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Kinetics of Anion Transfer across the Liquid | Liquid Interface of a Thin Organic Film Modified Electrode, Studied by Means of Square-Wave Voltammetry

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The electrochemical oxidation of lutetium bis(tetra-*tert*-butylphthalocyaninato) (LBPC) and decamethylferrocene (DMFC), as well as the reduction of LBPC, lutetium bis-(phthalocyaninato) (LPC), and lutetium (tetra-*tert*-butyl-phthalocyaninato hexadecachlorphthalocyaninato) (LB-PCl), has been studied in a thin nitrobenzene (NB) film deposited on the surface of a graphite electrode (GE) by means of square-wave voltammetry (SWV). The organic film-modified electrode was immersed in an aqueous (W) electrolyte solution and used in a conventional three-electrode configuration. When the aqueous phase contains ClO_4^-, NO_3^-, or Cl^- (ClO_4^-, or NO_3^- only, in the case of DMFC), both LBPC and DMFC are oxidized to stable monovalent cations in the organic phase. The electron transfer at the GE | NB interface is accompanied by a simultaneous anion transfer across the W | NB interface to preserve the electroneutrality of the organic phase. LBPC, LPC, and LBPCl are reduced to stable monovalent anions accompanied by expulsion of the anion of the electrolyte from the organic into the aqueous phase. In all cases, the overall electrochemical process comprises simultaneous electron and ion transfer across two separate interfaces. Under conditions of SWV, the overall electrochemical process is quasireversible, exhibiting a well-formed "quasireversible maximum" that is an intrinsic property of electrode reactions occurring in a limiting diffusion space. For all the redox compounds that have been studied, the kinetics of the overall electrochemical process is controlled by the rate of the ion transfer across the liquid | liquid interface. Based on the quasireversible maximum, a novel and simple methodology for measuring the rate of ion transfer across the liquid | liquid interface is proposed. A theoretical background explaining the role of the ion-transfer kinetics on the overall electrochemical process at the thin organic film modified electrode under conditions of SWV is presented. Comparing the positions of the theoretical and experimental quasireversible maximums, the kinetics of ClO_4^-, NO_3^-, and Cl^- across the W | NB interface was estimated. The kinetics of the overall process at the thin organic film modified electrode, represented by the second-order standard rate constant, is 91 ± 8, 90 ± 4, and 133 ± 10 cm⁴ s⁻¹ mol⁻¹, for the transfer of ClO_4^-, NO_3^-, and Cl^- respectively.

The importance of the liquid | liquid interface for living systems is well recognized and have been intensively studied over the past decades.[1] Most of the knowledge about charge transfer across the liquid interface has been collected by electrochemical measurements at the interface between two immiscible electrolyte solutions (ITIES). Several conceptually different experimental arrangements have been developed for studying both the electron and the ion transfer across the liquid interface,[2−19] among which
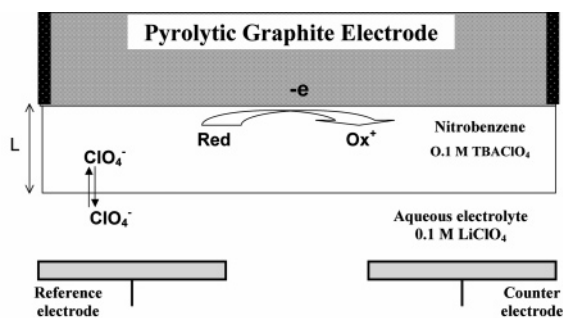
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(1) *Liquid interfaces in chemical, biological, and pharmaceutical applications,* 1st ed.; Volkov, A. G. Ed.; Marcel Dekker: New York, 2001.
(2) Shi, C.; Anson, C. *Anal. Chem.* **1998,** *70,* 3114−3118.
(3) Shi, C.; Anson, C. *J. Phys. Chem. B.* **1998,** *102,* 9850−9854.
(4) Shi, C.; Anson, F. C. *J. Phys. Chem. B* **1999,** *103,* 6283−6289.
(5) Chung, T. D.; Anson, F. C. *Anal. Chem.* **2001,** *73,* 337−342.
(6) Shi, C.; Anson, C. *J. Phys. Chem. B* **2001,** *105,* 1047−1049.
(7) Shi, C.; Anson, C. *J. Phys. Chem. B* **2001,** *105,* 8963−8969.
(8) Scholz, F.; Komorsky-Lovrić, Š.; Lovrić, M. *Electrochem. Commun.* **2000** *2,* 112−118.
(9) Gulaboski, R.; Riedl, K.; Scholz, F. *Phys. Chem. Chem. Phys.* **2003,** *5,* 1284−1289.
(10) Komorsky-Lovrić, Š.; Riedl, K.; Gulaboski, R.; Mirčeski, V.; Scholz, F. *Langmuir* **2002** *18,* 8000−8005.
(11) Mirčeski, V.; Scholz, F. *J. Electroanal. Chem.* **2002,** *522,* 189−198.
(12) Gulaboski, R.; Scholz F. *J. Phys. Chem. B* **2003,** *107,* 5650−5657.
(13) Gulaboski, R.; Mirčeski, V.; Scholz, F. *Amino Acids* **2003** *24,* 149−154.
(14) Bouchard, G.; Galland, A.; Carrupt, P.-A.; Gulaboski, R.; Mirčeski, V.; Scholz, F.; Girault, H. *Phys. Chem. Chem. Phys.* **2003,** *5,* 3748−3751.
(15) Gulaboski, R.; Galland, A.; Bouchard, G.; Caban, K.; Kretschmer, A.; Carrupt, P.-A.; Girault, H. H.; Scholz, F. *J. Phys. Chem. B* **2004,** *108,* 4565−4572.
(16) Zang, J.; Unwin, P. R. *Langmuir* **2002,** *18,* 2313−2318.
(17) Li, F.; Chen, Y.; Sun, P.; Zhang, M.; Gao, Z.; Zhan, D.; Shao, Y. *J. Phys. Chem., B* **2004,** *108,* 3295−3302.

Scheme 1. Pyrolytic Graphite Electrode Covered with a Thin Film of a Nitrobenzene Solution Containing 2 mM Redox Probe and 0.1 M Tetrabuthylammonium Perchlorate (TBAClO₄), Immersed in a 0.1 M LiClO₄ Aqueous Electrolyte


GE/ 0.002 M Red$_{(nb)}$, 0.1 M TBAClO$_{4(nb)}$ / 0.1 M LiClO4$_{(w)}$ / KCl sat$_{(w)}$ / AgCl / Ag

Chart 1. Compounds Used as Redox Probes

R = H	FC (ferrocene)	R = R' = H , n = m = 4	LPC
R = CH₃	DMFC	R = R' = C(CH₃)₃, n = m = 1	LBPC
		R = C(CH₃)₃, n = 1 ; R' = Cl , m = 4	LBPCl

the four-electrode configuration is mostly used.[20] Whereas scanning electrochemical microscopy requires sophisticated electrochemical instrumentation and considerable experimental proficiency,[16−19] the thin-film[2−7] and three-phase electrodes[8−15] are particularly attractive due to their simplicity and wide applicability.

The thin-film electrode[2−7,21] consists of a solid graphite electrode covered by a film of a water-immiscible organic solvent containing an electroactive redox system (Scheme 1). The film electrode is immersed in an aqueous electrolyte solution and used in a conventional three-electrode voltammetric configuration. Most frequently, the conductivity of the thin organic film is provided by an added electrolyte or by the electrolyte of the aqueous phase, by partition. The potential difference between the organic (O) and aqueous (W) phases is predominantly controlled by the concentrations of a common ion present in the two phases. The electrode reaction of the redox compound occurring at the graphite electrode | organic solution interface (GE | O), producing or consuming charged species at the electrode surface, disturbs the electroneutrality of the organic phase. Consequently, the electron-transfer reaction at the GE | O interface affects the concentration profiles of all ionic species in the organic film, inducing an additional ion transfer across the W | O interface to preserve the charge neutrality of the organic phase. Thus, the ion transfer across the W | O interface is driven by the electrode reaction occurring at the GE | O interface. The overall electrochemical process couples two charge-transfer reactions occurring simultaneously at two separate interfaces.

