Mechanism of Lecithin Adsorption at a Liquid|Liquid Interface

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Adsorption of L-α-lecithin (dipalmitoyl) at the water|1,2-dichloroethane interface has been studied by cyclic voltammetry. It has been found that the voltammetric peak in acidic medium corresponds to the desorption of the protonated form of lecithin. Its surface concentration is controlled by a surface chemical reaction of the zwitterionic form of adsorbed lecithin with hydroxonium ion. The whole process is complemented by the potential dependent adsorption/desorption equilibrium of the protonated form of lecithin. Its concentration in the organic phase is affected by the acid−base equilibrium.

1. Introduction

Ion transfer across a liquid|liquid interface modified by adsorption of phospholipids has been of increasing interest in recent decades not only because it can mimic one side of a biological membrane but also from the point of view of how it influences the structure of the interphase and the role it plays in the charge transfer kinetics. The relevant studies have focused primarily on the formation and description of the adsorbed monolayer. Girault and Schiffrin[1] have shown that surface tension in the presence of lecithin at the water|1,2-dichloroethane (1,2-DCE) interface in an unbuffered or a slightly acidic medium is strongly potential dependent. This has been explained by the potential dependent protonation of the phosphate moiety of the adsorbed zwitterion. The decrease in the interfacial tension at negative potentials has been related to the adsorption of phospholipid as a zwitterion, while the increase at positive potentials has been accounted for by the adsorption of the cationic form of the phospholipid.[1] Later it has been pointed out that the surface tension increase at positive potentials can be ascribed to desorption of the lipid,[2−5] and an attempt has been made to maintain the surface coverage constant during a voltammetric cycle by controlling the surface pressure using the electrochemical Langmuir trough.[4,5] An explanation of the phospholipid desorption has been offered on the basis of polarographic and drop time experiments in concentrated solutions of a phospholipid where micellization cannot be ruled out. The authors[6] have suggested formation of a complex between hydrophilic cations in the aqueous phase and a phospholipid layer followed by the desorption of the complex from the interface. However, analysis of the lipid desorption process is still lacking.

In this paper we show that the voltammetric current observed in acidic medium at positive potentials corresponds to desorption of the protonated form of lecithin. Two reaction mechanisms involving a surface chemical reaction of the zwitterionic form of adsorbed lecithin with hydroxonium ion, and adsorption/desorption equilibrium of the protonated lecithin are proposed. The second mechanism includes an additional follow-up reaction of the desorbed lecithin in the organic phase. The effect of this reaction on the analysis of voltammograms is illustrated.

2. Experimental Section

2.1. Chemicals. Reagent grade chemicals from Fluka AG (LiCl, HCl, tetrabutylammonium chloride (TBACl), tetrabutylammonium tetraphenylborate (TBATPB), potassium tetrakis(4-chlorophenyl)borate (KTPBCl), potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTPBCF3), and Serva (L-α-lecithin, dipalmitoyl) were used as received. TBATPBCl was prepared by mixing acetone solutions of TBACl and KTPBCl. KCl was filtered out and TBATPBCl was crystallized from the filtrate. Highly purified and deionized water (<0.1 S cm^{-1}, GORO system, Czech Republic) was used to prepare the aqueous solutions. 1,2-DCE (Fluka AG) was purified by passing it twice through columns of basic alumina.

2.2. Apparatus and Cell. Cyclic voltammetry measurements were carried out in a four-electrode cell[7] with a flat water|1,2-DCE interface having an area of 25.9 mm^2. An EG&G 263A potentiostat (Princeton Applied Research, U.S.A.) equipped with a homemade four-electrode adapter was used for cyclic voltammetry measurements. The impedance measurements were performed with a Frequency Response Analyzer SI 1255 and an Electrochemical Interface SI 1287 (Solartron Instruments, England). The interfacial tension at the water|1,2-DCE interface was measured using drop shape analysis in a four-electrode arrangement with an aqueous pendant drop electrode.[8]

The potential E of the cell was related to the formal potential difference for tetrabutylammonium ion $\Delta_o^w\phi^0_{TBA^+} = -0.226$ V.[9] The measurements were carried out at 296 ± 2 K.

