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.

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.

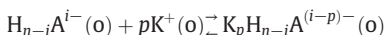The acid-base equilibria of the weak acid are the following:

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

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 $i = 0, \dots n$. 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:

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

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 $i = 1 \dots n$), $c^\alpha_{H_{n-i}A^{i-}}(0,t)$ 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:

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

$$c^o_{H_nAtot} = c^o_{H_nA} + \sum_{i=1}^{n} c^o_{H_{n-i}A^{i-}} + \sum_{i=1}^{n}\sum_{p=1}^{i} c^o_{K_pH_{n-i}A^{(i-p)-}}. \tag{6}$$

According to the boundary conditions, the flux of species across the interface is expressed by:

$$D^w \frac{\partial c^w_{H_nAtot}(0,t)}{\partial x} = D^o \frac{\partial c^o_{H_nAtot}(0,t)}{\partial x} = f_{H_nAtot}(t). \tag{7}$$

The total interfacial concentrations are expressed as a function of the convolution integrals using Laplace transforms [77,78]:

$$c^w_{H_nAtot}(0,t) = c^{w,*}_{H_nAtot} - \frac{1}{(\pi D^w)^{\frac{1}{2}}} \int_0^t \frac{f_{H_nAtot}(\tau)d\tau}{(t-\tau)^{\frac{1}{2}}} = c^{w,*}_{H_nAtot} - \frac{J(t)}{(D^w)^{\frac{1}{2}}} \tag{8}$$

$$c^o_{H_nAtot}(0,t) = c^{o,*}_{H_nAtot} + \frac{1}{(\pi D^o)^{\frac{1}{2}}} \int_0^t \frac{f_{H_nAtot}(\tau)d\tau}{(t-\tau)^{\frac{1}{2}}} = c^{o,*}_{H_nAtot} + \frac{J(t)}{(D^o)^{\frac{1}{2}}} \tag{9}$$

where $c^{a,*}_{H_nAtot}$ being the total concentration of weak acid in the α-phase at $t = 0$ and for all x values and are defined as follows:

$$c^{w,*}_{H_nAtot} = c^w_{H_nA}(x,0) + \sum_{i=1}^{n} c^w_{H_{n-i}A^{i-}}(x,0) \tag{10}$$

$$c^{o,*}_{H_nAtot} = c^o_{H_nA}(x,0) + \sum_{i=1}^{n} c^o_{H_{n-i}A^{i-}}(x,0) + \sum_{i=1}^{n}\sum_{p=1}^{i} c^o_{K_pH_{n-i}A^{(i-p)-}}(x,0). \tag{11}$$

The total initial concentration of all species in each α phase may be calculated at $t = 0$ as a function of the total initial concentration of weak acid ($c^{init}_{H_nA}$) introduced into the electrochemical cell before the experiment [20,21,61,62]:

$$c^{init}_{H_nA} = c^w_{H_nAtot}(x,0) + c^o_{H_nAtot}(x,0) = c^{w,*}_{H_nAtot} + c^{o,*}_{H_nAtot}. \tag{12}$$

The total interfacial concentration of weak acid species in the system is obtained from Eqs. (8) and (9) eliminating the convolution integrals:

$$c^*_{H_nAtot} = c^w_{H_nAtot}(0,t) + \xi c^o_{H_nAtot}(0,t) \tag{13}$$

where $\xi = (\frac{D^o}{D^w})^{\frac{1}{2}}$.

By using Eq. (13) it is possible to obtain all the concentration values at the interface at all simulation times.

By numerical integration of the convolution integrals:

$$J(t) = (D^w)^{\frac{1}{2}}\left[c^{w,*}_{H_nAtot} - c^w_{H_nAtot}(0,t)\right] \tag{14}$$

it is possible to know the total current-potential response of the system:

$$I(t) = FAf_{H_nAtot}(t). \tag{15}$$

1.1.1. Activity coefficients

Electrolyte solutions are non-ideal, with an increasing shift from the ideal behaviour by increasing the concentration [79–86]. Local electrostatic effects are generally considered to be the major source of non-ideality in electrolyte solutions and they are taken into account by using activity co-efficients, γ_i, that can be calculated according to classical Debye-Hückel (DH) theory [87,88] or by Fraenkel's smaller-ion shell (SiS) model [89–93]. The latter model is a fundamental generalization of the DH theory that takes into account the different sizes of spherically symmetric charged species to calculate their activity coefficients. The activity coefficients for the different species are given by [91]:

$$\log(\gamma^\alpha_+) = -z_+^2 \frac{A_\alpha}{B_\alpha}\left(\frac{\kappa_\alpha}{1+\kappa_\alpha a_\alpha}\right)\left\{1 - \frac{2\exp[\kappa_\alpha(a_\alpha - b_{+,\alpha})] - \kappa_\alpha(a_\alpha - b_{+,\alpha}) - 2}{1 + \kappa_\alpha b_{+,\alpha}}\right\} \tag{16}$$

$$\log(\gamma^\alpha_-) = -z_-^2 \frac{A_\alpha}{B_\alpha}\left(\frac{\kappa_\alpha}{1+\kappa_\alpha a_\alpha}\right)\left\{1 - \frac{2\exp[\kappa_\alpha(b_{-,\alpha} - a_\alpha)] - \kappa_\alpha(b_{-,\alpha} - a_\alpha) - 2}{1 + \kappa_\alpha b_{-,\alpha}}\right\} \tag{17}$$

where $\kappa_\alpha = [\frac{8\pi\delta_\alpha\sigma_\alpha N_A}{10^3} \times I_\alpha]^{\frac{1}{2}}$; $I_\alpha = \frac{1}{2}\sum_i m_i z_i^2$; $\delta_\alpha = \frac{q_e^2}{4\pi\varepsilon_0\varepsilon_\alpha k_B T}$; $B_\alpha = [\frac{8\pi\delta_\alpha\sigma_\alpha N_A}{10^3}]^{\frac{1}{2}}$ and $A_\alpha = (\frac{\delta_\alpha}{2\ln 10})B_\alpha$. When the identity of the ions is defined in an experiment, the closest internuclear distances for the specific ions used in the ionic solution between cation-cation ($b_{+,\alpha}$), anion-anion ($b_{-,\alpha}$) and anion-cation (a_α) can be used to explicitly solve Eqs. (16) and (17). Recently, the activity coefficients of individual ions using an ionic liquid salt bridge inserted in a Harned cell have been experimentally determined by the group of Prof. Kakiuchi [94,95] and successfully contrasted with the theory of NIES developed by Prof. Fraenkel [89–93].

Without loss of generality, we consider that all ions have the same size, $a_\alpha = b_{+,\alpha} = b_{-,\alpha}$, in order to include the smallest set of parameters in the analysis to be carried out in the last section of this paper. In this sense, the expressions of the activity coefficients given by the DH theory are obtained [88,91]:

$$\log(\gamma_+^\alpha) = -z_+^2 \frac{A_\alpha}{B_\alpha} \left(\frac{\kappa_\alpha}{1 + \kappa_\alpha a_\alpha} \right) \tag{18}$$

$$\log(\gamma_-^\alpha) = -z_-^2 \frac{A_\alpha}{B_\alpha} \left(\frac{\kappa_\alpha}{1 + \kappa_\alpha a_\alpha} \right). \tag{19}$$

When the sizes of ions are experimentally available, Eqs. (16) and (17) can be easily included in the current model.

