Proton transfer across a liquid-liquid interface facilitated by phospholipid interfacial films

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Modelling of certain interactions occurring at biological cell membranes is one important aspect of studies of interfaces between two immiscible electrolyte solutions (ITIES). The formation of phospholipid films formed by L-α-dipalmitoylphosphatidylcholine (DPPC) at the water-organic solvent interfaces and some properties of these films have previously been studied electrochemically, using two-phase liquid systems composed of a weakly acidic aqueous electrolyte solution and an electrolyte solution in 1,2-dichloroethane [1,2]. Cyclic voltammetric measurements and determination of surface tension at the interface have led to the formulation of a five-step mechanism for the formation of a DPPC layer at the interface and for its interactions with the components of the two phases [1],

\[
\begin{align*}
\text{L}^\pm(\text{o}) & \rightleftharpoons \text{L}^\pm(\text{ads}) + \text{H}^+(\text{w}) \\
& \rightleftharpoons \text{HL}^+(\text{ads}) \\
& \rightleftharpoons \text{HL}^+(\text{o}) + \text{A}^-(\text{o}) \\
& \rightarrow \text{HLA}(\text{o}) \\
& \rightarrow \text{HA}(\text{o}) + \text{L}^\pm(\text{o}).
\end{align*}
\] (1)

In the first step, the DPPC zwitterion L\(^\pm\) present in the organic phase (\(\text{o}\)), is adsorbed at the interface, attaining an adsorption steady state or equilibrium. Subsequently it undergoes an acid-base interaction with the hydrogen ions present in the aqueous phase (\(\text{w}\)), which leads to a steady state or even an equilibrium in the adsorbed state (step 2). The protonated form attains an adsorption/desorption steady state or equilibrium in step 3 and then it takes part in homogeneous reactions in the organic phase. These reactions (steps 4 and 5) involve the organic base anion, \(\text{A}^-\), and lead first to the formation of ion pair HLA\(_{(\text{o})}\) and then to regeneration of the DPPC zwitterion which can again be adsorbed at the interface, regardless of the potential difference across it.

In view of the general importance of controllable proton transfer across interfaces (see, e.g., modelling of biological membranes, or numerous technological applications), the present paper is concerned with a more detailed study of the crucial steps of mechanism [3]. To be able to estimate their rates in relation to some experimental parameters, an attempt is made at formulation of a simplified mathematical model and at a comparison of the computed values with the experimental data.

It is demonstrated that the theoretical and experimental values match semiquantitatively, supporting the proposed mechanism, and that the critical parameter is rate constant of step 5. Therefore, it can be assumed that the regeneration of the DPPC zwitterion is the reaction rate determining step in the whole five step cycle.

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