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Enhanced ion transfer rate due to the presence of zwitterionic phospholipid monolayers at the ITIES☆

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Abstract

The transfer of cations across phospholipid monolayers at ITIES is studied both experimentally and theoretically. Further evidence of the enhanced rate for cation transfer due to the presence of the monolayer is presented, and a theoretical model that can explain these observations is worked out. The system considered experimentally is Li^+ ion transfer across a hemispherical water | 1,2-dichloroethane interface covered by distearoyl phosphatidylcholine. The theoretical description is based on the electrical double layer correction to the Butler–Volmer equation, coupled with a solution of the Poisson–Boltzmann equation across the interfacial region. The phospholipid monolayer is modelled as two parallel planes of charge, with the negative charge located at the ITIES and the positive charge located at a distance d into the aqueous phase. The enhancement factors predicted are found to be in agreement with our experimental results as well as with those obtained by other authors. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: ITIES; Ion transfer; Phospholipid monolayers; Poisson–Boltzmann equation

1. Introduction

Monolayers of organic surfactants, especially phospholipid monolayers, are artificial systems which have been widely used to simulate the properties of biological membranes [1,2]. The permeation studies have shown a blocking effect, which depends on the state of the monolayer and invariably decreases the rate of solute transfer across it [3,4]. Similarly, the early studies on ion transfer across phospholipid monolayers adsorbed at the interface between two immiscible electrolyte solutions (ITIES) found a retardation effect [5–7], which was related to the size of the transferring ion and the state of the monolayer [8]. More recent studies of ion transfer across phospholipid monolayers at ITIES have reported that the rate of ion transfer is either not retarded [9,10], or in some cases enhanced [11–14], due to the presence of the monolayer. It is important to mention, however, that there is no contradiction between these studies because they have focused on different types of monolayers. While most studies reporting an enhanced rate for ion transfer have used pure phosphatidylcholines, the early works studied phospholipid mixtures (e.g. lecithins).

The experimental evidence for the enhancement of the rate of ion transfer across phospholipid monolayers is rather broad. Kakiuchi et al. studied perchlorate, tetramethylammonium and tetraethylammonium ion transfer at the water | nitrobenzene interface by ac impedance [11,15]. Kontturi et al. studied tetraethylammonium ion transfer across water | 1,2-dichloroethane (DCE) microinterfaces using short potential step techniques [12]. Chesniuk et al. studied the transfer of alkali and alkaline-earth cations across phospholipid monolayers at water | 1,2-DCE macrointerfaces by cyclic voltammetry and noticed either an enhancement of the current or a blocking of the transfer process, depending on the nature of the cation and its concentration [13,14].

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The theoretical efforts to explain the enhancement effect have been unsatisfactory so far. Frumkin was the first to notice that a layer of organic surfactants covering an electrode surface should modify the rate of the electrode reaction not only because of the blocking effect, but also because the surfactants modify the electrical potential difference affecting the reaction [16]. Similarly, Kakiuchi et al. attributed the enhancement to electrical double layer effects, but could not explain the observations in terms of a Frumkin-type correction [11,15]. A detailed picture of the electrical double layer structure and its influence on the rate of ion transfer was lacking.

The phosphatidylcholine head group is zwitterionic, with the ammonium group at the end and the phosphonic group close to the tail. At first glance, the monolayers of zwitterionic phospholipids are electrically neutral and should not influence the rate of interfacial ion transfer. However, it has been found that zwitterionic phospholipid monolayers behave similarly to ionic ones in relation to their interaction with ions in solution, and exhibit unexpected ion uptake behaviour. These phenomena have been explained satisfactorily by considering the electrical structure of the monolayer and solving the Poisson–Boltzmann (PB) equation [17,18].

In this paper, we present both additional experimental evidence of the enhanced cation transfer across a hemispherical water | 1,2-DCE interface covered by distearoyl phosphatidylcholine (DSPC) obtained with a syringe experimental set-up described elsewhere [9], and a theoretical model that can explain these observations. The ion transfer is described by the Butler–Volmer (BV) equation including the electrical double layer correction, which is determined in turn from the solution of the PB equation across the interfacial region. A key issue in this solution is the orientation of the zwitterionic head groups. At air | water interfaces, Standish and Pethica [19] and Ter-Minassian-Saraga [20] showed that the head group is oriented parallel to the interface. The phosphatidylcholine head group is aligned approximately at a right angle to the hydrocarbon chain. In lipid multilayers between quartz plates, Seeling et al. concluded that the head groups align parallel (within 30°) to the plane of the membrane at least in the case of phosphatidylcholine, phosphatidylethanolamine and phosphatidylglycerol [21,22]. In lipid bilayers in electrolyte solutions, however, Ashcroft et al. concluded [23] that the phosphatidylcholine head group changed its orientation with respect to the membrane | solution interface from normal in 1 mM KCl to parallel in 1000 mM KCl (see also Ref. [18]). In the case of liquid | liquid interfaces, as far as we know there is no conclusive study on the orientation of the head groups, although the idea of parallel alignment to the interface has been invoked by Kakiuchi et al. [24] in relation to capacitance studies.