On the other hand, IP describes the association of oppositely charged ions in electrolyte solutions to form distinct chemical species called ion-pairs. Different treatment can be employed to describe the ion-pair activity coefficient depending on its overall charge [76,83,85,96–99]. A simple way to treat the overall charged ion-pair is to assign a mean ionic activity coefficient that is generally calculated on the basis of the overall charge of the cation and anion [84,85,100]. Considering an overall charged ion-pair constituted by one anion and one cation ($z_+ \neq z_-$), its mean ionic activity coefficient in the organic phase can be calculated by the following equation:

$$\log\left(\gamma_{\pm, \text{ion pair}}^o\right) = -|z_+ z_-| \frac{A_o}{B_o} \left(\frac{\kappa_o}{1 + \kappa_o a_o} \right). \tag{20}$$

This equation can be replaced by the following simplified expression: $\gamma_{\pm, \text{ion pair}}^o = \sqrt{\gamma_+^o \gamma_-^o}$.

It is important to remark that, an ion-pair of zero overall charge cannot be treated like a neutral molecule [76,85,96,101,102]. At best, it can be regarded as a dipolar molecule, but it is probably more closely related to a charge-separated ion. The activity coefficient of an ion-pair with zero overall charge is given by [85,96,101,102]:

$$\ln\left(\gamma_{\text{ion pair}}^o\right) = \left[\frac{V^{\text{intr}} \left(V^{\text{intr}} - V^0 \right)}{10^3 \kappa_T RT} \right] I_o \tag{21}$$

where V^{intr} is the sum of the intrinsic volumes of the cation and anion, V^0 is the standard partial molar volume of the electrolyte [85,101–108]; I_o is the ionic strength of the electrolyte in the organic phase and κ_T is the isothermal compressibility of the non-aqueous solvent [109,110].

1.1.2. Corrections by non-ideality for equilibrium constants

For simplicity, the apparent i-acid dissociation constants, $K_{a,i}^{'\alpha}$, in the α phase are defined by:

$$K_{a,(i+1)}^{'\alpha} = \left(\frac{\gamma_{H_{n-i}A^{i-}}^\alpha}{\gamma_{H_{(n-i-1)}A^{(i+1)-}}^\alpha \gamma_{H^+}^\alpha} \right) K_{a,(i+1)}^\alpha = \frac{c_{H_{(n-i-1)}A^{(i+1)-}}^\alpha c_{H^+}^\alpha}{c_{H_{n-i}A^{i-}}^\alpha} \tag{22}$$

and the apparent ion-pair association constants, $K_{K_p H_{n-i} A^{(i-p)-}}^{'o}$, are defined by:

$$K_{K_p H_{n-i} A^{(i-p)-}}^{'o} = \left[\frac{\gamma_{H_{n-i}A^{i-}}^o \left(\gamma_{K^+}^o \right)^p}{\gamma_{K_p H_{n-i} A^{(i-p)-}}^o} \right] K_{K_p H_{n-i} A^{(i-p)-}}^o = \frac{c_{K_p H_{n-i} A^{(i-p)-}}^o}{c_{H_{n-i}A^{i-}}^o \left(c_{K^+}^o \right)^p}. \tag{23}$$

In the case of the partition constant of the neutral species, K_{D,H_nA}, we assume that the activity coefficient in both phases ($\gamma_{H_nA}^w$ and $\gamma_{H_nA}^o$) are close to unity [84].

1.2. Half-wave potential as a function of pH

The mid-peak potential, $\Delta_o^w \phi_{\text{mid}}$, can be determined experimentally from cyclic voltammetry by a simple relationship between the peak potentials of the forward and reverse scans: $\frac{1}{2}(\Delta_o^w \phi_{\text{peak}}^{\text{forward scan}} + \Delta_o^w \phi_{\text{peak}}^{\text{reverse scan}})$. These potentials are reported in terms of the Galvani potential difference referred to an extra thermodynamic assumption. Such assumption is that the ion transfer standard Gibbs free energies of the anions and cations of tetraphenylarsonium tetraphenylborate are the same for all pairs of immiscible liquids [111]. The $\Delta_o^w \phi_{\text{mid}}$ value of the ion transfer not only highly depends on IP but also on non-ideality of electrolyte solutions. As a matter of fact, the term half-wave potential, $\Delta \phi_{1/2}$, has its origin in the polarography literature, where it represents the potential at half the limiting current from a sigmoidally shaped polarogram [112]. Considering that all the systems analysed in this work are electrochemically reversible and the transfer of charged species is a diffusion-controlled process, the mid-peak potential can be regarded as the $\Delta \phi_{1/2}$ [74].

For the half-wave potential, where $\Delta_o^w \phi = \Delta_o^w \phi_{1/2}$, the Nernst equation for H^+ species can be written as:

$$\Delta_o^w \phi_{1/2} = \Delta_o^w \phi_{H^+}^o + \frac{RT}{F} \ln \left[\frac{a_{H^+}^o \left(0, \Delta_o^w \phi_{1/2} \right)}{a_{H^+}^w \left(0, \Delta_o^w \phi_{1/2} \right)} \right] = \Delta_o^w \phi_{H^+}^o + \frac{RT}{F} \ln \left(\frac{\gamma_{H^+}^o}{\gamma_{H^+}^w} \right) + \frac{RT}{F} \ln \left[\frac{c_{H^+}^o \left(0, \Delta_o^w \phi_{1/2} \right)}{c_{H^+}^w \left(0, \Delta_o^w \phi_{1/2} \right)} \right]. \tag{24}$$

According to Eq. (24), $c_{H^+}^o$ is needed to determine $\Delta \phi_{1/2} \cdot c_{H^+}^w$ is constant due to the presence of a buffer solution [61] and it is defined by $c_{H^+}^w = (\gamma_{H^+}^w)^{-1} 10^{-pH}$. The total concentration of weak acid species in the system can be calculated according to Eq. (13).

Now, we will focus on the calculation of $\Delta\phi_{1/2}$ for a single anionic species $H_{(n-j)}A^{j-}$ as a function of every other species present in the electrochemical system. When the potential matches the half-wave potential, $c^o_{H_{(n-j)}A^{j-}}(0, \Delta^w_o\phi_{1/2})$ is equal to half the initial concentration of weak acid, $c^{init}_{H_nA}$, which is equivalent to the sum of all other interfacial concentrations: $c^w_{H_{(n-j)}A^{j-}}(0, \Delta^w_o\phi_{1/2}), c^\alpha_{H_nA}(0, \Delta^w_o\phi_{1/2}), c^o_{K_pH_{(n-i)}A^{(i-p)-}}(0, \Delta^w_o\phi_{1/2})$ and $c^\alpha_{H_{(n-i)}A^{i-}}(0, \Delta^w_o\phi_{1/2})$ (with $i \neq j$) [74]:

$$\begin{cases} \dfrac{c^{init}_{H_nA}}{2} = c^w_{H_nA}\left(0, \Delta^w_o\phi_{1/2}\right) + \xi c^o_{H_nA}\left(0, \Delta^w_o\phi_{1/2}\right) + \displaystyle\sum_{i=1}^n c^w_{H_{(n-i)}A^{i-}}\left(0, \Delta^w_o\phi_{1/2}\right) + \\[2mm] \quad \xi \displaystyle\sum_{\substack{i=1 \\ i \neq j}}^n c^o_{H_{(n-i)}A^{i-}}\left(0, \Delta^w_o\phi_{1/2}\right) + \xi \sum_{\substack{i=1 \\ i \neq j}}^n \sum_{p=1}^i c^o_{K_pH_{(n-i)}A^{(i-p)-}}\left(0, \Delta^w_o\phi_{1/2}\right) \\[4mm] \dfrac{c^{init}_{H_nA}}{2} = \xi c^o_{H_{(n-j)}A^{j-}}\left(0, \Delta^w_o\phi_{1/2}\right) + \xi \displaystyle\sum_{p=1}^j c^o_{K_pH_{(n-j)}A^{(j-p)-}}\left(0, \Delta^w_o\phi_{1/2}\right). \end{cases} \tag{25}$$

