Ion transfer of weak acids across liquid|liquid interfaces

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A B S T R A C T

The main purpose of this paper is to develop a model for the ion transfer of weak acids across liquid|liquid interfaces including ion pairing and non-ideal electrolyte solutions to calculate the half-wave potential. The main equation derived in this model allows the simulation of different chemical systems, comprising multiple acid-base equilibria, hydrophilic and hydrophobic neutral weak acids, and different anions, including ion-pair formation in the organic phase. Hence, several representative chemical systems are analysed in detail in order to demonstrate the usefulness of the model. In addition, simple criteria to evaluate the presence of ion-pairs in the organic phase as well as the calculation of the apparent ion-pair formation constants are included.

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1. Introduction

The transfer of protonated species across liquid|liquid interfaces is reported in several experimental works in the literature [1–7]. In many of these studies, the transfer of weak acids and bases has been found to depend on the pH of the aqueous phase and on their partition coefficient [8–39]. In particular, the transfer of ions of weak acids has been extensively studied using experimental techniques in several works since the beginning of research in the area [19,22,28,40–60]. A theoretical approach for modelling the transfer of weak acids and weak bases across liquid|liquid interfaces was developed by several authors [21,25,33,34,38,61,62].

Girault and coworkers [19] proposed complete potential–pH diagrams of weak acids and bases at liquid|liquid interfaces based on the equiconcentration boundaries as a function of the interfacial Galvani potential difference and the aqueous pH. These ionic partition diagrams were calculated by taking into account the thermodynamic equilibria governing the distribution of the various acidic and basic forms of the molecules involved in the transfer. Therefore, the diagrams define the domains of predominance of each species either in the aqueous or in the organic phase, and they offer a global and direct visualisation of all the transfer mechanisms [1–5,7]. In recent years, a large number of ionisable drugs, such as acids, bases, ampholytes or zwitterionic species, have been characterized using these ionic partition diagrams, showing the usefulness of the methodology [18–20,22,26,46–51,56,58,59,63–73]. However, due to the assumptions involved in the model [19], these diagrams do not reproduce satisfactorily the boundary lines where two processes coexist. Additionally, they do not include ion pairing, or the effect of non-ideality of electrolyte solutions.

In a recent paper, we developed a model for the facilitated proton transfer or protonated species transfer across liquid|liquid interfaces including ion pairing to calculate the half-wave potential [74]. This paper discussed extensively the effect of ion pairing on the domains of the potential–pH diagrams. The main purpose of the present work is to generalize the model for the ion transfer of weak acids across liquid|liquid interfaces, including ion pairing (IP) and non-ideal electrolyte solutions (NIES). The main equation derived in this model allows the simulation of different chemical systems, comprising multiple acid-base equilibria, hydrophilic and hydrophobic neutral weak acids, and different anions, including ion-pair formation in the organic phase. Hence, several representative chemical systems are analysed in detail in order to demonstrate the usefulness of the model. In addition, simple criteria to evaluate the presence of ion-pairs in the organic phase as well as the calculation of the apparent ion-pair formation constants are included.

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1.1. Theory

In order to derive the current-potential equation for ion transfer of weak acids across liquid|liquid interfaces, the following suppositions are made:

