous and organic phases contain supporting electrolytes with a common anion or cation, depending on the particular experiment. The corresponding counterions in the organic and aqueous phase are strongly lipophilic and hydrophilic, respectively; hence, the counterions do not significantly partition between the two immiscible phases. After immersion of the film electrode into an aqueous solution, the organic film was sandwiched between the electrode surface and the aqueous phase. Accordingly, no three-phase boundary line is formed, which is the important difference with the TPE configuration.

For experiments with TPEs, 0.2 μL of the organic solution was deposited on the graphite electrode with the help of a micropipette. The organic solution spontaneously spread over the electrode surface, forming a very thin film of the organic solution. Due to the minute volume of the organic solution, the electrode surface was only partly covered with the organic film, causing the formation of a three-phase boundary line when the modified electrode is immersed in the aqueous electrolyte.^{22,23} The organic solution contained the redox probe only, and no supporting electrolyte was added to the organic phase.

Cyclic voltammetry (CV) and square-wave voltammetry (SWV) are conducted using an Autolab equipment (EcoChemie, Utrecht, Netherlands). A KCl saturated calomel electrode (SCE) is the reference, and a platinum wire is the auxiliary electrode. All experiments were conducted at 25 ± 0.1 °C.

3. Results and Discussion

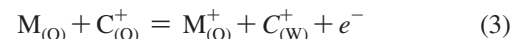
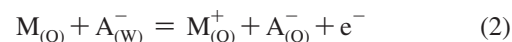
3.1. Thermodynamics of Ion Transfer Reactions Studied by Thin-organic-film Electrodes. An electrochemical process at organic-film modified electrodes proceeds as a complex, coupled electron–ion transfer reaction. The ion transfer at the WINPOE interface is driven by the electrode reaction of the

redox probe at the graphite/organic solution interface (GEIO). As noted in the previous section, both liquid phases contain an electrolyte with a common ion. In the course of the voltammetric experiment, the transfer of the common ion accompanies the electrode reaction of the redox probe. Both electrochemical processes are virtually simultaneous, resulting in a single voltammetric response that represents the overall electron-ion transfer reaction. Besides being a transferring ion, the purpose of the common ion is to control the potential difference at the LIL interface. The concentration of the common ion in both liquid phases is significantly larger than the redox probe. Consequently, its surface concentration at the liquid interface is considered as being constant in the course of the voltammetric experiment, buffering the interfacial potential difference at the liquid interface, which is defined by the following equation:

$$\Delta_{\text{W}}^{\text{O}}\varphi_{\text{i}} = \Delta_{\text{W}}^{\text{O}}\varphi_{\text{i}}^{\ominus} + \frac{RT}{zF} \ln \frac{a_{\text{i(w)}}}{a_{\text{i(o)}}} \quad (1)$$

where $\Delta_{\text{W}}^{\text{O}}\varphi_{\text{i}}$ is the Galvani potential difference, $\Delta_{\text{W}}^{\text{O}}\varphi_{\text{i}}^{\ominus}$ is the standard potential for the transfer of the ion (i) from the aqueous to the organic phase, z is the charge number of the ion (i), a denotes the activity, and other symbols have their usual meaning.

As elaborated in our previous studies, $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ can be oxidized and reduced in an organic medium in one-electron reversible processes to a chemically stable cation and anion, respectively.^{35,36} Both monovalent ionic forms are strongly lipophilic and remain confined within the organic film of the modified electrode. Depending of the common ion present in both electrolytes, the overall reaction corresponding to the oxidation probe can be represented by the following reactions:



Neglecting the activity coefficients and approximating the activities as being equal with the concentrations, the formal potential $E_{\text{c}}^{\ominus'}$ corresponding to these reactions is defined by eq 4,

$$E_{\text{c}}^{\ominus'} = E_{\text{M}_{(\text{O})}^{\ominus}/\text{M}_{(\text{O})}}^{\ominus} + \Delta_{\text{W}}^{\text{O}}\varphi_{\text{i}}^{\ominus} + \frac{RT}{zF} \ln \frac{c_{\text{i(w)}}}{c_{\text{i(o)}}} \quad (4)$$

where $E_{\text{M}_{(\text{O})}^{\ominus}/\text{M}_{(\text{O})}}^{\ominus}$ is the standard potential of the redox couple $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2^{\ominus}/\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ in the organic phase.

In the same manner, the reduction processes of $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ can proceed according to following equations.



Equation 5 refers to the case where the common ion is a cation, whereas eq 6 holds when an anion is common to both liquid phases. The formal potential for eqs 5 and 6 is defined as follows,

$$E_{\text{c}}^{\ominus'} = E_{\text{M}_{(\text{O})}^{\ominus}/\text{M}_{(\text{O})}}^{\ominus} + \Delta_{\text{W}}^{\text{O}}\varphi_{\text{i}}^{\ominus} + \frac{RT}{zF} \ln \frac{c_{\text{i(w)}}}{c_{\text{i(o)}}} \quad (7)$$

with $E_{\text{M}_{(\text{O})}^{\ominus}/\text{M}_{(\text{O})}}^{\ominus}$ being the standard potential of the redox couple $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2^{\ominus}/\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ in the organic phase.

From eqs 4 and 7, it follows that the standard potential of an ion transfer can be evaluated by measuring the formal potential of the system, provided the standard potential of the redox probe and the activities of the common ion are known. The standard

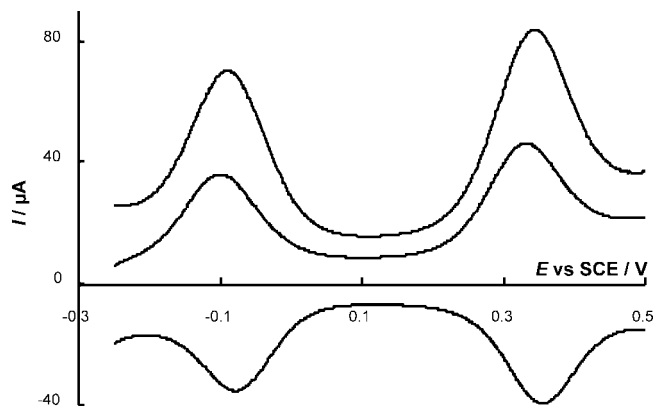


Figure 1. SWV response of $\text{Lu}[(\text{tBu})_4\text{Pc}]_2$ recorded on an organic film electrode in contact with 0.1 mol/L LiClO_4 aqueous solution. The organic phase is a NPOE solution containing 2 mmol/L of redox probe and 0.1 mol/L of Bu_4NClO_4 . The instrumental parameters are: frequency $f = 8$ Hz, amplitude $E_{\text{sw}} = 50$ mV, and step potential $\Delta E = 1$ mV.