We propose that the orientation of the head groups might be approximately, but not exactly, parallel to the interface. Taking into account that the dipole moment of the phosphatidylcholine head group has been estimated to be 19 D [21], even a small inclination will produce a large effect on the electric potential distribution at the interface. The reasons for this orientation could be found either in the effect of the electric field at the polarised ITIES [25,26], or in the tendency of the head groups to move deeper into the aqueous phase and minimise their electrostatic energy (due to both hydration and image charge effects). Following previous work on the electrostatic properties of lipid membranes [23] and zwitterionic micelles [17,27], and considering the aqueous supporting electrolyte concentration to be in the range 10–1000 mM, we propose a value of 3–4 Å for the distance d between the positive and negative charges in the head group in the direction normal to the interface.

Another key aspect of the theoretical approach is that it allows for the presence of ions in the interfacial region occupied by the phospholipid head groups, which has proved to be useful in the solution of related problems [8]. While an impermeable region results in a linear electric potential profile, an ion-permeable layer might result in a quite different electric potential distribution, especially when the supporting electrolyte concentration is high [28]. Note, finally, that the theoretical modelling presented below incorporates only electrostatic effects, and therefore cannot be applied to highly condensed phospholipid monolayers, where the idea of an ion-permeable interfacial region would not be valid and other effects might become more important than the electrostatic ones.

2. Experimental

A two-terminal electrochemical apparatus was used and the cell was as given in Scheme 1.

The aqueous solution was 1 M LiCl + 1 mM carbonate–bicarbonate buffer (pH 8.7). The organic solution was prepared with high-grade 1,2-DCE and 20 mM $TPeATPBCl_4$ (tetrapentylammonium tetrakis-(4-

$$\underset{\text{(s)}}{\text{Ag}} \;\Big|\; \underset{\text{(s)}}{\text{AgTPBCl}_4} \;\Big|\; \underset{\text{(1,2-DCE)}}{\text{20 mM TPeATPBCl}_4} \;\Big\|\; \underset{\text{(aq.)}}{\text{1 M LiCl, 1 mM CO}_3^{2-}/\text{HCO}_3^-} \;\Big|\; \underset{\text{(s)}}{\text{AgCl}} \;\Big|\; \underset{\text{(s)}}{\text{Ag}}$$

Scheme 1.

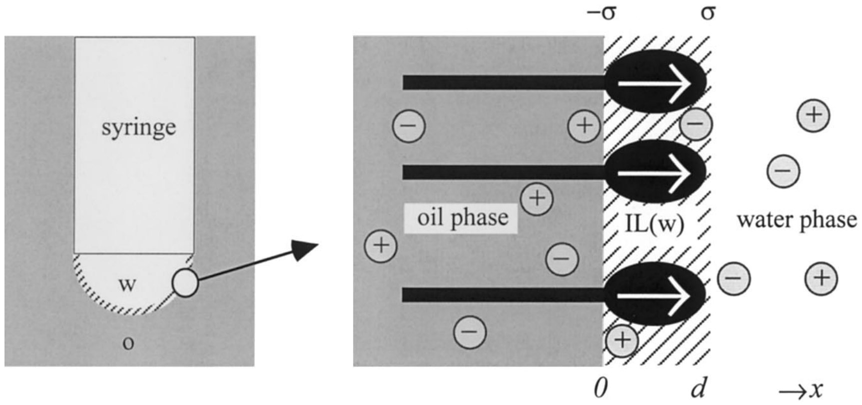

Fig. 1. Schematic drawing of the phospholipid monolayer at the ITIES showing the dipole moment of the head groups and the interfacial ion distribution.

chlorophenyl)borate). The ITIES was formed at the tip of a syringe containing the aqueous solution and was hemispherical in shape. DSPC was added to the organic phase. The head group of this phospholipid was in zwitterionic form at this pH. Details of the experimental set-up and the preparation of the organic salt and the counter/reference electrode can be found elsewhere [29]. The current density at the Ag | AgTPBCl$_4$ electrodes was less than 1 nA cm^{-2} under working conditions, and no instability problems were observed.

3. Theory

3.1. System description

Fig. 1 shows schematically the system under study. Due to the relatively large drop radius, the system is described as one-dimensional with the ITIES located at $x = 0$ and the aqueous medium in the positive x region. The current due to cations transferring from aqueous to organic electrolyte solution is considered to be positive.

The negative phosphonic groups are considered to be located at the ITIES, $x = 0$, and therefore a negative charge density $-\sigma$ is associated with this plane. The positive amine groups are at a distance d into the water phase, being $d \approx 3$–4 Å [18,23,27]. The plane $x = d$ is modelled as an ion-penetrable plane with a charge density $\sigma > 0$.

Since the presence of the phospholipid head groups is likely to affect the water structure in the interfacial region, a dielectric permittivity ε^i (whose value is intermediate between that of the organic phase, ε^o, and that of the aqueous phase, ε^w) is considered in this region [23,30].