3. Results and Discussion

Cyclic voltammograms of 0.01 M TBATPBCl and 25 μM lecithin in the organic phase and 0.01 M HCl in the aqueous phase are shown in Figure 1. Voltammograms were recorded after an 8 s delay at the initial potential $E_i = 0.2$ V in order to restore the adsorbed layer of lecithin. The forward peak current is proportional to the polarization rate v and at $v < 1$ V/s, the potentials of the forward and of the reverse peaks are almost equal. The difference between the half-peak potential and the peak potential for the forward peak is about 0.025 V larger compared to that of the diffusion controlled ion transfer reaction. The reverse and forward peak current ratio is about 0.6. These

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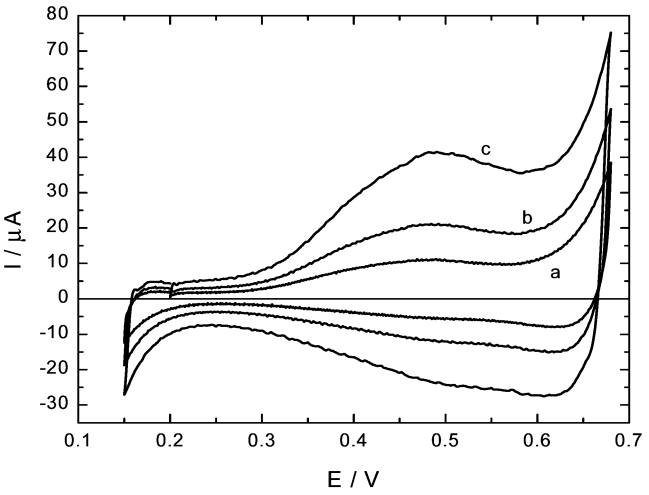

Figure 1. Cyclic voltammograms recorded in the presence of 25 μM lecithin in the organic phase. Organic phase: 0.01 M TBATPBCl in 1,2-DCE. Aqueous phase: 0.01 M HCl. Polarization rate: (a) 0.5; (b) 1; (c) 2 V s^{-1}.

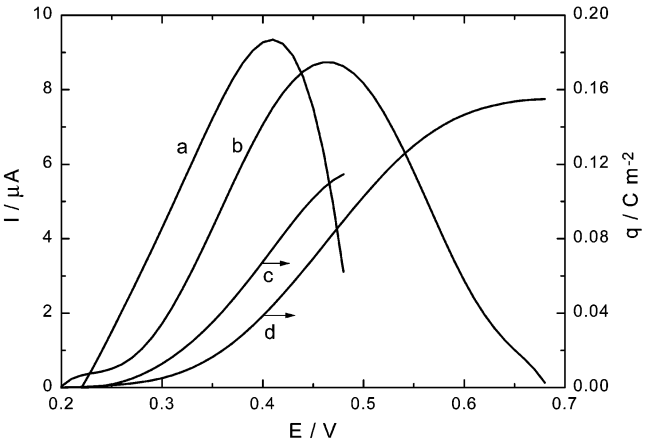

Figure 2. Forward scans of the voltammograms in the presence of 25 μM lecithin in the organic phase corrected for the base electrolyte current and the passed electrical charge q. Organic phase (1,2-DCE): (a, c) 0.01 M TBATPB; (b, d) 0.01 M TBATPBCl. Aqueous phase: (a−d) 0.01 M HCl. Polarization rate: 0.5 V s^{-1}.

facts indicate that the measured current is related to the change of the interfacial capacity and that lecithin desorbs from the interface.

When the base electrolyte TBATPBCl in the organic phase is replaced by TBATPB, the forward peak current is almost the same, but its potential is shifted by 0.06 V to less positive values. The forward scans of voltammograms of both systems corrected for the base electrolyte current are shown in Figure 2. Supposing that the forward voltammetric peak is connected with desorption of the positively charged lecithin $HL^+_{(ads)}$, the passed electric charge q corresponds to the decrease of the initial surface concentration of the adsorbed lecithin $L^{\pm}_{(ads)}$. In the system with TBATPBCl, the total passed charge is $q_{max} = 155$ mC m^{-2}, (curve d in Figure 2), which yields 1.6×10^{-6} mol m^{-2} for the initial surface concentration of lecithin. The passed charge at the peak potential is just one-half of the total charge. This observation can be used to estimate the total charge passed in the cell with TBATPB where the potential range on the forward scan is limited by the transfer of TPB^- from the organic to the aqueous phase. The total charge is estimated to be $2 \times 75 = 150$ mC m^{-2}, which corresponds to the lecithin initial surface concentration of 1.55×10^{-6} mol m^{-2}.