As in the film electrode, the same electrochemical events occur at the three-phase electrode consisting of a paraffin-impregnated graphite electrode at the surface of which a droplet of an organic solvent containing a neutral redox probe is attached. The unique feature of this system is the presence of a three-phase interface represented by a single line where the electrode, the organic
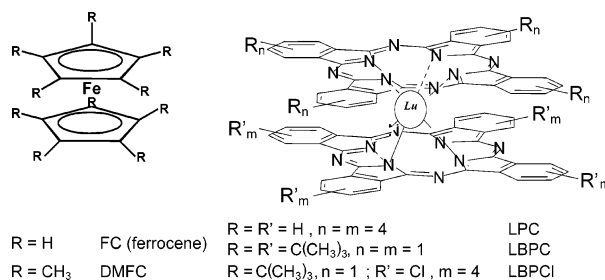
solution, and the aqueous phase meet. As suggested by Nakatani and Sekine,[22,23] the droplet of the organic solvent could be imagined as a series of thin films of different thicknesses, starting from the molecular dimension at the three-phase boundary line, up to macroscopic dimension at the center of the droplet. The edge of the droplet consists of very thin films in which the partition of the aqueous electrolyte provides conditions for commencing of the electrochemical reaction. Once the electrochemical reaction is initiated, the conductivity of the organic phase progressively increases due to the formation of charged species at the electrode surface and the ingress of the counterions from the aqueous phase. For these reasons, the three-phase electrode, in combination with a highly sensitive technique such as square-wave voltammetry (SWV),[24] provides an excellent voltammetric response under a large variety of experimental conditions, without addition of any electrolyte in the organic phase. This methodology enabled an assessment of the thermodynamic properties of a large series of inorganic[9] and organic ions,[10] cationic and anionic forms of amino acids and peptides,[12,13] and anionic forms of a large series of pharmacologically active compounds.[14,15]

Besides the applicability of the film and three-phase electrodes for the study of thermodynamics of ion transfer, attempting to apply these methods for assessing the kinetics of the ion transfer is a challenge. Although many works have been devoted to the kinetics of ion transfer across the liquid interface,[25−30] the parameters for the transfer of many common inorganic ions are still unknown, which indicates the necessity of a simple experimental method for kinetic measurements. With this motivation, in a very recent paper one of us developed a theoretical model for the measurements by SWV of a kinetically controlled simple electrode reaction occurring in finite diffusion space.[31] Instead of the finite difference backward implicit method,[32] the model was based on the modified step-function method,[33] yielding a solution

(18) Barker, A. L.; Gonsalves, M.; Macpherson, J. V.; Slevin. C. J.; Unwin, P. R., *Anal. Chim. Acta* **1999**, *385*, 223−240.

(19) Peng, S.; Yhiquan, Z.; Zhao, G.; Yuanhua, S. *Angew. Chem., Int. Ed.* **2002**, *1*, 3445−34488.

(20) Girault, H. H.; Schiffrin, D. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1989; Vol. 15, pp 1−141.

(21) Buck, R. P.; Mădăraş, M. B.; Mäckel, R. *J. Electroanal. Chem.* **1994**, *366*, 55−68.

(22) Nakatani, K.; Sekine, T. *J. Colloid Interface Sci.* **2000**, *225*, 251−253.

(23) Nakatani, K.; Sekine, T. *Langmuir* **2000**, *16*, 9256−9260.

(24) Lovrić, M., In *Electroanalytical methods, Guide to experiments and applications*, Scholz, F., Ed.; Springer-Verlag: Berlin, 2002; pp 111−133.

(25) Samec, Z., In *Liquid−Liquid Interfaces. Theory and Methods*; Volkov, A. G., Deamer, D. W., Eds.; CRC Press: Boca Raton, FL, 1996; pp 155−178.

(26) Manzanares, J. A.; Allen, R. M.; Kontturi, K. *J. Electroanal. Chem.* **2000**, *483*, 188−196.

(27) Murtomaki, L.; Kontturi, K.; Schiffrin, D. J. *J. Electroanal. Chem.* **1999**, *474*, 89−93.

(28) Samec, Z.; Langmaier, J.; Trojanek, A. *J. Electroanal. Chem.* **1999**, *463*, 232−241.

(29) Manzanares, J. A.; Lahtinen, R.; Quinn, B.; Kontturi, K.; Schiffrin, D. J. *Electrochim. Acta* **1998**, *44*, 59−71.

(30) Buck, R. P.; Bronner, W. E. *J. Electroanal. Chem.* **1986**, *197*, 179−181.

(31) Mirčeski, V, *J. Phys. Chem. B* **2004**, *108*, 13719−13725.

(32) Ball, J. C.; Compton, R. G. *J. Phys. Chem. B* **1998**, *102*, 3967−3973.

(33) Mirčeski, V. *J. Electroanal. Chem.* **2003**, *545*, 29−37.

that is represented by two simple recursive formulas.[31] This theoretical study predicted that the thin-film electrode reaction under conditions of SWV exhibits the highest response when it is controlled by the kinetics of the electron exchange. This specific property, known as a "quasireversible maximum", enables estimation of the redox kinetics by a simple and fast procedure.[31] In the present study, we apply the method of quasireversible maximum to study the kinetics of the electrochemical oxidation of the lutetium bis(tetra-*tert*-butylphthalocyaninato) (LBPC) and decamethylferrocene (DMFC), as well as the reduction of LBPC, lutetium bis(phthalocyaninato) (LPC), and lutetium (tetra-*tert*-butylphthalocyaninato hexadecachlorphthalocyaninato) (LBPCl) (Chart 1), dissolved in a film of nitrobenzene (NB) at the surface of a graphite electrode. Under conditions of SWV, all compounds behave quasireversibly, exhibiting a well-developed quasireversible maximum.

EXPERIMENTAL SECTION

LBPC, LPC, and LBPCl were synthesized and purified according to the procedure already described.[34,35] Decamethylferrocene was a product of Fluka. All other chemicals and nitrobenzene were of high purity and used as received. All redox compounds were dissolved in water-saturated NB (2 mmol/L). Besides the redox compound, NB contained an electrolyte, 0.1 mol/L tetrabutylammonium (TBA) salt of either perchlorate or nitrate, or tetrahexylammonium chloride, the anion being the same as the one in the aqueous electrolyte.

A disk electrode (0.32 cm^2) of graphite has been used; this is the section of a cylinder of highly oriented pyrolytic graphite, perpendicular to the graphitic planes. The graphite cylinder is connected to a brass shaft, both being protected from contact with the aqueous solution by heat-shrinkable polyethylene tubing. Before spreading 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. In most experiments, 1 μL of the NB solution was deposited on the graphite electrode with the help of a micropipet, the film forming by spontaneous spreading of the organic solution. The film-modified electrode was then immersed into the aqueous electrolyte and used in a conventional three-electrode cell.

Square-wave voltammograms were recorded using an Autolab instrument (Eco-Chemie, Utrecht, Netherlands). A saturated calomel electrode was used as a reference and a platinum wire as the auxiliary electrode. Nitrobenzene-saturated water (Millipore Q) was used to prepare all aqueous solutions.