3.2. Kinetics of interfacial ion transfer

The nature of the ion transfer process is still open to discussion. In the traditional BV approach for ion transfer across ITIES [31], a sharp interface was considered and the transfer rate was related to the difference between the change in the standard potential of the transferring ion, $\Delta_o^w\phi_i^0$, and the electrical potential difference $\Delta_o^w\phi_2 \equiv \phi_2^w - \phi_2^o$ between the positions of closest approach of this ion to the ITIES, x_2^w and x_2^o. Since the transfer across the interface was implicitly assumed to be the rate-determining step, other steps involved in the process such as the ion transport across the diffusion boundary layers [32] and across the diffuse electrical double layer [33] were often neglected. Currently, there seems to be agreement in describing the ion transfer as a combination of an electrodiffusion process and a desolvation–resolvation process [34]. This latter process is related to the change $\Delta_o^w\phi_i^0$, which takes place over some short distances in the interfacial region rather than abruptly at a sharp interface. However, a satisfactory theory based on this current view that can explain all the experimental data is still lacking [34]. Thus, although other possible descriptions have been suggested [32,35], the BV equation:

$$j_i = k_i^0[c_i(x_2^w)e^{\alpha z_i f(\Delta_o^w\phi_2 - \Delta_o^w\phi_i^0)} - c_i(x_2^o)e^{(\alpha - 1)z_i f(\Delta_o^w\phi_2 - \Delta_o^w\phi_i^0)}] \tag{1}$$

is still widely used [36]. In Eq. (1), k_i^0 is the true standard rate constant (which does not depend on the potential distribution), α is the forward transfer coefficient, z_i is the charge number of the transferring ion, and $f \equiv F/RT$, where F is Faraday's constant, R is the gas constant, and T is the absolute temperature.

Alternatively, the flux density j_i can be expressed in terms of the ion concentrations, c_i^w and c_i^o, and electrical potentials, ϕ^o and ϕ^w, at the positions x_0^w and x_0^o just outside the diffuse electrical double layer. In this case, the BV equation takes the form [37,38]:

$$j_i = k_{i,app}^0[c_i^w e^{\alpha z_i f(\Delta_o^w\phi - \Delta_o^w\phi_i^0)} - c_i^o e^{(\alpha - 1)z_i f(\Delta_o^w\phi - \Delta_o^w\phi_i^0)}] \tag{2}$$

where:

$$k_{i,app}^0 = k_i^0 e^{(1-\alpha)z_i f(\phi^w - \phi_2^w)} e^{-\alpha z_i f(\phi_2^o - \phi^o)} \tag{3}$$

is an apparent standard rate constant that depends on the potential distribution. In Eq. (2), $\Delta_{\rm o}^{\rm w}\phi = \phi^{\rm w} - \phi^{\rm o}$ is the total potential difference across the ITIES, i.e. the sum of the potential drops across the aqueous diffuse layer, the inner layer and the organic diffuse layer. Since the potential drops in the aqueous and organic diffuse layers are different from each other, Eq. (3) implies that the apparent standard rate constant $k^0_{\rm i,app}$ differs from the true constant $k^0_{\rm i}$ even when the transfer coefficient α is equal to 1/2.

In the early stages of liquid | liquid electrochemistry there was some controversy about the experimental determination of the potential drop across the inner layer, $\Delta_{\rm o}^{\rm w}\phi_2$. While some authors [37,38] believed it to be non-negligible and varying with the potential drop $\Delta_{\rm o}^{\rm w}\phi$, other authors concluded that it was practically zero [39,40]. Currently, the controversy on the value of $\Delta_{\rm o}^{\rm w}\phi_2$ has become less important because the concept of the inner layer itself is questioned [34,41]. In other words, the present view is that neither the sharp interface nor the inner layer model provide an accurate representation of the interfacial structure. Nevertheless, they can both be used in combination with the BV equation to describe ion transfer processes reasonably. Hence, for the sake of simplicity, we will use the sharp interface model and neglect the finite size of the transferring ion, so that $x_2^{\rm w} = x_2^{\rm o} = 0$ and $\Delta_{\rm o}^{\rm w}\phi_2 = 0$. Furthermore, in agreement with most experimental results, we take $\alpha \approx 1/2$. Under these approximations, the relation between the apparent rate constant and the electrical potential at the ITIES, $\phi(0)$, simplifies to [28]:

$$k^0_{\rm i,app} = k^0_{\rm i} {\rm e}^{-z_{\rm i} f\tilde{\phi}(0)} \tag{4}$$

where $\tilde{\phi}(0) \equiv \phi(0) - (\phi^{\rm w} + \phi^{\rm o})/2$ represents the potential at the ITIES measured with respect to the average potential of the aqueous and the organic phase. (The use of $\tilde{\phi}(0)$ is recommended not only because of the formal simplicity of Eq. (4), but also because of its relevance to the electric potential distribution in the absence of lipids, as shown below in Eq. (5).)