3.1. Mechanism without a Follow-up Reaction. These results indicate that the adsorption of lecithin proceeds as a three-step process at least. In the first step, the diffusion controlled step, lecithin $L^{\pm}_{(o)}$ dissolved in the organic phase is adsorbed at the interface in its zwitterionic form $L^{\pm}_{(ads)}$. This step is followed by interfacial protonation of the phosphate group of the adsorbed lecithin. In the last step, the positively charged lecithin $L^+_{(ads)}$ desorbs from the interface into the organic phase. The overall mechanism can be written as

$$L^{\pm}_{(o)} \overset{1}{\rightleftarrows} L^{\pm}_{(ads)} + H^+_{(w)} \overset{2}{\rightleftarrows} HL^+_{(ads)} \overset{3}{\rightleftarrows} HL^+_{(o)} \qquad (1)$$

Assuming that current I is controlled by charging the electrical double layer, we can write

$$I = \upsilon A \, dq/dE \qquad (2)$$

A is the area of the interface, and the charge q passed during time t of the potential sweep is due to desorption of the positively charged lecithin $HL^+_{(ads)}$. Obviously, this equation describes well the voltammetric behavior, because the voltammetric current I is proportional to the polarization rate υ.

Independence of the passed charge q on the polarization rate υ indicates that all steps in the desorption of lecithin should proceed under equilibrium conditions. In the proposed mechanism (eq 1), the surface concentration of $HL^+_{(ads)}$ is established by equilibrium of the surface chemical reaction (step 2). The nonzero surface concentration of $HL^+_{(ads)}$ is the driving force for the desorption step 3 controlled by the adsorption/desorption equilibrium of HL^+.

The surface concentration of the protonated form of adsorbed lecithin HL^+ can be then expressed as

$$\Gamma_{HL^+}(t,E) = \Gamma_{L^{\pm}}(t,E) \, \Gamma_{H^+}(E)/K_w \qquad (3)$$

where K_w is dissociation constant of step 2 in mechanism 1. K_w is related to the aqueous phase, where the polar heads of adsorbed lecithin are located. According to this mechanism, the surface concentration of the zwitterionic form of lecithin $\Gamma_{L^{\pm}}(t,E)$ can be calculated from its initial concentration $\Gamma^0_{L^{\pm}} = q_{max}/F$ by

$$\Gamma_{L^{\pm}}(t,E) = \Gamma^{\circ}_{L^{\pm}} - \Gamma_{HL^+}(t,E) - \Gamma_{HL^+_{(o)}}(t,E) \qquad (4)$$

where $\Gamma_{HL^+_{(o)}}(t,E)$ represents the hypothetical surface concentration of the desorbed lecithin $HL^+_{(o)}$ near the interface. Because the voltammetric scan is short, one can assume that, during its duration, the desorbed protonated lecithin remains at the organic side of the interface. Thus, the surface concentration of the desorbed lecithin can be calculated from the passed charge q

$$\Gamma_{HL^+_{(o)}}(t,E) = q/F \qquad (5)$$

The equilibrium in step 3 in mechanism 1 is given by the ratio of the rate constants k_1 and k_2 of desorption and adsorption, which for a linear adsorption isotherm is equal to the ratio of the surface concentrations

$$\Gamma_{HL^+_{(o)}}(t,E)/\Gamma_{HL^+}(t,E) = k_1/k_2 \qquad (6)$$

In contrast to the charge-transfer reaction, the adsorption/desorption process does not involve transfer of ions from one phase to the other one. If the adsorbed ions penetrate only a small distance from the interface, the electrical driving force for ion desorption will include only a part of the overall potential difference, $x\Delta^w_o\phi$, where x denotes the position of the adsorbed

ions.[10,11] Thus, the potential dependence of the rate constants can be defined as

$$k_1 = k_s \exp[\alpha x F(E - E^0)/RT] \quad (7)$$

$$k_2 = k_s \exp[-\beta x F(E - E^0)/RT] \quad (8)$$

where α and β are the charge-transfer coefficients. The potential dependence of the rate constant ratio can be expressed as

$$k_1/k_2 = \exp[(\alpha + \beta)xF(E - E^0)/RT] \quad (9)$$

3.2. Mechanism with a Follow-up Reaction. Mechanism 1 does not involve possible follow-up reactions of the protonated form of lecithin $HL^+_{(o)}$ in the organic phase. It can be assumed that the acid−base equlibrium of the protonated form of lecithin in the organic phase can be established due to the high amount of water (0.11 M) in 1,2-DCE. This equilibrium can be influenced by reaction of a proton with the anion of the organic base electrolyte. The existence of an equilibrium is accounted for by adding step 4 to mechanism 1:

$$L^{\pm}_{(o)} \overset{1}{\rightleftarrows} L^{\pm}_{(ads)} + H^+_{(w)} \overset{2}{\rightleftarrows} HL^+_{(ads)} \overset{3}{\rightleftarrows} HL^+_{(o)} \overset{4}{\rightleftarrows} H^+_{(o)} + L^{\pm}_{(o)} \quad (10)$$

