

Lutetium Bis(tetra-*tert*-butylphthalocyaninato): A Superior Redox Probe To Study the Transfer of Anions and Cations Across the Water|Nitrobenzene Interface by Means of Square-Wave Voltammetry at the Three-Phase Electrode

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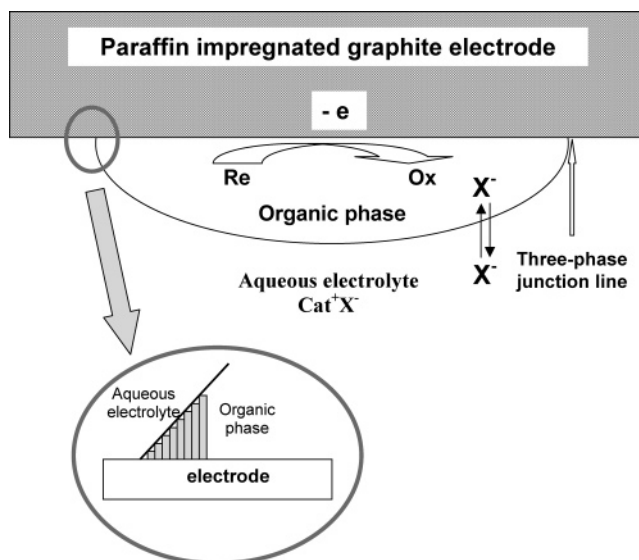
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The redox properties of lutetium bis(tetra-*tert*-butylphthalocyaninato) (LBPC) have been studied in nitrobenzene that is deposited as a microfilm on the surface of highly oriented pyrolytic graphite electrodes. The behavior of the modified electrode, which is immersed in an aqueous electrolyte solution, is typical for the three-phase electrode (Scholz, F.; Komorsky-Lovrić, Š.; Lovrić, M. *Electrochem. Comm.* **2000**, 2, 112–118). LBPC can be both oxidized and reduced in one electron reversible processes. The oxidation and the reduction of LBPC at the graphite|nitrobenzene interface is accompanied by the transfer of anion or cation, respectively, from the aqueous phase into the organic layer. Thus, using LBPC as a redox probe for the three-phase electrode, the transfer of both anions and cations across the water|nitrobenzene interface can be studied in a single experiment. The hydrophobicity of LBPC is so high that it enables inspection of cations and anions with $\Delta_w^{\text{nb}} G_{\text{Cat}^+}^\theta \leq 43$ kJ/mol and $\Delta_w^{\text{nb}} G_{\text{X}^-}^\theta \leq 50$ kJ/mol, respectively. The direct transfer of Na^+ and Li^+ from water to nitrobenzene, mutually saturated, is achieved for the first time at a macroscopic water|nitrobenzene interface.

1. Introduction

In past years the three-phase electrode emerged as a simple and powerful tool for studying the ion transfer across the liquid|liquid (L|L) interface.^{1–8} This modified electrode consists of a paraffin-impregnated graphite electrode (PIGE) at the surface of which a droplet of a water-immiscible organic solvent (O) is deposited (Scheme 1). The organic solvent contains only a neutral redox probe. The modified electrode is immersed in an aqueous electrolyte solution (W) and used in a conventional three-electrode arrangement. The electrochemical transformation of the neutral redox probe at the PIGE|O interface disturbs the charge neutrality of the organic phase, hence promoting the transfer of an ion across the W|O interface. Both electron and ion transfers occur simultaneously and cannot be separated on the time scale of a conventional voltammetric experiment. Therefore, in the overall electrochemical process, the electrode reaction at the PIGE|O interface serves as a driving force for the ion transfer across the W|O interface. This experimental arrangement is different from the conventional four-electrode method for studying the interface between two immiscible electrolyte solutions (ITIES)⁹ where the ion transfer is accomplished by external potentiostatic control of the potential difference at the L|L interface. For these reasons the use of the ITIES method is limited to organic solvents forming a polarizable interface with the water phase. This limitation is overcome by the three-phase electrode, as demonstrated in the study of anion transfer across the water|*n*-octanol interface.¹⁰ Note that *n*-octanol, which is the organic solvent used for the study of drug lipophilicity, does not form a polarizable interface with an aqueous electrolyte solution; hence it cannot be studied by standard ITIES methods.

SCHEME 1: Schematic Representation of the Three-Phase Electrode



Furthermore, the three-phase electrode in combination with a sensitive voltammetric technique such as square-wave voltammetry (SWV),¹¹ provides a well-defined voltammetric response in the absence of any added electrolyte in the organic phase.¹² This unique ability of the three-phase electrode arises from the low ohmic drop of the three-phase boundary junction, i.e., the region in which the electrode reaction is mainly constrained. Along the three-phase boundary line, the organic phase provides the redox active material, the aqueous phase supplies charge compensating counterions, and the electrode serves as a source or a sink of electrons. Thus, the three-phase line fulfills all requirements for initiating the electrochemical reaction