The presence of the phospholipids can affect the rate of ion transfer across the ITIES in two ways. On the one hand, the phospholipids alter the electrical potential $\tilde{\phi}(0)$, and hence the exponential term in Eq. (4). On the other hand, they can also modify the true standard rate constant $k^0_{\rm i}$. The second effect is expected to be noticeable only in relatively condensed monolayers and would account for the observed partial blocking of the ion transfer. The first effect, however, can result in either a decrease or an enhancement of the rate of ion transfer and is expected to be dominant in relatively dilute monolayers. The present study is restricted to the electrostatic effect. In particular, for every value of $\Delta_{\rm o}^{\rm w}\phi$, we define the enhancement factor as the ratio of apparent rate constants in the presence and in the absence of phospholipids, $k^0_{\rm i,app}({\rm presence})/k^0_{\rm i,app}({\rm absence}) = \exp\{-z_{\rm i} f[\tilde{\phi}(0)_{\rm presence} - \tilde{\phi}(0)_{\rm absence}]\}$, and compare it with the ratio of currents across the ITIES observed at this $\Delta_{\rm o}^{\rm w}\phi$ in the presence and in the absence of phospholipids.

3.3. Evaluation of the electric potential at the ITIES

In the absence of phospholipids, the condition of continuity of electric displacement at the ITIES can be used to match the Gouy–Chapman electric potential profiles in the aqueous and organic diffuse layers and obtain the following expression for $\tilde{\phi}(0)$ [42,43]:

$$f\tilde{\phi}(0) = 2\,{\rm arctanh}\left[\frac{r-1}{r+1}\tanh\left(\frac{f\Delta_{\rm o}^{\rm w}\phi}{4}\right)\right] \tag{5}$$

where $r = \varepsilon^{\rm w}\kappa^{\rm w}/(\varepsilon^{\rm o}\kappa^{\rm o})$, and $\kappa^{\rm w} = (2F^2c^{\rm w}/\varepsilon^{\rm w}RT)^{1/2}$, $\kappa^{\rm o} = (2F^2c^{\rm o}/\varepsilon^{\rm o}RT)^{1/2}$ are the reciprocal Debye lengths in the aqueous and organic electrolyte solutions, respectively.

In the presence of zwitterionic phospholipids, the determination of $\tilde{\phi}(0)$ requires the solution of the PB equation in the aqueous region in between the two planes of charge, $0 < x < d$ [28]. Since only the aqueous supporting electrolyte ions can be present in this region, the PB equation takes the form:

$$f\frac{{\rm d}^2\phi}{{\rm d}x^2} = \kappa^{{\rm i}2}\sinh[f(\phi - \phi^{\rm w})] \tag{6}$$

where $\kappa^{\rm i} = (2F^2c^{\rm w}/\varepsilon^{\rm i}RT)^{1/2}$ is the reciprocal Debye length in this region. The solution of Eq. (6) must be coupled to the two Gouy–Chapman electric potential profiles in the aqueous and organic diffuse layers ($x > d$ and $x < 0$, respectively) by the conditions of continuity of electrical potential at $x = 0$ and $x = d$, and discontinuity of electric displacement:

$$\varepsilon^{\rm i}\left(\frac{{\rm d}\phi}{{\rm d}x}\right)_{x=0+} - \varepsilon^{\rm o}\left(\frac{{\rm d}\phi}{{\rm d}x}\right)_{x=0-} = \sigma \tag{7a}$$

$$\varepsilon^{\rm w}\left(\frac{{\rm d}\phi}{{\rm d}x}\right)_{x=d+} - \varepsilon^{\rm i}\left(\frac{{\rm d}\phi}{{\rm d}x}\right)_{x=d-} = -\sigma \tag{7b}$$

In order for the potential profiles to satisfy these boundary conditions, the potentials $\phi(0)$ and $\phi(d)$ must be obtained by solving a system of two equations.

The first of these two equations arises from the integration of Eq. (6):

$$f^2\left(\frac{{\rm d}\phi}{{\rm d}x}\right)^2_{x=d-} - f^2\left(\frac{{\rm d}\phi}{{\rm d}x}\right)^2_{x=0+} = 2\kappa^{{\rm i}2}(\cosh\{f[\phi(d) - \phi^{\rm w}]\} - \cosh\{f[\phi(0) - \phi^{\rm w}]\}) \tag{8}$$

Making use of Eqs. (7a) and (7b) and the Gouy–Chapman equations for the electrical potential gradients:

$$f\left(\frac{{\rm d}\phi}{{\rm d}x}\right)_{x=0-} = 2\kappa^{\rm o}\sinh\{f[\phi(0) - \phi^{\rm o}]/2\} \tag{9a}$$

$$f\left(\frac{d\phi}{dx}\right)_{x=d+} = -2\kappa^{w}\sinh\{f[\phi(d)-\phi^{w}]/2\} \tag{9b}$$

Eq. (8) can be transformed to:

$$\begin{aligned}(\varepsilon^{w^2}\kappa^{w^2}-\varepsilon^{i^2}\kappa^{i^2})\sinh^2\{f[\phi(d)-\phi^{w}]/2\}\\ -\varepsilon^{w}\kappa^{w}f\sigma\sinh\{f[\phi(d)-\phi^{w}]/2\}\\ =\varepsilon^{o^2}\kappa^{o^2}\sinh^2\{f[\phi(0)-\phi^{o}]/2\}\\ -\varepsilon^{i^2}\kappa^{i^2}\sinh^2\{f[\phi(0)-\phi^{w}]/2\}\\ +\ \varepsilon^{o}\kappa^{o}f\sigma\sinh\{f[\phi(0)-\phi^{o}]/2\}\end{aligned} \tag{10}$$

