



Distribution of ionic components between two immiscible solutions. Partition of weak bases

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ABSTRACT

Theoretical aspects concerning the calculation of the distribution potential at the interface between two immiscible electrolyte solutions are examined. In particular, we analyze the effect of the ratio between the volumes of each phase (r) on the distribution potential for several systems with different levels of complexity. First, we examine the effect of water autoprotolysis for a system composed of completely dissociated electrolytes and weak bases. Finally, the effect of including the ion-pair formation on the potential distribution is considered. In all cases, the algebraic expressions for the equilibrium distribution potential, at $r \rightarrow 0$ and at $r \rightarrow \infty$, are developed. The results presented in this work are of fundamental importance for gaining further understanding of the basic properties of the partition of weak bases, with direct application in drug partitions, and in the theoretical treatments of ion-selective electrodes and of liquid extraction.

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1. Introduction

The distribution of ionic components and the distribution potential between two immiscible solutions have a fundamental importance in diverse physicochemical phenomena [1,2]. In electrochemistry, particularly, at the interface between two immiscible electrolyte solutions (ITIES), all the equilibrium properties of the system are a function of the distribution potential [3,4].

The distribution of ionic components and the distribution potential which characterize a two-phase system in a final distribution of equilibrium were exhaustively studied by Hung [4–6]. He has developed the general equations for several systems with different levels of complexity. Later, Kakiuchi [3,7,8] described a theoretical approach for the partition equilibria of ionic components between two immiscible liquids exhibiting an interesting limiting behaviour when the volume ratio of the two phases is either extremely small or large.

The effect of the volume ratio of the two phases on the equilibrium potential difference for the ITIES model of the liquid-membrane ion-selective electrode (ISE) was analyzed by Samec and Girault [9]. The ITIES model was regarded as a two-phase liquid system $IA(w)||IX(o)$ with the common cation I^+ . The authors con-

cluded that a Nernstian behaviour can be observed in the range of the potential differences $\Delta_0^w \phi$ that fulfill the condition $\Delta_0^w \phi_{A^-}^o \ll \Delta_0^w \phi \ll \Delta_0^w \phi_{X^-}^o$ or $\Delta_0^w \phi_{X^-}^o \ll \Delta_0^w \phi \ll \Delta_0^w \phi_{A^-}^o$. Hence, in designing the ISE for a specific target ion, careful attention should be paid to the selection of the counterions for both, the aqueous and the ISE membrane phases.

Uehara et al. [10] devised an electrochemical method for studying the distribution of weak acids at the aqueous|organic solution interface. The authors developed the general equation that describes the distribution ratio of different species of a weak acid for different experimental conditions. In addition, they obtained a set of several thermodynamic parameters from experimental studies.

Recently, Lepková et al. [11] developed a novel approach to controlling the electrodeposition of metal nanoparticles at a liquid|liquid interface. The authors demonstrated that the size distribution of gold nanoparticles co-deposited in a polymer matrix can vary by modifying the Galvani potential difference established at the water|1,2-dichloroethane interface.

The central aim of this work is to analyze the effect of the phase volume ratio on the distribution potential for several systems with different levels of complexity. First, we examine the effect of the water autoprotolysis on a system composed of completely dissociated electrolytes (Section 3.1) and weak bases (Section 3.2). Finally, the results for systems with ion-pair formation are shown in Section 3.3.

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2. Theory

The initial compositions of the aqueous and organic phase are defined as follows:

The aqueous phase (w) of volume V_w contains a base electrolyte, MX and the protonatable species, HLX.

The organic phase (o) of volume V_o contains a base electrolyte, OY.

The volume ratio of the two phases is defined as $r = V_o/V_w$.

In both phases, HL^+ is considered weak acid species. The ion-pair formation for all species in both phases is explicitly considered.

According to the previous works of Hung [5,6], Kakiuchi [8] and Uehara et al. [10], the equilibrium concentrations of ionic species and the distribution potential can be calculated from the initial concentrations of ions, the standard Gibbs energy of ion transfer, the ion-pair formation constants, the acid–base dissociation constants and the volume ratio of the two phases.

