

Electrode Potential Induced Reorientation of a Phospholipid Monolayer on a Mercury Electrode Surface

Shaowei Chen and Héctor D. Abruña*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

Received April 25, 1994. In Final Form: July 5, 1994[⊗]

Rapid scan cyclic voltammetry has been employed to probe the potential induced transitions of a dioleoylphosphatidylcholine (diOPC) monolayer deposited onto a mercury surface. By employing two different types of electrodes, a hanging mercury drop electrode (HMDE) and a mercury-film-coated gold electrode (J-electrode), we were able to deposit the diOPC monolayer in tails-down and heads-down fashion, respectively. Comparison of the results for these two deposition methods suggests that the tails-down structure is the more stable one at potentials of up to -0.80 V. Cycling of the potential to about -1.20 V for the electrode with the monolayer deposited in a heads-down fashion results in a complete reorientation of the monolayer to a tails-down configuration. We have studied this process in the presence of halides and find that whereas the onset of this process is independent of the halide, the rate depends strongly on the identity of the halide. We have, in addition, studied the pH and temperature dependencies of this transition. Finally, we propose a tentative mechanism for this transition.

Introduction

Phospholipid monolayers have been employed extensively as models for actual biological membranes in the study of membrane structural transitions and membrane transport.¹⁻⁴ Such studies have involved a variety of techniques such as X-ray diffraction and reflectivity measurements,⁵⁻⁸ infrared⁹⁻¹¹ and Raman spectroscopies,¹² electrochemistry,^{4,13,18-24} and electron microscopy.¹⁴⁻¹⁷ Due to their high mechanical stability and their strong resistance to applied potentials, electrochemistry has proven to be an effective method to investigate the electrical properties of these model membranes, in combination with Langmuir-Blodgett or self-assembly techniques. As the phospholipid molecules are generally charged, and their charge is a function of pH, there have been numerous studies geared at the understanding of the electrical properties of phospholipid layers especially as a function of pH, ionic strength, and electrolyte

composition.^{4,13,18-24} One of the basic aims of these studies has been a correlation of membrane function with its electrical properties.

Recently, Nelson has employed electrochemical techniques to study potential-induced structural changes/reorientation of phospholipid monolayers adsorbed onto a hanging mercury drop electrode.¹⁹ The electrochemical responses exhibited two well-defined peaks which were ascribed to the flipping of the monolayer and the formation of the bilayer, respectively, based on the model he proposed which involved a "flipping" of the apolar tails and the polar heads so that the monolayer goes from tails down to heads down followed by the formation of a bilayer, thus exposing half of the electrode surface to the solution.²¹ The observed electrochemical responses, especially the double layer capacitance vs potential, can then be interpreted, according to this model. He also carried out simulations of the proposed potential induced reorientation of the phospholipid monolayer.²³ In all of these studies, the monolayer initially had a tails-down structure so that the apolar hydrocarbon tails were in contact with the mercury surface.

Here we report an electrochemical study of dioleoylphosphatidylcholine (diOPC, Figure 1) monolayers adsorbed onto mercury surfaces with an initial heads-down structure. We find that the voltammetric response for such a system evolves from one that is quite different to one that is virtually identical to that reported by Nelson.

We have also carried out studies where deposition of the monolayer was carried out under potential control and in the presence of halide anions or in the absence of any electrolyte. In addition, we have investigated the

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1994.

(1) Blank, M.; Miller, I. R. *J. Colloid Interface Sci.* **1967**, *26*, 26.
 (2) Phillips, M. C.; Chapman, D. *Biochim. Biophys. Acta* **1968**, *163*, 301.
 (3) Ghosh, D.; Williams, M. A.; Tinoco, J. *Biochim. Biophys. Acta* **1973**, *291*, 351-362.
 (4) Sakurai, I.; Kawamura, Y. *Biochim. Biophys. Acta* **1987**, *904*, 405-409.
 (5) Kjaer, K.; Als-Nielsen, J.; Laxhuber, L. A.; Möhwald, H. *Phys. Rev. Lett.* **1987**, *58* (21), 2224-2227.
 (6) Als-Nielsen, J.; Christensen, F.; Pershan, P. S. *Phys. Rev. Lett.* **1982**, *48*, 1107.
 (7) Breslau, A.; Deutsch, M.; Pershan, P. S.; Bohr, J. *Phys. Rev. Lett.* **1985**, *54*, 114.
 (8) Eisenberger, P.; Marra, W. C. *Phys. Rev. Lett.* **1981**, *46*, 1981.
 (9) Duevel, R. V.; Corn, R. M.; Liu, M. D.; Leidner, C. R. *J. Phys. Chem.* **1992**, *96* (1), 468-73.
 (10) Hunt, R. D.; Mitchell, M. L.; Dluhy, R. A. *J. Mol. Struct.* **1989**, *214*, 93-109.
 (11) Dluhy, R. A.; Wright, N. A.; Griffiths, P. R. *Appl. Spectrosc.* **1988**, *42* (1), 138-41.
 (12) Mendelsohn, R.; Taraschi, T.; van Holten, R. W. *J. Raman Spectrosc.* **1979**, *8* (5), 279-83.
 (13) Liu, M. D.; Leidner, C. R.; Facci, J. J. *J. Phys. Chem.* **1992**, *96* (7), 2804-2811.
 (14) Neuman, R. D.; Ferestehkhou, S.; Ovalle, R. J. *Colloid Interface Sci.* **1984**, *101* (2), 309-313.
 (15) Fischer, A.; Sackmann, E. *J. Phys.* **1984**, *45* (3), 517-27.
 (16) Cornell, D. G.; Carroll, R. J. *Colloids Surf.* **1983**, *6* (4), 385-93.
 (17) Reinhardt-Schlegel, H.; Kawamura, Y.; Furuno, T.; Sasabe, H. *J. Colloid Interface Sci.* **1991**, *147* (2), 295-306.