RESULTS AND DISCUSSION

Reversibility of the Electrochemical Processes of DMFC and Lutetium Bisphthalocyanines in Thin Nitrobenzene Film under Conditions of Square-Wave Voltammetry. The SW voltammetric response of a reversible electrode reaction occurring in a restricted diffusion space depends predominantly on the thickness parameter defined as $\Lambda = L(f/D)^{1/2}$ (for the meaning

of the symbols see Table 1). Theory has shown[36] that the dimensionless net SW peak current $\Delta\Psi_p$ ($\Delta\Psi_p = \Delta I_p/(nFSc^*_{Red}(Df)^{1/2})$) increases sigmoidally with the thickness parameter. For this reason, the ratio of the real net peak current and the square root of the frequency, $(\Delta I_p/f^{1/2})$, increases sigmoidally with frequency, as shown in Figure 1A (curve 1); it is worth pointing out that this ratio is not frequency dependent when the reversible reaction occurs under semi-infinite diffusion conditions.[24]

If the thin-film electrode reaction is kinetically controlled, besides the thickness parameter, the response is affected by the kinetic parameter $K = (k_s/(Df)^{1/2})$, where k_s is the standard heterogeneous electron exchange rate constant (in units of cm s^{-1}). The dimensionless net peak current is a parabolic function of the logarithm of the kinetic parameter, with the maximum being positioned within the quasireversible region (see Figure 1A, curve 2). Note that the net peak current of an electrode reaction under semi-infinite diffusion conditions depends sigmoidally on the kinetic parameter reaching a maximal constant value within the reversible region. The parabolic dependence of the dimensionless net peak current on the kinetic parameter is an intrinsic property of the kinetically controlled thin-film electrode reaction, which, by analogy with surface electrode processes, is called "quasireversible maximum".[37,38] Consequently, in a real experiment the ratio $(\Delta I_p/f^{1/2})$ is expected to be also a parabolic function of the frequency of the potential modulation, due to the influence of the kinetic parameter K. The importance of the quasireversible maximum stems from the fact that its position can be used for estimating the standard heterogeneous electron exchange rate constant. Calculating theoretically the critical value of the kinetic parameter K_{max}, which is associated with the position of the theoretical quasireversible maximum, and measuring experimentally the corresponding critical frequency f_{max}, one can estimate the standard rate constant through the simple formula

$$k_s = K_{max}\sqrt{Df_{max}} \qquad (1)$$

In the present study, quasireversible maximums were measured for oxidation of LBPC and DMFC, as well as for reduction of LBPC, LPC, and LBPCl, in a thin nitrobenzene film spread over the graphite electrode. LBPC can be electrochemically oxidized to a stable cation in the organic phase. Provided the aqueous phase contains ClO_4^-, NO_3^-, or Cl^- ions, the electrode reaction of LBPC is accompanied by the anion transfer across the W | NB interface. The same holds for DMFC in the presence of ClO_4^- and NO_3^- ions, chloride ions being avoided in that case due to the instability of DMFC$^+$ in the presence of coordinating species.[39] The electrochemical oxidation for both compounds can be described by the following general scheme:

$$Red_{(nb)} + X^-_{(w)} \rightleftarrows Ox^+_{(nb)} + X^-_{(nb)} + e \qquad (2)$$
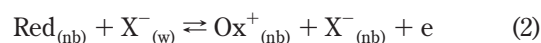
Besides oxidation, LBPC, LPC, and LBPCl can also be reduced to a stable anion.[35] The reduction of LBPC, LPC, and LBPCl in

(34) Pondaven, A.; Cozien, Y.; L'Her, M. *New J. Chem.* **1992**, *16*, 711−718.

(35) L'Her, M.; Pondaven, A. Electrochemistry of phthalocyanines. In *The Porphyrin Handbook. Phthalocyanines: Spectroscopic and Electrochemical Characterization;* K. Kadish, K., Guilard, R., Smith, K., Eds.; Academic Press: New York 2003; Vol. 16, pp 117−170.

(36) Mirčeski, V.; Gulaboski, R.; Scholz, F. *J. Electroanal. Chem.* **2004**, *566*, 351−360.

(37) Komorsky-Lovrić, Š.; Lovrić, M. *Anal. Chim. Acta* **1995**, *305*, 248−255.

(38) Mirčeski, V.; Lovrić, M.; Jordanoski, B. *Electroanalysis* **1999**, *11*, 660−663.

Table 1. List of Symbols and Abbreviations

symbol	meanings of the symbols and abbreviations	units
β	charge-transfer coefficient	1
c_{Ox}	concentration of the oxidized form	mol cm^{-3}
c_{Red}	concentration of the reduced form	mol cm^{-3}
c_{Ox}^{*}	bulk concentration of the oxidized form in the film	mol cm^{-3}
c_{X^-}	concentration of the transferring ion	mol cm^{-3}
$c_{X^-}^{*}$	bulk concentration of the transferring ion	mol cm^{-3}
D	diffusion coefficient	cm^2 s^{-1}
d	main time increment	s
d'	subtime increment	s
dE	step of the potential	V
$\Delta_w^{nb}\,\varphi_{X^-}^{\varnothing}$	standard potential of ion transfer from water to nitrobenzene	V
E	electrode potential	V
$E_{Ox/Red}^{\varnothing}$	standard redox potential	V
$E^{\varnothing\prime}$	formal potential	V
f	square-wave frequency	s^{-1}
f_{max}	frequency associated with the position of the quasireversible maximum	s^{-1}
F	Faraday constant	C/mol
φ	dimensionless potential	1
I	current	A
ΔI_p	real net peak current	A
K	dimensionless kinetic parameter for the first-order electrode reaction	1
K'	dimensionless kinetic parameter for the second-order electrode reaction	1
k_s	first-order heterogeneous standard rate constant	cm s^{-1}
k_s'	second-order heterogeneous standard rate constant	cm^4 s^{-1} mol^{-1}
L	thickness of the film	cm
Λ	dimensionless thickness parameter	1
R	gas constant	J mol^{-1} K^{-1}
ρ	concentration ratio	1
S	electrode surface area	cm^2
t	time	s
T	thermodynamic temperature	K
x	distance	cm
Ψ	dimensionless current	1
$\Delta\Psi_p$	dimensionless net peak current	1

the nitrobenzene film is accompanied by expulsion of ClO_4^- from the organic into the aqueous phase, according to the following scheme:

$$Ox_{(nb)} + X^-_{(nb)} + e \rightleftarrows Red^-_{(nb)} + X^-_{(w)} \qquad (3)$$

For all systems, the cyclic voltammograms showed an excellent stability along repetitive cycling of the potential.

The overall processes 2 and 3 combine the electron transfer taking place at the GE | NB interface and the ion transfer across the W | NB interface. Although these two processes occur at separate interfaces, they are simultaneous and cannot be separately identified. The electron-transfer reaction of the redox probe at the graphite surface is the driving force for the ion transfer across the W | NB interface which, on a molecular level, can occur according to (i) a pure electrochemical mechanism, excluding any chemical interactions between the redox probe and the transferring ion, or (ii) a chemical mechanism in which the chemical coupling between them takes place. The "electrochemical mechanism" refers to the situation in which the electron transfer, by producing charged species in the organic phase (Ox^+ for the

(39) Prins, R.; Korswagen, A. R.; Kortbeek, A. G. T. G. *J. Organomet. Chem.* **1972**, *39*, 335−344.

oxidation or Red^- for the reduction), modifies the gradient of the electrochemical potential at the W | NB interface, forcing X^- to cross the interface. In the "chemical mechanism", the ion transfer is followed by a reaction between the ionic species of the redox probe and the transferring ion; this is equivalent to an EC mechanism at solid electrodes. For the electrochemical mechanism, the thermodynamics and kinetics of the ion transfer will be independent of the chemical nature of the redox couple, whereas in the chemical mechanism the overall properties of the ion transfer will be influenced by the redox couple and also by the nature of the electrolyte. For these reasons, different redox probes, both oxidation and reduction processes, and various electrolytes have been used.

Figure 1B illustrates the influence of the frequency on the ratio $(\Delta I_p/f^{1/2})$ for the thin-film experiments for the oxidation of LBPC and DMFC measured in contact with a 0.1 mol/L $LiClO_4$ aqueous solution. In both cases, the quasireversible maximum was well developed, indicating that under conditions of SWV both processes are kinetically controlled.