potential of ion transfer ($\Delta_{\text{W}}^{\text{O}} \phi_i^{\ominus}$) can be transformed into Gibbs energy of ion transfer ($\Delta_{\text{W}}^{\text{O}} G_i^{\ominus}$) according to the following relation: $\Delta_{\text{W}}^{\text{O}} G_i^{\ominus} = -zF\Delta_{\text{W}}^{\text{O}} \phi_i^{\ominus}$. In addition, the Gibbs energy is related with the partition coefficient of the ion for the biphasic system studied as $P_i = \exp(-\Delta_{\text{W}}^{\text{O}} G_i^{\ominus}/RT)$. The Gibbs energy, or the partition coefficient, is of exceptional importance, because it is a quantitative evaluation of the lipophilicity of a studied ion.

In the present experiments, the formal potential is determined by precisely measuring the net peak potential (E_p) of the SW voltammetric response at TFE, at a low SW frequency, in order to meet the criteria for a reversible electrochemical process.¹³ A SWV for the oxidation and reduction of $\text{Lu}[(\text{tBu})_4\text{Pc}]_2$ accompanied by transfer of ClO_4^- ions across WINPOE is depicted in Figure 1. The aqueous and the organic phase contain 0.1 mol/L LiClO_4 and 0.1 mol/L Bu_4NClO_4 , respectively. The SW peak at 0.344 V corresponds to the oxidation of $\text{Lu}[(\text{tBu})_4\text{Pc}]_2$, accompanied by the transfer of ClO_4^- from W to NPOE, whereas the peak at -0.091 V represents the reduction of $\text{Lu}[(\text{tBu})_4\text{Pc}]_2$ coupled with the expulsion of ClO_4^- from NPOE. The forward and backward components of the SW response for both redox systems are well-developed bell-shaped curves, with almost identical peak potentials and peak currents, implying a reversible electrochemical processes.¹⁴ The potential separation of 0.435 V between the two net SW peaks corresponds to the difference between the standard potentials of the two redox couples, as can be deduced by subtracting eqs 4 and 7. It is interesting to note that the standard potential difference of 0.435 V in NPOE is higher than the corresponding value of 0.38 V that is frequently measured in various organic solvents different to NPOE,^{24,35,36,37} which is most likely due to the formation of ion pairs in the latter solvent.³¹

To confirm that the common ClO_4^- ion is the transferring ion for both electrode reactions of $\text{Lu}[(\text{tBu})_4\text{Pc}]_2$, the dependence of the net peak potentials on the aqueous concentration of ClO_4^- is studied, while keeping the concentration in the organic phase constant. Two sets of experiments are performed in which the concentration of the ion in the organic phase is 0.1 and 0.05 mol/L, and Figure 2 displays the dependence (E_p) versus $\log [c(\text{ClO}_4^-(\text{o}))/c(\text{ClO}_4^-(\text{w}))]$, curves 1 and 2 correspond, respectively, to the oxidation and reduction processes. The dependence is linear for both redox processes, with practically an identical slope of 60 mV. These results confirm that the electrochemical processes for the oxidation and reduction of the redox probe proceed according to reactions 2 and 6, whereas the net peak

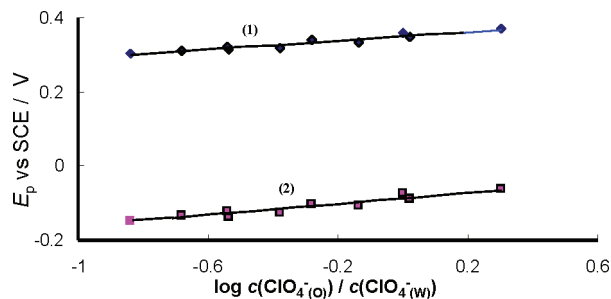


Figure 2. Dependence of the net SW peak potential for the oxidation (1) and reduction (2) process of $\text{Lu}[(\text{tBu})_4\text{Pc}]_2$ on the logarithm of the concentration ratio $c(\text{ClO}_4^-(\text{o}))/c(\text{ClO}_4^-(\text{w}))$. The concentration ratio is varied by adjusting the concentration of the common ion in the aqueous phase while keeping the concentration in the organic phase at 0.1 mol/L or 0.05 mol/L. All other conditions are the same as for Figure 1.

potentials vary in agreement with equations 4 and 7, respectively. For each concentration of the transferring ion in the aqueous phase the net peak potential separation of 0.430 V remains virtually unaltered, corresponding to the difference in the standard potentials of the two redox couples.

Applying the same methodology, the response of the thin-film electrode has been examined when Br^- , SCN^- , Cl^- , NO_3^- , Me_4N^+ , Et_4N^+ , Pr_4N^+ , Bu_4N^+ , Pen_4N^+ , Hex_4N^+ , Na^+ , and K^+ are the transferring ions. In each case, a linear relationship between the peak potentials and the logarithm of the aqueous concentration of the ion is observed, for both oxidation and reduction processes of $\text{Lu}[(\text{tBu})_4\text{Pc}]_2$ (Table 1). The data in Table 1 show that the potential difference between the oxidation and reduction SW peaks remains practically constant and equal to 0.432 ± 0.008 V for all the ions investigated. According to eqs 4 and 7, the formal potentials for the oxidation and reduction processes depend linearly on the standard potential of ion transfer. In an idealized case, the slope of the dependence E_c^{\ominus} versus $\Delta_{\text{W}}^{\text{O}} \phi_i^{\ominus}$ is equal to 1, and the intercept is equal to $E^{\ominus} + (RT/zF) \ln(c_{i(\text{w})}/c_{i(\text{o})})$, as a consequence, for $c_{i(\text{w})} = c_{i(\text{o})}$, the intercept is equal to the standard potential of the redox couple. This is illustrated in Figure 3A, for the oxidation and reduction processes of $\text{Lu}[(\text{tBu})_4\text{Pc}]_2$, whereas Figure 3B displays the net SWVs corresponding to various tetraalkylammonium cations. The $\Delta_{\text{W}}^{\text{O}} \phi_i^{\ominus}$ values are taken from ref 38. When the lipophilicity of the tetraalkylammonium cation increases, the SW peak moves toward more positive potential. For both redox systems, the evolution of E_c^{\ominus} versus $\Delta_{\text{W}}^{\text{O}} \phi_i^{\ominus}$ is linear (Figure 3A), with slopes of 0.95 (for the oxidation process) and 0.94 (for the reduction process), which are close to the theoretically predicted values. The experimental data presented in Figure 3A correspond to the case when $c_{i(\text{w})} = c_{i(\text{o})}$, so that the intercepts of the lines corresponds to the standard potentials of the redox couples, which are $E^{\ominus}(\text{Lu}[(\text{tBu})_4\text{Pc}]_2^+/\text{Lu}[(\text{tBu})_4\text{Pc}]_2) = 0.223$ V and $E^{\ominus}(\text{Lu}[(\text{tBu})_4\text{Pc}]_2/\text{Lu}[(\text{tBu})_4\text{Pc}]_2^-) = -0.210$ V versus SCE. It has to be emphasized that all values for $\Delta_{\text{W}}^{\text{O}} \phi_i^{\ominus}$ used for the calibration line in Figure 3A are based on the extra-thermodynamic hypothesis assuming that the energies for the transfer of tetraphenylarsonium (TPAs^+) and tetraphenylborate (TPB^-) ions are equal.³⁹ These standard potentials of the redox couples being established, one can estimate the standard potential of the transfer of a particular common ion.