The second relation between $\phi(0)$ and $\phi(d)$ is:

$$\int_0^d \frac{d\phi}{d\phi/dx} = d \tag{11}$$

where the electrical potential gradient in this region can be obtained from Eq. (6) as:

$$\begin{aligned}\frac{d\phi}{dx} = \pm\frac{1}{f\varepsilon^{i}}\{[f\sigma-2\varepsilon^{w}\kappa^{w}\sinh\{f[\phi(d)-\phi^{w}]/2\}]^2\\ -2\varepsilon^{i^2}\kappa^{i^2}[\cosh\{f[\phi(d)-\phi^{w}]\}-\cosh\{f[\phi-\phi^{w}]\}]\}^{1/2}\end{aligned} \tag{12}$$

where the sign is that of the potential difference $\phi(d)-\phi(0)$; note that $d\phi/dx$ can vanish only when $\Delta_o^w\phi$ is negative and large in magnitude. Thus, Eqs. (10) and (11) allow for the determination of $\phi(0)$ and $\phi(d)$ for given values of σ and $\Delta_o^w\phi$.

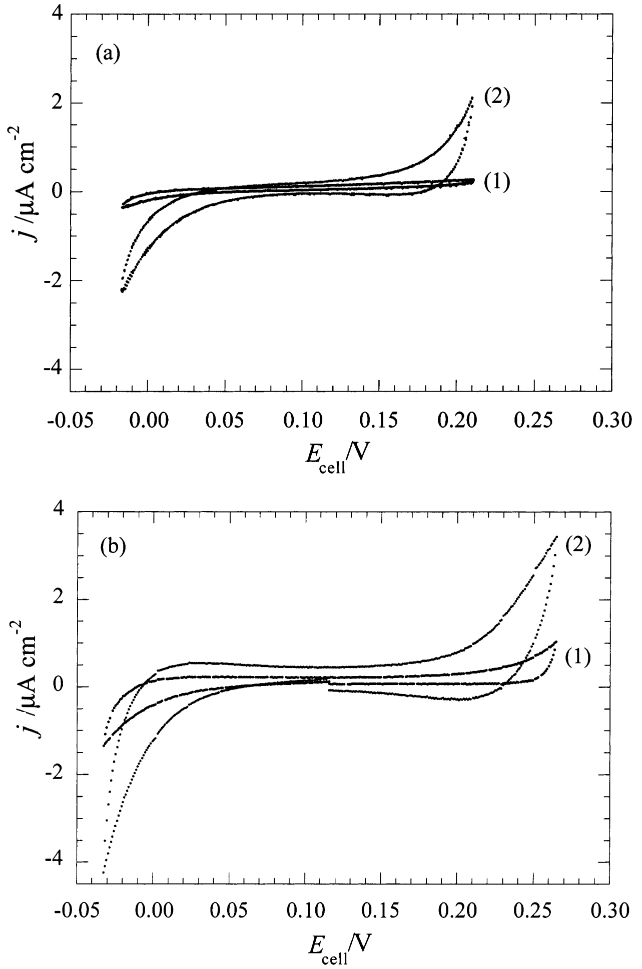

Fig. 2. (a) Comparison of cyclic voltammograms obtained before (1) and after addition (2) of 59 μM DSPC to the organic phase. Sweep rate: 1 mV s^{-1}. (b) Comparison of cyclic voltammograms obtained before (1) and after addition (2) of 10 μM DSPC to the organic phase. Sweep rate: 10 mV s^{-1}.

4. Results and discussion

As we have already mentioned, our primary concern is to describe the experimental observations of the effect of zwitterionic phospholipids on the transfer of a cation across the ITIES from the aqueous to the organic phase, and to explain those observations in the light of the theory presented above.

Fig. 2(a and b) shows the current density measured in the cell described in Section 2 before (1) and after (2) the addition of DSPC. The area of the ITIES is ca. 5.5×10^{-4} cm^2 in all experiments. It is observed that the current density increases at both sides of the window. At the positive side of the window, Li$^+$ ion transfers from the aqueous to the organic phase. At the negative side, the transferring ion could be either the TPeA$^+$ ion from organic to aqueous phase or the Cl$^-$ ion transfer from aqueous to organic phase. The enhancement factor (i.e. the ratio of current densities at fixed cell potential) observed for the Li$^+$ ion transfer varies slightly with cell potential, and takes values between 5 and 10.

Similarly, the enhancement factors observed in Ref. [11] (by ac impedance) and Ref. [12] (by potential steps) were also only a few units. The cyclic voltammetry study in Ref. [13] reported much larger enhancement factors, and considered the effect of the cation nature, the concentration of the transferring ion and the applied potential. The enhancement was shown to be larger at low applied potentials and at low concentrations of the transferring ion.