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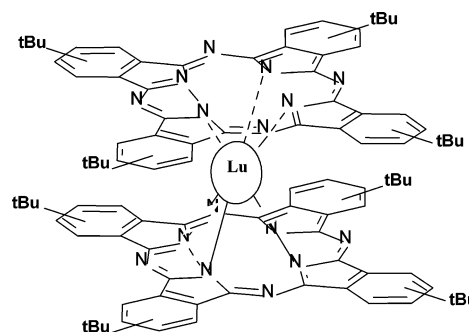
regardless of the electrical conductivity of the organic phase. Furthermore, the region of the droplet close to the three-phase boundary line can be represented as a series of ultrathin films in which the partition of the aqueous electrolyte provides conductivity for initiating the electrochemical reaction (see Scheme 1). For these reasons, the electrode reaction is not restricted only to the three-phase boundary line but expands in the edge region of the droplet. Accordingly, in a recent study it has been demonstrated that the voltammetric response at the three-phase electrode under conditions of SWV has the properties of an electrode reaction occurring in a limiting diffusion space.¹² It is important to emphasize another feature of the three-phase electrode; i.e., once the electrochemical reaction is initiated in the region of the three-phase junction, the conductivity of the organic phase rapidly increases in the course of the voltammetric experiment, due to the formation of the charge species in the organic phase and to the simultaneous ingress of an equivalent amount of counterions from the aqueous phase.¹³ The ability of the system to increase the conductivity of the organic phase is responsible for the progression of the electrochemical process from the edge of the droplet toward its center when the time of electrolysis is sufficiently long, e.g., in cyclic voltammetry at a slow scan rate.^{1,14} Consequently, despite the absence of the electrolyte in the organic phase, the uncompensated resistance does not significantly affect the voltammetric response.

The presence of a single electrolyte only in the aqueous phase simplifies the system facilitating the identification of the ion crossing the L|L interface, which is sometimes not straightforward in classical ITIES experiments.⁹ The ionic current could be either the transfer of ions of the redox probe, created electrochemically at the PIGE|O, leaving the organic phase, or the transfer of counterions from the aqueous electrolyte into the organic phase. This depends on the relative affinity of the oxidized, or reduced, redox probe and of the aqueous ions for both phases. As long as the lipophilicity of the redox probe is higher than the hydrophilicity of the aqueous ions, the ionic current is only due to the transfer of the aqueous ions to the organic phase. Consequently, highly lipophilic redox species are required for the study of hydrophilic ions.

A large series of hydrophilic inorganic anions,^{1,2} miscellaneous organic anions,³ anionic forms of amino acids and peptides,^{5,6} and the anionic forms of many pharmacologically active compounds were studied,^{7,8} using the oxidation of decamethylferrocene (DMFC) to decamethylferrocenium ion (DMFC⁺) as a driving force for anion transfer. Nitrobenzene (NB) being the organic solvent, the anions with Gibbs energy of transfer $\Delta_w^{\text{nb}} G_{\text{X}^-}^\theta \leq 37.21$ kJ/mol can be studied with DMFC. On the other hand, cations have been studied on the basis of a complex electrode mechanism of iodine reduction in the presence of chloride ions in the aqueous phase.¹⁵ Cation transfer can be more efficiently studied from the reduction of Fe(III) tetraphenylporphyrin chloride (FePorph).¹⁶ However, this method is applicable only to cations with $\Delta_w^{\text{nb}} G_{\text{Cat}^+}^\theta \leq 23$ kJ/mol; the transfer of the alkali ions such as Li⁺ and Na⁺, as well as those of cationic forms of many important organic ions, e.g., the cationic forms of amino acids, cannot be studied. It must also be emphasized that the redox probes used previously are quick to have chemical side reactions following the electron transfer. DMFC⁺, as the ferricinium derivatives, is not stable in the presence of coordinating species, halide ions for example; iron porphyrin redox properties depend on possible axial ligand exchange reactions and iodine forms trihalides.

From all the previous studies with the three-phase electrode, it follows that the performance of the system for studying the

CHART 1: Molecular Structure of Lutetium Bis(tetra-*tert*-butylphthalocyaninato) (LBPC)



ion transfer depends predominantly on the properties of the redox probe. To extend the capabilities of the method, it is of crucial importance to find a highly hydrophobic and chemically stable compound, undergoing reversible redox transformation in the organic phase. A compound fulfilling all these requirements is lutetium bis(tetra-*tert*-butylphthalocyaninato) (LBPC) (Chart 1).^{17,18} LBPC undergoes monoelectronic oxidation and reduction in nitrobenzene, yielding stable LBPC⁺ and LBPC⁻ ions. Thus, LBPC enables the study of both anions and cations of the aqueous electrolyte in a single experiment with the three-phase electrode. The hydrophobicity of LBPC, as well as its chemical stability, is significantly higher than that of DMFC and FePorph, which improves markedly the overall performances of the three-phase electrode. Furthermore, a highly oriented pyrolytic graphite electrode has been used in the present study, demonstrating that the three-phase electrode is not restricted to the use of paraffin impregnated graphite electrode. With this experimental arrangement, we report herein for the first time, electrochemical experiments for the transfer of Li⁺ and Na⁺ across a macroscopic W|NB interface, without using any facilitating agents in the organic phase. Similar results have been reported only by using microscopic W|NB interface with no added supporting electrolyte in the water phase.¹⁹

2. Experimental Section

LBPC was synthesized and purified according to the procedure already described.^{17,18} All other chemicals and nitrobenzene were of high purity and used as received. LBPC was dissolved in water-saturated nitrobenzene (2 mmol/L).