A more direct approach to estimate the standard redox potentials based on the latter extra-thermodynamic hypothesis is to measure the formal potentials in two separate experiments in which TPAs^+ and TPB^- are the common ions. Because $\Delta_{\text{W}}^{\text{O}} \phi_{\text{TPB}^-}^{\ominus} = -\Delta_{\text{W}}^{\text{O}} \phi_{\text{TPAs}^+}^{\ominus}$, from eq 4, it follows that $E_{\text{M}(\text{o})/\text{M}(\text{o})}^{\ominus} = (E_c^{\ominus}(\text{TPAs}^+) + E_c^{\ominus}(\text{TPB}^-))/2$, where $E_c^{\ominus}(\text{TPAs}^+)$ and

TABLE 1: The Net Peak Potentials Measured with SWV at Thin-film Electrodes for the Oxidative and Reductive Processes^a, the Slope of the Dependence E_p ^b, and the Net Peak Potential Difference between the Oxidative and Reductive System for the Same Transferring Ion

transferring common ion	aqueous electrolyte	organic electrolyte	M ⁺ /M		M/M ⁻		$\Delta E_p/V$
			slope/mV	E_p/V	slope/mV	E_p/V	
ClO ₄ ⁻	LiClO ₄	Bu ₄ NClO ₄	60	0.349	75	-0.087	0.436
NO ₃ ⁻	KNO ₃	Oc ₄ NNO ₃	66	0.556	66	0.123	0.433
Br ⁻	LiBr	Oc ₄ PBr	60	0.610	57	0.165	0.445
Cl ⁻	KCl	Oc ₄ NCl	55	0.691	54	0.252	0.439
SCN ⁻	KSCN	Pen ₄ NSCN	58	0.435	64	0.005	0.430
TPB ⁻	NaTPB	Bu ₄ NTPB	70	-0.102	64	-0.547	0.445
Me ₄ N ⁺	Me ₄ NBr	Me ₄ NTPBCl	52	0.110	55	-0.320	0.430
Et ₄ N ⁺	Et ₄ NCl	Et ₄ NTPBCl	55	0.213	56	-0.205	0.418
Pr ₄ N ⁺	Pr ₄ NCl	Pr ₄ NTPBCl	54	0.345	55	-0.081	0.426
Bu ₄ N ⁺	Bu ₄ NCl	Bu ₄ NTPBCl	60	0.453	59	0.027	0.426
Pen ₄ N ⁺	Pen ₄ NCl	Pen ₄ NTPBCl	50	0.542	58	0.110	0.432
Hex ₄ N ⁺	Hex ₄ HSO ₄	Hex ₄ TPBCl	52	0.197	58	0.626	0.429
Na ⁺	NaCl	NaTPBF	65	-0.151	65	-0.575	0.424
K ⁺	KNO ₃	KTPBCl	67	-0.110	66	-0.543	0.433
TPAs ⁺	TPAsCl	TPAsTPBCl	51	0.554	62	0.109	0.445

^a For a series of transferring ions, when the concentration of the ion was equal in both liquid phases. ^b Versus the logarithm of the $c(A_{(NPOE)})/c(A_{(w)})$ or $c(C_{(w)})/c(C_{(NPOE)})$ ratio.

$E_c^{\ominus}(\text{TPB}^-)$ are the formal potential for the oxidation process measured when TPAs⁺ or TPB⁻ are the common ion in the organic and aqueous phases. An analogous equation can be derived from eq 7, referring to the redox couple $M_{(o)}/M_{(o)}^-$. With this experimental approach, the standard potentials of the two redox couples are $E^{\ominus}(\text{Lu}[(t\text{Bu})_4\text{PCl}_2]^+/\text{Lu}[(t\text{Bu})_4\text{PCl}_2]) = 0.226$ V and $E^{\ominus}(\text{Lu}[(t\text{Bu})_4\text{PCl}_2]/\text{Lu}[(t\text{Bu})_4\text{PCl}_2]^-) = -0.219$ V versus SCE. These values are in good agreement with those previously obtained and are used to estimate the Gibbs energy of transfer for a series of ions and to compare them with the literature data (Table 2). Figure 4 shows a correlation diagram between the values estimated with thin-film electrodes and literature data.³⁸ The regression line is attributed with a slope of 1.041, intercept 1.863, and a correlation coefficient (R) of 0.998, confirming the applicability of thin-film electrodes for assessing thermodynamic parameters of the ion transfer reactions. The only disadvantage of this approach is that one requires corresponding salts with a common ion to be dissolved in the two liquid phases, which in some cases could not be obtained.