a) The interface between the aqueous and the organic phase is stationary and planar.
b) Both phases contain enough inert electrolytes so that migration of the transferring ion can be neglected.
c) The rates of the acid-base association and dissociation processes are sufficiently large in comparison with the corresponding diffusion rates, so that it may be assumed that acid-base association and dissociation are at equilibrium even when current is flowing.
d) The transfer of all species through the interface is reversible and diffusion controlled. The diffusion occurs in the x coordinate, normal to the interface. The interface is defined at $x = 0$.
e) Double layer effects and adsorption are not considered in the model, as well as acid dissociation constant change between the bulk and the interface.
f) The distribution constant of the neutral weak acid H_nA does not depend on the potential applied and is defined by: $K_{D,H_nA} = \frac{a^o_{H_nA}}{a^w_{H_nA}}$.
g) All the charged species are perturbed by the potential applied to the interface and depend on the Nernst equation.
h) The diffusion coefficients in one phase are the same for all species. Of course, this assumption is not real for the H^+ in the aqueous phase, but it is necessary to apply Matsuda's approach [75]. This assumption allows an important simplification of the mass balance equations which may in this way be reduced to standard mass transport equations, similar to Fick's laws for the total concentrations. Furthermore, the electrochemical signal in the limiting current region is always controlled by the diffusion of the weak acid species in aqueous buffered solutions.
   i) The total buffer concentration is higher than the total weak acid concentration so that the $pH[= -\log(a^w_{H^+})]$ value is constant.
   j) Ion-pair formation is considered only in the organic phase. Ion-pair association and dissociation are at equilibrium even when current is flowing, since the rates of the ion-pair association and dissociation processes are sufficiently high in relation to the corresponding diffusion rates. Bulk concentration of the counterion of the supporting electrolyte is much higher than that of the transferred anionic species.
   k) Free H^+ transfer is negligible in the potential range where the ion transfer of weak acids is observed and the free proton activity in the organic phase is also negligibly small.

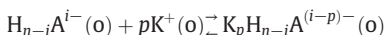The acid-base equilibria of the weak acid are the following:

$$H_{n-i}A^{i-} \overset{\rightarrow}{\underset{\leftarrow}{}} H^+ + H_{(n-i-1)}A^{(i+1)-}.$$

The i-acid dissociation constant in the α phase is defined by:

$$K^\alpha_{a,(i+1)} = \frac{a^\alpha_{H_{(n-i-1)}A^{(i+1)-}} a^\alpha_{H^+}}{a^\alpha_{H_{n-i}A^{i-}}} \tag{1}$$

for $i = 0, \ldots n$. and $\alpha = $ organic phase (o) or aqueous phase (w).

The ion-pair equilibria of the anionic species with the cation (K^+) of the supporting electrolyte in organic phase are the following:

$$H_{n-i}A^{i-}(o) + pK^+(o) \overset{\rightarrow}{\underset{\leftarrow}{}} K_pH_{n-i}A^{(i-p)-}(o)$$

where the net charge of the ion-pair $(i-p)$ may not be necessarily zero [76]. The overall ion-pair association constant is defined by:

$$K^o_{K_pH_{n-i}A^{(i-p)-}} = \frac{a^o_{K_pH_{n-i}A^{(i-p)-}}}{a^o_{H_{n-i}A^{i-}}\left(a^o_{K^+}\right)^p}. \tag{2}$$

The distribution of charged species at the interface is defined by the following Nernst equation:

$$\frac{c^o_{species}(0,t)}{c^w_{species}(0,t)} = \frac{\gamma^w_{species}}{\gamma^o_{species}} \exp\left[\frac{z_{species}F}{RT}\left(\Delta^w_o\phi - \Delta^w_o\phi^o_{species}\right)\right], \tag{3}$$

for species = H^+ or $H_{n-i}A^{i-}$ (for $i = 1 \ldots n$), $c^\alpha_{H_{n-i}A^{i-}}(0,t)$ the i-anionic species concentration and $c^\alpha_{H_{n-i}A^{i-}}(0,t)$ the proton concentration at the interface ($x = 0$) at any time. $\Delta^w_o\phi^o_{H^+}$ is the standard transfer potential of the H^+ species, $\Delta^w_o\phi^o_{H_{n-i}A^{i-}}$ is the standard transfer potential of the i-anionic species and $\gamma^w_{species}$ and $\gamma^o_{species}$, are the activity coefficients of charged species in the aqueous and organic phase, respectively.

The diffusion equation for the total weak acid is defined by Fick's laws:

$$\frac{\partial c^\alpha_{H_nAtot}}{\partial t} = D^\alpha \frac{\partial^2 c^\alpha_{H_nAtot}}{\partial x^2} \tag{4}$$

where the diffusion coefficients (D^α) are assumed to be the same for all species in each phase (assumption (h)).

The total concentration of H_nA is defined by the mass balance equation in each phase:

$$c^w_{H_nAtot} = c^w_{H_nA} + \sum_{i=1}^n c^w_{H_{n-i}A^{i-}} \tag{5}$$