Rewriting equation system, Eq. (25), as a function of $c^o_{H^+}(0, \Delta^w_o\phi_{1/2})$ and $c^w_{H_nA}(0, \Delta^w_o\phi_{1/2})$, the following equations are obtained:

$$\begin{cases} \dfrac{c^{init}_{H_nA}}{2} = c^w_{H_nA}\left(0, \Delta^w_o\phi_{1/2}\right)\left\{1 + \xi K_{D,H_nA} + \displaystyle\sum_{i=1}^n \dfrac{\prod_{m=1}^i K'^w_{a,m}}{\left(c^w_{H^+}\right)^i} + \xi K_{D,H_nA}\sum_{\substack{i=1 \\ i \neq j}}^n \dfrac{\prod_{m=1}^i K'^o_{a,m}}{\left[c^o_{H^+}\left(0, \Delta^w_o\phi_{1/2}\right)\right]^i}\left[1 + \sum_{p=1}^i K'^o_{K_pH_{(n-i)}A^{(j-p)-}}\left(\alpha c^o_{SE}\right)^p\right]\right\} \\[4mm] \dfrac{c^{init}_{H_nA}}{2} = \xi K_{D,H_nA}c^w_{H_nA}\left(0, \Delta^w_o\phi_{1/2}\right)\dfrac{\prod_{m=1}^j K'^o_{a,m}}{\left[c^o_{H^+}\left(0, \Delta^w_o\phi_{1/2}\right)\right]^j}\left[1 + \sum_{p=1}^j K'^o_{K_pH_{(n-j)}A^{(j-p)-}}\left(\alpha c^o_{SE}\right)^p\right] \end{cases} \tag{26}$$

where c^o_{SE} is the bulk concentration of the organic supporting electrolyte and $\alpha(= c^o_{ion}/c^o_{SE})$ is the degree of its dissociation in the organic phase. The fraction of free ions can be calculated from the apparent ion-pair association constant of the supporting electrolyte, $K'^o_{SE}(= \frac{\gamma^o_{K^+}\gamma^o_{Y^-}}{\gamma^o_{KY}}K^o_{SE})$, and c^o_{SE} by $K'^o_{SE} = \frac{1-\alpha}{\alpha^2 c^o_{SE}}$. This approximation is valid when the bulk concentration of the counterion of the supporting electrolyte is much higher than that of the transferred anionic species.

By substitution we obtain a polynomial equation of degree n in $c^o_{H^+}(0, \Delta^w_o\phi_{1/2})$ which can be solved analytically when $n \leq 3$:

$$\begin{aligned} &\xi K_{D,H_nA}\left\{\dfrac{\prod_{m=1}^j K'^o_{a,m}}{\left[c^o_{H^+}\left(0, \Delta^w_o\phi_{1/2}\right)\right]^j}\left[1 + \sum_{p=1}^j K'^o_{K_pH_{(n-j)}A^{(j-p)-}}\left(\alpha c^o_{SE}\right)^p\right] - \sum_{\substack{i=1 \\ i \neq j}}^n \dfrac{\prod_{m=1}^i K'^o_{a,m}}{\left[c^o_{H^+}\left(0, \Delta^w_o\phi_{1/2}\right)\right]^i}\left[1 + \sum_{p=1}^i K'^o_{K_pH_{(n-i)}A^{(j-p)-}}\left(\alpha c^o_{SE}\right)^p\right]\right\} = \\[3mm] &1 + \xi K_{D,H_nA} + \displaystyle\sum_{i=1}^n \dfrac{\prod_{m=1}^i K'^w_{a,m}}{\left(c^w_{H^+}\right)^i}. \end{aligned} \tag{27}$$

In the case that $n > 3$, Eq. (27) can be solved using a numerical method [113,114]. From this main equation, we can calculate the half-wave potential for any species in all the experimental conditions, including IP and NIES.

Below, the analytical expressions for $\Delta\phi_{1/2}$ for $n \leq 2$ are detailed. According to Eq. (27), the pH dependence of $\Delta\phi_{1/2}$ for a monoprotic weak acid ($n = 1$ and $j = 1$) can be expressed as:

$$\Delta\phi_{1/2} = \Delta^w_o\phi^{o'}_{1/2,A^-} - \frac{RT}{F}\ln\left[1 + \frac{c^w_{H^+}(1 + \xi K_{D,HA})}{K'^w_{a,1}}\right] + \frac{RT}{F}\ln(f_{KA}) \tag{28}$$

where $\Delta^w_o\phi^{o'}_{1/2,A^-} = \Delta^w_o\phi^o_{H^+} + \frac{RT}{F}\ln(\frac{\gamma^o_{H^+}}{\gamma^w_{H^+}}) + \frac{RT}{F}\ln(\xi) + \frac{RT}{F}\ln(\frac{K_{D,HA}K'^o_{a,1}}{K'^w_{a,1}})$ and $f_{KA} = 1 + K'^o_{KA}\alpha c^o_{SE}$.

In the case of a diprotic weak acid, the pH dependence of the $\Delta\phi_{1/2}$ can be written as follows:
for $n = 2$ and $j = 1$:

$$\begin{aligned} \Delta^w_o\phi_{1/2} &= \Delta^w_o\phi^{o'}_{1/2,HA^-} + \\ &\frac{RT}{F}\ln\left\{\frac{K'^w_{a,1}}{2c^w_{H^+}\mathcal{T}\left(c^w_{H^+}\right)}\left\{f_{K_pHA^{(1-p)-}} + \left[\left(f_{K_pHA^{(1-p)-}}\right)^2 - 4f_{K_pA^{(2-p)-}}K'^o_{a,2}\left(\xi K_{D,H_2A}K'^o_{a,1}\right)^{-1}\mathcal{T}\left(c^w_{H^+}\right)\right]^{\frac{1}{2}}\right\}\right\} \end{aligned} \tag{29}$$

where $\Delta_o^w \phi_{1/2,HA^-}^{o'} = \Delta_o^w \phi_{H^+}^o + \frac{RT}{F} \ln\left(\frac{\gamma_{H^+}^o}{\gamma_{H^+}^w}\right) + \frac{RT}{F} \ln(\xi) + \frac{RT}{F} \ln\left(\frac{K_{D,H_2A}K_{a,1}'^o}{K_{a,1}'^w}\right)$, $\Upsilon(c_{H^+}^w) = 1 + \xi K_{D,B} + \frac{K_{a,1}'^w}{c_{H^+}^w} + \frac{K_{a,1}'^w K_{a,2}'^w}{(c_{H^+}^w)^2}$, $f_{K_pHA^{(1-p)-}} = 1 + K_{KHA}'^o \alpha c_{SE}^o$ and $f_{K_pA^{(2-p)-}} =$