(18) Britten, J. S.; Blank, M. *Bioelectrochem. Bioenerg.* **1977**, *4*, 209-216.

(19) Nelson, A.; Benton, A. *J. Electroanal. Chem.* **1986**, *202*, 253-270.

(20) Nelson, A.; Auffret, N. *J. Electroanal. Chem.* **1988**, *244*, 99-113.

(21) Nelson, A.; Leermakers, F. A. M. *J. Electroanal. Chem.* **1990**, *278*, 73-83.

(22) Nelson, A.; Auffret, N.; Borlakoglu, J. *Biochim. Biophys. Acta* **1990**, *1021*, 205-216.

(23) Leermakers, F. A. M.; Nelson, A. *J. Electroanal. Chem.* **1990**, *278*, 53-72.

(24) Nelson, A. *J. Chem. Soc., Faraday Trans.* **1993**, *89* (15) 2799-2805.

(25) Terrettaz, S.; Vogel, H.; Grätzel, M. *J. Electroanal. Chem.* **1992**, *326*, 161-176.

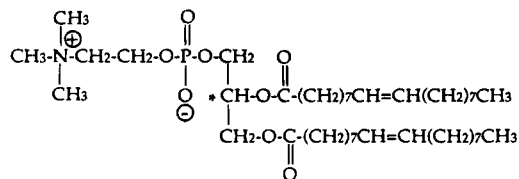


Figure 1. Molecular structure of L- α -dioleoylphosphatidylcholine (diOPC).

effects of pH and temperature on this process and finally propose a mechanism for these potential-induced conformational changes of the diOPC monolayer under the above mentioned conditions.

Experimental Section

1. Materials. Dioleoylphosphatidylcholine (diOPC) was used as received from Fluka. Solutions of 0.2 mg of diOPC per mL of chloroform were prepared just prior to use.

Electrolyte solutions were prepared with ultrapure salts (Aldrich) which were at least 99.99+% pure. These were dissolved (0.20 M) in water which was purified with a Millipore Milli-Q system and buffered with high-purity phosphate or acetate salts or hydrochloric acid depending on the desired pH.

2. Equipment. Electrochemical experiments were carried out with an EG&G PARC 173 potentiostat and 175 universal programmer. Data were collected on a Nicolet 4094 digital oscilloscope and transferred to a personal computer for analysis using Sigma Plot.

A sodium-saturated calomel electrode (SSCE) was used as a reference electrode and a large area platinum coil was used as a counter electrode. A two-compartment cell without frits was employed in all experiments. The cell had standard joints for all electrodes and for degassing.

3. Electrodes. Two types of electrodes were employed. A Kemula type (micrometer driven) hanging mercury drop electrode (HMDE) was used to obtain a monolayer with the tails-down orientation as described in ref 19.

The second type of electrode (J-electrode) consisted of a mercury-film-coated gold disk sealed in a J-shaped piece of glass tubing. The mercury thin film was obtained either by electrochemical deposition from a mercury solution (eg. $\text{Hg}(\text{NO}_3)_2$) or by simple immersion into a high-purity mercury pool (electronic grade, 99.9998% from Johnson Matthey). From electrolytic dissolution of the deposited mercury we estimate a thickness of approximately 100 equivalent monolayers of mercury.

4. Monolayer Deposition. In the case of the HMDE, the procedure was similar to that described in ref 19. The electrode was slowly lowered into the electrochemical cell containing degassed (for at least 30 min using high-purity nitrogen that was additionally passed through oxygen and hydrocarbon traps from MG Industries) electrolyte onto which a measured volume of the chloroform solution of the diOPC had been spread dropwise with a microliter syringe so as to achieve a monolayer coverage. The chloroform was allowed to evaporate (15 min) prior to immersion of the electrode. After deposition, the electrode was maintained below the solution level to preclude further deposition.

In the case of the J-electrode, it was hung vertically into a beaker containing degassed electrolyte which was placed on a high precision laboratory jack. Subsequently, a monolayer coverage of diOPC over the solution surface was achieved by the same procedure as described above. The deposition was effected by slowly lowering the jack manually so that the J electrode passed the electrolyte surface slowly and the monolayer was deposited onto the mercury thin film surface with the polar heads down. Afterward the electrode was transferred to the electrochemical cell containing degassed electrolyte where voltammetric measurements were carried out.