An alternative way to determine the standard potentials of the redox couples in NPOE is to conduct a conventional voltammetric experiment, using ferrocene as an internal standard. Figure 5 shows linear sweep and net SWVs for the reduction and oxidation of $\text{Lu}[(t\text{Bu})_4\text{PCl}_2]$ recorded at a Pt microelectrode and vitreous carbon electrode in a water saturated NPOE solution, containing 0.01 mol/L of Hex₄NTPBCl and 0.1 mol/L of Bu₄NClO₄, respectively, as a supporting electrolyte. The peak potential difference of SWV is 0.430 V, whereas the half-wave potential difference between LSV is 0.440 V, representing the potential difference between the standard potentials of the two redox couples. These values are in excellent agreement with that measured by means of organic-film modified electrodes in the presence of various transferring ions. Assuming that the standard potential of ferrocenium/ferrocene couple is known (Strehlow assumption),^{39,40} the standard potentials of the present redox couples in NPOE are: $E^{\ominus}(\text{Lu}[(t\text{Bu})_4\text{PCl}_2]^+/\text{Lu}[(t\text{Bu})_4\text{PCl}_2]) = 0.041$ V and $E^{\ominus}(\text{Lu}[(t\text{Bu})_4\text{PCl}_2]/\text{Lu}[(t\text{Bu})_4\text{PCl}_2]^-) = -0.389$ V versus SCE. Therefore, using the latter values for the standard redox potentials and measuring the formal potentials with TFEs, one can estimate the standard potentials of ion transfer based on the Strehlow assumption. As in the case of NB,²⁴ the difference between the two hypothesis is significant (17 kJ mol⁻¹).

3.2. Thermodynamics of Ion Transfer Reactions Studied by TPEs. The TPE configuration is characterized by the absence of electrolyte in the organic phase, an important difference with TFEs. The TPE configuration is much simpler than the TFEs. As a consequence, the number of possible ion transfer reactions is significantly reduced at TPEs. For instance, using a strongly hydrophobic redox probe such as $\text{Lu}[(t\text{Bu})_4\text{PCl}_2]$, the oxidation and reduction reaction are accompanied only by the transfer of anions and cations from water to the organic phase, respectively, whereas reactions 3 and 6 do not occur due to the absence of a significant amount of ions in the organic phase. The disadvantage of the three-phase configuration is that the potential difference across the L/L interface is not constant, as in the case of organic film electrodes, but changes with the electrode reaction as the charge transfer modifies the organic phase composition. Nevertheless, as shown below, this obstacle does not impede precise determination of the energy of transfer of strongly hydrophilic ions that otherwise cannot be measured with other electrochemical methods.

The other important characteristic of the TPE configuration is the presence of a three-phase boundary line, where the three phases (electrode, organic solution, and aqueous phase) meet. The role of the three-phase boundary line and the overall electrochemical mechanism has been elaborated in detail in a series of previous studies.^{18,22,23,41,42} The coupled electron-ion transfer reaction commences in the three-phase boundary region. In the course of the voltammetric experiment, the conductivity of the organic phase progressively increases due to electrochemical formation of ions by the electrode reaction, as well as by the simultaneous ingress of aqueous ions into the organic phase. The oxidation of the redox probe to a monovalent cation is coupled with ingress of the aqueous anion, as described by reaction 2, whereas the reduction mechanism proceeds according to reaction 6. The formal potentials at the TPEs are defined by the following equations,²⁰⁻²²

$$E_c^{\ominus'} = E_{M_{(o)}^+/M_{(o)}}^{\ominus} + \Delta_{\text{w}}^{\text{O}}\varphi_i^{\ominus} - \frac{RT}{F} \ln c_{A_{(w)}} + \frac{RT}{F} \ln \frac{c_{M_{(o)}}}{2} \quad (8)$$

$$E_c^{\ominus'} = E_{M_{(o)}/M_{(o)}^-}^{\ominus} + \Delta_{\text{w}}^{\text{O}}\varphi_i^{\ominus} + \frac{RT}{F} \ln c_{C_{(w)}} - \frac{RT}{F} \ln \frac{2}{c_{M_{(o)}}} \quad (9)$$

which refer to reactions 2 and 5, respectively. Here, $c_{M_{(o)}}$ is the concentration of $\text{Lu}[(t\text{Bu})_4\text{PCl}_2]$ in the organic phase. Figure 6

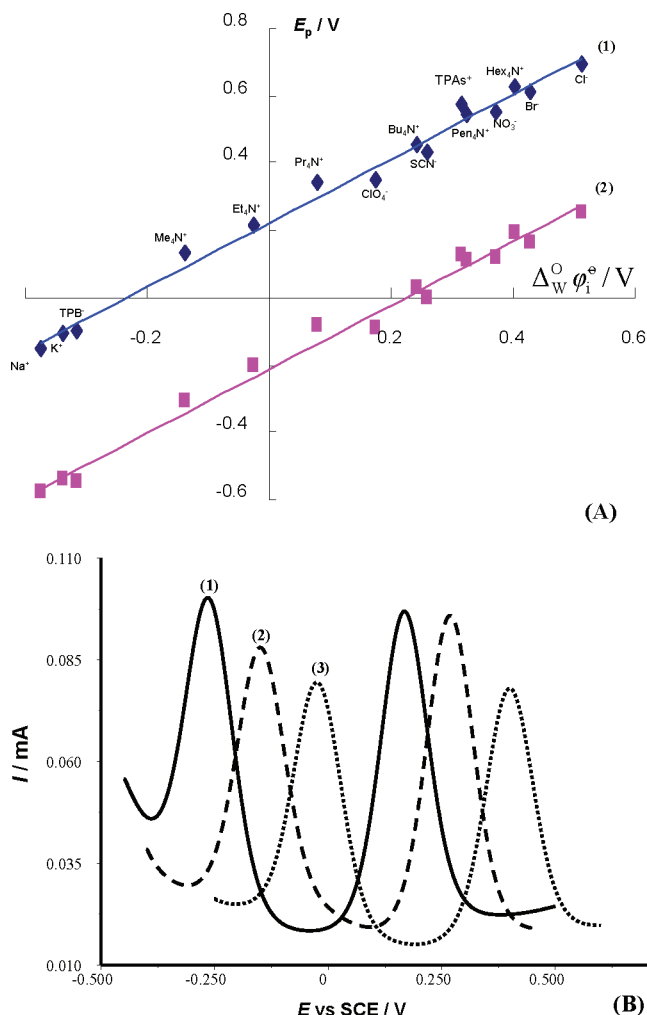


Figure 3. (A) Dependence of the net SW peak potentials for the oxidation (1) and reduction (2) of $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ on the standard ion transfer potential of different transferring ions (the data being taken from 38). The concentrations of the transferring ion in both liquid phases are equal. (B) Net SWVs corresponding to the transfer of Me_4N^+ (1), Et_4N^+ (2), and Pr_4N^+ (3) cations. The aqueous phase contains 0.5 mol/L of the chloride salt of the corresponding cation, whereas the organic phase contains 0.05 mol/L of the tetrakis(4-chlorophenyl)-borate salt of the corresponding cation. The other conditions are the same as for Figure 1.