$1 + K_{KA}'^o \alpha c_{SE}^o + K_{K_2A}'^o (\alpha c_{SE}^o)^2$. With the following mathematical condition for the aqueous proton concentration:

$$c_{H^+}^w \geq 4 f_{K_pA^{(2-p)-}} K_{a,2}'^o \left\{ -K_{a,1}'^w + \sqrt{\left(K_{a,1}'^w\right)^2 - 4K_{a,1}'^w K_{a,2}'^w \left\{ \xi K_{D,H_2A}\left[1 - K_{a,1}'^o \left(f_{K_pHA^{(1-p)-}}\right)^2 \left(4f_{K_pA^{(2-p)-}} K_{a,2}'^o\right)^{-1}\right] - 1\right\}} \right\}$$
$$\left\{ 2\xi K_{D,H_2A}\left[4f_{K_pA^{(2-p)-}} K_{a,2}'^o - \left(f_{K_pHA^{(1-p)-}}\right)^2 K_{a,1}'^o\right] - 8f_{K_pA^{(2-p)-}} K_{a,2}'^o \right\}^{-1} \tag{30}$$

and, for $n = 2, j = 2$:

$$\Delta_o^w \phi_{1/2} = \Delta_o^w \phi_{1/2,A^{2-}}^{o'} +$$
$$\frac{RT}{F} \ln\left\{ \frac{K_{a,1}'^w K_{a,2}'^w}{2c_{H^+}^w K_{a,2}'^o \Upsilon\left(c_{H^+}^w\right)} \left\{ -f_{K_pHA^{(1-p)-}} + \left[\left(f_{K_pHA^{(1-p)-}}\right)^2 + 4f_{K_pA^{(2-p)-}} K_{a,2}'^o \left(\xi K_{D,H_2A} K_{a,1}'^o\right)^{-1} \Upsilon\left(c_{H^+}^w\right)\right]^{\frac{1}{2}} \right\} \right\} \tag{31}$$

where $\Delta_o^w \phi_{1/2,A^{2-}}^{o'} = \Delta_o^w \phi_{H^+}^o + \frac{RT}{F} \ln\left(\frac{\gamma_{H^+}^o}{\gamma_{H^+}^w}\right) + \frac{RT}{F} \ln(\xi) + \frac{RT}{F} \ln\left(\frac{K_{D,H_2A}K_{a,1}'^o K_{a,2}'^o}{K_{a,1}'^w K_{a,2}'^w}\right)$.

2. Results and discussion

In this section we present four representative chemical systems to demonstrate the usefulness of the model developed in Section 1.1. It is important to note that the pH range that defines the different transfer mechanisms depends on the chemical systems selected to illustrate the capability of the model. In the first case (Section 2.2), we analyse two chemical systems: a monoacid (HA) and a diacid (H$_2$A), without considering ion-pair formation in the organic phase and NIES. In Section 2.3, we study the effect of the ion-pair formation on the half-wave potential and finally, in Section 2.4, we show the effect of IP and non-ideality altogether.

In every case, the initial potential will be taken as positive, i.e., the voltammetric scans will always start from the positive side of the potential window. By convention, the transfer of a negative (positive) charge from the aqueous (organic) phase to the organic (aqueous) phase will produce a net negative (positive) current. In this sense, the different charge transfer mechanisms are always described from the positive values of the potential window.

2.1. Hydrophobic weak acid: $n = 1$

Fig. 1 shows the pH dependence of the $\Delta\phi_{1/2}$ for a particular hydrophobic weak acid obtained by evaluating Eq. (27) for $n = 1$ without considering neither ion pairing nor non-ideality of the electrolyte solutions. As it can be readily seen from the figure, the behaviour of the pH dependence can be divided into two zones, as follows: if pH > 8.0, the transfer

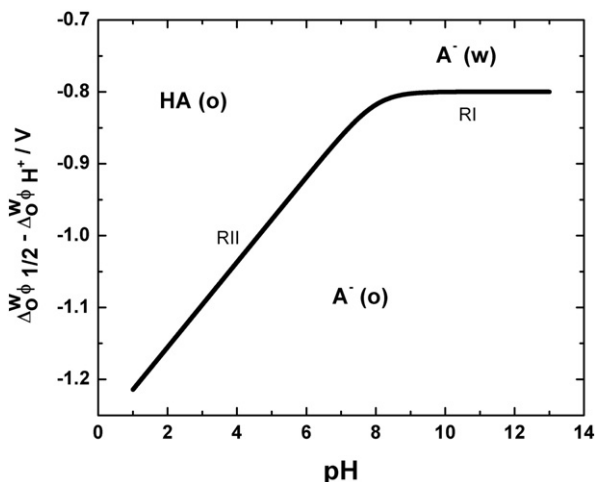**Fig. 1.** Dependence of $\Delta\phi_{1/2}$ on the pH of the aqueous phase for a hydrophobic weak acid ($n = 1$). Simulation parameters: $pK_{a,HA}^w = 6.00$; $\log(K_{D,HA}) = 2.00$; $\Delta_o^w \phi_{A^-}^{o'} = 0.250V$ and $\xi = 1.00$.

of A$^-$ formed in the aqueous phase to the organic phase occurs; in this transfer process $\Delta\phi_{1/2}$ is independent of pH of the aqueous phase. On the other hand, if pH < 8.0, the transfer process occurs by proton transfer by interfacial deprotonation of the weak acid present in the organic phase. Consequently, the dependence of $\Delta\phi_{1/2}$ on pH values is a straight line with a slope of $2.303 \frac{RT}{F}$.

It is possible to postulate a general transfer mechanism consisting in two different processes: a general transfer reaction (transfer of A$^-$ formed previously in the aqueous phase):

$$A^-(w) \overset{\rightarrow}{\leftarrow} A^-(o) \tag{RI}$$

and proton transfer by interfacial deprotonation of the weak acid present in the organic phase:

$$HA(o) \overset{\rightarrow}{\leftarrow} H^+(w) + A^-(o). \tag{RII}$$

These proposed mechanisms for each case, represent the limiting behaviours of a unique transfer reaction because the aqueous phase is bufferized [35].

Finally, the analytical expression for the pH dependence of $\Delta\phi_{1/2}$ without considering neither IP nor non-ideality of the electrolyte solutions can be written as:

$$\Delta\phi_{1/2} = \Delta_o^w \phi_{1/2,A^-}^{o'} - \frac{RT}{F} \ln\left[K_{a,1}^w + c_{H^+}^w \left(1 + \xi K_{D,HA}\right)\right] - \frac{RT}{F} \ln\left(K_{a,1}^w\right). \tag{32}$$

This expression is equivalent to the pH dependence of the $\Delta\phi_{1/2}$ developed by Senda and coworkers (Eq. (2) in Ref. [43]).