The law of mass conservation of the different species in the system reads as follows:

$$rc_{OY,o}^{init} = c_{O^+}^w + c_{OY}^w + c_{OX}^w + c_{O(HO)}^w + r(c_{O^+}^o + c_{OY}^o + c_{OX}^o + c_{O(HO)}^o) \quad (1)$$

$$c_{MX,w}^{init} = c_{M^+}^w + c_{MY}^w + c_{MX}^w + c_{MHO}^w + r(c_{M^+}^o + c_{MY}^o + c_{MX}^o + c_{MHO}^o) \quad (2)$$

$$c_{HLX,w}^{init} = c_{HL^+}^w + c_L^w + c_{HLY}^w + c_{HLX}^w + r(c_{HL^+}^o + c_L^o + c_{HLY}^o + c_{HLX}^o) \quad (3)$$

$$rc_{OY,o}^{init} = c_{Y^-}^w + c_{OY}^w + c_{MY}^w + c_{HLY}^w + c_{HY}^w + r(c_{Y^-}^o + c_{OY}^o + c_{MY}^o + c_{HLY}^o + c_{HY}^o) \quad (4)$$

$$c_{MX,w}^{init} + c_{HLX,w}^{init} = c_{X^-}^w + c_{OX}^w + c_{MX}^w + c_{HLX}^w + c_{HX}^w + r(c_{X^-}^o + c_{OX}^o + c_{MX}^o + c_{HLX}^o + c_{HX}^o) \quad (5)$$

The conditions of the electroneutrality for each phase are the following:

$$c_{O^+}^w + c_{M^+}^w + c_{H^+}^w + c_{HL^+}^w = c_{Y^-}^w + c_{X^-}^w + c_{HO^-}^w \quad (6)$$

or

$$c_{O^+}^o + c_{M^+}^o + c_{H^+}^o + c_{HL^+}^o = c_{Y^-}^o + c_{X^-}^o + c_{HO^-}^o \quad (7)$$

where c_i^α , is the concentration of the i -species in the α -phase ($\alpha = w$ or o).

The acid–base equilibria for HL^+ , HX and HY in the α -phase are defined as:



$$K_{a,HL^+}^\alpha = \frac{c_{H^+}^\alpha c_L^\alpha}{c_{HL^+}^\alpha} \quad (8)$$



$$K_{a,HJ}^\alpha = \frac{c_{H^+}^\alpha c_{J^-}^\alpha}{c_{HJ}^\alpha} \quad (9)$$

where $J^- = Y^-$ or X^- .

The ion-pair equilibria in the α -phase are given by:



with the association constant defined as:

$$K_{KA}^\alpha = \frac{c_{KA}^\alpha}{c_{K^+}^\alpha c_{A^-}^\alpha} \quad (10)$$

where $K^+ = O^+$; M^+ or HL^+ and $A^- = Y^-$, X^- or HO^- .

According to the Nernst equation, the concentration ratio, c_i^o/c_i^w , can be expressed as:

$$\frac{c_i^o}{c_i^w} = \left(\frac{\gamma_i^w}{\gamma_i^o} \right) (\theta_{eq} \theta_i)^{z_i} \quad (11)$$

where $\theta_{eq} = \exp\left(\frac{F}{RT} \Delta_o^w \phi_{eq}\right)$, $\theta_i = \exp\left(-\frac{F}{RT} \Delta_o^o \phi_i^o\right)$, $\Delta_o^w \phi_{eq}$ is the distribution potential and $\Delta_o^o \phi_i^o$ is the standard transfer potential of the i -species. Although the activity coefficients, γ_i^α , are functions of the composition of the solution phase, we neglect the concentration dependence of the activity coefficients for simplicity.

Water autoprotolysis is explicitly considered as:



The water autoprotolysis constant is defined by:

$$K_w = c_{H^+}^w c_{HO^-}^w \quad (12)$$

Replacing Eqs. (10) and (11) in Eqs. (1)–(3), we can obtain the following equations as a function of the $c_{H^+}^w$, $c_{Y^-}^w$ and $c_{X^-}^w$, and $\Delta_o^w \phi_{eq}$:

$$\begin{aligned} c_{O^+}^w &= rc_{OY,o}^{init} \left\{ 1 + K_{OY}^w c_{Y^-}^w + K_{OX}^w c_{X^-}^w + K_{O(HO)}^w \frac{K_w}{c_{H^+}^w} \right. \\ &\quad \left. + r \theta_{O^+} \left[\theta_{eq} + \frac{K_{OY}^o c_{Y^-}^o}{\theta_{Y^-}} + \frac{K_{OX}^o c_{X^-}^o}{\theta_{X^-}} + \frac{K_{O(HO)}^o K_w}{c_{H^+}^o \theta_{HO^-}} \right] \right\}^{-1} \\ c_{M^+}^w &= c_{MX,w}^{init} \left\{ 1 + K_{MY}^w c_{Y^-}^w + K_{MX}^w c_{X^-}^w + K_{M(HO)}^w \frac{K_w}{c_{H^+}^w} \right. \\ &\quad \left. + r \theta_{M^+} \left[\theta_{eq} + \frac{K_{MY}^o c_{Y^-}^o}{\theta_{Y^-}} + \frac{K_{MX}^o c_{X^-}^o}{\theta_{X^-}} + \frac{K_{M(HO)}^o K_w}{c_{H^+}^o \theta_{HO^-}} \right] \right\}^{-1} \\ c_{HL^+}^w &= c_{HLX,w}^{init} \left\{ 1 + \frac{K_{a,HL^+}^w}{c_{H^+}^w} + K_{HLY}^w c_{Y^-}^w + K_{HLX}^w c_{X^-}^w \right. \\ &\quad \left. + r \left[\theta_{HL^+} \left[\theta_{eq} + \frac{K_{HLY}^o c_{Y^-}^o}{\theta_{Y^-}} + \frac{K_{HLX}^o c_{X^-}^o}{\theta_{X^-}} \right] + \frac{K_{a,HL^+}^o K_{D,L}}{c_{H^+}^o} \right] \right\}^{-1} \end{aligned} \quad (13)$$

where $K_{D,L}$ is the partition coefficient of the neutral species, L .

By using Eqs. (4)–(7) and (9)–(12) the following system of equations can be obtained:

$$\begin{cases} rc_{OY,o}^{init} = c_{Y^-}^w \left[1 + \frac{c_{H^+}^w}{K_{a,HL^+}^w} + K_{OY}^w c_{O^+}^w + K_{MY}^w c_{M^+}^w + K_{HLY}^w c_{HL^+}^w \right] \\ \quad + r \frac{c_{Y^-}^o}{\theta_{Y^-}} \left[\frac{1}{\theta_{eq}} + \frac{c_{H^+}^o}{K_{a,HL^+}^o} \theta_{H^+} + K_{OY}^o c_{O^+}^o \theta_{O^+} + K_{MY}^o c_{M^+}^o \theta_{M^+} + K_{HLY}^o c_{HL^+}^o \theta_{HL^+} \right] \\ c_{MX,w}^{init} + c_{HLX,w}^{init} = c_{X^-}^w \left[1 + \frac{c_{H^+}^w}{K_{a,HJ}^w} + K_{OX}^w c_{O^+}^w + K_{MX}^w c_{M^+}^w + K_{HLX}^w c_{HL^+}^w \right] \\ \quad + r \frac{c_{X^-}^o}{\theta_{X^-}} \left[\frac{1}{\theta_{eq}} + \frac{c_{H^+}^o}{K_{a,HJ}^o} \theta_{H^+} + K_{OX}^o c_{O^+}^o \theta_{O^+} + K_{MX}^o c_{M^+}^o \theta_{M^+} + K_{HLX}^o c_{HL^+}^o \theta_{HL^+} \right] \\ c_{O^+}^w + c_{M^+}^w + c_{H^+}^w + c_{HL^+}^w = c_{Y^-}^w + c_{X^-}^w + \frac{K_w}{c_{H^+}^w} \\ (\theta_{eq})^2 [c_{O^+}^w \theta_{O^+} + c_{M^+}^w \theta_{M^+} + c_{H^+}^w \theta_{H^+} + c_{HL^+}^w \theta_{HL^+}] = \frac{c_{Y^-}^w}{\theta_{Y^-}} + \frac{c_{X^-}^w}{\theta_{X^-}} + \frac{K_w}{c_{H^+}^w \theta_{HO^-}} \end{cases} \quad (14)$$

By combining Eqs. (13) and (14), we obtain a system of 4-non-linear equations in 4-variables ($\Delta_o^w \phi_{eq}$, $c_{H^+}^w$, $c_{Y^-}^w$ and $c_{X^-}^w$). This system of equations may be solved numerically or analytically, with given values of the initial concentrations, the standard ion transfer potentials for charged species, the partition coefficient, and the association constant for the ion-pair formation. The method used for finding the zero of Eq. (14) is based on a modification of the Powell hybrid method [12–14]. This is a powerful tool for solving complex systems of N -nonlinear equations in N -variables without previous algebraic rearrangements.