Changing the frequency, the shape of all components of the SW voltammetric response, together with the half-peak width of the net component, were carefully inspected. Typical SW voltammetric responses of the two redox compounds are presented in Figure 2. All voltammetric curves were particularly well developed
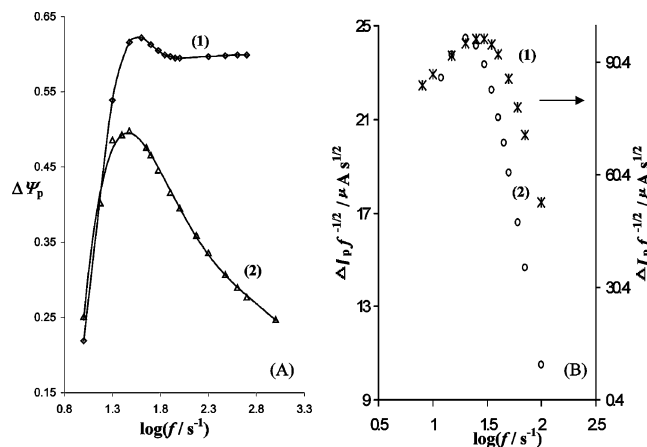
Figure 1. (A) Dependence of the dimensionless net peak current of a reversible[36] (curve 1) and quasireversible[31] (curve 2) reaction on the logarithm of the frequency of the potential modulation. Simulation conditions: film thickness $L = 5$ μm, diffusion coefficient $D = 1 \times 10^{-5}$ cm^2 s^{-1}, SW amplitude $nE_{sw} = 50$ mV, potential step $dE = 10$ mV. For curve 2, the standard electron exchange rate constant was $k_s = 1 \times 10^{-4}$ cm s^{-1}, and the electron-transfer coefficient $\alpha = 0.5$. The dimensionless net peak current was defined as $\Delta\Psi_p = \Delta I_p/(nFSc^*_{Red}(Df)^{1/2})$. (B) Dependence of the ratio $(\Delta I_p/f^{1/2})$ on the logarithm of the frequency for the SWV thin-film experiment with LBPC (curve 1) and DMFC (curve 2) measured in 0.1 mol/L aqueous solution of LiClO$_4$. The electrode was covered with a 1-μL nitrobenzene solution containing 0.1 mol/L TBAClO$_4$ and 2 mmol/L of the corresponding redox compound. The other experimental conditions were: amplitude of the potential modulation $E_{sw} = 50$ mV and the step of the staircase ramp $dE = 0.15$ mV.
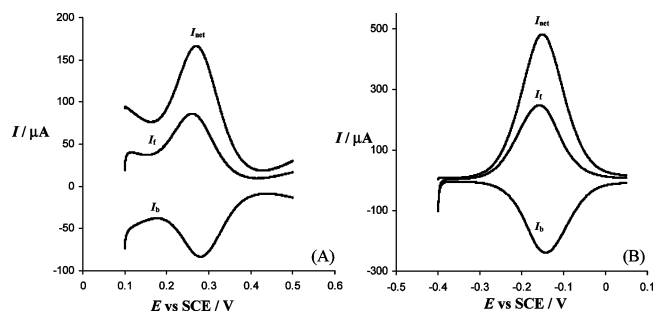

Figure 2. Typical SW voltammetric response of LBPC (A) and DMFC (B) recorded in 0.1 mol/L LiClO$_4$ aqueous solution at a frequency of $f = 20$ Hz. All other conditions were same as in the caption of Figure 1B. The subscripts f, b, and net correspond to the forward, backward, and net components of the SW voltammetric response, respectively.

within the frequency region of the quasireversible maximum. Furthermore, both the peak potential and the half-peak width of the net component diminished slightly with increasing frequency. Therefore, no uncompensated resistance was observed while measuring the quasireversible maximum.[36] It is particularly important to note that, in the two sets of experiments with the different redox compounds but the same counteranions in the aqueous phase, the positions of the quasireversible maximum are identical.

Figure 3 depicts a series of quasireversible maximums measured by changing the amount of the solution spread over the electrode surface, which corresponds to the variation of the film thickness. Theory predicts that K_{max}, the critical value of the kinetic parameter, depends slightly on the film thickness.[31]
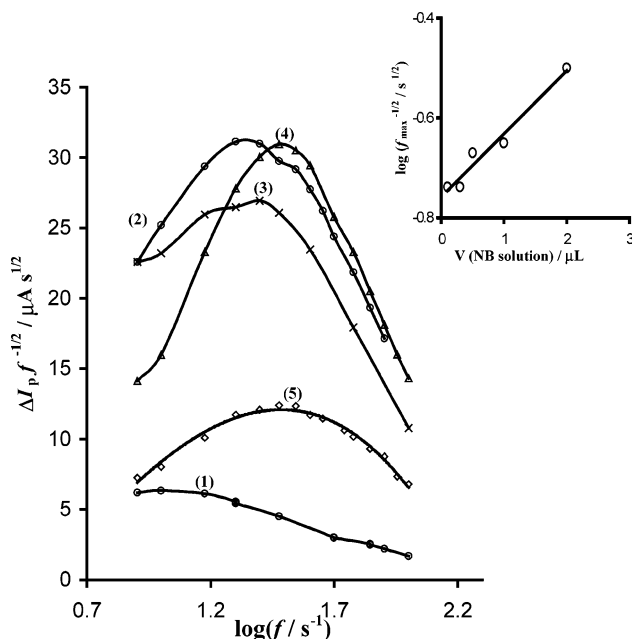

Figure 3. Effect of the volume of the organic solution imposed on the graphite electrode on the position of the quasireversible maximums of LBPC measured in 0.1 mol/L aqueous solution of LiClO$_4$. The volumes of the organic solution were 2 (1), 1 (2), 0.5 (3), 0.3 (4), and 0.1 μL (5). All other conditions were same as in the caption of Figure 1B. The inset shows the dependence of the logarithm of the inverse square root of the critical frequency on the volume of the organic solution.

Simulations revealed a linear relationship between $\log(K_{max})$ and the thickness parameter Λ, with a positive slope, so that the quasireversible maximum will shift toward lower critical frequencies by increasing the film thickness. It must be pointed out that in the experiments the thickness of the thin film cannot be exactly controlled. Considering the roughness of the electrode material, it is clear that the film does not have a uniform thickness over the electrode surface. Moreover, due to the wetting angle, the edge of the organic film is expected to be different. Nevertheless, the larger the volume of the organic phase deposited on the electrode, the larger the average thickness of the film. Figure 3 shows the quasireversible maxima measured in 0.1 mol/L LiClO$_4$ aqueous solution, for different volumes of the nitrobenzene LBPC solution spread over the graphite electrode surface. The experimental data are in general accordance with theoretical predictions. For a relatively thick film corresponding to 2 μL of the organic solution, the quasireversible maximum is positioned at lower frequency and only its descending part is observed (see curve 1 in Figure 3). On the contrary, for smaller volumes of the organic solution, the maximum is shifted toward higher frequencies (see curves 2−5 in Figure 3), as expected. The inset in Figure 3 shows the linear dependence of $\log(1/(f_{max})^{1/2})$ versus the volume of the organic solution, with a positive slope, which is in good agreement with the prediction.[31]