2.2. Hydrophobic weak acid: $n = 2$

Fig. 2a shows the pH dependence of $\Delta\phi_{1/2}$ for a hydrophobic weak acid obtained by evaluating Eqs. (29) and (31) for $n = 2$ without considering neither IP nor non-ideality of the electrolyte solutions. The behaviour of the pH dependence can be divided into different zones. The domains of predominance of each species are defined by $\Delta\phi_{1/2}$ for HA$^-$ ($j = 1$) and A^{2-} ($j = 2$). First, we analysed the pH dependence of the half-wave potential for the A^{2-} species. The general behaviour can be compared with the behaviour obtained by hydrophobic weak acid with $n = 1$ (see Fig. 1) and can be divided into two types, as follows: if pH > 10.0, the transfer of A^{2-} formed in the aqueous phase to the organic phase occurs, in this transfer process the $\Delta\phi_{1/2}$ is independent of pH values of the aqueous phase. On the other hand, if pH < 10.0, the proton transfer process occurs by interfacial deprotonation of the HA$^-$ present in the organic phase. Consequently, the dependence of half-wave potential on pH
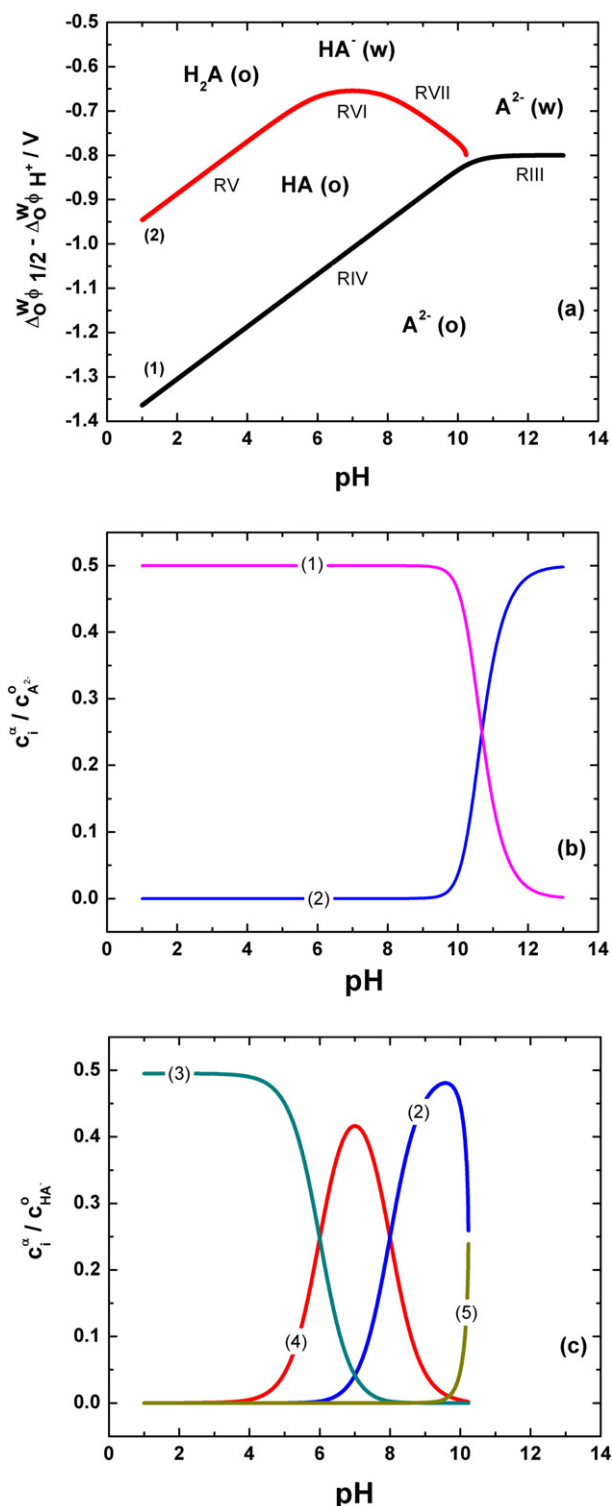
and an proton transfer process that occurs by interfacial deprotonation of the HA^- present in the organic phase:

$$HA^-(o) \underset{\leftarrow}{\overset{\rightarrow}{}} H^+(w) + A^{2-}(o). \tag{RIV}$$

On the other hand, the pH dependence of the $\Delta\phi_{1/2}$ for HA^- can be divided into three zones, as follows: if pH < 6.0, the proton transfer occurs by interfacial dissociation of the H_2A species present in organic phase. The dependence of half-wave potential on pH values is a straight line with a slope of $2.303\frac{RT}{F}$. On the other hand, if $6.0 < pH < 8.0$, the transfer of HA^- formed in the aqueous phase to the organic phase occurs, in this transfer process the $\Delta\phi_{1/2}$ is independent of pH of the aqueous phase. Finally, if pH > 8.0, the transfer process occurs by facilitated proton transfer by interfacial protonation. Consequently, the dependence of half-wave potential on pH values is a straight line with a slope of $-2.303\frac{RT}{F}$. It is possible to postulate a general transfer mechanism consisting of three different processes. A proton transfer by interfacial dissociation of the H_2A species:

$$H_2A(o) \underset{\leftarrow}{\overset{\rightarrow}{}} H^+(w) + HA^-(o) \tag{RV}$$

a simple HA^- transfer:

$$HA^-(w) \underset{\leftarrow}{\overset{\rightarrow}{}} HA^-(o) \tag{RVI}$$

and, facilitated proton transfer by interfacial protonation:

$$H^+(w) + A^{2-}(w) \underset{\leftarrow}{\overset{\rightarrow}{}} HA^-(o). \tag{RVII}$$

The analytical expressions for the pH dependence on the half-wave potential can be written as follows:

for $n = 2$ and $j = 1$ $\left(f_{K_p HA^{(1-p)-}} = f_{K_p A^{(2-p)-}} = 1 \text{ and } \gamma^\alpha_{species} = 1 \right)$:

$$\Delta^w_o\phi_{1/2} = \Delta^w_o\phi^{o'}_{1/2,HA^-} + \frac{RT}{F} \ln\left\{ \frac{K^w_{a,2}}{2c^w_{H^+} \Upsilon(c^w_{H^+})} \left\{ 1 + \left[1 - 4K^o_{a,2} \left(\xi K_{D,H_2A} K^o_{a,1} \right)^{-1} \Upsilon(c^w_{H^+}) \right]^{\frac{1}{2}} \right\} \right\} \tag{33}$$

where $\Delta^w_o\phi^{o'}_{1/2,HA^-} = \Delta^w_o\phi^o_{H^+} + \frac{RT}{F}\ln(\xi) + \frac{RT}{F}\ln\left(\frac{\xi K_{D,H_2A}K^o_{a,1}}{K^w_{a,1}}\right)$ and $\Upsilon(c^w_{H^+}) = 1 + \xi K_{D,B} + \frac{K^w_{a,1}}{c^w_{H^+}} + \frac{K^w_{a,1}K^w_{a,2}}{(c^w_{H^+})^2}$. With the following mathematical condition for the aqueous proton concentration:

$$c^w_{H^+} \geq 4K^o_{a,2} \left\{ -K^w_{a,1} + \sqrt{ \left(K^w_{a,1} \right)^2 - 4K^w_{a,1}K^w_{a,2} \left\{ \xi K_{D,H_2A} \left[1 - K^o_{a,1} \left(4K^o_{a,2} \right)^{-1} \right] - 1 \right\} } \right\} \\ \left\{ 2\xi K_{D,H_2A} \left[4K^o_{a,2} - K^o_{a,1} \right] - 8K^o_{a,2} \right\}^{-1} \tag{34}$$

and, for $n = 2, j = 2$ $(f_{K_p HA^{(1-p)-}} = f_{K_p A^{(2-p)-}} = 1$ and $\gamma^\alpha_{species} = 1)$:

$$\Delta^w_o\phi_{1/2} = \Delta^w_o\phi^{o'}_{1/2,A^{2-}} + \frac{RT}{F} \ln\left\{ \frac{K^w_{a,1}K^w_{a,2}}{2c^w_{H^+}K^o_{a,2}\Upsilon(c^w_{H^+})} \left\{ \left[1 + 4K^o_{a,2} \left(\xi K_{D,H_2A}K^o_{a,1} \right)^{-1} \Upsilon(c^w_{H^+}) \right]^{\frac{1}{2}} - 1 \right\} \right\} \tag{35}$$

where $\Delta^w_o\phi^{o'}_{1/2,A^{2-}} = \Delta^w_o\phi^o_{H^+} + \frac{RT}{2F}\ln(\xi) + \frac{RT}{2F}\ln\left(\frac{K_{D,H_2A}K^o_{a,1}K^o_{a,2}}{K^w_{a,1}K^w_{a,2}}\right)$.

From the model it is possible to determine the concentrations of the different species in the biphasic system at the half-wave potential. Fig. 2b and 2c show the species distribution as a function of pH for the half-wave potential of A^{2-} (Fig. 2b) and HA^- (Fig. 2c), respectively. As it was previously demonstrated [74], these distributions can be used to determine which are the species involved in each boundary line in the ionic partition diagram. The analysis of species distributions is a useful tool to understand which species are responsible for transfer processes at each pH value for different chemical systems.