shows typical net SWVs recorded with TPEs in contact with different aqueous electrolytes: KNO_3 , NaCl , and LiBr . It is obvious that the reductive peak is sensitive to the nature of the aqueous cation, shifting toward negative potentials when the hydrophilicity of the transferring cation increases; similarly, the oxidation peak shifts toward higher potentials when the anion of the aqueous electrolyte has more affinity for water. These experimental findings are in accord with the electrochemical processes (reactions) 2 and 5. In addition, Figure 7 shows the dependence of the net peak potentials on the standard potentials of ion transfers for a series of transferring ions. For both electrochemical processes, a linear dependence is found, with slopes of 0.93 (curve 1) and 1.1 (curve 2), in agreement with eqs 8 and 9. The slight deviation of the slope from the theoretical value of 1 is a consequence of the uncertainty and scattering of available literature data, rather than due to a certain drawback of the TPE configuration. Note that with the TFE system, the corresponding slopes also deviate from the theoretical value [i.e., the slopes are 0.95 and 0.94 (See Figure 3A)], despite the fact that the potential difference at the WINPOE interface is precisely

TABLE 2: Comparison of the Gibbs Energies of Ion Transfer Taken from Literature³⁸ and Measured with Three-phase (TPE) and Thin-film Electrodes (TFE)

transferring ion	$\Delta_W^O G_i^{\ominus}$ data taken from ref 38/kJ mol ⁻¹	$\Delta_W^O G_i^{\ominus}$ (TPE)/kJ mol ⁻¹	$\Delta_W^O G_i^{\ominus}$ (TFE)/kJ mol ⁻¹
Hex ₄ N ⁺		-46.1	-38.6
Pen ₄ N ⁺	-31.25		-30.6
Bu ₄ N ⁺	-23.3	-27.6	-22.0
Pr ₄ N ⁺	-7.7	-7.4	-11.4
Et ₄ N ⁺	2.5	5.7	1.25
Me ₄ N ⁺	13.4	14.5	11.2
K ⁺	32.7	34.0	32.3
Na ⁺	36.3	40.7	36.3
TPAs ⁺	-30.5	-28.9	-31.6
Li ⁺	46.5*	42.5	
ClO ₄ ⁻	16.9	16.7	11.9
SCN ⁻	25.1	23.2	20.3
NO ₃ ⁻	35.9	34.5	31.9
Br ⁻	41.3	38.7	37
Cl ⁻	49.5	46.6	45
TPB ⁻	-30.5		-31.6
F ⁻		70	

* Taken from ref 48.

controlled by the distribution of the common ion. With the aid of eqs 9 and 10 and the intercept of calibration lines given in Figure 7, one can estimate the standard potentials of the two redox couples in the organic phase, which are $E^\ominus(\text{Lu}[(t\text{Bu})_4\text{Pc}]_2^+/\text{Lu}[(t\text{Bu})_4\text{Pc}]_2) = 0.250$ V and $E^\ominus(\text{Lu}[(t\text{Bu})_4\text{Pc}]_2/\text{Lu}[(t\text{Bu})_4\text{Pc}]_2^-) = -0.231$ V versus SCE. These values are in fair agreement with the corresponding values measured with TFEs of 0.223 and -0.210 V, respectively. Obviously, the standard redox potential measured with TPEs for the oxidative and reductive processes are more positive and more negative, respectively, compared to the corresponding values observed with thin-film electrodes. This deviation might be partly caused by the uncompensated resistance of the organic phase of the TPE. Therefore, the calibration line constructed by the TPE might involve some error in the intercept of the line. For these reasons, it is recommendable to use the values for the standard redox potentials estimated with TFEs, where the effect of uncompensated resistance is minimized. In spite of the latter drawback, an important advantage of the TPE is the capability to study the transfer of strongly hydrophilic ions, F^- and Li^+ being examples in the current study (Table 2), that otherwise are difficult to assess by other electrochemical techniques. The

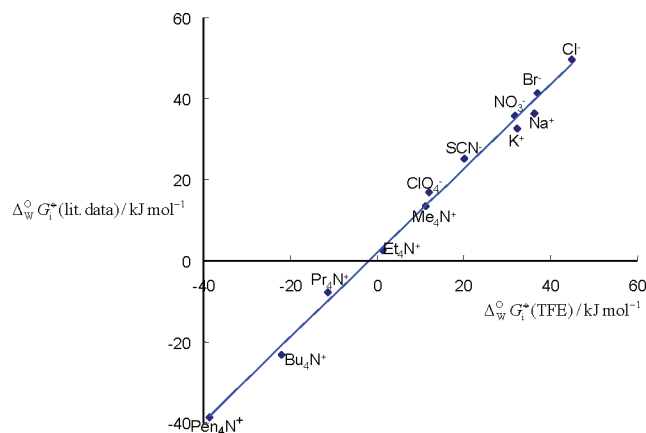


Figure 4. Correlation between the standard potentials of ion transfer measured with thin-film electrodes and literature data taken from ref 38.

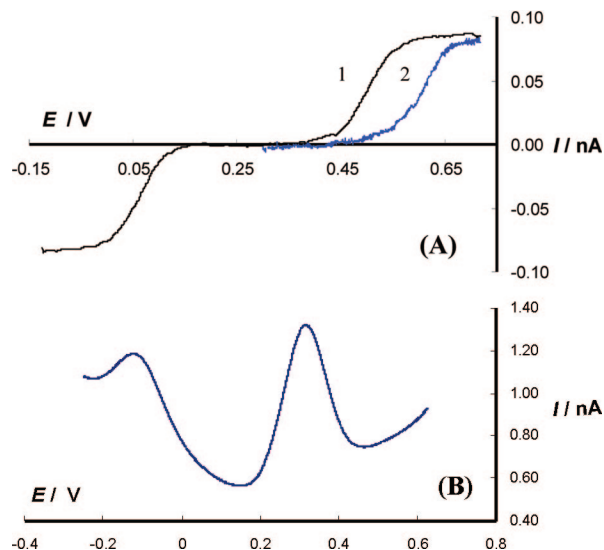


Figure 5. (A) LSV of 2.5 mmol/L $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ recorded at a Pt-microdisc electrode ($r = 10 \mu\text{m}$) in a water-saturated NPOE containing 0.01 mol/L $\text{Hex}_4\text{NTPBCl}$ as a supporting electrolyte, using an Ag/THATPBCl as a reference electrode ($\nu = 1 \text{ mV/s}$). The voltammograms (1) and (2) corresponds to the electrode reactions of $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ and ferrocene, respectively. (B) SWV of 1.25 mmol/L $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ recorded at a vitreous carbon electrode using an Ag/AgCl reference electrode. The parameters of the potential modulation are $f = 8 \text{ Hz}$, $E_{\text{sw}} = 40 \text{ mV}$, and $\Delta E = 1 \text{ mV}$.