We should mention that in both cases the systems were under a nitrogen flow throughout the entire procedure and the deposition process was carried out at open circuit. In order to investigate the effects of the electrical properties of the mercury-water interface on the deposition of the diOPC monolayer, we also carried out experiments where the deposition was under potential control or where the deposition was carried out in degassed pure water without any electrolyte. In the case of

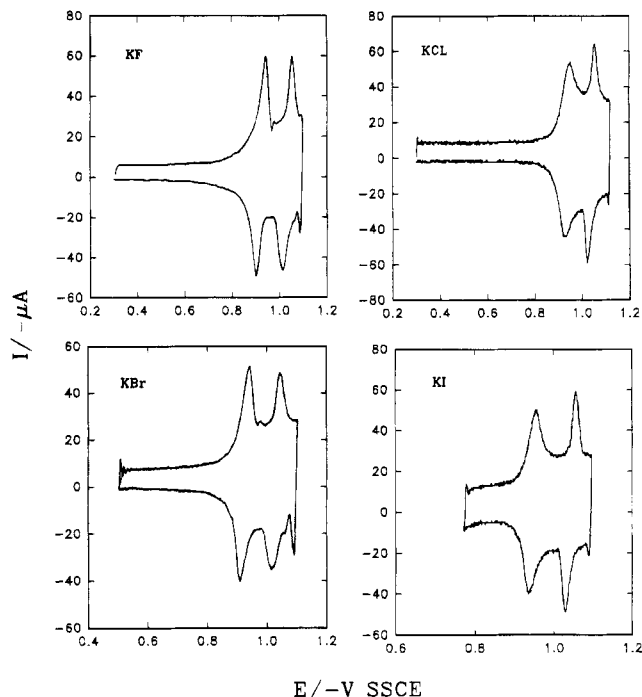


Figure 2. Cyclic voltammograms of diOPC monolayers on HMDE (area = $2.20 \pm 0.05 \text{ mm}^2$) in 0.20 M KX (X = F^- , Cl^- , Br^- , and I^-) in phosphate buffer (pH = 8.5). Scan rate = 100 V/s. (Initial scan and steady-state scans are virtually identical.)

deposition under potential control, the applied potentials were kept close to, or negative of, the corresponding point of zero charge (E_{pzc}) for the mercury electrode in contact with the various anions. The specific applied potentials employed for the different anions were as follows: F^- , -0.50 V ; Cl^- , -0.60 V ; Br^- , -0.70 V ; I^- , -0.80 V (all vs SSCE).

In terms of the temperature effects on the reorientation process, we have carried out a series of experiments in 0.20 M KCl with 0.01 M K_2HPO_4 - KH_2PO_4 (pH 6.7) by varying the solution temperature from 7 to 36 °C. Here the identical open circuit deposition procedure was followed at room temperature (21 °C). After the deposition, the electrode was transferred to an electrochemical cell (with degassed electrolyte) which had been placed into an Allied water circulation pool (Fisher Scientific Model 800). At least 10 min was allowed to achieve a temperature equilibrium between the electrolyte and the monolayer before the electrochemical measurements were carried out.

Results and Discussions

1. Effect of Halides. (a) Deposition at Open Circuit. We begin with a description of the voltammetric responses for the diOPC monolayers deposited at open circuit in the presence and absence of halide-containing electrolytes. As can be ascertained from Figures 2 and 3, the steady-state ($v = 100 \text{ V/s}$) cyclic voltammetric responses are very similar for both the HMDE and J-electrode with the appearance of two well-defined peaks at about -0.9 and -1.0 V , respectively. The precise potential values at which these peaks appear are a function of the identity of the halides, and these aspects will be discussed further on. As mentioned earlier, the HMDE case corresponds to the tails-down structure of the monolayer while the J-electrode corresponds, initially, to the heads-down structure. Thus, in order to account for the similar steady-state responses from initially different orientations on the mercury surface, one might suspect that after some number of scans, either monolayer experiences a total reorientation from one structure into the other.

In order to test for the possibility of such a reorientation process, we focused on the initial voltammetric scans. As

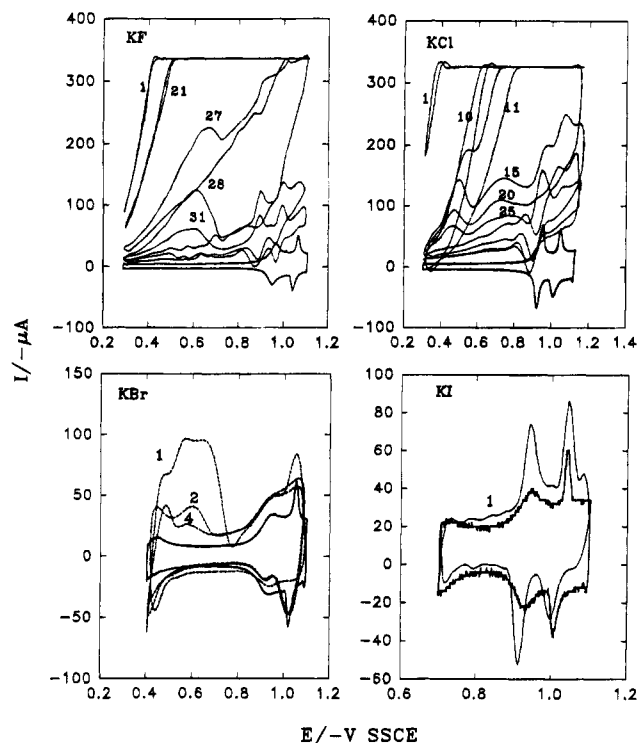


Figure 3. Initial scans (dashed lines) of cyclic voltammograms of diOPC monolayers deposited at open circuit on a J electrode in 0.20 M potassium halides (KX) buffered with 0.02 M K_2HPO_4 (pH = 8.5). Numbers shown are the scan numbers. Sweep rate = 100 V/s except for KF, 50 V/s. Corresponding steady-state scans are shown as solid lines.

can be seen in Figure 2, in the case of the HMDE even the first scan exhibited the twin-peak feature while the J-electrode exhibited dramatically different behavior. As can be ascertained from Figure 3, the first scans did not show anything resembling the twin-peak feature. However, and as mentioned earlier, the responses eventually evolved into the twin peaks. In the case of J-electrode there is clearly a structural reorientation of the monolayer which is ascribed as being due to a change from a heads-down to a tails-down configuration. Thus, it appears that the heads-down structure represents a metastable state which is driven into the more stable tails-down configuration through potential scanning. The fact that for the HMDE, where the monolayer is initially in the tails-down configuration, the twin-peak response is observed even for the very first scan is consistent with the above arguments.