The theory presented above accounts for the electrostatic effects on the apparent rate constant for ion transfer (and therefore the observed current densities) and requires the value of the electrical potential at the ITIES $\phi(0)$ because, under the approximations employed (particularly, $\Delta_o^w\phi_2=0$), any change in $k^0_{i,app}$ is directly related to a change in $c_i^w(0)$, or equivalently to $\phi(0)$. In the following, we present theoretical results obtained for the water | 1,2-DCE interface ($\varepsilon_r^w=78.39$, $\varepsilon_r^o=10.36$), with a relative permittivity of the interfacial region $\varepsilon_r^i=30$ [30], and a separation between the charged planes $d=3$ Å (except in Fig. 5, where different values are considered). The surface charge concentration σ is expressed as a molecular area for the zwitterionic head groups, the maximum surface charge

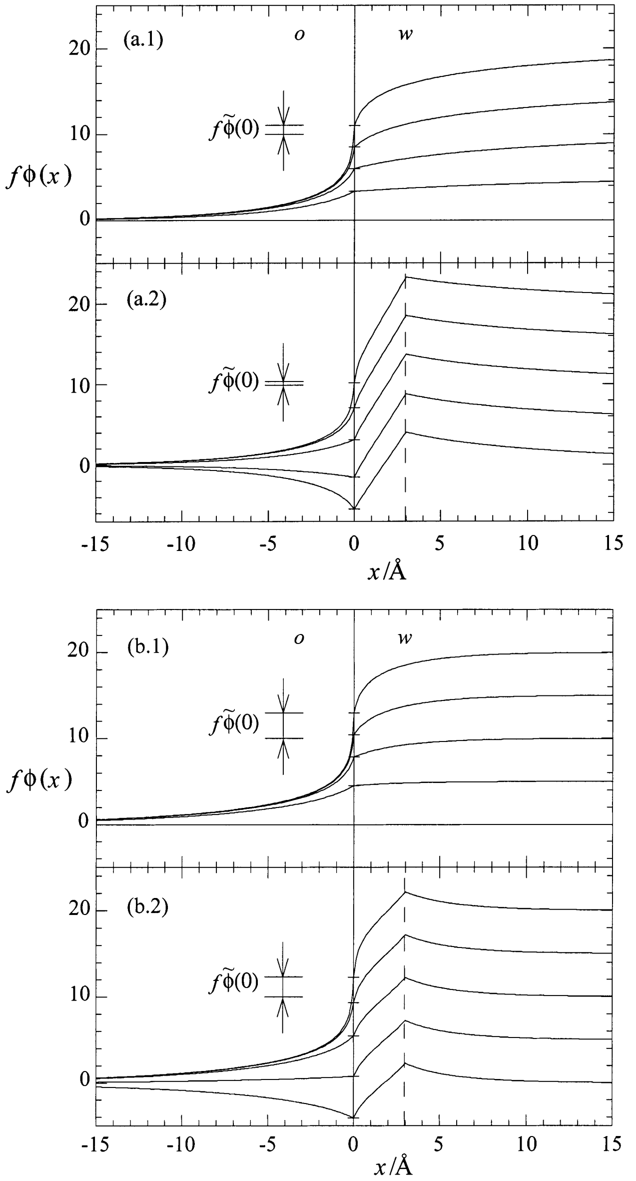

Fig. 3. Simulated electrical potential profiles in the absence (1) and in the presence (2) of a phospholipid monolayer of molecular area 50 Å^2 at the water | 1,2-DCE interface. The potential in the bulk of the organic phase has been set equal to zero in this plot, $\phi^o = 0$. The negative phosphonic groups are assumed to be located at $x = 0$, and the positive ammonium groups at $x = d = 3$ Å. Galvani potential differences $f\Delta_o^w\phi = 0$, 5, 10, 15 and 20 are considered. All $\phi(0)$ values have been marked with a small horizontal line. For the sake of clarity, only the $f\tilde{\phi}(0)$ values corresponding to $f\Delta_o^w\phi = 20$ have been shown. Electrolyte concentrations are: (a) $c^w = c^o = 50$ mM, (b) $c^w = 1000$ mM, $c^o = 20$ mM.

concentration corresponding to a compact DSPC monolayer of 37 Å^2 [7]. (As an example of the equivalence between these magnitudes, note that a molecular area of 50 Å^2 corresponds to $\sigma = 32.0$ μC cm^{-2}.) Since the molecular area is not well characterised in the experiments considered, different values ranging from condensed to very dilute monolayers are given to σ.

When a potential difference is applied to the ITIES, there must be a charge separation across the ITIES through the formation of the electrical double layers, which in turn affects the rate of ion transfer. The presence of the phospholipids modifies the electrical double layer and their influence is expected to be greatest for the lowest ionic strength, since then there are less ions to screen the zwitterionic charges. Furthermore, the effect of the phospholipids is determined by the charge separation due to the polar head groups in relation to the charge separation due to the applied potential difference. Since the latter is larger for higher applied potentials, it is expected that the effect of the phospholipids will decrease with the applied potential difference.