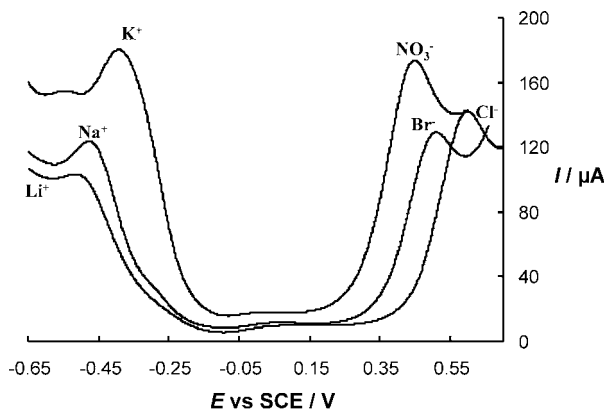


Figure 6. Net SW voltammograms of $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ recorded at a TPE in contact with an aqueous solution containing 1 mol/L of LiBr , KNO_3 , and NaCl . The other conditions are the same as for Figure 1.

corresponding values for the Gibbs energy of transfer of these ions are $\Delta G_{\text{W}}^{\text{NPOE}} G_{\text{F}^-}^{\text{O}} = 70 \text{ kJ mol}^{-1}$ and $\Delta G_{\text{Li}^+}^{\text{NPOE}} G_{\text{Li}^+}^{\text{O}} = 42.5 \text{ kJ mol}^{-1}$. Table 2 summarizes the data for the standard Gibbs energy of transfer from water to NPOE for a series of ions measured with thin-film and three-phase electrodes. For a comparison, the second column lists the literature data taken from ref 38. The correlation line between the data measured with three-phase and thin-film electrodes is associated with a slope of 0.923, an intercept of 0.594, and a correlation coefficient (R) of 0.994, showing a good consistency of the data obtained with the two electrode configurations.

3.3. Kinetics of Ion Transfers Across the WINPOE Interface. We have previously shown that kinetic information on the ion transfer reactions across the LIL interface can be obtained using TFEs in combination with SWV.^{10–12,25} The methodology is based on the specific feature of the SWV response in thin-film voltammetry,^{43,44} known as a “quasireversible maximum”. The measurement is experimentally simple, requiring only inspection of the net SW peak currents as a

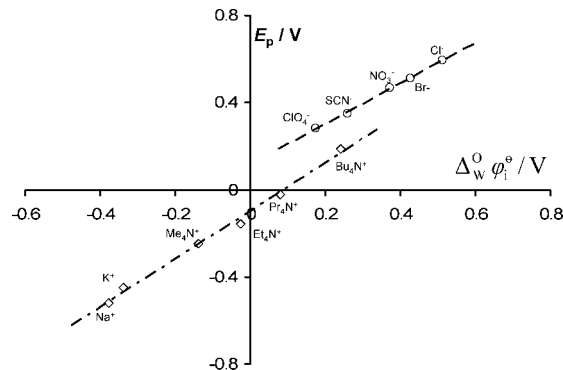


Figure 7. Dependence of the net SWV peak potentials for the oxidation (1) and reduction (2) of $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ at a TPE on the standard potential of transfer for various ions present in the aqueous phase at a concentration of 0.1 mol/L (the data being taken from ref 38). All other conditions are the same as for Figure 1.

function of the time-window of the voltammetric experiment, represented by the frequency of the potential modulation. The phenomenological standard rate constant (k_s) of the ion transfer can be estimated through the simple formula $k_s = K_{\text{max}} \sqrt{D f_{\text{max}}}$, where K_{max} is the critical kinetic parameter calculated by the simulations, f_{max} is the critical frequency associated with the position of the experimentally measured quasireversible maximum, and D is the diffusion coefficient.^{10–12,43,44}

As previously described,^{10–12} the overall electrochemical process at organic film electrodes couples the electron transfer at the EPGE|NPOE with the ion transfer at the NPOE|W interface. Using $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ as a redox probe, it has already been shown that the ion transfer is the rate-determining step, for the WINB^{10–12} and Wln-octanol interfaces.²⁵ When the ion transfer is the rate-controlling step, the position of the quasireversible maximum shifts toward higher critical frequencies by increasing the concentration of the transferring ion in the aqueous phase. This feature is an important diagnostic criterion for a coupled electron–ion transfer reaction controlled by the kinetics of the ion transfer.^{10,11} According to the theory,¹¹ the plot $\log(f_{\text{max}}^{-0.5})$ versus $\log(c_{i(\text{W})})$ is a line with a slope dependent on the transfer coefficient. On the contrary, if the electron transfer at the EPGE|organic film interface controls the rate of the overall process, then the position of the maximum is insensitive to the concentration of the transferring ion.¹¹

Before applying SWV to kinetic measurements, the response of the organic film electrodes has been thoroughly inspected by cyclic voltammetry in order to examine its reproducibility and stability by repetitive cycling of the potential. Typical repetitive cyclic voltammograms corresponding to the electrolysis of the $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$ in the organic film coupled with the transfer of ClO_4^- ions are given in Figure 8A. The stability of the response of the modified electrode is obvious. As ClO_4^- is the common ion in equilibrium between the two liquid phases; it is transferred for both oxidative and reductive processes, as described by reactions 2 and 7, respectively. The results in Figure 8B represent $\Delta I_p f^{-0.5}$ versus $\log f$ for the oxidation (1) and reduction (2) of the $\text{Lu}[(t\text{Bu})_4\text{Pc}]_2$. The two maximums have the same position, implying identical kinetics for the two electrochemical systems. Because the two processes involve different electron transfer reactions but the same ion transfer reaction, it is obvious that the latter is the rate-determining step. This is in accord with the previous results on ion transfers across the WINB interface.^{10–12} In addition, the