3. Results and discussion

In this section the effect of water autoprotolysis on the distribution potential is analyzed. The results are divided into three subsections where the distribution of completely dissociated electrolytes and weak bases, with and without ion-pair formation, are analyzed.

For all simulations the temperature is fixed at 298.15 K.

3.1. Distribution of completely dissociated electrolytes

In this section, a two-phase system with base electrolyte in both phases is analyzed.

According to Eqs. (13) and (14), the system of equations to be solved is the following:

$$\begin{cases} c_{O^+}^w = r c_{OY,o}^{\text{init}} [1 + r \theta_{\text{eq}} \theta_{O^+}]^{-1} \\ c_{M^+}^w = c_{MX,w}^{\text{init}} [1 + r \theta_{\text{eq}} \theta_{M^+}]^{-1} \\ c_{Y^-}^w = r c_{OY,o}^{\text{init}} [1 + \frac{r}{\theta_{\text{eq}} \theta_{Y^-}}]^{-1} \\ c_{X^-}^w = c_{MX,w}^{\text{init}} [1 + \frac{r}{\theta_{\text{eq}} \theta_{X^-}}]^{-1} \\ c_{O^+}^w + c_{M^+}^w + c_{H^+}^w = c_{Y^-}^w + c_{X^-}^w + \frac{K_w}{c_{H^+}^w} \\ (\theta_{\text{eq}})^2 [c_{O^+}^w + c_{M^+}^w + c_{H^+}^w] = \frac{c_{Y^-}^w}{\theta_{Y^-}} + \frac{c_{X^-}^w}{\theta_{X^-}} + \frac{K_w}{c_{H^+}^w \theta_{HO^-}} \end{cases} \quad (15)$$

From Eq. (15) after some rearrangement we obtain system of 2-nonlinear equations in 2-variables ($\Delta_o^w \phi_{\text{eq}}$ and $c_{H^+}^w$).

In the particular case of a system without water autoprotolysis ($c_{H^+}^w = c_{HO^-}^w = 0$), the distribution potential is the limiting behaviour reported by Kakiuchi [8]. The expressions of the distribution potential are the following:

For $r \rightarrow 0$, Eq. (15) takes the form of:

$$\Delta_o^w \phi_{\text{eq}} = \frac{1}{2} (\Delta_o^w \phi_{M^+}^o + \Delta_o^w \phi_{X^-}^o) \quad (16)$$

and, for $r \rightarrow \infty$:

$$\Delta_o^w \phi_{\text{eq}} = \frac{1}{2} (\Delta_o^w \phi_{O^+}^o + \Delta_o^w \phi_{Y^-}^o). \quad (17)$$

The behaviour of the distribution potential as a function of the r values is shown in Fig. 1a. In addition, Fig. 1b and c shows the concentration profiles for the species in the aqueous and organic phase, respectively. At both, the negative and positive extremes of $\log(r)$, $\Delta_o^w \phi_{\text{eq}}$ reaches limiting values, 0.036 and 0.000 V, respectively. The limiting behaviour observed in Fig. 1a derives from the fact that the deviations of the concentrations of ionic components in the larger phase from the initial values are negligible.

The comparison between the behaviour of the distribution potential for three different total electrolyte concentrations is shown in Fig. 2a. The distribution potential profile number (1) was obtained without considering the water autoprotolysis process (Eq. (15) with $c_{H^+}^w = c_{HO^-}^w = 0$). The concentration profiles in