The passed charge q in eq 5 now corresponds to the sum

$$\Gamma_{HL^+_{(o)}}(t,E) + \Gamma_{L^{\pm}_{(o)}}(t,E) = q/F \quad (11)$$

The dissociation constant K_o of step 4 together with eq 11 can be used to calculate the concentration of the protonated form of lecithin in the organic phase:

$$\Gamma_{HL^+_{(o)}}(t,E) = (c_{H^+_{(o)}}(E)q/F)/(K_o + c_{H^+_{(o)}}(E)) \quad (12)$$

where $c_{H^+_{(o)}}(E)$ is the concentration of protons at the organic side of the interface. This concentration can be calculated using the Nernst equation and the formal potential of proton transfer $\Delta^w_o\phi^0_{H^+} = 0.55$ V.[9] Formal introduction of the reaction layer thickness to convert surface concentrations in the organic phase into volume concentrations is senseless because these terms cancel in the expression for the equilibrium of step 4 in mechanism 10.

Analysis of experimental data using the above equations requires that the surface concentration of $H^+_{(w)}$, $\Gamma_{H^+}(E)$, introduced in eq 3 is estimated. In the first approximation this concentration can be calculated from the surface charge density q_w obtained from ac impedance data of the base electrolyte system. These data were analyzed using a simple Randles type equivalent circuit. Plots of the double-layer capacitance C_{dl} versus the potential difference E for 0.01 or 0.1 M HCl in water and 0.01 M TBATPB in 1,2-DCE or 0.01 M HCl and 0.01 M TBATPBCl are shown in Figure 3, curves a, b, and c, respectively. The potential dependences of the surface charge density q_w plotted in Figure 3, curves d−f, were calculated supposing that the potential of zero charge E_{pzc} coincides with the potential of the minimum of C_{dl}.

Both mechanisms 1 and 10 were used to analyze the voltammograms of lecithin desorption at different experimental conditions. The difference in mechanisms 1 and 10 lies in the evaluation of the concentration $\Gamma_{HL^+_{(o)}}(t,E)$ of the protonated form of lecithin in the organic phase. For mechanism 1, $\Gamma_{HL^+_{(o)}}(t,E)$ is calculated from eq 5 while, for mechanism 10, it is calculated from eq 12. The surface concentration of H^+ in the aqueous phase was calculated in both cases from $\Gamma_{H^+}(E) = q_w/F$. The potential dependence of the ratio of the rate constants k_1/k_2 calculated from eq 6 was approximated by eq 9. Only solutions yielding E^0 close to the peak potential E_p were taken into account. One can expect that the current maximum occurs at a potential where the rate constants of desorption and adsorption are equal. According to eq 9 this occurs for $E = E^0$.

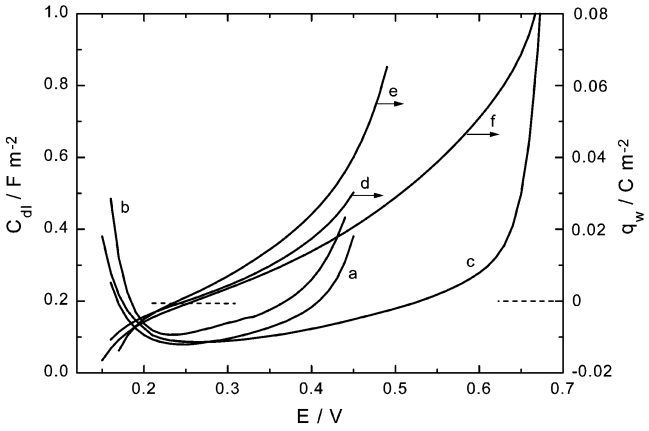

Figure 3. Double-layer capacitance C_{dl} and the surface charge density q_w of the base electrolyte system. Organic phase (1,2-DCE): (a, b, d, e) 0.01 M TBATPB; (c, f) 0.01 M TBATPBCl. Aqueous phase: (a, c, d, f) 0.01 M HCl; (b, e) 0.1 M HCl. C_{dl} minimum: (a) 0.25; (b) 0.23; (c) 0.26 V.

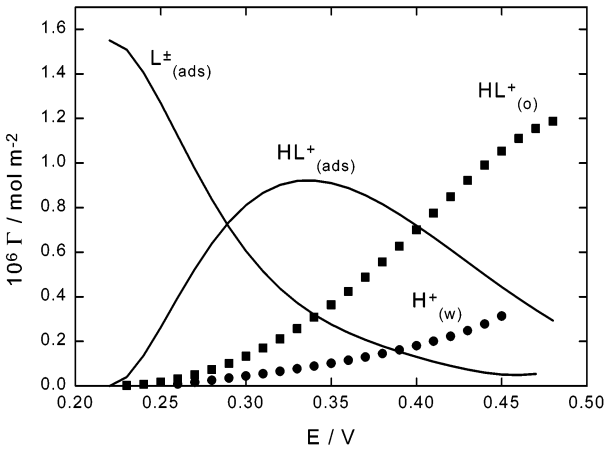

Figure 4. Surface concentration of $L^{\pm}_{(ads)}$ and $HL^+_{(ads)}$ calculated according to mechanism 1: (■) $\Gamma_{HL^+_{(o)}}(t,E) = q/F$; (●) $\Gamma_{H^+}(E) = q_w/F$. Experimental data are given in Figure 2, curves a and c.