Besides the thickness of the film, the amplitude of the potential modulation (E_{sw}) slightly affects the position of the quasireversible maximum. For the quasireversible maximums of LBPC in 0.1 mol/L LiClO$_4$ aqueous solution, the critical frequency is 18, 25, and 35 Hz for values of $E_{sw} = 20$, 50, and 80 mV, respectively.
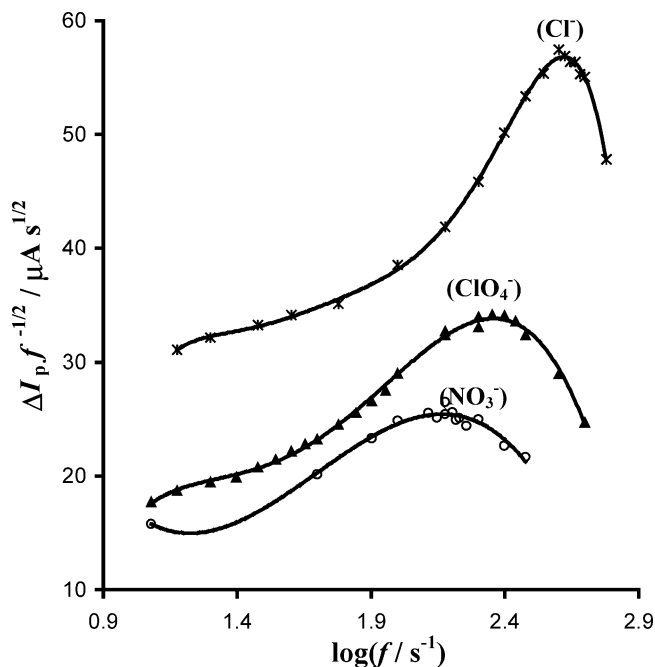
Figure 4. Effect of the type of aqueous ions on the position of the quasireversible maximums of LBPC. The concentration of the aqueous solutions was 1 mol/L. In the case of perchlorate the cation was Li^+, and for both nitrate and chloride it was K^+. All other conditions were same as in the caption of Figure 1B.

The dependence of $\log(f_{max})$ versus E_{sw} is a line with a negative slope (regression coefficient $R = 0.98$), in accordance with theory.[31]

Keeping the volume of the organic solution and the amplitude of the potential modulation constant, the position of the quasireversible maximum is solely determined by the standard heterogeneous electron exchange rate constant of the electrochemical process in the thin-film voltammetry.

The properties of the quasireversible maximum of other redox probes with respect to the thickness of the film and the amplitude are analogous to those of LBPC (data not shown). Therefore, the electrochemical processes of all redox probes under conditions of SWV are quasireversible and their voltammetric properties are in good qualitative agreement with the theoretical model of a simple, kinetically controlled, electrode reaction in thin-film SW voltammetry.[31]

Influence of the Aqueous Ions on the Kinetics of the Electrochemical Processes of DMFC and Lutetium Bis-(phthalocyanines) in a Thin Nitrobenzene Film, under Conditions of Square-Wave Voltammetry. The overall processes at the thin organic film modified electrode (reactions 2 and 3) couple the electron transfer at the GE | NB interface with the ion transfer at the W | NB interface. Which of these two simultaneous processes controls the kinetics of the overall electrochemical process is a crucial question even if from published data it appears that the heterogeneous electron rate transfer (k_s (ferrocenium/ferrocene) = 3.7 cm s^{-1} in CH_3CN[40]) is faster than the ion transfer through the liquid | liquid interface.[25,30] To reveal the rate-determining step, the evolution of quasireversible maximums in different aqueous electrolyte solutions has been examined for various compounds. Figure 4 shows the quasireversible maximums for LBPC measured in 1 mol/L aqueous solutions contain-

ing NO_3^-, ClO_4, or Cl^- ions. The quasireversible maximum occurs at remarkably different critical frequencies for the three anions. The values are f_{max} = 150, 225, and 400 Hz for NO_3^-, ClO_4^-, and Cl^-, respectively. This indicates a strong influence of the anion on the overall kinetics of the electrochemical process. In a separate set of experiments using 0.5 mol/L aqueous solutions, the quasireversible maximums were positioned at 110 Hz for both NO_3^- and ClO_4^- and at 200 Hz for Cl^-.

The positions of the quasireversible maximums for DMFC oxidation in the presence of the same anions are almost identical; of course, Cl^- was not used in the experiments with DMFC. For instance, the maximums for LBPC and DMFC, measured in 1 mol/L NO_3^- aqueous solution, occur at 150 and 130 Hz, respectively. In 1 mol/L ClO_4^-, critical frequencies are 225 and 200 Hz. The same conclusion follows from data presented in Figure 1B, referring to quasireversible maximums measured for the two compounds in 0.1 mol/L ClO_4^- solution (maximum for LBPC at f_{max} = 20 Hz and at 25 Hz for DMFC).

Furthermore, quasireversible maximums have been measured for the reduction of LBPC, LPC, and LBPCl in contact with a 0.1 mol/L aqueous solution of $LiClO_4$. For LBPC and LPC, the critical frequencies are f_{max} = 30 Hz, and f_{max} = 20 Hz for LBPCl. The critical frequencies measured for the reduction of these three redox compounds are in very good agreement with the frequencies corresponding to the oxidation of LBPC (f_{max} = 20 Hz) and DMFC (f_{max} = 25 Hz).

All these experimental results strongly suggest that the overall electrochemical process at the film electrode, LBPC, LPC, LBPCl, or DMFC being the redox probe in the organic film, is controlled by the kinetics of the anion transfer across the W | NB interface. They also indicate that the kinetics of ion transfer is independent of the redox probe in the organic film. Furthermore, the kinetics is independent of the type of electron transfer, i.e., oxidation or reduction. It should be pointed out that these findings are in accord with the results of Lovrić et al.,[41] who indicated that the electrochemical oxidation of DMFC in a nitrobenzene droplet at the three-phase electrode, in the presence of various inorganic ions in the aqueous phase, is a quasireversible process under conditions of SWV. No difference is detectable for some probe species or electrolyte anion, at least for the precision of the present experimental method, so that there is no evidence of chemical interaction; the overall processes appear to be pure charge transfers.

Figure 5A depicts the evolution of the quasireversible maxima for LBPC with the concentrations of ClO_4^- in the aqueous phase. An increase of ClO_4^- concentration in the aqueous phase shifts the LBPC maximum toward higher f_{max} values (Table 2), indicating a corresponding increase of the overall rate of the electrochemical process. These results strongly support the conclusion that the ion transfer across the liquid interface controls the overall kinetics.

To explain the influence of the aqueous ions on the kinetics of the overall electrochemical process occurring at the film electrode, it is necessary to extend to a more complex case the theoretical treatment previously established,[31] considering the simultaneous electron ion-coupled transfer reaction. A brief description

(40) Mirkin, M. V.; Richard T. C.; Bard A. J. *J. Phys. Chem.* **1993**, *97*, 7672–7677.
(41) Komorsky-Lovrić, Š.; Lovrić, M.; Scholz, F. *Collect. Czech. Chem. Commun.* **2001**, *66*, 434–444.

Table 2. Analysis of the Quasireversible Maximum of LBPC Measured in the Aqueous Solution Containing Different Concentrations of LiClO₄[a]

f_{max}/Hz	20		110		220		350		474	
$c^*_{X_{(w)}^-}$/mol L^{-1}	0.1		0.5		1		2		3	
$\log(\Lambda)$	$\log(K'_{max})$	$k_{app} \times 10^2$/cm s^{-1}	$\log(K'_{max})$	$k_{app} \times 10^2$/cm s^{-1}	$\log(K'_{max})$	$k_{app} \times 10^2$/cm s^{-1}	$\log(K'_{max})$	$k_{app} \times 10^2$/cm s^{-1}	$\log(K'_{max})$	$k_{app} \times 10^2$/cm s^{-1}
−0.4	−0.5	0.4	−0.10	2.6	0	4.7	0.2	9.4	0.25	12.25
−0.30	−0.35	0.6	0.00	3.3	0.15	6.6	0.3	11.8	0.40	17.31
−0.22	−0.20	0.9	0.10	4.2	0.3	9.3	0.4	14.9	0.50	21.79
−0.15	−0.10	1.1	0.20	5.3	0.4	11.8	0.4	18.7	0.60	27.44
−0.10	−0.23	1.4	0.35	7.4	0.5	14.8	0.7	29.6	0.80	43.48
$(k_{app})_{av} \times 10^2$/cm s^{-1}		0.9		4.6		9.5		16.9		24.46
k'_s/cm^4 s^{-1} mol^{-1}		90.18		91.23		94.58		84.40		81.52