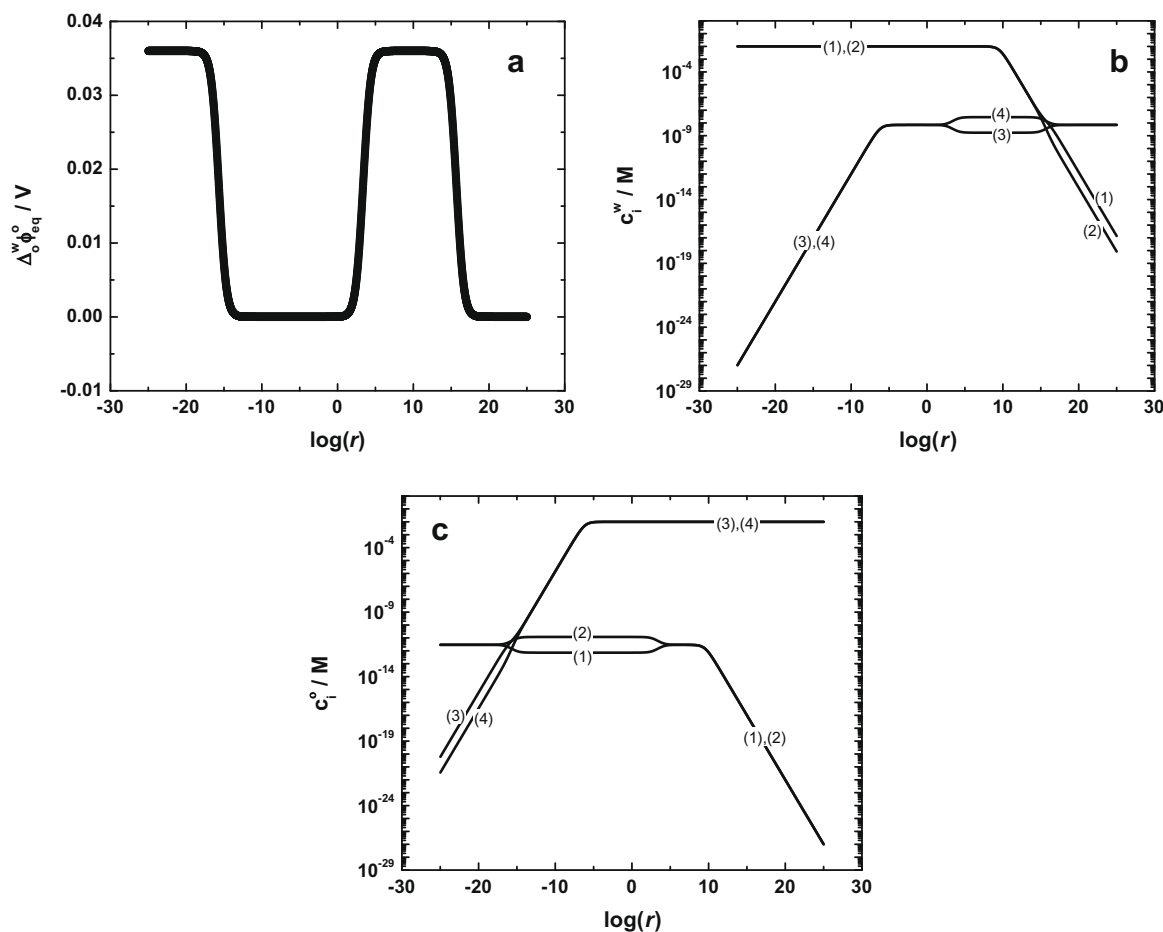


Fig. 1. Effect of the volume ratio on the distribution potential (a) and on the equilibrium concentrations of the different species in the aqueous (b) and organic phase (c). Panels (b) and (c): $c_{M^+}^o$ (1), $c_{X^-}^o$ (2), $c_{O^+}^o$ (3) and $c_{Y^-}^o$ (4). $c_{MX,w}^{\text{init}} = 1.0 \times 10^{-2}$ M, $c_{OY,o}^{\text{init}} = 1.0 \times 10^{-2}$ M, $\Delta_o^w \phi_{M^+}^o = 0.600$ V, $\Delta_o^w \phi_{X^-}^o = -0.528$ V, $\Delta_o^w \phi_{O^+}^o = -0.364$ V and $\Delta_o^w \phi_{Y^-}^o = 0.364$ V.