We looked further into the details of this conformational change by acquiring the first 100 voltammetric scans and observing the time evolution of the voltammetric profiles. This was additionally done in the presence and absence of KF, KCl, KBr, and KI. We find that in the presence of KF, the transition was quite sluggish requiring about 30 scans for the transition to be complete, whereas in the presence of KI, even the initial scan showed the twin-peak feature. In the presence of KCl and KBr the behavior was intermediate between the two extremes represented by KF and KI. In the time evolution of the voltammetric profiles, some transient peaks were observed between -0.50 and -0.80 V, which were tentatively ascribed to halide adsorption/desorption processes on the mercury surface.

As mentioned earlier, for the studies just described for the J-electrode, the deposition was carried out at open circuit and in the presence of the various halides. Thus, it was anticipated that prior to deposition of the diOPC

monolayer, the mercury surface might have been actually covered by a layer of adsorbed halide. We have also performed studies where the deposition step was carried out in the absence of halides and the electrode was subsequently placed in halide-containing solution. The voltammetric results from this series of experiments were qualitatively very similar to those described earlier where the deposition of the phospholipid monolayer was carried out in the presence of halides. Here we should note that the point of zero charge (E_{pzc}) of the mercury/diOPC interface is approximated to be -0.44 V (vs SSCE).¹⁹ Prior to halide diffusion into this interface, the open circuit potential would be approximately equal to the corresponding E_{pzc} , which is much more positive than the E_{pzc} 's of Hg electrode in the presence of specific adsorption of halides: F^- , 0.47; Cl^- , -0.51 ; Br^- , -0.58 ; I^- , -0.73 V (all vs SSCE).²⁶ Thus, it was believed that halides diffused into the polar head/Hg interface, through edge or defect sites, due to electrostatic interaction and/or hydrogen bonding, and consequently in both instances the diOPC monolayer was on top of the halide adlayer with stabilization being provided, in part, by the interactions between the polar head groups and the adsorbed halide layer.

The above argument is also supported by the observation that the potentials of the desorption peaks shift positively as the desorption proceeds. As the negatively charged halides are desorbed from the electrode interface through potential sweeping, the interfacial potential would become increasingly positive and, hence, the positive shift of the corresponding desorption peaks.

If such a model was an apt description of the system, one might expect that the halide adlayer could help initiate the reorientation process once the potential was swept negative of the E_{pzc} since in that potential regime the halide anions would be desorbed, leaving the mercury surface available for direct interaction with the diOPC molecules. Since at potentials close to the point of zero charge the mercury surface is hydrophobic, it would be reasonable to have a transition so that the hydrocarbon tails, rather than the polar head groups, would be in direct contact with the mercury surface. Thus we believe that the initial scans reflect such a flipping process of the diOPC molecules from heads down to tails down.

(b) Deposition under Potential Control. In order to further ascertain the role of the state of charge of the mercury surface on the above-mentioned transition, we have carried out studies with the J-electrode where the deposition of the diOPC monolayer was under potential control and in the presence of halides. In this case the applied potentials were -0.50 , -0.60 , -0.70 , and -0.80 V (vs SSCE) in the presence of F^- , Cl^- , Br^- , and I^- , respectively, all at 0.20 M concentration in phosphate buffers (pH 7.5–8.5). In all cases the applied potentials were chosen to be close to or more negative than the potential of zero charge so as to preclude adsorption of the halide prior to deposition of the diOPC monolayer. In this series of experiments, and for all the halides, the first scans of cyclic voltammograms exhibited the twin-peak feature (Figure 4), just like for the HMDE. This suggests that instead of there being a specific interaction of the halide with the monolayer, the reorientation process is more likely controlled by the direct interaction of the surface with the diOPC molecules. However, in order to achieve such direct interaction, a sufficiently negative potential must be applied so as to preclude adsorption of the halides and thus the dependence of the reorientation

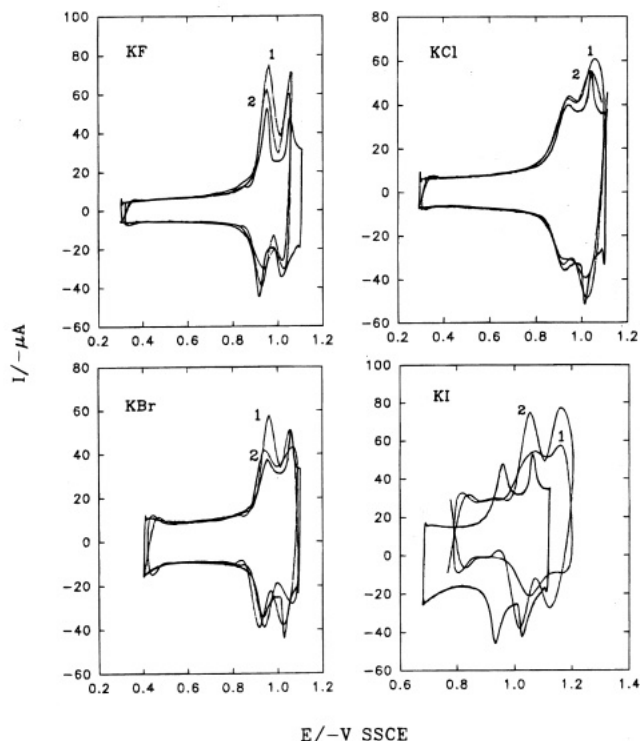


Figure 4. Initial scans (dashed lines) of cyclic voltammograms of diOPC monolayers deposited under potential control on a J electrode in 0.20 M KX/0.02 M K_2HPO_4 (pH = 7.5–8.5). Applied potentials for the different halides were as follows: F^- , -0.50; Cl^- , -0.6; Br^- , -0.70; I^- , -0.80 V vs SSCE. Numbers shown are the scan numbers. Scan rate = 100 V/s. Steady-state scans are shown as solid lines.

process on the potential applied during deposition, particularly in the presence of halides.