A disk electrode (0.32 cm²) of graphite has been used; this is the section of a cylinder of highly oriented pyrolytic graphite, perpendicular to the graphitic planes (EPGE). The graphite cylinder is connected to a brass shaft, both being protected from contact with the aqueous solution by heat shrinkable polyethylene tubing. Before depositing the organic solution on the electrode surface, graphite was abraded with SiC paper (600), sonicated for 30 s in water, rinsed with pure water and acetone, and dried in air. The nitrobenzene solution deposited on the graphite electrode with the help of a micropipet spreads spontaneously over the electrode surface, rather than forming droplet as on PIGE. However, due to the very small volume of nitrobenzene solution deposited on the electrode (0.2 μ L), the organic phase does not cover completely the surface and spreads as an ultrathin film, thus forming a three-phase boundary line after immersing the electrode into the aqueous phase. In such a configuration, a larger part of the organic solution is electrochemically active in comparison with the macroscopic droplet attached to the paraffin-impregnated electrode,¹ due to the very low thickness of the film. Consequently, the three-phase electrode in the present case provides a more intense and more

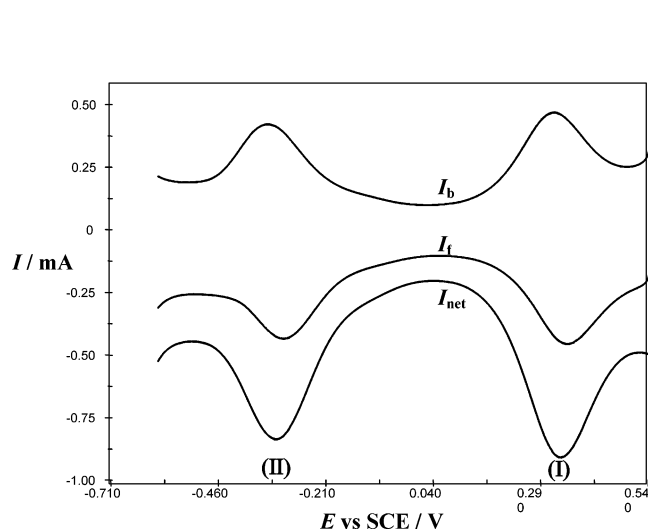


Figure 1. Square-wave voltammogram of LBPC recorded in 0.5 mol/L KNO_3 aqueous solution starting from +0.540 to -0.550 V. The organic phase contains 2 mmol/L LBPC. The other experimental conditions were frequency of the potential modulation $f = 100$ Hz, height of the potential pulses $E_{sw} = 50$ mV, and potential step of the staircase ramp $dE = 0.15$ mV. The subscripts f, b, and net refer to the forward (reduction), backward (oxidation), and net component of the SW voltammetric response.

reproducible response with respect to the peak currents of the SW voltammetric response.

Square-wave voltammograms were recorded using an AUTOLAB equipment (Eco-Chemie, Utrecht, Netherlands). A saturated calomel electrode was used as a reference and a platinum wire as the auxiliary electrode. Water (Millipore Q) was saturated with nitrobenzene to prevent dissolution of the organic solvent in the aqueous phase.

3. Results and Discussion

A typical SW voltammogram of LBPC at the three-phase electrode, recorded in contact with a 0.5 mol/L aqueous KNO_3 solution is depicted in Figure 1. LBPC is oxidized (peak I) and reduced (peak II), giving rise to two net SW peaks. Both oxidation and reduction of LBPC undergo one-electron reversible reactions to monovalent chemically stable ions.¹⁸ The forward and backward components of the SW response for both electrode reactions are well-developed bell-shaped curves, of almost identical heights, implying that both mechanisms are reversible. The two peak potentials of SW response are virtually unaffected by the frequency of the potential modulation, over the interval from 8 to 100 Hz. No deviation in the peak shape or increase of the net half-peak width have been observed, implying the absence of uncompensated resistance effects.¹² For both electrode mechanisms, it is interesting to note that the backward (oxidation) and forward (reduction) components of the SW response are positioned at more negative and more positive potentials, respectively (Figure 1). Such an inverse position of the oxidation and reduction components of the SW response is typical for a reversible electrode reaction occurring in a limiting diffusion space.¹²

Figure 2 shows a series of subsequent net SW voltammograms, recorded at the same three-phase electrode. The peak potentials of both net SW peaks are unaffected by the resting time of the electrode in the aqueous phase, whereas the peak currents increase with time, reaching constant values after the sixth SW voltammogram. These results illustrate the role of the partition of the aqueous electrolyte in the organic phase, which