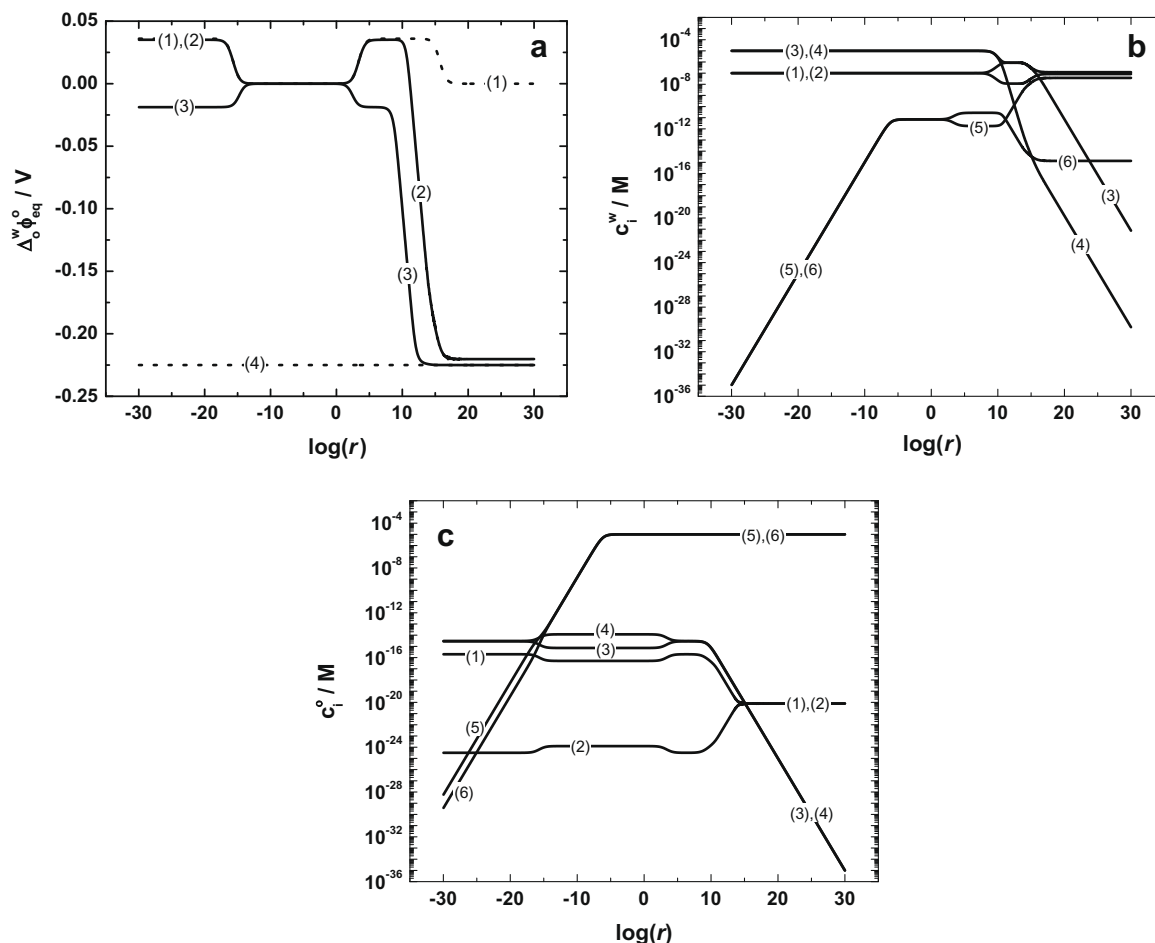


Fig. 2. Effect of the volume ratio on the distribution potential (a) and on the equilibrium concentrations of the different species in the aqueous phase (b) and organic phase (c). Panel (a): $c_{MX,w}^{init} = c_{OY,o}^{init} = 1.0 \times 10^{-2}$ M (without considering the water autoprotolysis process) (1), $c_{MX,w}^{init} = c_{OY,o}^{init} = 1.0 \times 10^{-5}$ M (2), $c_{MX,w}^{init} = c_{OY,o}^{init} = 1.0 \times 10^{-8}$ M (3) and $c_{MX,w}^{init} = c_{OY,o}^{init} = 0.0$ M (4). Panels (b) and (c): $c_{H^+}^z$ (1), $c_{HO^-}^z$ (2), $c_{M^+}^z$ (3), $c_{X^-}^z$ (4), $c_{O^+}^z$ (5), $c_{Y^-}^z$ (6). $\Delta_o^w \phi_{H^+}^o = 0.550$ V, $\Delta_o^w \phi_{HO^-}^o = -1.00$ V and $pK_w = 14.0$. Other parameters as in Fig. 1.

the aqueous and organic phases for $c_{MX,w}^{init} = c_{OY,o}^{init} = 0.01$ mM are shown in Fig. 2b and c, respectively. In general, $\Delta_o^w \phi_{eq}$ decreases when the electrolyte concentration value decreases for the limiting r values. In contrast, for r values close to one, the distribution potential remains unchanged. At positive extremes of $\log(r)$, $\Delta_o^w \phi_{eq}$ reaches the limiting values, 0.000; -0.220 and -0.225 V for total concentration values equal to 10.0 mM; 10.0 and 0.01 μ M, respectively.