Fig. 3(a and b) show electrical potential distributions for different values of $\Delta_o^w\phi$. Fig. 3(a) corresponds to the concentrations $c^w = c^o = 50$ mM employed in some experiments reported in Ref. [13]. Fig. 3(b) corresponds to the concentrations $c^w = 1000$ mM and $c^o = 20$ mM employed in the experiments shown in Fig. 2(a and b). In all cases, a phospholipid molecular area of 50 Å^2 has been assumed. The ITIES has been marked with a continuous vertical line, and the plane where amine groups are assumed to be located has been marked with a dashed line. The potential distributions in the region $0 < x < d$ are non-linear due to the presence of aqueous ions. For every value of the applied potential $\Delta_o^w\phi$, it is observed that the presence of the phospholipids (in particular the phosphonic groups assumed to be located at the ITIES) leads to a decrease in the value of the potential $\phi(0)$, which has been marked with a small horizontal line. The values of $f\tilde{\phi}(0)$ corresponding to $f\Delta_o^w\phi = 20$ have also been shown in order to clarify the meaning of this magnitude. Note, however, that the enhancement factors for cation transfer can be calculated from $\phi(0)$, since the equality $k^0_{i,app}(\text{presence})/k^0_{i,app}(\text{absence}) = \exp\{f[\tilde{\phi}(0)_{absence} - \tilde{\phi}(0)_{presence}]\} = \exp\{f[\phi(0)_{absence} - \phi(0)_{presence}]\}$ holds at fixed $\Delta_o^w\phi$.

Fig. 4 shows the enhancement factors calculated for the concentrations: (a) $c^w = c^o = 50$ mM, and (b) $c^w = 1000$ mM, $c^o = 20$ mM. Different values of the phospholipid molecular area have been considered. The Galvani potential difference $\Delta_o^w\phi$ varies from 0 to $15/f \approx 385$ mV at 25°C. It is observed that the enhancement factor increases with increasing surface charge density (decreasing molecular area) and with decreasing $\Delta_o^w\phi$. These results are in agreement with the experimental observations in Refs. [12,13] and can be rationalised in terms of space charge distribution. The applied potential difference $\Delta_o^w\phi$ involves a charge separation that increases with increasing $\Delta_o^w\phi$. When this charge separation is low compared with the charge densities (σ and $-\sigma$) associated with the phospholipid head groups, large perturbations of the electric potential distributions are to be expected, as shown indeed by Fig. 4.

Note finally that the enhancement factors shown in Fig. 4 are larger when $c^w = 50$ mM (case a) than when $c^w = 1000$ mM (case b), which is in agreement with the experimental observations in Ref. [13] and in Fig. 2(a and b). Evidently, the larger enhancement factors calculated in case (a) of Fig. 4 are directly related to the larger decrease (in magnitude) of $\phi(0)$, $\phi(0)_{\text{presence}} - \phi(0)_{\text{absence}}$, observed in Fig. 3(a) (in comparison with the respective cases (b)).

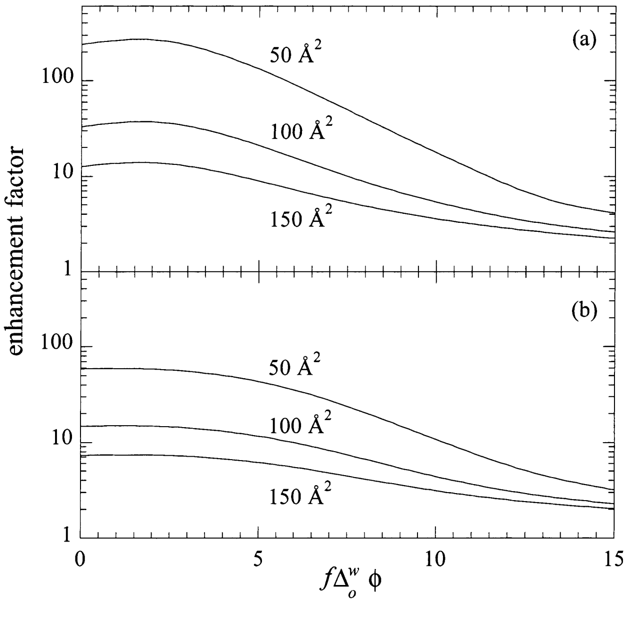

Fig. 4. Theoretical enhancement factor against Galvani potential difference for DSPC monolayers of different molecular areas (shown on the curves) and electrolyte concentrations: (a) $c^w = c^o = 50$ mM, (b) $c^w = 1000$ mM, $c^o = 20$ mM. The value of d is 3 Å.

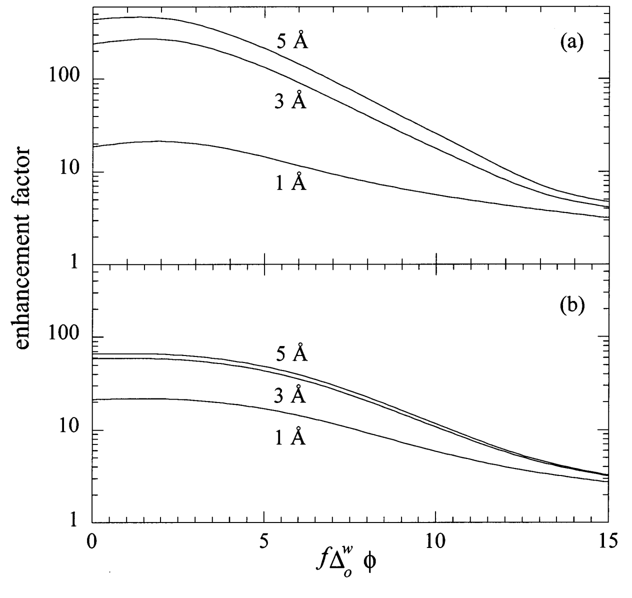

Fig. 5. Theoretical enhancement factor against Galvani potential difference for DSPC monolayers of different values of d (shown on the curves) and electrolyte concentrations: (a) $c^w = c^o = 50$ mM, (b) $c^w = 1000$ mM, $c^o = 20$ mM. The phospholipid molecular area is 50 Å^2.