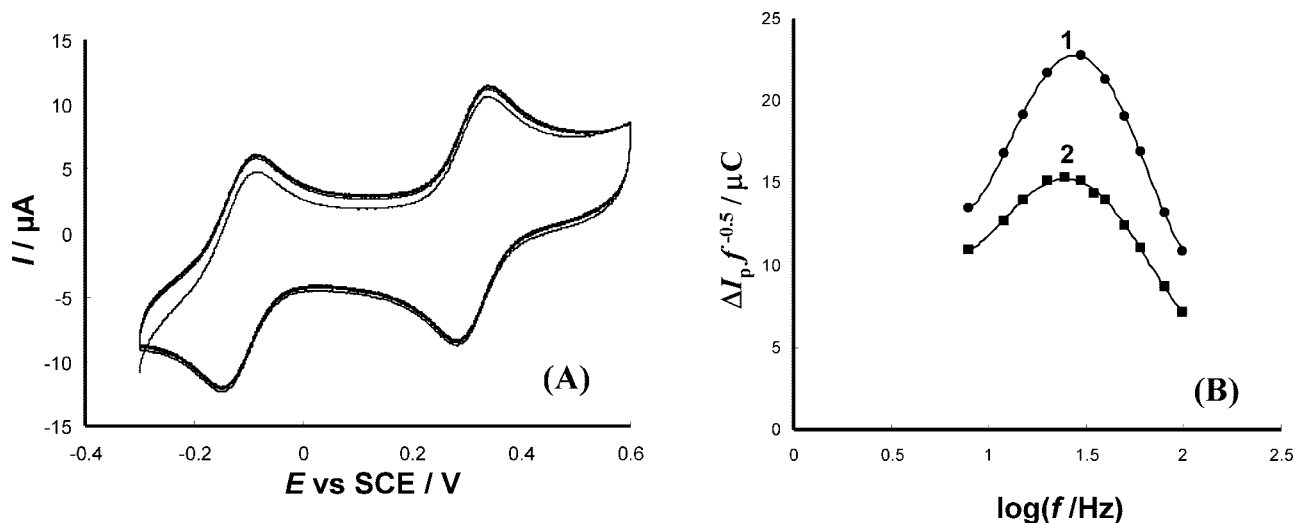


Figure 8. (A) Repetitive cyclic voltammograms for the oxidation and reduction of $\text{Lu}[(\text{tBu})_4\text{Pc}]_2$ coupled with the transfer of ClO_4^- across the WINPOE interface ($\nu = 50$ mV/s). (B) Quasireversible maximums corresponding to the transfer of ClO_4^- recorded by the oxidation (1) and reduction (2) of $\text{Lu}[(\text{tBu})_4\text{Pc}]_2$. For both panels the aqueous and the organic phase contain 1 mol/L LiClO_4 and 0.1 mol/L Bu_4NClO_4 , respectively.

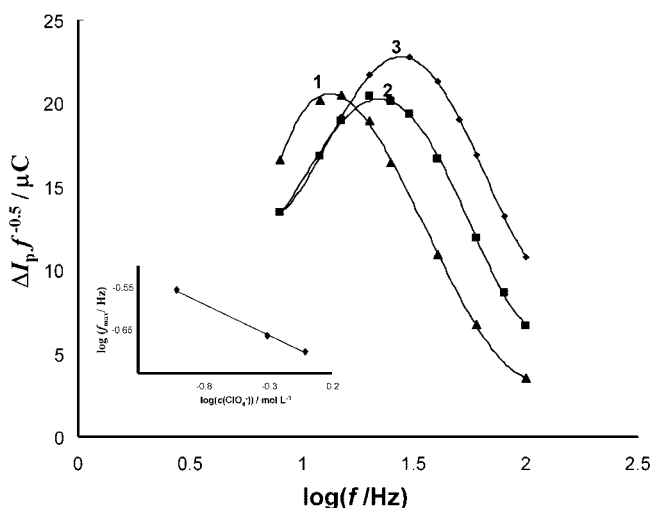


Figure 9. Quasireversible maximums recorded by oxidation of $\text{Lu}[(\text{tBu})_4\text{Pc}]_2$ for different concentrations of the transferring ClO_4^- ions in the aqueous phase. Aqueous phase contains 0.1 (1); 0.5 (2), and 1 mol/L (3). The organic phase contains 0.1 mol/L Bu_4NClO_4 . The parameters of the potential modulation are $E_{\text{sw}} = 50$ mV, $\Delta E = 0.15$ mV. The inset shows the dependence of the logarithm of the critical frequency on the logarithm of the concentration of the transferring ion in the aqueous phase.

evolution of the quasireversible maxima with the concentration of ClO_4^- is presented in Figure 9. The position of the quasireversible maximum shifts toward higher critical frequencies by increasing the concentration of the ion. The inset in Figure 9 shows a linear dependence between $\log(f_{\text{max}}^{-0.5})$ and $\log(c_{\text{ClO}_4^-})$ ($R = 0.999$), which is a clear confirmation that the transfer of ClO_4^- across the WINPOE interface is the rate-determining step.

Corresponding quasireversible maxima are successfully measured for the transfer of Me_4N^+ , Et_4N^+ , Pr_4N^+ , and Bu_4N^+ (see Figure 10). For all the studied ions the critical frequency is within the interval 15–20 Hz, when the concentrations of the transferring ion in the organic and aqueous phase is 0.1 and 0.5 mol/L. The very close values for the critical frequency imply similar transfer rates for these ions, which is a general feature already observed at various liquid interfaces.

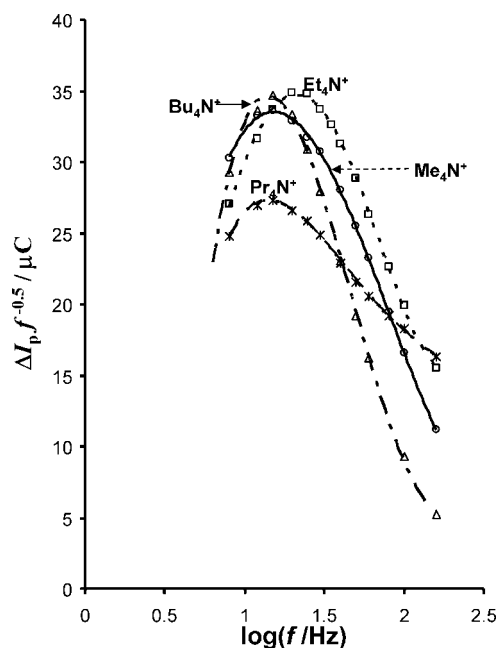


Figure 10. Quasireversible maximums for the transfers of tetraalkylammonium ions recorded by oxidation of $\text{Lu}[(\text{tBu})_4\text{Pc}]_2$. The aqueous and the organic phase contain 0.5 and 0.05 mol/L of the corresponding ion, respectively. The parameters of the potential modulation are $E_{\text{sw}} = 50$ mV and $\Delta E = 0.15$ mV.