[a] The concentrations of LBPC and perchlorate ions in the nitrobenzene phase were 2 mmol/L and 0.1 mol/L, respectively. The other experimental conditions are the same as in the caption of figure 1B. The values of the critical kinetic parameter K'_{max} were calculated theoretically for the same concentrations of the species as in the experiment. The other conditions of the simulations were as follows: charge-transfer coefficient $\beta = 0.5$, diffusion coefficient $D = 1 \times 10^{-5}$ cm^2 s^{-1}, amplitude of the potential modulation $nE_{sw} = 50$ mV, and step of the staircase ramp $dE = 10$ mV.
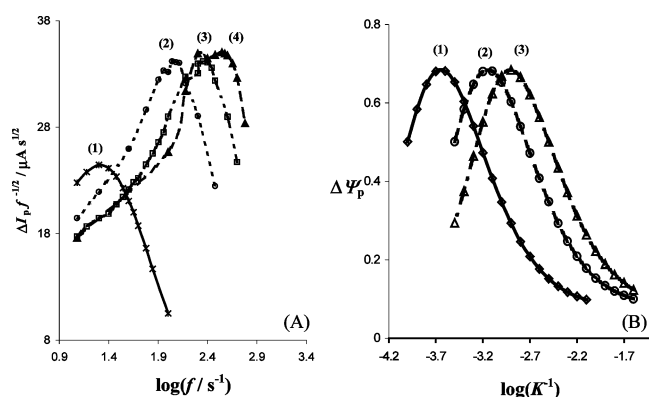

Figure 5. (A) Effect of the concentration of LiClO₄ in the aqueous phase on the quasireversible maximums of LBPC. The concentration of LiClO₄ were 0.1 (1); 0.5 (2), 1 (3), and 2 mol/L (4). All other conditions were same as in the caption of Figure 1B. (B) The influence of the concentration of the transferring ion in the aqueous phase on the position of the theoretically calculated quasireversible maximums. The quasireversible maxima were calculated according to the model given in the Supporting Information. Simulation condition: thickness parameter $\Lambda = 0.5$, amplitude of the potential modulation $nE_{sw} = 50$ mV, step of the staircase ramp $dE = 10$ mV, concentration of the redox compound in the film $c^*_{Red_{(nb)}} = 2$ mmol/L, and concentrations of the transferring ion in the film $c^*_{X_{(w)}^-} = 0.1$ mol/L, and in the aqueous phase $c^*_{X_{(w)}^-} = 1$ (1), 2 (2), and 3 mol/L (3).

of the theoretical model based on the electron−ion coupled electrochemical process 2 is presented in the Supporting Information. Assuming that the kinetics of reaction 2 is described by the Butler−Volmer formalism, the following kinetic equation holds:

$$I/FS = k'_s \exp(\beta\varphi)[(c_{Red_{(nb)}})_{x=0}(c_{X_{(w)}^-})_{x=L} - \exp(-\varphi)(c_{Ox^+_{(nb)}})_{x=0}(c_{X_{(nb)}^-})_{x=L}] \quad (4)$$

where k'_s is the second-order heterogeneous standard rate constant of ion transfer across the liquid | liquid interface (in units of cm^4 s^{-1} mol^{-1}) and β is the transfer coefficient. In addition, $\varphi = (F/RT)(E - E^{\varnothing'})$ is the dimensionless potential, $E^{\varnothing'} = E^{\varnothing}_{Ox/Red} + \Delta^{nb}_w \varphi^{\varnothing}_{X^-}$, being the formal potential of reaction 2, and L the thickness of the film. If the concentrations of the transferring ion

in both liquid phases are constant along the voltammetric experiment, eq 4 can be rewritten in the following form:

$$I/FS = k'_s c^*_{X_{(w)}^-} \exp(\beta\varphi_{X^-}) \exp(\beta\varphi_{Ox/Red})[(c_{Red_{(nb)}})_{x=0} - \exp(-\varphi)(c_{Ox^+_{(nb)}})_{x=0}\rho_1] \quad (5)$$

where $\varphi_{X^-} = (F/RT)(\Delta^{nb}_w\varphi - \Delta^{nb}_w\varphi^{\varnothing}_{X^-}) = \ln(c^*_{X_{(nb)}^-}/c^*_{X_{(w)}^-})$ is the dimensionless potential at the W | NB interface that is controlled by the concentration of the transferring ion in both phases. $\varphi_{Ox/Red} = (F/RT)(E - E^{\varnothing}_{Ox/Red})$ is the dimensionless potential at the GE | NB interface versus the standard redox potential of the redox couple in NB, $\rho_1 = (c^*_{X_{(nb)}^-}/c^*_{X_{(w)}^-})$ being the concentration ratio of the transferring ion. Equation 5 applies to the experiments in the present work, which all have been carried out in the presence of an excess of the transferring ion in both liquid phases, which concentration is at least 2 orders of magnitude higher than that of the redox compound.

Equation 5 is of crucial importance for understanding the behavior of the system. It reveals the complex influence of the concentration of the transferring ion on the overall kinetics of the system. All other concentrations being constant, an increase of the concentration of the transferring ion in the aqueous phase enhances the overall kinetics, through the term $k'_s c^*_{X_{(w)}^-}$; The variation of the concentration of the transferring ion in the aqueous phase also affects the kinetics of the system by changing the potential difference at the liquid | liquid interface. This effect is represented by the term $\exp(\beta\varphi_{X^-})$ in eq 5, which can be rewritten as $\exp(\beta \ln(c^*_{X_{(nb)}^-}/c^*_{X_{(w)}^-}))$.

Equation 5 also indicates that the apparent reversibility of the system under conditions of SWV will depend on the concentration ratio ρ_1 and, more importantly, on the dimensionless kinetic parameter K' defined as

$$K' = \frac{k'_s c^*_{X_{(w)}^-} \exp(\beta \ln(c^*_{X_{(nb)}^-}/c^*_{X_{(w)}^-}))}{\sqrt{Df}} \quad (6)$$

The variation of the quasireversible maximum with the concentration of the transferring ion in the aqueous phase can also be
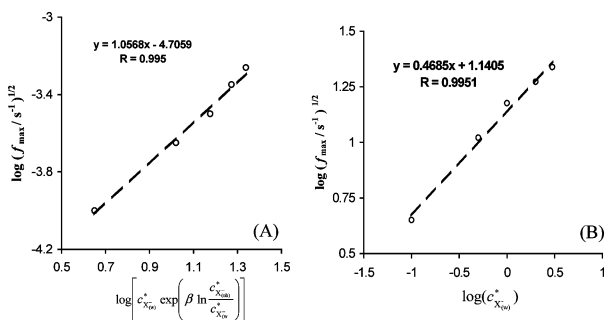
Figure 6. (A) Dependence of the critical frequency on the complex concentration parameter (see eq 7) for the quasireversible maximums of LBPC measured at different concentrations of LiClO₄ in the aqueous phase. (B) Dependence of the critical frequency on the concentration of the perchlorate ion in the aqueous phase (see eq 8). All other conditions were same as in the caption of Figure 1B.

deduced from K'. The logarithmic form of eq 6 at the position of the quasireversible maximum is

$$\log(\sqrt{f_{max}}) = \log\left(\frac{k'_s}{K'_{max}\sqrt{D}}\right) + \log\left[c^*_{X_{(w)}^-}\exp\left(\beta\,\ln\frac{c^*_{X_{(nb)}^-}}{c^*_{X_{(w)}^-}}\right)\right] \quad (7)$$