To account for the above described phenomena, one could consider two possibilities. On one case, one could postulate that after the monolayer was brought into contact with the electrolyte solution, the molecules rearranged into the tails-down structure prior to electrochemical interrogation such that the developing (breaking-in) process observed after deposition at open circuit (in the presence or absence of halides) could be attributed to desorption of the halides. This possibility can be eliminated by considering the results of a blank experiment where the identical procedure (except for monolayer adsorption) was followed. Under these conditions the cyclic voltammogram only showed featureless double layer current, even in the first scans. Compared to the rather sharp desorption peaks observed in the presence of the diOPC monolayer, this would imply that the deposited monolayer could actually enhance the adsorption of the halide species onto the mercury surface perhaps due to the interactions between the positively charged nitrogen of the polar head groups and the anionic halides.

The other possibility (Figure 5) is that initially the system is in a high (metastable) energy state as the polar head groups of the diOPC are in contact with the virtually hydrophobic mercury surface left by the desorbed halide species while the apolar hydrocarbon tails are exposed to the ionic solution (state I). As the potential is scanned negatively, the electrostatic repulsion between the negative electrode surface and the hydrated polar head groups increases (recall that the pH is about 8 where the diOPC is present in the zwitterionic form) so that the molecules are repelled from the electrode surface, probably in the form of activated clusters (state II). However, since this intermediate structure alters the energetic state within the monolayer, it could initiate a cooperative process

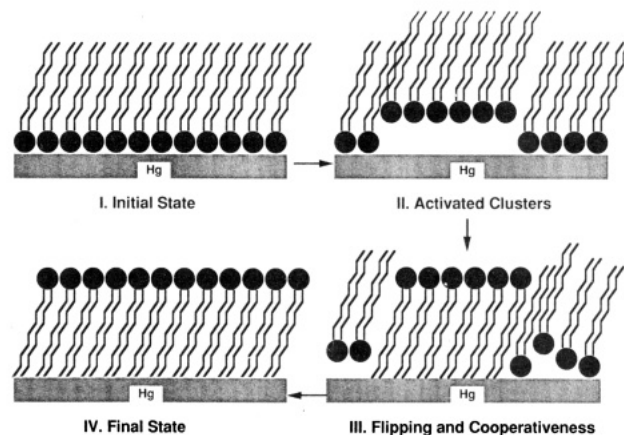


Figure 5. Proposed mechanism for the structural reorientation of diOPC monolayer on a mercury surface from heads-down to tails-down fashion.

(perhaps in a process akin to nucleation) with the neighboring molecules (state III) until all of them were reoriented into the tails-down structure (state IV) and thus subsequently behaved as a tails-down monolayer.

The relative rate of the reorientation process in the presence of halides is a bit perplexing since, based on the strength of adsorption, one would have predicted that the process would have been fastest in the presence of fluoride and slowest in the presence of iodide. One could envision two possibilities, one based on the interaction of the halide with the monolayer rather than with the mercury and an alternative one based on the interfacial potential during deposition.

In the first case, one could postulate that the F^- ions with their strong solvation sphere, strong hydrogen bonding capability, and relatively small size might interact more strongly with the monolayer than iodide anions. These interactions would be intermediate for chloride and bromide, consistent with the experimental observation.

Alternatively, one could envision that the interfacial potential during the deposition process could affect the kinetics of the reorientation with a faster rate being observed for more negative potentials. If one assumes that at open circuit and in the presence of the halide electrolytes the potential of the electrode will essentially be the E_{pzc} , then the values would be proportionally negative for the sequence, $F^- > Cl^- > Br^- > I^-$, as shown earlier. Thus the monolayer deposited at the least negative potential (F^-) would exhibit the slowest reorientation rate whereas the fastest rate would be predicted for deposition in the presence of iodide as was experimentally found. We find that the latter explanation is more plausible especially in light of the results obtained for deposition at controlled potential.

2. pH Effect. To investigate the effects of the interfacial potentials as well as the electrical properties of the monolayer, we varied the solution pH and carried out similar experiments to those described above with the intent to comparing the developing process of the twin-peaks feature.