3.3. Base Electrolyte TBATPB. The results of the calculation for 0.01 M HCl in water (voltammogram a, Figure 2) are plotted in Figures 4−6. The surface concentrations $\Gamma_{L^{\pm}}(t,E)$ and $\Gamma_{HL^+}(t,E)$ calculated according to mechanism 1 are shown in Figure 4. The surface concentration of the desorbed lecithin $\Gamma_{HL^+_{(o)}}(t,E)$ (points ■ in Figure 4) was calculated from the passed charge q (curve c, Figure 2). The surface concentration of H^+ (points ● in Figure 4) was derived from the surface charge density q_w for $E > 0.25$ V (curve d, Figure 3). The ratio of the rate constant k_1/k_2 calculated from eq 6 is shown in Figure 5, points ■. Application of eq 9 yields $E^0 = 0.402$ V ($E_p = 0.41$ V) and $(\alpha + \beta)x = 0.46$ (Figure 5, curve a). A small deviation of k_1/k_2 from the straight line in the log scale observed at potentials below 0.27 V indicates that close to the potential of zero charge E_{pzc} the surface charge density q_w does not correspond to $\Gamma_{H^+}(E)$. This is understandable, because $\Gamma_{H^+}(E)$ can hardly be zero or negative. The values of $\Gamma_{HL^+}(t,E)$ and $\Gamma_{L^{\pm}}(t,E)$ (Figure 4) at potentials close to E_{pzc} were calculated using eqs 6, 4, and 3; the potential dependence of the ratio log k_1/k_2 was extrapolated to $E = 0.22$ V. The dissociation constant

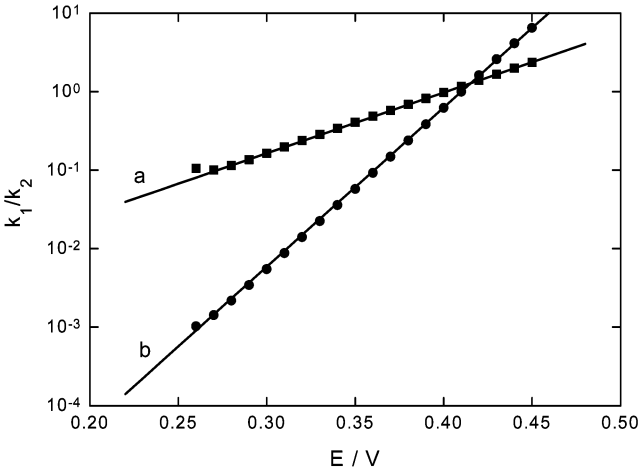

Figure 5. Potential dependence of the rate constant ratio k_1/k_2 calculated according to mechanisms 1 [■, a] and 10 [●, b]. Points (■, ●) were calculated by eq 6 for the experimental data in Figure 2, curves a and c. The fit (a, b) was by eq 9.

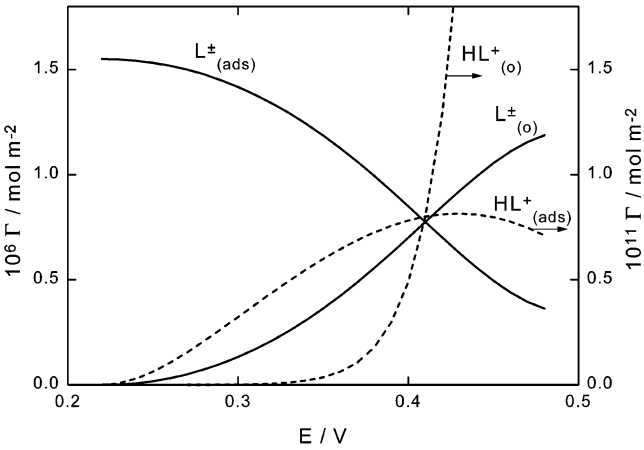

Figure 6. Surface concentration of $L^{\pm}_{(ads)}$, $HL^{+}_{(ads)}$, $L^{\pm}_{(o)}$, and $HL^{+}_{(o)}$ calculated according to mechanism 10 for pK_w = 1.7. Experimental data are given in Figure 2, curves a and c.