To calculate the critical kinetic parameter K_{max} and to estimate the standard rate constant of studied ion transfer reactions, a theoretical model has been developed based on the following kinetic equation,

$$\frac{I}{FA} = k_{\text{s, it}} \exp(\beta\phi) \left[\frac{(c_{\text{M}^+})_{x=0}}{(c_{\text{M}})_{x=0}} \right]^{-\beta} \left[(c_{\text{A}(\text{w})})_{x=L} - \exp(-\phi) (c_{\text{A}(\text{o})})_{x=L} \frac{(c_{\text{M}^+})_{x=0}}{(c_{\text{M}})_{x=0}} \right] \quad (10)$$

which is valid for the coupled electron–ion transfer reaction 2, controlled by the rate of the ion transfer.¹¹ (Note that in ref 11 there is a misprint, where the last term on the right-hand side of eq 10, i.e., $(c_{\text{M}^+})_{x=0}/(c_{\text{M}})_{x=0}$ is powered on β , which is

incorrect.) Here, $k_{s, it}$ is the phenomenological standard rate constant of the ion transfer reaction, β is the charge transfer coefficient of the ion transfer, $(c_{M^{+}})_{x=0}$ and $(c_M)_{x=0}$ are the surface concentrations of the redox species at the electrode surface, and $(c_{A(w)})_{x=L}$ and $(c_{A(o)})_{x=L}$ are the concentrations of the transferring ion at the liquid interface that is positioned at distance L from the electrode surface. In addition, $\varphi = (F/RT)(E_{GE|W} - E_c^\ominus)$ is the relative dimensionless potential, $E_{GE|W}$ is the potential difference between the graphite electrode and the aqueous phase, and E_c^\ominus is the formal potential of reaction 2.

The surface concentrations of all electroactive species have been calculated by solving differential equations for the second Fick's law, assuming semi-infinite linear diffusion for the ion in the aqueous phase and a linear diffusion within a limiting space, for all other species confined within the organic film with a thickness L .^{43,44} Due to the significant viscosity, the diffusion coefficients of species in NPOE are assumed to be an order of magnitude lower than in the aqueous phase. To derive the numerical solution, a modified step-function method is used, as described elsewhere.⁴⁵ The numerical simulations are conducted by MATHCAD software.⁴⁶ Generally speaking, the model used in the present study is more rigorous than the previous ones used for similar purposes.^{10–12,25} Note that in previous models a common diffusion coefficient was assumed for all electroactive species;^{10–12,25} also, the concentration of ions at the L/L interface was considered as being constant in the course of the voltammetric experiment.^{10,11,25}

Because of the complexity of the system considered, the value of the critical kinetic parameter associated with the position of the theoretical quasireversible maximum depends on several parameters, such as the concentration ratios $\rho_1 = c_{A(o)}^*/c_{M(o)}^*$ and $\rho_2 = c_{A(w)}^*/c_{M(o)}^*$, the diffusion coefficient ratio $\rho_D = D_{(o)}/D_{(w)}$, the film thickness L , and the charge transfer coefficient, β . $c_{A(o)}^*$ and $c_{A(w)}^*$ are the bulk concentrations of the ion in the corresponding liquid phase, $c_{M(o)}^*$ is the bulk concentration of the redox probe, $D_{(o)}$ is the diffusion coefficient common to all species in the organic phase, and $D_{(w)}$ is the corresponding parameter in water. The experimental system can be even more complex than the theoretical one, considering that ion-pairing effects in NPOE cannot be ignored, an important factor determining the actual concentration of the ion in the film.^{31,33} Furthermore, there are not precise data for the diffusion coefficients of all studied ions in NPOE. For all these reasons, a precise determination of the kinetic parameters is not possible, however relative values for a series of ions can be evaluated. Assuming that the diffusion coefficients in NPOE and water are 1×10^{-6} and $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, respectively, and that the actual concentrations of the ions in the organic phase are 0.05 mol/L, the critical kinetic parameter is $K_{\max} = 0.025$. The latter value is an average of the values for the critical kinetic parameter valid for film thickness of $1 \leq L/\mu\text{m} \leq 10$, transfer coefficient $0.3 \leq \beta \leq 0.7$, $c_{A(w)}^* = 0.5 \text{ mol/L}$, $c_{M(o)}^* = 2 \text{ mmol/L}$, and amplitude of the potential modulation $E_{sw} = 50 \text{ mV}$. Hence, the estimation of the standard rate constant for all studied ions yields a value on the order of $10^{-4} \text{ cm s}^{-1}$. This value is an order of magnitude lower than the corresponding one measured by our method at the WINB interface^{11,12} and is practically proportional to the inverse ratio of the viscosities of the organic solvents.⁴⁷ Note that our rate constants are in agreement with those measured by Manzanares et al.,³³ as both systems refer to the ion transfers at a nonpolarizable L/L interface. The rate constants measured at the polarizable

L/L interface are usually about 2 orders of magnitude higher,³⁴ implying the sensitivity of the rate of the ion transfer on the experimental conditions and structure of the L/L interface.

Conclusion

In conclusion, organic-solution-modified electrodes are experimentally simple but powerful system for studying both thermodynamics and kinetics of ion transfer reactions across L/L interfaces. The electrode system can be assembled in two configurations, that is, as thin-film and three-phase electrodes. A comparative thermodynamic study with the two electrode configurations provided a consistent set of data for the energy of ion transfer reactions for a large series of monovalent ions. In a thin-film configuration, the potential difference at the L/L interface is precisely controlled, thereby enabling accurate determination of the standard potential of the redox probe and the energy of ion transfer reaction. On the other hand, the TPE configuration enables determination of the transfer energy of strongly hydrophilic ions that otherwise are inaccessible with other electrochemical techniques, F^- being an example in the current study ($\Delta W_{\text{NPOE}}^{\text{NPOE}} G_{F^-}^\ominus = 70 \text{ kJ mol}^{-1}$).

From a kinetic point-of-view, TFEs in combination with SWV is particularly suited system for assessment of the rate of ion transfer reactions across a nonpolarizable L/L interface. Using the method of "quasireversible maximum," the kinetics of ClO_4^- and a series of tetraalkylammonium cations has been estimated. All studied ions exhibit a similar kinetics of transfer across a WINPOE interface, attributed with an apparent standard rate constant that is approximately an order of magnitude lower compared to the WINB system measured by the same method.

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