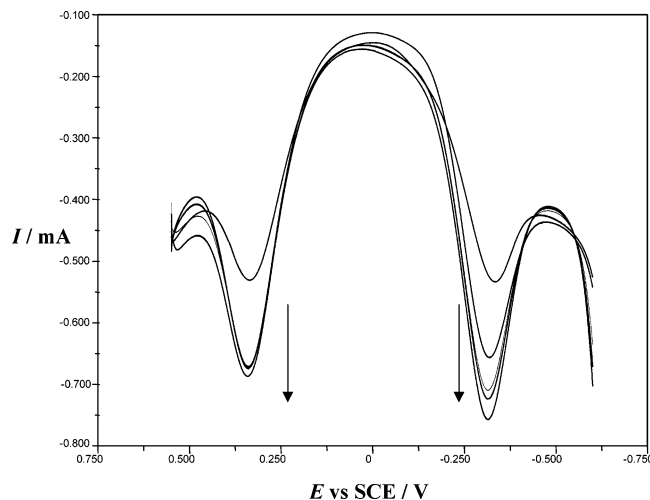


Figure 2. Successive SW voltammograms of LBPC recorded in 0.5 mol/L KNO_3 aqueous solution. All other experimental conditions were same as in the caption of Figure 1.

influences only the peak currents of both electrode processes of LBPC. At the beginning of the experiment, the current is sensitive to the contact time of the electrode with the aqueous phase. As the concentration of the aqueous electrolyte increases in the organic phase, its conductivity becomes higher, enabling a larger part of the film to be electrochemically active. Obviously, after a few minutes this process is accomplished, yielding a stable and reproducible peak current of the voltammetric response. Nevertheless, it should be added that besides the partition, the conductivity of the organic phase increases due to the electrode reaction that produces charged species at the electrode surface accompanied by ingress of counterions from the aqueous phase. At the starting potential of the experiment shown in Figure 2, i.e., 0.540 V vs SCE, LBPC is oxidized to LBPC^+ accompanied by an equivalent amount of NO_3^- ions, which enter the organic phase to compensate the charge excess. Thus, besides the partition of the aqueous electrolyte, the ions present in the organic phase due to the overall electrochemical process contribute in the conductivity of the organic phase.

The difference between the formal potentials of the oxidation and reduction processes of LBPC is dependent on the aqueous electrolyte. The peak potential separation increases with the hydrophilicity of the aqueous electrolyte ions. This behavior is illustrated by net SW voltammograms recorded in contact with 0.5 mol/L aqueous solution of KNO_3 , NaCl , and LiBr (see Figure 3). The net SW peak corresponding to the oxidation of LBPC shifts toward more positive potentials by increasing the standard Gibbs energy ($\Delta_w^{\text{nb}} G_{\text{ion}^-}^\theta$) of the anion transfer from water to nitrobenzene; the peak potentials measured in the presence of NO_3^- , Br^- , and Cl^- are 0.337, 0.368, and 0.427 V, corresponding to $\Delta_w^{\text{nb}} G_{\text{X}^-}^\theta$ of 26.6, 30.5, and 38.2 kJ/mol,²⁰ respectively. These results indicate that the anion transfer from the aqueous to the organic phase accompanies the oxidation of LBPC to LBPC^+ . The overall electrochemical process is described by the following scheme:



to which the following Nernst equation is ascribed:

$$E = E_{\text{LBPC}^+_{(\text{nb})}|\text{LBPC}_{(\text{nb})}}^\theta + \Delta_w^{\text{nb}} \phi_{\text{X}^-}^\theta + \frac{RT}{F} \ln \frac{a_{\text{LBPC}^+_{(\text{nb})}} a_{\text{X}^-_{(\text{nb})}}}{a_{\text{LBPC}_{(\text{nb})}} a_{\text{X}^-_{(\text{w})}}} \quad (\text{II})$$

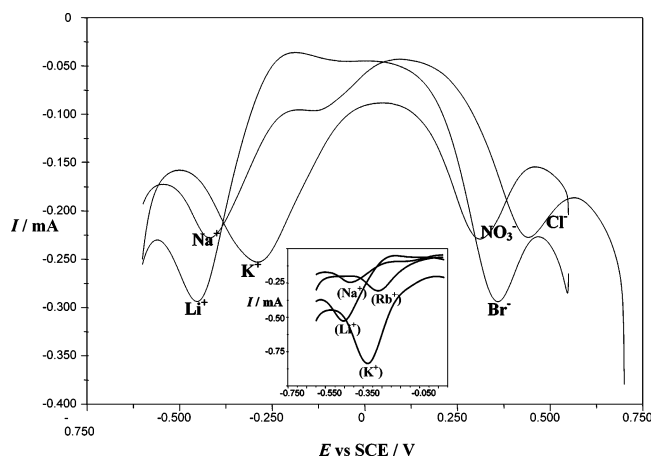


Figure 3. Net SW voltammograms of LBPC recorded in 0.5 mol/L aqueous solutions of KNO₃, NaCl, and LiBr. The transferring ion is indicated in the plot. The frequency of the potential modulation was $f = 50$ Hz. The inset shows the reduction peak recorded in 0.5 mol/L chloride solution of the corresponding cations that are indicated on the plot. All other conditions were the same as in Figure 1.