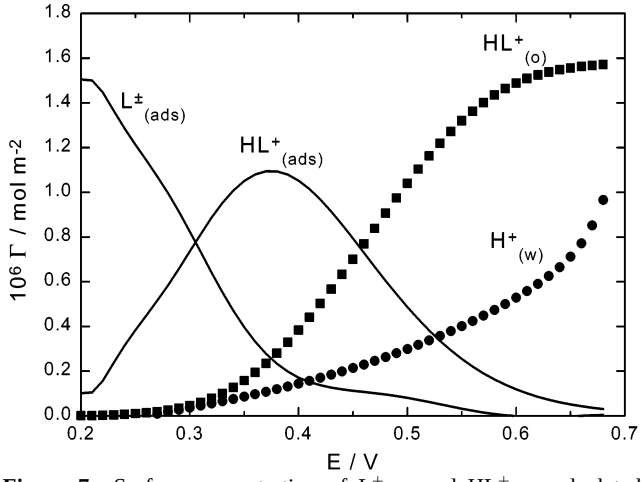

Figure 7. Surface concentration of $L^{\pm}_{(ads)}$ and $HL^{+}_{(ads)}$ calculated according to mechanism 1: (■) $\Gamma_{HL^{+}_{(o)}}(t,E) = q/F$; (●) $\Gamma_{H^+}(E) = q_w/F$. Experimental data are given in Figure 2, curves b and d.

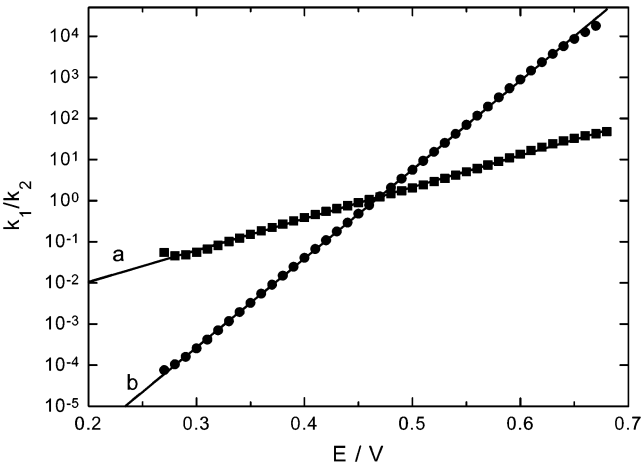

Figure 8. Potential dependence of the rate constant ratio k_1/k_2 calculated according to mechanisms 1 [■, a] and 10 [●, b]. Points (■, ●) were calculated by eq 6 for the experimental data in Figure 2, curves b and d. The fit (a, b) was by eq 9.

K_w (eq 3) is invariant in the whole potential range, and its value $K_w = 3.3 \times 10^{-8}$ mol m^{-2} corresponds to pK_w = 7.5.

Analysis of the voltammogram according to mechanism 10 does not provide the dissociation constants K_w and K_o but only their ratio $K_o/K_w = 33$ m^{-1}. The potential dependence of the ratio log k_1/k_2 (points ●, Figure 5) does not change in the range of K_w between 1×10^{-5} and 1 mol m^{-2}. Fit by eq 9 (curve b, Figure 5) yields $E^0 = 0.41$ V and $(\alpha + \beta)x = 1.2$. These data and pK_w = 1.7 found for the phosphate group of dimyristoyl phosphatidylethanolamine[12] were used to calculate the surface concentrations of $L^{\pm}$ and HL^{+} shown in Figure 6.

The positions of the voltammetric peaks of lecithin desorption/adsorption depend on the pH of the aqueous phase, because production of the protonated form of lecithin (reaction mechanisms 1 and 10, step 2) depends on the H^+ concentration. The forward peak potential of the voltammogram shifts by 0.06 V to less positive potentials ($E_p = 0.35$ V) if 0.01 M HCl in water is replaced by 0.1 M HCl. Analysis of the voltammogram using eqs 1−6 and 9 (mechanism 1) yields the same value of $K_w = 3.3 \times 10^{-8}$ mol m^{-2} as with 0.01 M HCl. Fit of eq 9 to the potential dependence of the ratio of the rate constants k_1/k_2 calculated from eq 6 yields $E^0 = 0.34$ V and $(\alpha + \beta)x = 0.47$. Analysis of the same voltammogram according to mechanism 10 yields $E^0 = 0.347$ V, $(\alpha + \beta)x = 1.08$, and the dissociation constants' ratio $K_o/K_w = 34$ m^{-1}. The surface concentration of $\Gamma_{H^+}(E) = q_w/F$ was derived in both analyses from the surface charge density q_w in 0.1 M HCl (Figure 3, curve e).