This last equation predicts a linear relationship between $\log(f_{max}^{1/2})$ and the complex concentration parameter $\log\,[c^*_{X_{(w)}^-}\exp(\beta\,\ln(c^*_{X_{(nb)}^-}/c^*_{X_{(w)}^-}))]$, where f_{max} is the critical frequency measured at various concentrations of the transferring ion. Figure 6A shows this dependence for the quasireversible maximums of LBPC measured with ClO_4^- in the aqueous phase, assuming $\beta = 0.5$. In agreement with eq 7, $\log(f_{max}^{1/2})$ varies linearly with a slope close to 1 (1.06). Furthermore, eq 7 can be rewritten in a form in which the concentrations of the transferring ion in the two liquid phases are separated:

$$\log(\sqrt{f_{max}}) = \log\left(\frac{k'_s}{K'_{max}\sqrt{D}}\right) + (1-\beta)\log(c^*_{X_{(w)}^-}) +$$
$$\beta\log(c^*_{X_{(nb)}^-}) \quad (8)$$

This equation also predicts a linear dependence of $\log(f_{max}^{1/2})$ versus $\log(c^*_{X_{(w)}^-})$, the slope being equal to $1-\beta$. As seen in Figure 5A, the quasireversible maximum for the experimental system LBPC−ClO_4^- shifts toward higher frequencies by increasing the concentration of the aqueous ion, the other parameters being constant. The linear variation is illustrated in Figure 6B, the correlation coefficient of the regression line being $R = 0.995$ and the slope 0.47, which corresponds to $\beta = 0.53$.

This again confirms that the kinetics of the electrochemical reaction 2 is controlled by the ion transfer across the liquid | liquid interface. For an accurate estimation of the second-order standard rate constant of the ion transfer, the model described in the Supporting Information must be used. Using the numerical solution derived in the Supporting Information, theoretical quasireversible maximums have been calculated for the same concentration ratios of transferring ion as used in the experimental analysis for the system LBPC−ClO_4^-. For the sake of comparison with the experimental data, the theoretical quasireversible maxi-

mums are presented in Figure 5B. The shift of the maximum is analogous in both experimental and theoretical analyses.

To estimate the second-order standard rate constant k'_s, the critical kinetic parameter K'_{max} was calculated for conditions corresponding to the transfer of ClO_4^- across the W | NB interface. Table 2 summarizes the data of this analysis. It must be pointed out that, for rigorous treatment, knowledge of the exact film thickness is required, since the latter affects slightly the critical kinetic parameter K'_{max}. Calculating the film thickness on the basis of the geometrical surface area of the electrode (0.32 cm²) and the volume of the deposited organic solvent (1 μL), assuming an ideal smooth surface, yields a film thickness of ∼31 μm. For such a thick film examined by SWV, the electrode reaction would be characterized by a thickness parameter, $\log(\Lambda) \geq 0.5$, which implies that the reaction would occur under semi-infinite diffusion conditions.[31] This is impossible as the existence of a quasireversible maximum is characteristic of a kinetically controlled electrode reaction in a restricted diffusion space only.[31] Accordingly, the present study clearly shows that the reaction takes place in much thinner film. A typical interval for the thickness parameter associated with the quasireversible maximum is $-0.4 \leq \log(\Lambda) \leq -0.1$,[31] which corresponds to a film thickness of about 4−8 μm. For these reasons, in further calculations, instead of using a single value of the critical kinetic parameter K_{max}', corresponding to a particular film thickness, an average K_{max}' will be used, corresponding to the interval $-0.4 \leq \log(\Lambda) \leq -0.1$.

In the theoretical model, the kinetic parameter K' is defined as $K' = (k'_s c^*_{X_{(w)}^-}/(Df)^{1/2})$. Thus, the second-order standard rate constant of the ion transfer is calculated according to the simple relation

$$k'_s = K'_{max}\frac{\sqrt{Df_{max}}}{c^*_{X_{(w)}^-}} \quad (9)$$

where K'_{max} is the critical parameter associated with the theoretical quasireversible maximum, f_{max} being experimentally measured at a given concentration of the transferring ions in the aqueous phase. For all five concentrations, estimations are in good agreement (see Table 2), yielding an average second-order standard rate constant of $k'_s = 91 \pm 8$ cm⁴ s⁻¹ mol⁻¹ for the transfer of perchlorate ion across the W | NB interface.

Commonly, the rate of the electrode reactions in electrochemistry is expressed by using first-order rate constants. Hence, to get an impression about the rate of the electrochemical process, it is recommended to define conditions under which the rate could be formally described by the corresponding apparent first-order standard rate constant (in units of cm s⁻¹). Formally, the apparent first-order rate constant k_{app}, can be calculated as a product of the second-order rate constant and the corresponding concentration, $k_{app} = k'_s c^*_{X_{(w)}^-}$. These values of the apparent first-order rate constant are listed in Table 2. The values are different for different concentrations of the transferring ion due to the fact that the real rate at which the ion enters into the organic phase depends on the potential difference across the W | NB interface, which is controlled by the term $\log\,(c^*_{X_{(w)}^-}/c^*_{X_{(nb)}^-})$. When $c^*_{X_{(w)}^-} = c^*_{X_{(nb)}^-}$, a zero potential difference is imposed across the liquid interface that corresponds to the conditions of the standard rate constant of the ion transfer. Under such conditions, the basic kinetic eq 5

simplifies to the first-order-like kinetic equation:

$$I/FS = k'_s c^*_{X^-_{(w)}} \exp(\beta\varphi_{Ox/Red})[(c_{Red_{(nb)}})_{x=0} -$$
$$\exp(-\varphi_{Ox/Red})(c_{Ox^+_{(nb)}})_{x=0}] \quad (10)$$

since the terms $\exp(\beta\varphi_{X^-}) = \exp(\beta \ln(c^*_{X^-_{(nb)}}/c^*_{X^-_{(w)}}))$ and ρ_1 in eq 5 equal 1. Substituting the product $k'_s c^*_{X^-_{(w)}} = k_{s,app}$, the last equation transforms into the first-order-like kinetic equation. Therefore, kinetics could be formally expressed by an apparent first-order standard rate constant, $k_{s,app}$, of ion transfer when the concentrations of the transferring ion in both phases are equal. In the experimental analysis, this is fulfilled when $c^*_{X^-_{(w)}} = c^*_{X^-_{(nb)}} = 0.1$ mol/L. Under such conditions, the second-order standard rate constant is $k'_s = 90.18$ cm⁴ s⁻¹ mol⁻¹. Thus, the apparent first-order standard rate constant of perchlorate transfer across the W | NB interface is estimated $k_{s,app} = 0.93 \times 10^{-2}$ cm s⁻¹.

The comparison of this apparent first-order standard rate constant of ion transfer with that evaluated by impedance measurements using a four-electrode configuration[25,30] is not straightforward due to the significant differences in the experimental conditions. Samec[25] has mentioned the important variations observed for the ion-transfer constants $(10^{-4}-10^{-3} < k_s/\text{cm s}^{-1} < 1)$ and discussed the reasons for that;[25] however, he concludes that the order of magnitude is 0.1 cm s⁻¹. Different configurations of the liquid | liquid interface lead to different constants because the estimation of that parameter is never straightforward; e.g., the solution resistance, which is much higher than the kinetic resistance, must be correctly evaluated. The present results are the first measured using an organic thin-layer electrode and SWV. From what is already known about ion transfers at ITIES and electron transfer between a solid electrode and a redox species in solution, it looks probable that the limiting process for the overall reaction at the complex-modified electrode is the transfer of ions. It must be pointed out that the different ions studied have comparable constants, which is consistent with previous works at liquid | liquid interfaces examined through more conventional electrochemical methods and confirms the hypothesis about the limitation of the kinetics by ions. It is also useful to note that the effect of the nonhomogeneous polarization of the interface in such an electrode could play a role. Moreover, it has also been suggested that the thermal fluctuations at the interface should influence the ion-transfer rate, and in this respect, the interface between two bulky liquid phases should be really different from that between water and a thin layer of the solvent wetting a graphite surface.