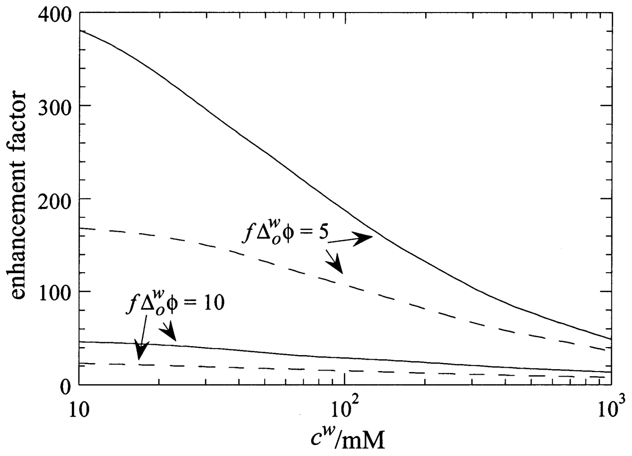

Fig. 6. Theoretical enhancement factor against electrolyte concentration in the aqueous phase for two values of the Galvani potential difference (shown on the curves) and two electrolyte concentrations in the organic phase: (—) $c^o = 10$ mM, (– – –) $c^o = 50$ mM. The DSPC molecular area is 50 Å^2. The value of d is 3 Å.

Since the orientation of the phospholipid head group with respect to the ITIES is likely to change with electrolyte concentration or applied potential difference, the effect of varying d on the enhancement factor has been analysed in Fig. 5. In particular, the values $d = 1$, 3 and 5 Å have been considered. As expected, the enhancement factors increase with increasing d, and two facts are worth mentioning. First, that even a small deviation from the parallel orientation, $d = 1$ Å, leads to significant enhancement factors. Second, that the same change in the magnitude of d (from 1 to 3 Å as compared with the change from 3 to 5 Å) leads to much larger changes in the enhancement factor when d is small. Both facts reveal the importance of small deviation angles (of the order of 30° or less) from the parallel orientation of the polar head groups with respect to the ITIES. Unfortunately, the lack of accurate experimental information on the variation of d with c^w and $\Delta_o^w\phi$ obtained from phospholipid monolayers at ITIES makes it unreasonable to introduce such dependence into the theoretical calculations at the present stage.

Fig. 6 analyses the effect of the electrolyte concentration in both the aqueous and the organic phase. The continuous lines correspond to a fixed electrolyte concentration in the organic phase $c^o = 10$ mM and two values of the Galvani potential difference. The dashed lines correspond to a fixed electrolyte concentration in the organic phase $c^o = 50$ mM and the same two values of the Galvani potential difference. These theoretical results are in agreement with the experimental observations by Chesniuk et al. [13], who observed that the current enhancement due to the phospholipid monolayer was much more important in dilute solutions than in concentrated solutions. Moreover, it is shown that a decrease in the electrolyte concentration in the organic phase has a similar effect to a decrease in the electrolyte concentration in the aqueous phase.

5. Conclusions

A two-terminal electrochemical apparatus has been used to show that the Li^+ ion transfer across the water | 1,2-DCE interface formed at an extruded drop at the tip of a syringe is enhanced due to the presence of adsorbed DSPC. This result is in agreement with recent studies of ion transfer across phospholipid monolayers at ITIES. Although the electrical double layer correction for the kinetics of ion transfer across ITIES has not been very fruitful in the past (and sometimes it has even been controversial), a theoretical approach based on such a correction is proposed to explain the observed enhancement. Since the phospholipid head groups are in the zwitterionic form at the pH considered, the charges in these groups must modify the electrical potential difference affecting the ion transfer process. If the orientation of the head groups is such that the phosphonic group remains closer to the ITIES than the ammonium groups, the local concentration of cations is increased at the ITIES and hence the current observed due to cation transfer is larger than in the absence of phospholipids at the interface. This enhancement is evaluated from the solution of the PB equation, and calculations have been carried out for the conditions of the experiments presented here, as well as for those in Ref. [13]. The theoretical results turn out to be in good agreement with both experimental studies, thus showing the importance of the electrostatic correction on the rate of ion transfer across an ITIES with adsorbed phospholipids. It must be mentioned, however, that the present theoretical approach neglects ion size effects and might lead to unrealistically high ion concentrations in the case of large potential differences $\Delta_o^w\phi$. Furthermore, it has to be stressed that other effects such as steric hindrance giving rise to partial blocking of ion transfer might be important in the case of more condensed monolayers.

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