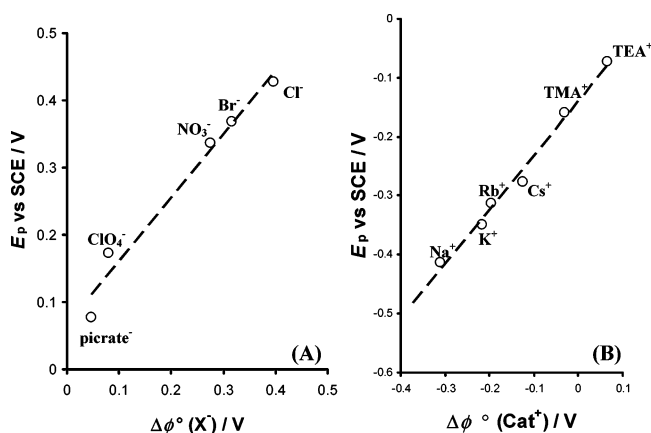


Figure 4. Dependence on standard potentials of ion transfer of the peak potentials of the net SW response corresponding to the process of oxidation (A) and reduction (B) of LBPC. The concentration of anions was 0.5 mol/L (for A), and the concentration of cations was 0.1 mol/L (for B). All other conditions were the same as in Figure 1.

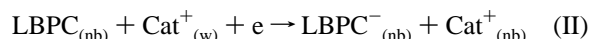
The formal potential $E_c^{\theta'}$ is defined as¹

$$E_c^{\theta'} = E_{\text{LBPC}^+_{(\text{nb})}|\text{LBPC}^+_{(\text{nb})}}^{\theta} + \Delta_w^{\text{nb}} \phi_{X^-}^{\theta} - \frac{RT}{F} \ln(a_{X^-}) + \frac{RT}{F} \ln\left(\frac{a_{\text{LBPC}^+_{(\text{nb})}}^*}{2}\right) \quad (2)$$

where $E_{\text{LBPC}^+_{(\text{nb})}|\text{LBPC}^+_{(\text{nb})}}^{\theta}$ is the standard potential of the LBPC⁺/LBPC redox couple in nitrobenzene, $\Delta_w^{\text{nb}} \phi_{X^-}^{\theta}$ being the standard potential for the transfer of X[−] from water to nitrobenzene, $a_{\text{LBPC}^+_{(\text{nb})}}^*$ is the initial activity of LBPC in the organic phase, and the other symbols having their usual meanings. Notice that the standard potential of the ion transfer is related with the standard Gibbs energy $\Delta_w^{\text{nb}} G_{\text{ion}^\pm}^{\theta}$ through $\Delta_w^{\text{nb}} \phi_{\text{ion}^\pm}^{\theta} = -(\Delta_w^{\text{nb}} G_{\text{ion}^\pm}^{\theta}/zF)$, where z is the charge of the transferring ion.⁹

The net SW peak potential of a reversible electrode reaction is equivalent to the formal potential of the reaction.¹¹ Hence, eq 2 predicts a linear dependence of the peak potential on the standard potential of the anion transfer, with a slope equal to 1. Figure 4A shows this dependence for a series of anions. The standard Gibbs energies for ion transfer²⁰ refer to the extra-thermodynamic assumption based on the equal contribution of

both ions to the transfer of tetraphenylarsonium tetraphenylborate (TPATPB). As expected, the dependence is linear, with a regression coefficient $R = 0.986$ and a slope 0.947, in good agreement with eq 1. The formal potential of the reduction process of LBPC is sensitive only to the cation present in the aqueous phase (Figure 3). The higher is the energy of the cation transfer, the more negative is the formal potential of the reduction process. The inset of Figure 3 shows more clearly the variation of the position of the reduction peak in the presence of highly hydrophilic alkali cations present in the aqueous phase. For, Rb⁺, K⁺, Na⁺, and Li⁺, the peak potentials are −0.313, −0.347, −0.412, and −0.435 V, which is in agreement with the standard Gibbs energy of cation transfer, $\Delta_w^{\text{nb}} G_{\text{Cat}^+}^{\theta} = 19, 21, 30,$ and 36 kJ/mol,¹⁹ respectively. These results strongly indicate that the reduction of LBPC follows:



The formal potential of the electrochemical process (II) is¹⁶

$$E_c^{\theta'} = E_{\text{LBPC}^-_{(\text{nb})}|\text{LBPC}^-_{(\text{nb})}}^{\theta} + \Delta_w^{\text{nb}} \phi_{\text{Cat}^+}^{\theta} + \frac{RT}{F} \ln(a_{\text{Cat}^+_{(\text{w})}}) + \frac{RT}{F} \ln\left(\frac{2}{a_{\text{LBPC}^-_{(\text{nb})}}^*}\right) \quad (3)$$

The experimental dependence of the reduction peak potential on the standard potentials of the cation transfer is depicted in Figure 4B. The linear regression coefficient, $R = 0.994$, and the slope, 0.918, are in good agreement with eq 3. Furthermore, the dependence of the peak potential on the logarithm of the cation concentration is a line with a positive slope. As an example, the slope is 58 mV ($R = 0.994$) for Li⁺ and 62 mV ($R = 0.985$) for K⁺, in accordance with eq 3. All these results clearly demonstrate that the reduction of LBPC is capable of driving the transfer of strongly hydrophilic cations, such as Na⁺ and Li⁺. To the best of our knowledge, this is the first electrochemical experiment showing the transfer of Li⁺ and Na⁺ at the macroscopic W|NB interface in the absence of facilitating agents in the organic phase.