Fig. 2. Dependence of $\Delta\phi_{1/2}$ on the pH of the aqueous phase for a hydrophobic weak acid ($n = 2$) (a). A^{2-} (1) and HA^- (2). Species distributions as a function of the pH of the aqueous phase for a hydrophobic weak acid ($n = 2$) ((b) and (c)). HA^- in the organic (1) and aqueous phase (4); A^{2-} in the aqueous (2) and organic phase (5); and H_2A in the organic phase (3). Simulation parameters: $pK^w_{a1,H_2A} = 4.00$; $pK^w_{a2,HA^-} = 8.00$; $\log(K_{D,H_2A}) = 2.00$; $\Delta^w_o\phi^{o'}_{HA^-} = -0.100V$; $\Delta^w_o\phi^{o'}_{A^{2-}} = -0.250V$ and $\xi = 1.00$.

values is a straight line with a slope of $2.303\frac{RT}{F}$. It is possible to postulate a general transfer mechanism consisting of two different processes:

a simple A^{2-} transfer :
$$A^{2-}(w) \underset{\leftarrow}{\overset{\rightarrow}{}} A^{2-}(o) \tag{RIII}$$

In the case of $\Delta\phi_{1/2}$ for A^{2-} (Fig. 2b), for pH comprised between 9.0 and 13.0, the predominant species are A^{2-} in aqueous phase and HA^- in organic phase. Therefore, the global transfer mechanism and the half-wave potential for A^{2-} are defined by reactions (RIII) and (RIV) (see Fig. 2b). On the other hand, for $\Delta\phi_{1/2}$ for HA^- and pH comprised between 8.0 and 10.0, the predominant species are HA^- and A^{2-} in aqueous phase. Therefore, the global transfer mechanism for HA^- is defined by reactions (RVI) and (RVII) (see Fig. 2c). Finally, for pH comprised between 4.0 and 6.0, the predominant species are HA^- in aqueous phase and H_2A in organic phase. Therefore, the global transfer mechanism is defined by reactions (RV) and (RVI) (see Fig. 2c).

It is important to note that this model relies on using the same diffusion coefficients for all species in each phase. Unequal diffusion coefficients can modify the difference between the two half-wave potentials of the two anionic species. This change would be most noticeable when these values were comparable (i.e. around pH 10 in the case of Fig. 2a).

2.3. Effect of ion pairing on the half-wave potential

Ion-pair formation in the organic phase is only negligible in solvents with high dielectric constant. In the frequently used organic solvents in liquid|liquid systems, ion-pair formation cannot be ignored [76,85,115–121]. The effect of IP on the half-wave potential depends not only on the association constant between the anionic species and the counterion of the supporting electrolyte but also on the availability of counterions. Hence, the value of the ion-pair association constant between the supporting electrolyte ions directly affects the half-wave potential. In general, in low polarity solvents, such as 1,2-dichloroethane, these values for monovalent ions range between $10^1 \, M^{-1}$ and $10^3 \, M^{-1}$ for supporting electrolytes whereas they are approximately $10^4 \, M^{-1}$ for other ion-pairs [116–118,122–130].

In order to show how it is possible to analyse this effect on $\Delta\phi_{1/2}$, in this section we show the most relevant results using a hydrophobic weak acid with $n = 2$, as an example. Fig. 3 illustrates the pH dependence of $\Delta\phi_{1/2}$ for this hydrophobic weak acid in presence of IP. Similar to the results present in previous report for protonated species [74], the five zones shown in Fig. 2 are also present when incorporating ion-pair formation. However, the reactions taking place in each one of these zones are different and the boundary lines depend on the value of the ion-pair association constant for the different species.
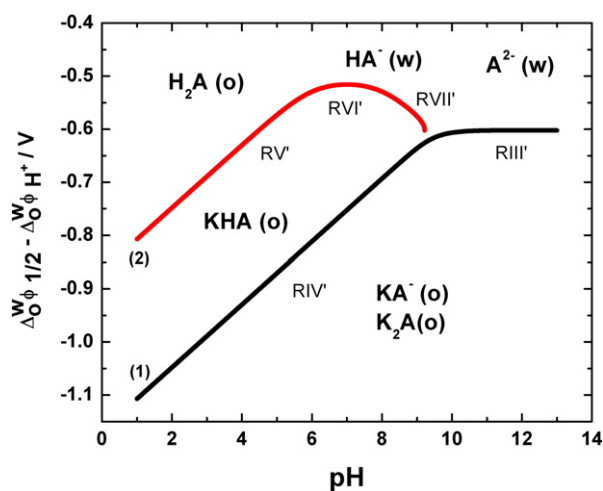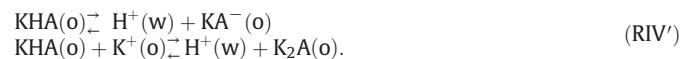
The following reactions apply when IP occurs. Facilitated A^{2-} transfer by IP with K^+:

$$A^{2-}(w) + K^+(o) \underset{\leftarrow}{\rightarrow} KA^-(o)$$
$$A^{2-}(w) + 2K^+(o) \underset{\leftarrow}{\rightarrow} K_2A(o) \tag{RIII'}$$

and an proton transfer processes occur by interfacial deprotonation of the ion-pair, KHA, present in the organic phase:

$$KHA(o) \underset{\leftarrow}{\rightarrow} H^+(w) + KA^-(o)$$
$$KHA(o) + K^+(o) \underset{\leftarrow}{\rightarrow} H^+(w) + K_2A(o). \tag{RIV'}$$

A proton transfer by interfacial dissociation of the H_2A species following by IP:

$$H_2A(o) + K^+(o) \underset{\leftarrow}{\rightarrow} H^+(w) + KHA(o) \tag{RV'}$$
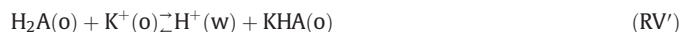
and facilitated HA^- transfer by IP with K^+:

$$HA^-(w) + K^+(o) \underset{\leftarrow}{\rightarrow} KHA(o). \tag{RVI'}$$

Facilitated HA^- transfer by K^+ coupled to the interfacial protonation of the A^{2-} species in the aqueous phase:

$$H^+(w) + A^{2-}(w) + K^+(o) \underset{\leftarrow}{\rightarrow} KHA(o). \tag{RVII'}$$
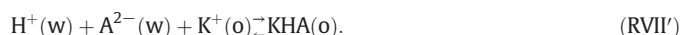
The fractions of each one of the species given by reactions (RIII–RVII) and (RIII'–RVII') strongly depend on the ion-pair association constants values. When the ion-pair association constants between the different anionic species of the weak acid and the counterion of the supporting electrolyte are of the same order, the general behaviour is comparable but at higher potential than observed in the absence of IP. In contrast, the behaviour changes when the constant value of IP between HA^- and K^+ is lower than the other ones [74].

Measuring the half-wave potential as a function of the concentration of supporting electrolyte represents the easiest way to experimentally verify the formation of ion-pairs in the organic phase.