To control the quality of the estimated kinetic parameters, theoretical voltammograms have been simulated for second-order standard rate constant values varying within the interval $83 \leq k'_s/(\text{cm}^4 \text{ s}^{-1} \text{ mol}^{-1}) \leq 99$, and the complete SW voltammetric response was compared with the experimental voltammograms. Figure 7 shows an example of the comparison between the theoretical voltammogram simulated for $k'_s = 90$ cm⁴ s⁻¹ mol⁻¹ and $\beta = 0.53$ and the experimental voltammogram of DMFC, after normalization and subtraction of the blank currents. The voltammogram of DMFC is the same as the one presented in Figure 2B. The concentration of the transferring ion in both liquid phases and the amplitude and frequency of the potential modulation are
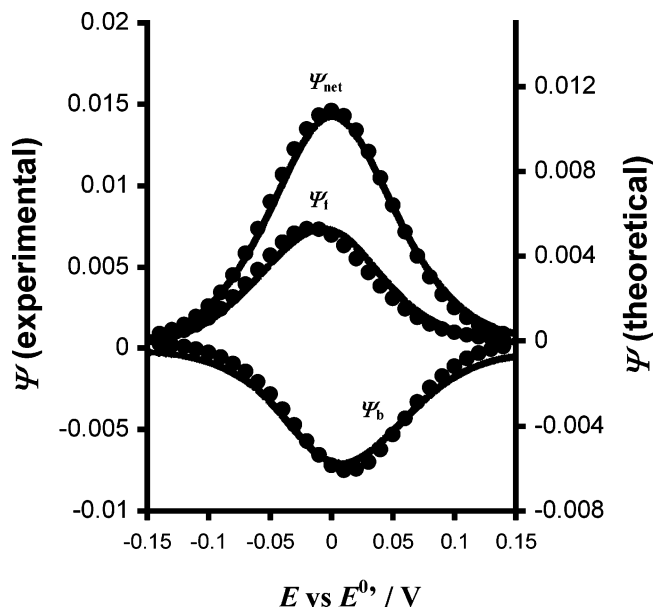
Figure 7. Comparison of the experimental (lines, left ordinate) and theoretical (dots, right ordinate) SW voltammograms for the transfer of ClO_4^- across the W | NB interface at the organic film modified graphite electrode. The experimental conditions were the same as in Figure 2B. The blank voltammogram was recorded under the same experimental conditions and subtracted from the DMFC voltammogram. The normalization of the real current values of the DMFC voltammogram has been performed by assuming $n = 1$, $D = 6 \times 10^{-6}$ cm²/s and $S = 0.32$ cm². Simulation parameters: $K_s = 90$ cm⁴ s⁻¹ mol⁻¹, $\beta = 0.53$, $D = 6 \times 10^{-6}$ cm² s⁻¹, $f = 20$ Hz, $nE_{sw} = 50$ mV, $dE = 10$ mV, $L = 4$ μm, $c^*_{X^-_{(nb)}} = c^*_{X^-_{(w)}} = 0.1$ mol/L, and $c^*_{Red_{(nb)}} = 2$ mmol/L. The dimensionless current for both experimental and theoretical voltammogram is defined as $\Psi = I/(nFSc^*_{X^-_{(w)}}(Df)^{1/2})$. The subscripts f, b, and net correspond to the forward, backward, and net components of the SW voltammetric response, respectively.

identical in both the simulation and the experiment. The thickness of the film in the simulation was $L = 4$ μm, corresponding to the thickness parameter $\log(\Lambda) = -0.14$. A very good agreement between the theoretical and experimental voltammograms, with respect to the parameters of the SW voltammetric response, the peak potentials, half-peak widths, and relative ratio of the forward and backward peak currents, supports strongly the correctness of the overall methodology presented in this study. Although for estimation of the kinetic parameters only the net SW peak currents have been used, the theoretical model is obviously capable of describing all the properties of the experimental response in a rigorous way. The differences between the dimensionless current values of the experimental and theoretical voltammograms are due to the uncertainty of the real active surface area of the graphite electrode.

The rate constants of nitrate and chloride ion transfers from water to nitrobenzene have been estimated similarly. For chloride $k'_s = 133 \pm 10$ cm⁴ s⁻¹ mol⁻¹ and $k_{s,app} = 1.26 \times 10^{-2}$ cm s⁻¹. The corresponding constants for NO_3^- ions are $k'_s = 90 \pm 4$ cm⁴ s⁻¹ mol⁻¹ and $k_{s,app} = 0.93 \times 10^{-2}$ cm s⁻¹.

CONCLUSION

This work reports the first attempt to use the thin-film electrode for the study of the kinetics of ion transfer across the liquid interface. To the best of our knowledge, it is a very convenient

experimental methodology to assess such an important phenomenon as the rate of ion transfer, more simple to use than four-electrode electrochemistry at the liquid | liquid interface. The experimental analysis requires only measurements of the net SW peak current at different frequencies. Each series of measurements to find out the position of the quasireversible maximum is carried out at a single modified electrode, due to the excellent stability of the organic liquid film at the electrode surface. The voltammetric response can be simulated with two relatively simple recursive formulas, presented in the Supporting Information, which can be easily introduced in any spreadsheet or mathematical commercially available program. The kinetic rate constant can be calculated simply requiring only the knowledge of the critical kinetic parameter, calculated with the help of the model, and the measurement of the critical frequency of the quasireversible maximum.

The present study demonstrates how powerful and suitable is square-wave voltammetry for studying the phenomena at the liquid | liquid interface. It utilizes low scan rates but, at the same time, the short time window of the voltammetric experiment. For instance, the scan rate at a relatively high frequency of 200 Hz and potential step of the staircase ramp of $dE = 0.1$ mV is only $v = 20$ mV/s. For these reasons, the shape of all components of the SW response is well developed and the properties of the response such as the peak current, peak potential, and half-peak width are readily measurable. On the other hand, the time window, τ, for inspecting the ion transfer is very short, i.e., $\tau = (1/2f)$. For the latter example, the time window for studying the ion transfer at each potential of the staircase ramp, is only 5 ms, thus providing insight into the kinetics of this process. Therefore, although this appears contradictory at the first sight, SWV utilizes at the same time a low scan rate and a short time window for assessing the charge-transfer reaction. These properties enable one to avoid completely the effect of uncompensated resistance that usually accompanies voltammetric methods used in liquid | liquid electrochemistry, as well as to inspect the kinetics of the charge-transfer reaction. For comparison, to achieve the same time window in cyclic voltammetry, assuming a minimal potential path of 300 mV, the scan rate would be $v = 60$ V/s. Such a high scan rate cannot be applied at the macroscopic liquid | liquid interface without observing high ohmic drop.

It has to be pointed out that this experimental approach is intrinsically different from all other methods based on external potentiostatic control of the potential difference across the liquid | liquid interface to study the ion transfer. In the present method, the potential difference across the liquid | liquid interface is controlled by a common ion present in both liquid phases, which concentration in both phases is at least 2 orders of magnitude higher than the concentration of the redox probe. The structure of the liquid interface is not significantly disturbed during the voltammetric measurements; thus, no phenomenon leading to the instability of the interface has been observed. In combination with the three-phase electrode, the presented methodology is very promising to provide information on the kinetics of many hydrophilic ions that are inaccessible by the common four-electrode arrangement for studying ITIES.

Finally, one should be aware of the possible disadvantages of the proposed experimental arrangement such as nonhomogeneous polarization effects or the effect of the phase-volume ratio. It will be necessary to examine more carefully the origin of the differences in the standard rate constants for ion transfers measured previously and the apparent standard rate constants obtained in the present study; it must be known whether this is due to the underestimation of some phenomena or just because the liquid−liquid interface between the organic liquid film and water is different.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.