3.4. Base Electrolyte TBATPBCl. The shift of the voltammetric peaks of 0.06 V to positive potentials is observed when TBATPB is replaced by TBATPBCl without changing the concentration of HCl in the aqueous phase (Figure 2, curves a and b). This can be explained in terms of the proposed mechanisms by a decrease of the surface concentration of H^+. Indeed, the surface charge density q_w derived from the ac impedance measurement at potentials positive to E_{pzc} is lower in TBATPBCl than in TBATPB (curves f and d in Figure 3). Analysis of the voltammogram shown in Figure 2, curve b, using eqs 1−6 (mechanism 1) supposing that surface concentration $\Gamma_{H^+}(E)$ equals q_w/F (points ● in Figure 7), gives $K_w = 3.2 \times 10^{-8}$ mol m^{-2} and the k_1/k_2 potential dependence (points ■ in Figure 8). Fit of the log k_1/k_2 potential dependence (curve a in Figure 8) by eq 9 yields $E^0 = 0.457$ V and $(\alpha + \beta)x = 0.455$. The value of E^0 is close to the peak potential $E_p = 0.47$ V. The value of $(\alpha + \beta)x$ is close to that obtained in TBATPB, but the deviation of log k_1/k_2 from the straight line is larger than that in TBATPB. The surface concentration of the desorbed lecithin $\Gamma_{HL^{+}_{(o)}}(t,E)$ (points ■, Figure 7) was calculated from the passed charge q (curve d, Figure 2). Concentrations of $\Gamma_{HL^+}(t,E)$ and $\Gamma_{L^{\pm}}(t,E)$ (Figure 7) were calculated using a linear fit to the log k_1/k_2 potential dependence (curve a, Figure 8).

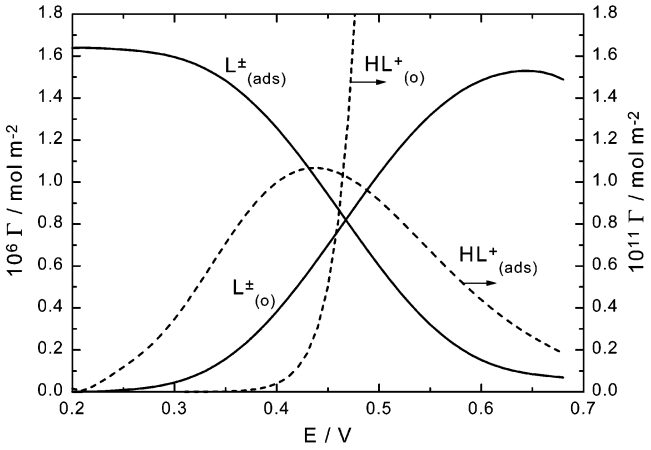

Figure 9. Surface concentration of $L^{\pm}_{(ads)}$, $HL^{+}_{(ads)}$, $L^{\pm}_{(o)}$, and $HL^{+}_{(o)}$ calculated according to mechanism 10 for $pK_w = 1.7$. Experimental data are given in Figure 2, curves b and d.

Analysis of the voltammogram according to mechanism 10 yields $E^0 = 0.465$ V, $(\alpha + \beta)x = 1.28$, and the ratio of dissociation constants $K_o/K_w = 225$ m^{-1}. These data and the value of $pK_w = 1.7$ (see above) were used to calculate the surface concentrations of $L^{\pm}$ and HL^{+} shown in Figure 9.

The value of the dissociation constant $pK_w = 7.5$ obtained in the analysis of the voltammograms both in TBATPB and TBATPBCl according to mechanism 1 is much higher than the expected value, <3.[12] Also, the value of $(\alpha + \beta)x$ close to 0.5, indicating that the position of the polar group of adsorbed lecithin should be located close to the midpoint of the potential difference across the interface,[10,11] that is, in the organic phase, contradicts the general concept of the lecithin monolayer structure. This concept assumes that the polar head of lecithin penetrates into the water phase, similarly as at the water|air interface.[13]