The limiting behaviour of $\Delta_o^w \phi_{eq}$ can be represented as follows:

For $r \rightarrow 0$, considering the electroneutrality of the aqueous phase, it can be demonstrated that $c_{H^+}^w = c_{HO^-}^w = \sqrt{K_w}$. Then, Eq. (15) reduces to:

$$\Delta_o^w \phi_{eq} = \frac{RT}{2F} \ln \left[\frac{\frac{c_{MX,w}^{init}}{\theta_{X^-}} + \sqrt{K_w}}{c_{MX,w}^{init} \theta_{M^+} + \sqrt{K_w} \theta_{H^+}} \right] \quad (18)$$

$\Delta_o^w \phi_{eq}$ strongly depends on the total concentration of the electrolyte in the aqueous phase. Two different limiting distribution potential values can be obtained:

for $c_{MX,w}^{init} \gg \sqrt{K_w} \left(\frac{\theta_{X^-}}{\theta_{HO^-}} \right)$ and $c_{MX,w}^{init} \gg \sqrt{K_w} \left(\frac{\theta_{H^+}}{\theta_{M^+}} \right)$, the limit of Eq. (18) is $\Delta_o^w \phi_{eq} = \frac{1}{2} (\Delta_o^w \phi_{M^+}^o + \Delta_o^w \phi_{X^-}^o)$, exhibiting the same values as those obtained in Eq. (16), and for $c_{MX,w}^{init} \ll \sqrt{K_w} \left(\frac{\theta_{X^-}}{\theta_{HO^-}} \right)$ and $c_{MX,w}^{init} \ll \sqrt{K_w} \left(\frac{\theta_{H^+}}{\theta_{M^+}} \right)$, the limit of Eq. (18) is:

$$\Delta_o^w \phi_{eq} = \frac{1}{2} (\Delta_o^w \phi_{H^+}^o + \Delta_o^w \phi_{HO^-}^o). \quad (19)$$

For $r \rightarrow \infty$, considering the electroneutrality of the organic phase, it can be demonstrated that $c_{H^+}^o = c_{HO^-}^o$. Then, Eq. (15) reduces to:

$$\Delta_o^w \phi_{eq} = \frac{RT}{2F} \ln \left[\frac{\frac{c_{OY,o}^{init}}{\theta_{O^+}} + \sqrt{\frac{K_w}{\theta_{H^+} \theta_{HO^-}}}}{c_{OY,o}^{init} \theta_{Y^-} + \sqrt{K_w} \theta_{H^+} \theta_{HO^-}} \right] \quad (20)$$

In this case, $\Delta_o^w \phi_{eq}$ largely depends on the total concentration of the electrolyte in the organic phase. Two different limiting distribution potential values can be obtained:

For $c_{OY,o}^{init} \gg \sqrt{K_w} \left(\frac{\theta_{O^+}}{\theta_{Y^-}} \right)$ and $c_{OY,o}^{init} \gg \sqrt{K_w} \left(\frac{\sqrt{\theta_{H^+} \theta_{HO^-}}}{\theta_{Y^-}} \right)$, the limit of Eq. (20) is $\Delta_o^w \phi_{eq} = \frac{1}{2} (\Delta_o^w \phi_{O^+}^o + \Delta_o^w \phi_{Y^-}^o)$, which gives the same values as those obtained in Eq. (17), and, for $c_{OY,o}^{init} \ll \sqrt{K_w} \left(\frac{\theta_{O^+}}{\theta_{Y^-}} \right)$ and $c_{OY,o}^{init} \ll \sqrt{K_w} \left(\frac{\sqrt{\theta_{H^+} \theta_{HO^-}}}{\theta_{Y^-}} \right)$, the limit of Eq. (20) is $\Delta_o^w \phi_{eq} = \frac{1}{2} (\Delta_o^w \phi_{H^+}^o + \Delta_o^w \phi_{HO^-}^o)$.

In addition, in this limiting case, it is possible to obtain an expression for the aqueous proton concentration as a function of the total organic base electrolyte:

$$c_{H^+}^w = \sqrt{\frac{K_w}{\theta_{H^+} \theta_{HO^-}}} \left(\frac{c_{OY,o}^{init} \theta_{Y^-} + \sqrt{K_w} \theta_{H^+} \theta_{HO^-}}{\frac{c_{OY,o}^{init}}{\theta_{O^+}} + \sqrt{\frac{K_w}{\theta_{H^+} \theta_{HO^-}}}} \right)^{\frac{1}{2}} \quad (21)$$