Here the solutions were 0.20 M KCl buffered with either phosphate or acetate buffers or hydrochloric acid over the pH range of 8.5–2.1. All other conditions were identical to those previously described. From the initial 100 scans of the voltammograms (Figure 6), we measured the area of the desorption peaks ($-\delta q$), which was assumed to be proportional to the amount of halides desorbed in one cycle of potential scanning. To calculate the total desorbed amount up to a given time, t , the integral (Q_t) from the first cycle was determined. These Q_t vs t plots were fitted

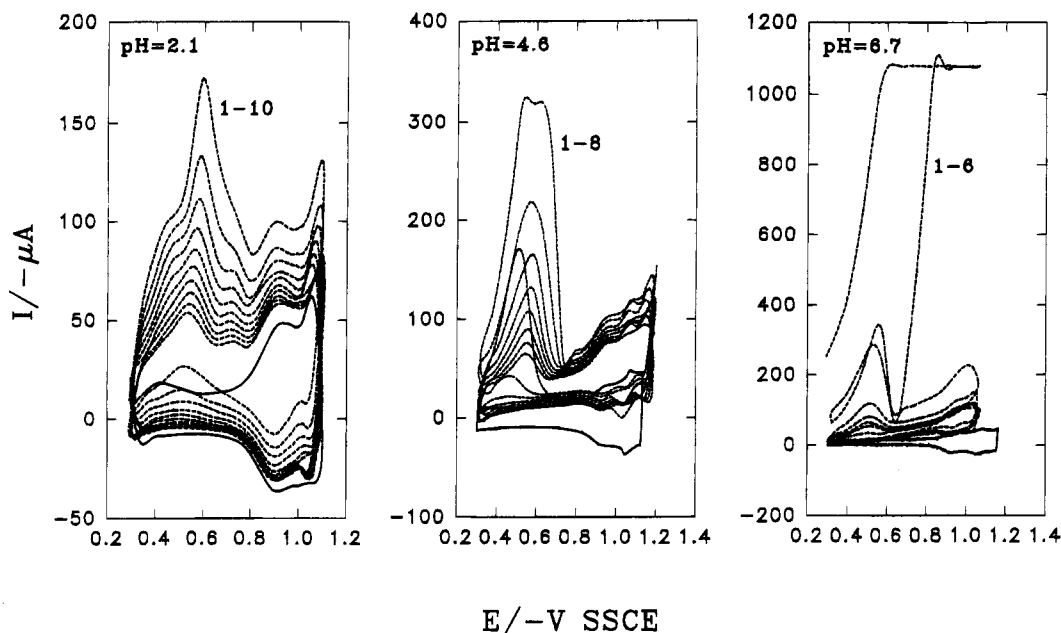


Figure 6. Initial scans (dashed lines) of cyclic voltammograms of diOPC monolayers in 0.20 M KCl buffered at different pH values. Numbers shown are the scan numbers. Scan rate = 100 V/s. Steady-state scans are shown as solid lines.

in order to obtain a mathematical expression describing the process and these were found to be of the form

$$Q_t = Q_0 \frac{t}{t + \tau} \quad (1)$$

where Q_0 is the total amount of halide initially adsorbed onto the electrode surface and τ is a constant depending on the particular system with units of time.

If Q_r is defined as the amount of halides remaining after desorption cycling for a time period t , then by conservation of mass we obtain that

$$Q_t = Q_0 - Q_r \quad (2)$$

From eqs 1 and 2, we can get

$$Q_0 - Q_r = Q_0 \frac{t}{t + \tau} \quad (3)$$

from which we can derive

$$1 - \theta = \frac{t}{t + \tau} \quad (4)$$

where $\theta = Q_r/Q_0$ is the fractional coverage. This last expression is essentially equivalent to eq 1. Figure 7b presents $(1 - \theta)$ data as a function of pH and is immediately apparent that there is an excellent correspondence between the data (symbols) and the fits (solid lines). From eq 4, θ can also be expressed as

$$\theta = \frac{\tau}{t + \tau} \quad (5)$$

Thus, we can obtain an expression for the kinetics of the desorption process

$$-\frac{d\theta}{dt} = \frac{\theta^2}{\tau} \quad (6)$$

which indicates that the desorption is second order with respect to fractional coverage. We should also note that τ is the time for half of the halides to be desorbed from the interface, that is, the half-life.

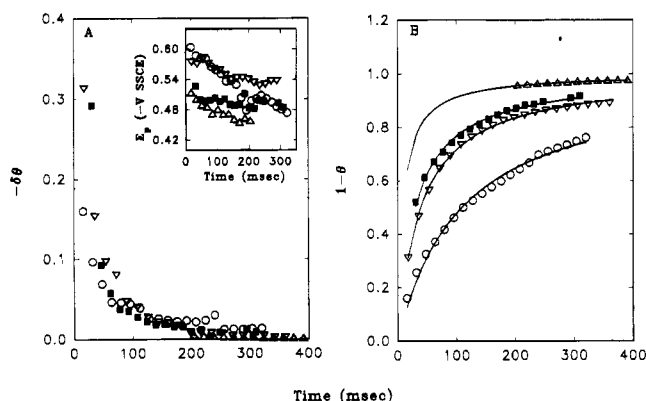


Figure 7. Effect of pH on the surface coverage of chloride (a, $-\delta\theta$; b, $1 - \theta$) as a function of the potential scanning (time, t). Inset shows the shift in the desorption peak potentials during the desorption/reorientation processes: O, pH = 2.1; ∇ , pH = 4.6; \blacksquare , pH = 6.7; Δ , pH = 8.5.

From the above derivation and eq 5, the amount of halides desorbed during a given cycle ($n - 1$ to n) should be

$$-\delta\theta = \frac{\tau t_0}{[\tau + (n - 1)t_0](\tau + nt_0)} \quad (7)$$

with t_0 being the period of one cycle and n the number of cycles so that $t = nt_0$. Such an expression indeed fits the data presented in Figure 7a quite well (not shown). Thus the desorption process is consistent with the above kinetic scheme over the pH range of 2.1–8.5.