Fig. 4 shows the half-wave potential (at two different pH values) and the dissociation degree of the ion-pair of the supporting electrolyte as a function of $\log(c_{SE}^o)$. For $\log(c_{SE}^o) \geq -3$, the half-wave potentials of HA^- and A^{2-}, present a linear relationship with a slope equal to

Fig. 3. Effect of IP on $\Delta\phi_{1/2}$ for a hydrophobic weak acid ($n = 2$). A^{2-} (1) and HA^- (2). Simulation parameters: $pK_{a1,H_2A}^w = 4.00$; $pK_{a2,HA^-}^w = 8.00$; $\log(K_{D,H_2A}) = 2.00$; $\Delta_o^w\phi_{HA^-}^{o'} = -0.100V$; $\Delta_o^w\phi_{A^{2-}}^{o'} = -0.250V$ and $\xi = 1.00$. Supporting electrolyte: $c_{SE}^o = 1.00M$, $\alpha = 0.02$ (considering $K_{SE}^o = 2 \times 10^3 \, M^{-1}$). Ion-pair formation constants: $K_{KHA}^o = 1 \times 10^4 \, M^{-1}$, $K_{KA^-}^o = 1 \times 10^5 \, M^{-1}$ and $K_{K_2A}^o = 1 \times 10^{10} \, M^{-2}$.
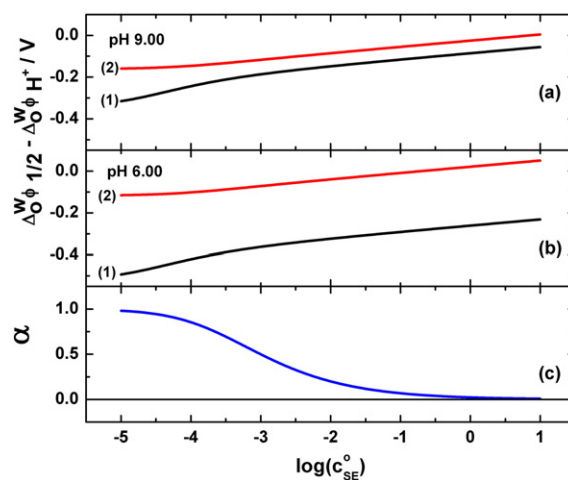

Fig. 4. Effect of supporting electrolyte concentration in organic phase on $\Delta\phi_{1/2}$ for a hydrophobic weak acid ($n = 2$). A^{2-} (1) and HA^- (2). Half-wave potential obtained at pH 6.00 (a) and 9.00 (b). Supporting electrolyte concentration dependence of the dissociation degree of the ion-pair of supporting electrolyte (c). Other parameters as in Fig. 3.

$30\,\mathrm{mV\,dec^{-1}}$. This value can be explained according to the limiting behaviour of the dissociation degree of the ion-pair of the supporting electrolyte for highly concentrated solutions. Considering that the dissociation degree can be written as $\alpha = \frac{\sqrt{1+4c_{SE}^{o}K'_{SE}}-1}{2c_{SE}^{o}K'_{SE}}$, if $4c_{SE}^{o}K'_{SE} \gg 1$ then $\alpha = \frac{1}{\sqrt{c_{SE}^{o}K'_{SE}}}$. The terms associated to the ion-pair formation can be rewritten as follows:

$$f_{K_{p}HA^{(1-p)-}} = 1 + K'^{o}_{KHA}\sqrt{\frac{c_{SE}^{o}}{K'_{SE}}} \tag{36}$$

and

$$f_{K_{p}A^{(2-p)-}} = 1 + K'^{o}_{KA^{-}}\sqrt{\frac{c_{SE}^{o}}{K'_{SE}}} + K'^{o}_{K_{2}A}\frac{c_{SE}^{o}}{K'_{SE}}. \tag{37}$$

Substituting Eqs. (36) and (37) in Eq. (29), considering that $(f_{K_{p}HA^{(1-p)-}})^{2} \gg 4f_{K_{p}A^{(2-p)-}}K'^{o}_{a,2}(\xi K_{D,H_{2}A}K'^{o}_{a,1})^{-1}\Upsilon(c_{H^{+}}^{w})$ and $K'^{o}_{KHA}\sqrt{\frac{c_{SE}^{o}}{K'_{SE}}} \gg 1$, and performing some rearrangement the following equation is obtained:

$$\Delta_{o}^{w}\phi_{1/2} = \Delta_{o}^{w}\phi^{o'}_{1/2,HA^{-}} + \frac{RT}{F}\ln\left[\frac{K'^{w}_{a,1}K'^{o}_{KHA}}{c_{H^{+}}^{w}\sqrt{K'_{SE}}\Upsilon(c_{H^{+}}^{w})}\right] + \frac{RT}{2F}\ln\left(c_{SE}^{o}\right). \tag{38}$$

On the other hand, substituting Eqs. (36) and (37) in Eq. (31), considering that $K'^{o}_{KHA}\sqrt{\frac{c_{SE}^{o}}{K'_{SE}}} \gg 1$ and $K'^{o}_{K_{2}A}\frac{c_{SE}^{o}}{K'_{SE}} \gg 1 + K'^{o}_{KA^{-}}\sqrt{\frac{c_{SE}^{o}}{K'_{SE}}}$, it is easy to show that:

$$\Delta_{o}^{w}\phi_{1/2} = \Delta_{o}^{w}\phi^{o'}_{1/2,A^{2-}} + \frac{RT}{F}\ln\left\{\frac{K'^{w}_{a,1}K'^{w}_{a,2}}{\xi K_{D,H_{2}A}K'^{o}_{a,1}c_{H^{+}}^{w}}\left(\frac{K'^{o}_{K_{2}A}}{\sqrt{K'_{SE}}K'^{o}_{KHA}}\right)\right\}$$
$$+ \frac{RT}{2F}\ln\left(c_{SE}^{o}\right). \tag{39}$$

Clearly, Eqs. (38) and (39) show the dependence of $\Delta\phi_{1/2}$ with $\log(c_{SE})$ and the slope of its graphical representation equals to $2.303\frac{RT}{F}$. This behaviour can be used as a simple criterion to verify the ion-pair formation in the organic phase. It is important to note that the values of characteristic parameters, such as acid-base dissociation constants in the organic phase, partition coefficient and formal transfer potential, calculated from experimental data can differ significantly from the actual values when IP is neglected. Therefore, this issue can be experimentally solved by using different concentrations of the supporting electrolyte in the organic phase. A simple procedure to calculate the characteristic parameters of the system from the half-wave potentials measured experimentally is presented as Supplementary Information.

2.4. Effect of ion pairing and non-ideality in electrolyte solutions on the half-wave potential

The effect of IP and NIES on $\Delta\phi_{1/2}$ is discussed in this section. Hence, the electrochemical system discussed in the previous section is here reviewed in the light of non-ideality calculated according to the equations shown in Section 1.1.1. Fig. 5 compares the pH dependence of the half-wave potential for HA^{-} and A^{2-} according to four different levels of the model. Clearly, Fig. 5 shows that taking into account non-ideality and IP in the model causes a decrease in the half-wave potentials for the transfer of both anions. This behaviour is the consequence of the ionic strength effect on the values of the formal transfer potentials for all the species, the apparent i-acid dissociation and ion-pair association constants. In general, the values of the

apparent i-acid dissociation constants in both phases increase according to the relationship between the activity coefficients, i.e. $\gamma_{H_{2}A}^{\alpha} > \gamma_{HA^{-}}^{\alpha} > \gamma_{A^{2-}}^{\alpha}$ (see Eq. (22)). The formal transfer potentials for the different anionic species are more positive than the standard transfer potentials because $\gamma_{HA^{-}}^{w} > \gamma_{HA^{-}}^{o}$ and $\gamma_{A^{2-}}^{w} > \gamma_{A^{2-}}^{o}$. These relationships between the activity coefficients are a consequence of the different dielectric permittivity and the size of ions in both phases. In the case of the apparent ion-pair association constants, the explanation is not trivial because they depend on the different treatments employed to describe the activity coefficient of the neutral or charged ion-pairs. Both ion-pair formation and non-ideality, shift the pH range where the half-wave potential of the HA^{-} species is defined. This behaviour must be taken into account to accurately calculate the partition coefficient values from direct measurement of the half-wave potential.