The significant change of $(\alpha + \beta)x$ from 0.5 to a value close to 1 is observed both in TBATPB and TBATPBCl when the acid−base equilibrium of desorbed lecithin in the organic phase is assumed. Even when dissociation constants cannot be inferred from the present results, their ratio $K_o/K_w = 33$ m^{-1} obtained in TBATPB indicates that the acidity of the protonated form of lecithin is higher in the organic phase than in the adsorbed state. The value of $K_o/K_w = 225$ m^{-1} obtained in TBATPBCl is even higher. This increase indicates that in the system with TBATPBCl the proposed mechanism (eq 10) may be more complicated. The surface concentration of $\Gamma_{HL^+}(t,E)$ can be affected by adsorption of $TPBCl^-$, which can compensate the positive charge of the adsorbed $HL^{+}_{(ads)}$. Adsorption of $TPBCl^-$ can be expected due to a decrease of the interfacial tension when TBATPB in 1,2-DCE is replaced by TBATPBCl (Figure 10). Adsorption of $TPBCl^-$ may be coupled with a surface reaction involving a cation present in the aqueous phase. The effect of the surface reaction can be observed in acidic medium at an aqueous electrolyte drop electrode (Figure 11). The product of this reaction is evidently HTPBCl,[14] which is insoluble in the organic phase and, due to the drop-shaped interface, moves up along the surface to the top of the drop electrode, where it accumulates and leaves the drop by forming a plume. The plume is observed at potentials positive to 0.4 V. In the presence of lecithin this reaction is enhanced and the plume begins to appear at about 0.3 V. It should be noted that the plume formation is not visible at a horizontal and flat interface, because the product of the surface reaction is not removed from the interface. Similar behavior is exhibited by other hydrophobic anions, such as tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($TPBCF^{3-}$) and

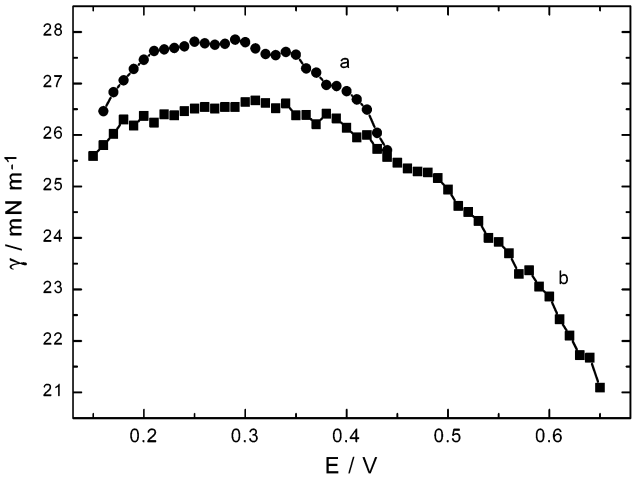

Figure 10. Surface tension γ at the 0.01 M LiCl in water and (a) 0.01 M TBATPB or (b) 0.01 M TBATPBCl in 1,2-DCE interface.

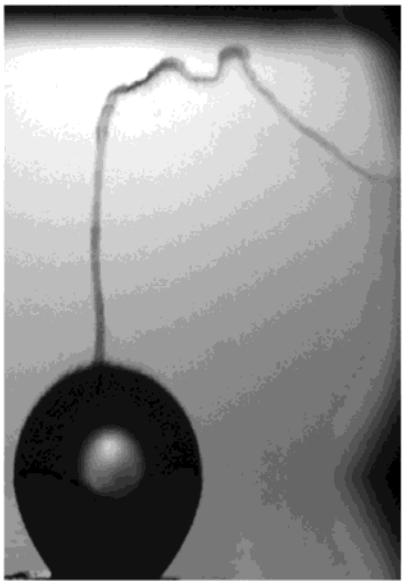

Figure 11. Formation of HTPBCl at the aqueous electrolyte drop electrode. Organic phase: 0.01 M TPBATPBCl. Aqueous phase: 0.01 M HCl. Applied potential: $E = 0.4$ V.

3,3′-como-bis(undecahydro-1,2-dicarba-3-cobalta-*closo*-dodecabor)ate (DCC^-). The lower rate of the formation of HTPB compared to that of HTPBCl[14] makes its effect on the acid−base equilibrium step 4 in mechanism 10 negligible in the time scale of the present experiments.

4. Conclusions

Two mechanisms of lecithin adsorption at a liquid|liquid interface have been proposed. Analysis of voltammograms according to the mechanism involving the acid−base equilibrium reaction of lecithin in the organic phase provides more reliable results. The acidity of lecithin seems to be higher in the organic phase than in the aqueous phase. However, the apparent increase of the dissociation constant ratio in the system with TBATPBCl is evidently due to the presence of another follow-up reaction in the organic phase in which unsoluble HTPBCl is formed. This reaction is enhanced by desorption of the protonated form of lecithin. After a proton is released, the zwitterionic form of lecithin is restored and can again adsorb. The overall mechanism is transfer of a proton from the aqueous to the organic phase. This is an example of the lecithin proton-

pump. The rate of this reaction increases with the increasing potential difference across the interface.

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