It is worth speculating as to the possible physical origin of the second-order dependence of the process on fractional coverage. If one assumes that the halide forms a relatively compact layer and that the diOPC molecules occupy bridgelike positions between two adsorbed halides, then one of the more favorable processes would be for two halides to be desorbed so that the diOPC molecules can contact the mercury surface directly. Although this would be plausible and consistent with experimental observation, we must reiterate that we have no direct experimental evidence in support of this.

Table 1. Half-Life of Chloride Desorption as a Function of Solution pH^a

pH	τ (ms)	pH	τ (ms)
2.1	109	6.7	30
4.6	40	8.5	10

^a The solutions were 0.20 M KCl buffered with 0.05 M Na₂HPO₄ (pH = 8.5), 0.025 M Na₂HPO₄-0.025 M NaH₂PO₄ (pH = 6.7), 0.01 M NaAc-HAc (pH = 4.6) or HCl (pH = 2.1).

Data for the desorption kinetics are presented in Table 1 where one can observe that there is a dramatic increase in the decay rate with increasing pH with the half-life (τ) decreasing by an order of magnitude from 109 at pH = 2.1 to 10 at pH = 8.5 (the corresponding rate constant, $1/\tau$, increases with an order of magnitude). We believe that these changes are likely due to the more negative electrode solution interface as the pH is increased. As we mentioned earlier, the more negative interfacial potential would tend to drive the reorientation process more quickly. Here we should note that at pH values much higher than the phosphate pK_a ($pK_{a, \text{phosphate}} = 1.4^{20}$), the polar head groups of the diOPC molecules are neutral although with a significant dipole moment due to its zwitterionic character (Figure 1). At lower pH, in the vicinity of the pK_a of the diOPC molecule, there would be a significant fraction of the polar head groups which would be positively charged instead of neutral. The presence of a significant number of positively charged species could give rise to a number of effects, including a different packing density or even the formation of a different phase. In addition, and perhaps more importantly, is that because of electrostatic attraction, the species that are positively charged will interact much more strongly with the electrode surface at negative potentials. Such an interaction would have to be overcome in order for the reorientation process to take place, thus giving rise to a significantly lower rate as observed. At pH = 2.1, the rate constant is about 1 order of magnitude lower than at higher pH values. This might be accounted for by considering the above mentioned interactions between the positively charged molecules and the negatively charged electrode. Such interactions will likely affect the formation of activated clusters which we believe are essential for the reorientation process. At higher pH, a less significant difference is observed which might be due to the fact that the charged state of the polar head groups of the monolayer molecules is quite similar.

Here one should also note the pH effect on the positive shift of the desorption peaks. As can be seen in Figure 7, there is a general trend of peak positions vs potential scanning where the peak positions shifted positively as more and more negatively charged halide species were desorbed from the electrode interface as a result of the interfacial potential change. However, some differences over this pH range can still be observed. It can be seen that the effect is more significant at low pH, say, pH = 2.1, than that in the higher pH range, which is consistent with the above argument. As discussed above, at low pH, there could be a significant fraction of phospholipid molecules which are charged. Thus the interfacial potential would be more sensitive to the desorption/reorientation process as now charges were involved, in contrast to the cases at higher pH where the phospholipid molecules were in the neutral, zwitterionic form, although with a large dipole.

3. Temperature Effect. We have also investigated the temperature dependence of the reorientation process (Figure 8). A similar procedure to that described in the previous section was followed in analyzing the desorption kinetics. The general expression of eq 1 was again found appropriate for the particular system studied here (Figure

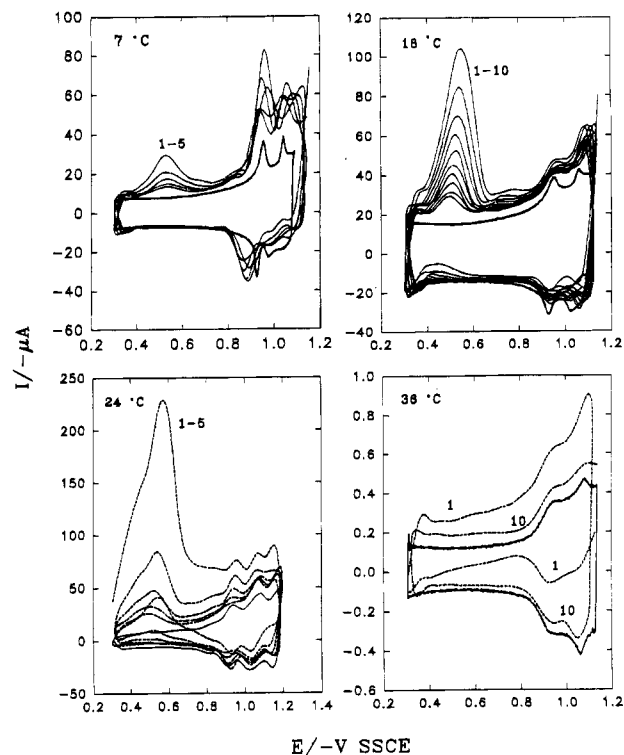


Figure 8. Initial scans (dashed lines) of cyclic voltammograms of diOPC monolayers in 0.20 M KCl/0.01 M K₂HPO₄-KH₂PO₄ (pH = 6.7) at different temperatures. Numbers shown are the scan numbers. Scan rate = 100 V/s. Steady-state scans are shown as solid lines.