Fig. 6 shows the half-wave potential (at two different pH values) and the dissociation degree of the ion-pair of the supporting electrolyte as a function of $\log(c_{SE}^{o})$. For comparison purposes, the half-wave potentials for both species calculated considering only the ion-pair formation are included. Notably at pH 9.00, the half-wave potential of the HA^{-} species is not defined over the full range of the explored concentrations. This behaviour will be observed in any situation in which the pH value is close to the intersection of two half-wave potentials of HA^{-} and A^{2-} (see Fig. 5). Therefore, the electrolyte concentration at which the half-wave potential of A^{2-} reaches a constant value strongly depends on the non-ideality. As discussed in the previous section, at pH 6.00 for $-4 < \log(c_{SE}^{o}) < -1$, the half-wave potentials of HA^{-} and A^{2-} present a linear relationship with the $\log(c_{SE}^{o})$ with a slope equal to $30\,\mathrm{mV\,dec^{-1}}$. On the other hand, for $\log(c_{SE}^{o}) > -1$, both half-wave potentials drastically decrease because the apparent equilibrium constants significantly change at high concentrations of the supporting electrolyte.

3. Conclusion

A model describing the half-wave potential for ion transfer of weak acids at liquid|liquid interfaces in the presence of ion pairing (IP) and
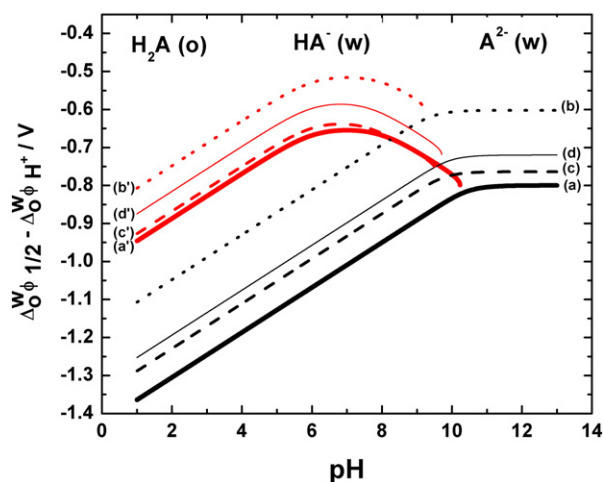

Fig. 5. Effect of IP and NIES on $\Delta\phi_{1/2}$ for a hydrophobic weak acid ($n = 2$). A^{2-} (lines (a)–(d)) and HA^{-} (lines (a')–(d')). Lines (a) and (a'): without IP and NIES; lines (b) and (b'): with IP and without NIES; lines (c) and (c'): without IP and with NIES and lines (d) and (d'): with IP and NIES. Simulation parameters: $pK_{a1,H_{2}A}^{w} = 4.00$; $pK_{a2,HA^{-}}^{w} = 8.00$; $\log(K_{D,H_{2}A}) = 2.00$; $\Delta_{o}^{w}\phi_{HA^{-}}^{o'} = -0.100\mathrm{V}$; $\Delta_{o}^{w}\phi_{A^{2-}}^{o'} = -0.250\mathrm{V}$; and $\xi = 1.00$. Supporting electrolyte: $c_{SE}^{o} = 1.00\mathrm{M}$, $\alpha = 0.02$ (considering $K_{SE}^{o} = 2 \times 10^{3}\mathrm{M^{-1}}$), buffer concentration: 0.100 M, supporting electrolyte concentration in the aqueous phase: 1.00 M. Ion-pair formation constants: $K_{KHA}^{o} = 1 \times 10^{4}\mathrm{M^{-1}}$, $K_{KA^{-}}^{o} = 1 \times 10^{5}\mathrm{M^{-1}}$ and $K_{K_{2}A}^{o} = 1 \times 10^{10}\mathrm{M^{-2}}$. NIES: $\varepsilon_{w} = 78.38$ [91], $\varepsilon_{1,2-DCE} = 10.36$ [4], $\sigma_{w} = 0.99704\,\mathrm{g\,cm^{3}}$ [91], $\sigma_{1,2-DCE} = 1.2458\,\mathrm{g\,cm^{3}}$ [4], $\kappa_{T,1,2-DCE} = 0.846\mathrm{GPa^{-1}}$ [109], $V_{KY}^{intr} = 380\,\mathrm{cm^{3}\,mol^{-1}}$, $V_{KY}^{0} = 450\,\mathrm{cm^{3}\,mol^{-1}}$, $v_{KHA}^{intr} = v_{K_{2}A}^{intr} = 250\,\mathrm{cm^{3}\,mol^{-1}}$ and $V_{KHA}^{0} = V_{K_{2}A}^{0} = 280\,\mathrm{cm^{3}\,mol^{-1}}$ [96,106,108,131,132].
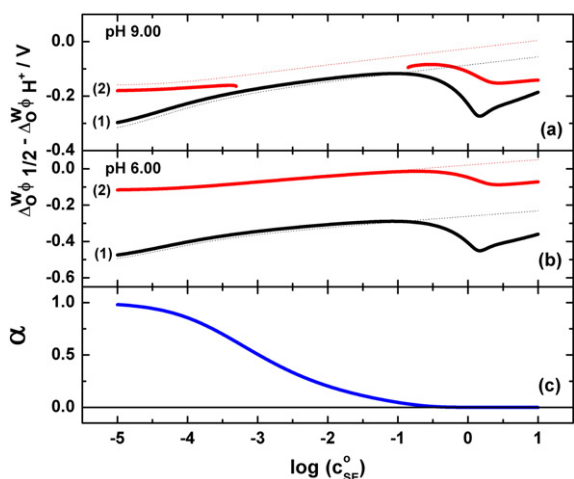
Fig. 6. Effect of supporting electrolyte concentration in organic phase on $\Delta\phi_{1/2}$ for a hydrophobic weak acid ($n=2$). A^{2-} (1) and HA^- (2). Half-wave potential obtained at pH 6.00 (a) and 9.00 (b). Dashed lines: with IP and without NIES. Supporting electrolyte concentration dependence of the dissociation degree of the ion-pair of supporting electrolyte (c). Other parameters as in Fig. 5.

non-ideal electrolyte solutions (NIES) is presented. The main equation (Eq. (27)) derived in this research allows the simulation of several chemical systems under different experimental conditions. It should be mentioned, that the current model does not consider some aspects that could influence the half-wave potentials, such as different diffusion coefficients for each species in each phase and the fact that acid dissociation constants at the interface can be slightly different from those in the bulk phases. Nevertheless, the proposed model is a powerful tool to understand the general behaviour of the ion transfer process of weak acids at liquid|liquid interfaces providing that the standard transfer potentials of all the involved ionic species, the acid-base dissociation constants in both phases, the partition coefficient of the neutral species, the ion-pair association constants and the characteristic parameters to describe non-ideality are available.

We used four representative chemical systems to demonstrate the usefulness of the model. In the absence of IP and considering ideally dilute solutions (infinite dilution), we presented the pH dependence of $\Delta\phi_{1/2}$ for calculated results, according to Eqs. (32), (33) and (35). These results clearly illustrate the different domains limiting the ion transfer of weak acids at liquid|liquid interfaces. Comparatively, the system with $n = 2$ is selected to analyse the effect of the formation of ion-pairs and the non-ideality of the electrolyte solutions. As a first step, the effect of IP considering ideal electrolyte solutions was analysed. As it has already been demonstrated in previous work for a protonated weak base [74], not only $\Delta\phi_{1/2}$ change but also the domains of predominance of each species. Finally, the effect of both contributions, the IP and the non-ideality of the electrolyte solutions, was analysed. The half-wave potential for both anions strongly depends on both contributions. This behaviour is a consequence of the change in the values of the formal transfer potential for all species, apparent i-acid dissociation and ion-pair association constants due to the change in ionic strength. In general, the value of the apparent i-acid dissociation constants in both phases increase according to the relation between the activity coefficients.

In the light of our results, the validity of parameters, like acid dissociation constants in the organic phase and partition coefficient of neutral species, measured from electrochemical experimental data deserves a critical revision. From now on, the calculation of these parameters must include the effect of ion pairing and non-ideality in electrolyte solutions.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jelechem.2016.05.012.

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