Evolutions of the peak potentials with the standard potentials of ion transfer, depicted in Figure 4, are calibration lines of the present three-phase system for both anion and cation transfers. It must be pointed out that the accuracy of the calibration depends on the quality of the data for the energy of ion transfer, available in the literature. Because the data obtained from different sources scatter significantly, care must be taken to select a consistent set. Knowing the standard potentials of the redox couples of LBPC in nitrobenzene, and measuring the peak potentials for both oxidation and reduction processes at the three-phase electrode, energies for the transfer of both anion and cation of an aqueous electrolyte can be determined.

The intercepts of the calibration lines with the ordinate enable estimation of the standard potentials of the two redox couples of LBPC in nitrobenzene. Approximating activities and concentrations, the intercept of the calibration line for the anion transfer is equal to

$$E_{\text{LBPC}^+_{(\text{nb})}|\text{LBPC}^+_{(\text{nb})}}^{\theta'} - \frac{RT}{F} \ln(c_{X^-}) + \frac{RT}{F} \ln\left(\frac{c_{\text{LBPC}^+_{(\text{nb})}}^*}{2}\right)$$

and

$$E_{\text{LBPC}^-_{(\text{nb})}|\text{LBPC}^-_{(\text{nb})}}^{\theta'} + \frac{RT}{F} \ln(c_{\text{Cat}^+}) + \frac{RT}{F} \ln\left(\frac{2}{c_{\text{LBPC}^-_{(\text{nb})}}^*}\right)$$

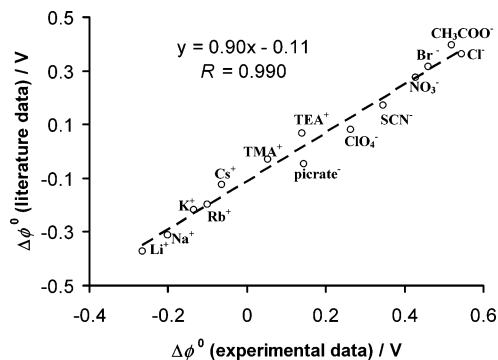


Figure 5. Correlation between the standard potentials of ion transfer across the W|NB interface measured with the three-phase electrode (experimental data, abscissa) with literature data taken from ref 20.

for the cation transfer. Thus, from data in Figure 4, the standard electrode potentials of the redox couples of LBPC in nitrobenzene are $E_{\text{LBPC}^+_{(\text{nb})}|\text{LBPC}_{(\text{nb})}}^\theta = +0.223$ V and $E_{\text{LBPC}_{(\text{nb})}|\text{LBPC}^-_{(\text{nb})}}^\theta = -0.257$ V vs SCE, these potentials being $+0.464$ V and -0.016 V vs NHE, respectively. These values are formal potentials and it must also be emphasized that they rely on the tetraphenylarsonium tetraphenylborate assumption because the potentials for the transfer of ions used for the calibration plots⁹ are based on this same assumption. The difference between the two redox systems of LBPC is $\Delta E^\theta = 0.48$ V, larger than the value obtained from direct electrochemical measurements, $\Delta E^\theta = 0.40$ V.^{17,18} This difference certainly stems from the uncertainties on the transfer potentials of the ions and consequently on the origin of the linear plots in Figure 4.

The formal potentials of the redox couples of LBPC can independently be measured in a conventional experiment carried out in the organic medium. This has been performed in a 0.1 mol/L solution of Bu_4NPF_6 in nitrobenzene saturated with water, using Pt and SCE as the working and reference electrodes, for LBPC as well as for ferrocene. The values for the formal potentials of the redox couples of LBPC, referring to the potential of ferrocenium/ferrocene (Fe^+/Fc), are $E_{\text{LBPC}^+_{(\text{nb})}|\text{LBPC}_{(\text{nb})}}^\theta = -0.093$ V and $E_{\text{LBPC}_{(\text{nb})}|\text{LBPC}^-_{(\text{nb})}}^\theta = -0.489$ V, ΔE^θ being very close to 0.40 V as in other solvents.¹⁸ Assuming that the potential of Fc^+/Fc is 0.392 V vs NHE,²¹ it is possible to refer the redox potentials for LBPC in nitrobenzene to the NHE scale (Strehlow's or "ferrocene" assumption): $E_{\text{LBPC}^+_{(\text{nb})}|\text{LBPC}_{(\text{nb})}}^\theta = 0.299$ V vs NHE and $E_{\text{LBPC}_{(\text{nb})}|\text{LBPC}^-_{(\text{nb})}}^\theta = -0.097$ V vs NHE. These experimental values of $E_{\text{LBPC}^+_{(\text{nb})}|\text{LBPC}_{(\text{nb})}}^\theta$ and $E_{\text{LBPC}_{(\text{nb})}|\text{LBPC}^-_{(\text{nb})}}^\theta$ enable independent measurements of the standard potential of ion transfer with the present three-phase electrode (eqs 2 and 3) on the basis of ferrocene assumption. Figure 5 shows the correlation between the standard ion potentials measured with the three-phase electrode and literature data.²⁰ Figure 5 is a comparison of two different extra thermodynamic assumptions because the experimental data measured with the three-phase electrode are based on the ferrocene assumption, whereas the literature data are based on the TPATPB assumption. The present study demonstrates that the two assumptions are in a fair agreement. The intercept of the linear plot with the abscissa axis represents the difference between the two different hypothesis, 0.11 V (10.6 kJ); this also includes the uncertainties and particularly those about the potentials for the transfers of the ions, as already mentioned.