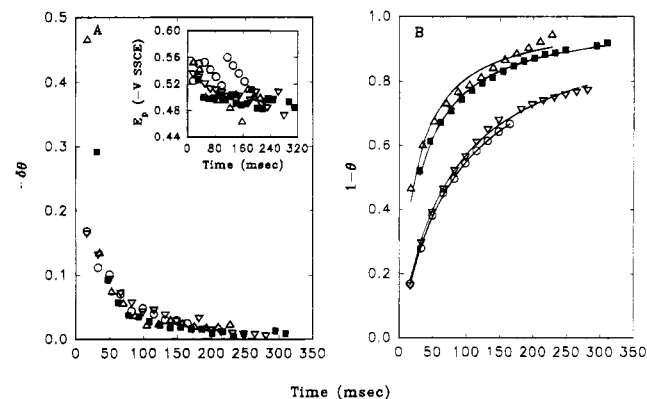


Figure 9. Effect of temperature on the surface coverage of chloride (a, $-\delta\theta$; b, $1 - \theta$) as a function of the potential scanning (time, t). Inset shows the shift in the desorption/reorientation peak potentials during the desorption/reorientation processes: \circ , $T = 7^\circ\text{C}$; ∇ , $T = 18^\circ\text{C}$; \blacksquare , $T = 21^\circ\text{C}$; \triangle , $T = 24^\circ\text{C}$.

9), which implied that within this temperature range the kinetics of the desorption process was still second order. However, one can find that as the temperature is increased, there is a slight effect on the desorption rate and the development of the twin peaks. In the voltammograms in Figure 8, one can see that the decay rate of the desorption current around -0.58 V is accelerated with an increase in temperature from 7°C to room temperature (21°C) and to 24°C . At even higher temperature, 36°C , even the first scan showed the twin-peak feature with no significant desorption current. Clearly, the higher temperature facilitated the desorption of the halide species, likely because the diOPC monolayer became less rigid such that it was physically easier for the halides to leave the electrode surface.

From Table 2, one can see the increasing trend of the desorption rate constants as a function of temperature.

Table 2. Temperature Effect on the Decay Rate of the Desorption Process in the System of 0.20 M KCl Buffered with 0.01 M K_2HPO_4 - KH_2PO_4 (pH 6.7)

temperature (°C)	τ (ms)	temperature (°C)	τ (ms)
7	82	24	24
18	75	36	
21	30		

However, the effect is less significant than that of pH, most probably because the temperature range under study is above the main transition temperature ($T_m = -7^\circ C^{27}$) of the diOPC molecules. Consequently the fluidity of the monolayer within this temperature would be very similar, giving rise to only a slight difference in the desorption processes as observed.

As to temperature effects on the desorption peak positions, again one can see that as the desorption proceeds, the peaks shift positively, just as expected from the previous discussion. However, within this temperature range, only small differences were observed, most probably due to the fact that charged state of the phospholipid molecules is not very sensitive to temperature.

Conclusions

We have employed rapid scan cyclic voltammetry to investigate structural transitions of diOPC monolayers on a mercury surface. Our observations suggest that the tails-down structure of the diOPC monolayer is energetically more favorable than the heads-down orientation. A mechanism is proposed to account for the structural reorientation from the heads-down to the tails-down configuration, which involves a cooperative process during the transition. Even though the onset of this reorientation process, from a heads-down to a tails-down fashion, is independent of the electrolyte species, its kinetic behavior is the combined result of many factors, such as the specific halide species, the temperature, and pH of the solutions. In the desorption/reorientation processes, the interfacial potential shifts positively, which is consistent with the interfacial structural changes as more and more negatively charged halide species are desorbed from the electrode surface. It was found that this phenomenon was independent of halide species, pH, or temperature of the working solutions. Based on fits to the data, the des-

orption/reorientation process was found to be second order with respect to fractional coverage within the temperature and pH ranges studied here. Some differences of the kinetic parameters were observed which were found consistent with the specific experimental conditions. These effects are summarized below:

(1) The reorientation rate of the monolayer increases in the order $F^- < Cl^- < Br^- < I^-$. This might be accounted for by the fact that the corresponding interfacial potentials were more negative, due to their specific points of zero charge (E_{pzc}), as the desorption of the halide, and thus the developing of the twin-peaks feature due to monolayer reorientation, is believed to be strongly affected by the interfacial potential. This conclusion is consistent with the mechanism proposed since the more negative the interfacial potential, the more easily state II can proceed, which is essential for the entire process.

(2) The reorientation rate is not very sensitive to pH when it is above the pK_a for diOPC. We ascribe this to the fact that the change in the interfacial electric effects will not be very dramatic nor will the changes in the charged state of the polar head groups of the deposited monolayer. However, at pH values close to the pK_a of the monolayer, dramatic effects were observed which were ascribed to attractive interactions between the positively charged molecules in the monolayer and the negatively charged electrode surface.

(3) Temperature has a moderate effect on the desorption/reorientation process when it is above the corresponding main transition temperature due to the similarity of the molecular fluidity. With an increase in temperature, the desorption process and thus the generation of the twin-peak feature was accelerated. As the charged state of the phospholipid molecules was not very sensitive to temperature, small differences were observed in the shift of the desorption peak positions within this temperature range under study.

We are continuing our investigations of this system by electrochemical and X-ray scattering techniques and results from these studies will be reported elsewhere.

Acknowledgment. This work was supported by the National Science Foundation through Grant DMR-9107116. The authors acknowledge the assistance from Mr. F. Ronning in collecting data. Discussions with Mr. H. S. Yee are gratefully acknowledged.

(27) Castelli, F.; Raciti, G. *Thermochim. Acta* **1991**, *186*, 205-215.