Capabilities of the three-phase electrode for studying ion transfer are limited by the potentials at which the solvent or the aqueous electrolyte are becoming electrochemically active,

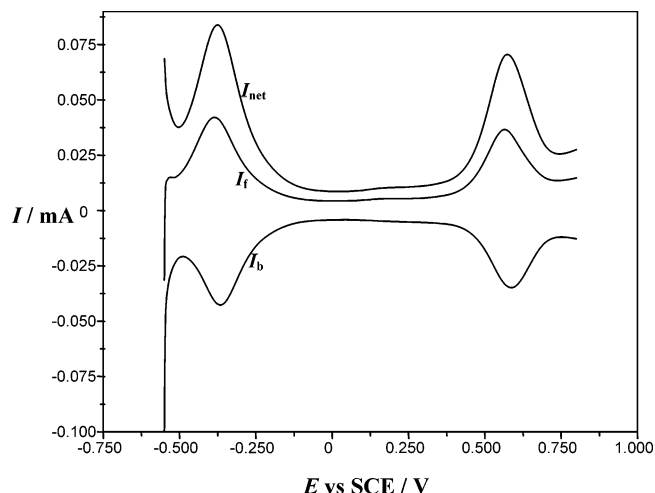


Figure 6. SW voltammetric response of the three-phase electrode recorded in the 2 mol/L aqueous Li_2SO_4 solution, starting from -0.550 to $+0.800$ V. The aqueous phase was not saturated with nitrobenzene, to increase the solubility of the electrolyte. The frequency of the potential modulation was 8 Hz. All other conditions were same as in Figure 1.

as well as by the transfer of the ions of the redox probe from the organic medium, where they are generated, into the aqueous phase. In the present three-phase electrode system, the negative potential limit is controlled by the reduction potential of nitrobenzene that commences at about -0.580 V vs SCE. The transfer of the ionic species LBPC^- does not occur at potentials higher than this limit of the domain. Therefore, the reduction of LBPC to LPBC^- at the three-phase electrode allows the study of cation transfers for which $\Delta_w^{\text{nb}} G_{\text{Cat}^+}^\theta \leq 44.2$ kJ/mol.

To determine the positive potential limit of the three-phase electrode, the oxidation of LBPC was investigated in contact with Li_2SO_4 aqueous solutions (Figure 6). The concentration of the electrolyte in the aqueous phase was 2 mol/L to increase as much as possible its concentration in the film, besides the very low affinity of the sulfate for the organic phase. The peak potential of the net SW peak corresponding to the oxidation of LBPC is 0.572 V, 100 mV more positive than in the presence of chloride. Even under such extreme conditions, when the partition of the aqueous electrolyte is infinitely low, the three-phase electrode, in combination with SWV, provides an excellent voltammetric response (Figure 6). As expected from eq 2, the oxidation peak shifts to more positive potentials when the concentration of sulfate decreases. However, the slope of the E_p vs $\log(c_{\text{SO}_4(\text{w})^{2-}})$ deviates from the expected values of 30 mV. Furthermore, at $c_{\text{SO}_4(\text{w})^{2-}} \leq 1$ mol/L, the oxidation peak suddenly shifts toward less positive potentials becoming insensitive to the variation of SO_4^{2-} concentration for $c_{\text{SO}_4(\text{w})^{2-}} \leq 1$ mol/L. Such a complex behavior for the oxidation of LBPC in the presence of sulfate could be due to the anion itself (e.g., precipitation of salts at the interface, complex evolution of the activity coefficients of this dianionic species) or to very close Gibbs energies for the transfers of SO_4^{2-} and LBPC^+ . Solving this question will require more experiments. Nevertheless, the position of the oxidation peak recorded in contact with an aqueous sulfate solution represents the potential limit for assessing the transfer of anions from water to nitrobenzene. In terms of energy for the transfer of anions from water to nitrobenzene, this corresponds to $\Delta_w^{\text{nb}} G_{\text{X}^-}^\theta \leq 50.78$ kJ/mol.

4. Conclusion

In this report a new three-phase electrode system has been described that can be used to study the transfer of anions as well as cations from water to nitrobenzene, using a single redox probe. From a methodological point of view, the present study demonstrates that the three-phase electrode system is not restricted to the paraffin-impregnated graphite electrode or to droplets of an organic solvent attached to the electrode surface, as used so far. The present three-phase electrode consists of a highly oriented pyrolytic graphite electrode, the surface of which is partly covered with a very thin nitrobenzene film. The combination of the highly oriented pyrolytic graphite electrode with the intrinsic properties of the lutetium bis(tetra-*tert*-butylphthalocyaninato) (LBPC) enabled experiments with nitrobenzene containing only 2 mmol/L of the redox probe. The chemical stability of LBPC, as well as its much lower affinity for the aqueous phase, allowed measurements at a concentration 2 orders of magnitude lower than that used so far at the paraffin impregnated graphite electrode. This is a real advantage as redox systems are not always freely soluble in water-saturated organic solvents; this also reduces the risk of precipitation reactions at the interface between the organic and aqueous phases. Despite the low concentration of the redox probe, the three-phase electrode in the present configuration provides well-developed voltammetric responses, even in the presence of an aqueous electrolyte such as Li_2SO_4 that does not partition appreciably into the organic phase. Besides the reproducibility of the peak potential, the present three-phase electrode provides also reproducible currents soon after the immersion of the modified electrode in the aqueous electrolyte. This feature is of particular importance because it implies that the three-phase electrode can also be applied to kinetics studies of the transfer processes.

The redox compound used, i.e., lutetium bis(tetra-*tert*-butylphthalocyaninato), is superior to all redox probes used so far to build up three-phase electrodes because it enables inspection of both anion and cation transfers in a single experiment. The energy of transfer of the LBPC^- ion from nitrobenzene to water is estimated larger than 44.2 kJ/mol, which allows the study of highly hydrophilic cations that have been so far inaccessible. To the best of our knowledge, this report presents for the first time the direct transfer of highly hydrophilic alkali cations such as Li^+ and Na^+ across the macroscopic water|nitrobenzene interface, in the absence of any facilitating agent. The present three-phase electrode system provides an access to the transfer of cation and anion with standard Gibbs

energies of about $\Delta_{\text{w}}^{\text{nb}} G_{\text{Cat}^+}^\theta \leq 43$ kJ/mol and $\Delta_{\text{w}}^{\text{nb}} G_{\text{X}^-}^\theta \leq 50$ kJ/mol, respectively. This interval corresponds to a potential window for studying of about 1 V.

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References and Notes

- (1) Scholz, F.; Komorsky-Lovrić, Š.; Lovrić, M. *Electrochem. Commun.* **2000**, 2, 112–118.
- (2) Gulaboski, R.; Riedl, K.; Scholz, F. *Phys. Chem. Chem. Phys.* **2003**, 5, 1284–1289.
- (3) Komorsky-Lovrić, Š.; Riedl, K.; Gulaboski, R.; Mirčeski, V.; Scholz, F. *Langmuir* **2002**, 18, 8000–8005.
- (4) Mirčeski, V.; Scholz, F. *J. Electroanal. Chem.* **2002**, 522, 189–198.
- (5) Gulaboski, R.; Mirčeski, V.; Scholz, F. *Amino Acids* **2003**, 24, 149–154.
- (6) Gulaboski, R.; Scholz, F. *J. Phys. Chem. B* **2003**, 107, 5650–5657.
- (7) Bouchard, G.; Galland, A.; Carrupt, P.-A.; Gulaboski, R.; Mirčeski, V.; Scholz, F.; Girault, H. *Phys. Chem. Chem. Phys.* **2003**, 5, 3748–3751.
- (8) Gulaboski, R.; Galland, A.; Bouchard, G.; Caban, K.; Kretschmer, A.; Carrupt, P.-A.; Girault, H. H.; Stojek, Z.; Scholz, F. *J. Phys. Chem. B* **2004**, 108, 4565–4572.
- (9) Girault, H. H.; Schiffrin, D. J. In *Electroanalytical Chemistry*; Bard, A. J. Ed.; Marcel Dekker: New York, 1989; Vol. 15, pp 1–141.
- (10) Gulaboski, R.; Mirčeski, V.; Scholz, F. *Electrochem. Commun.* **2002**, 4, 277–283.
- (11) Lovrić, M. In *Electroanalytical methods, Guide to experiments and applications*; Scholz, F., Ed.; Springer-Verlag: Berlin, Heidelberg, 2002; pp 111–133.
- (12) Mirčeski, V.; Gulaboski, R.; Scholz, F. *J. Electroanal. Chem.* **2004**, 566, 351–360.
- (13) Komorsky-Lovrić, Š.; Mirčeski, V.; Kabbe, Ch.; Scholz, F. *J. Electroanal. Chem.* **2004**, 566, 371–377.
- (14) Donten, M.; Stojek, Z.; Scholz, F. *Electrochem. Commun.* **2002**, 4, 324–329.
- (15) Mirčeski, V.; Gulaboski, R.; Scholz, F. *Electrochem. Commun.* **2002**, 4, 814–819.
- (16) Scholz, F.; Gulaboski, R.; Caban, K. *Electrochem. Commun.* **2003**, 5, 929–934.
- (17) Pondaven, A.; Cozien, Y.; L'Her, M. *New J. Chem.* **1992**, 16, 711–718.
- (18) L'Her, M.; Pondaven, A. *Electrochemistry of phthalocyanines*; In Kadish, K.; Guillard, R.; Smith, K., Eds.; The Porphyrin Handbook. Phthalocyanines: Spectroscopic and Electrochemical Characterization; Academic Press: New York, 2003; Vol. 16, pp 117–170.
- (19) Wilke, S. *J. Electroanal. Chem.* **2001**, 504, 184–194.
- (20) Electrochemical Data Base: <http://dcwww.epfl.ch/cgi-bin/LE/DB/InterrDB.pl>.
- (21) De Ligny, C. L.; Alfenaar, M.; Van Der Veen, N. G. *Recl. Trav. Chim. Pays-Bas.* **1968**, 87, 585–598.