If $c_{\text{OY},o}^{\text{init}} \gg \sqrt{K_w} \left(\frac{\theta_{\text{O}^+}}{\sqrt{\theta_{\text{H}^+} \theta_{\text{HO}^-}}} \right)$ and $c_{\text{OY},o}^{\text{init}} \gg \sqrt{K_w} \left(\frac{\sqrt{\theta_{\text{H}^+} \theta_{\text{HO}^-}}}{\theta_{\text{Y}^-}} \right)$, Eq. (22) presents an interesting limiting behaviour. Here, the expression for the pH takes the following form:

$$\text{pH} = \frac{1}{2} pK_w + \frac{F}{2.303RT} \left[\frac{1}{2} (\Delta_o^w \phi_{\text{O}^+}^o + \Delta_o^w \phi_{\text{Y}^-}^o) - \frac{1}{2} (\Delta_o^w \phi_{\text{H}^+}^o + \Delta_o^w \phi_{\text{HO}^-}^o) \right] \quad (22)$$

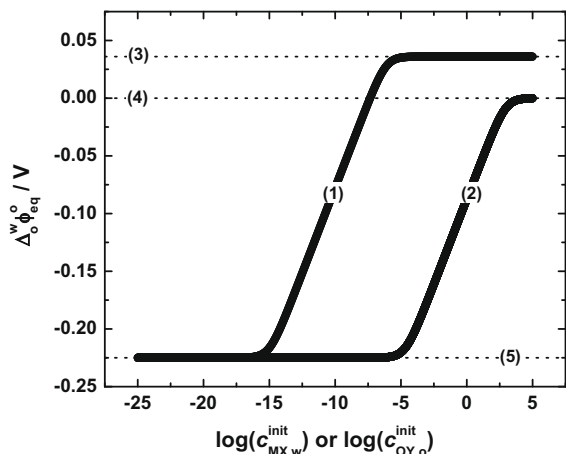


Fig. 3. Effect of the initial electrolyte concentrations on the extreme distribution potential. $r \rightarrow 0$ (1) and $r \rightarrow \infty$ (2). $\frac{1}{2} (\Delta_o^w \phi_{\text{M}^+}^o + \Delta_o^w \phi_{\text{X}^-}^o)$ (3), $\frac{1}{2} (\Delta_o^w \phi_{\text{O}^+}^o + \Delta_o^w \phi_{\text{Y}^-}^o)$ (4) and $\frac{1}{2} (\Delta_o^w \phi_{\text{H}^+}^o + \Delta_o^w \phi_{\text{HO}^-}^o)$ (5). Parameters as in Fig. 2.

Fig. 3 shows the shape of the two different limiting cases of Eq. (15) as a function of the total electrolyte concentration. For $r \rightarrow 0$, $\Delta_o^w \phi_{\text{eq}}^o$ reaches a constant value if $\log(c_{\text{MX},w}^{\text{init}}) > -5$ and if $\log(c_{\text{MX},w}^{\text{init}}) < -15$, equal to $\frac{1}{2} (\Delta_o^w \phi_{\text{M}^+}^o + \Delta_o^w \phi_{\text{X}^-}^o)$ and $\frac{1}{2} (\Delta_o^w \phi_{\text{H}^+}^o + \Delta_o^w \phi_{\text{HO}^-}^o)$, respectively. For $r \rightarrow \infty$ however, $\Delta_o^w \phi_{\text{eq}}^o$ reaches a constant values if $\log(c_{\text{OY},o}^{\text{init}}) < -5$, equal to $\frac{1}{2} (\Delta_o^w \phi_{\text{H}^+}^o + \Delta_o^w \phi_{\text{HO}^-}^o)$ and if $\log(c_{\text{OY},o}^{\text{init}}) > 3.5$, equal to $\frac{1}{2} (\Delta_o^w \phi_{\text{O}^+}^o + \Delta_o^w \phi_{\text{Y}^-}^o)$.

3.2. Distribution of weak bases

In this section, a two-phase system with a weak base is considered. The weak base is dissolved in the aqueous phase in the HLX form.

According to Eqs. (13) and (14), the system of equations to be solved is the following:

$$\begin{cases} c_{\text{HL}^+}^w = c_{\text{HLX},w}^{\text{init}} \left[1 + r \theta_{\text{eq}} \theta_{\text{HL}^+} + \frac{K_w^{\text{a,HL}^+}}{c_{\text{H}^+}^w} (1 + r K_{\text{D,L}}) \right]^{-1} \\ c_{\text{X}^-}^w = c_{\text{HLX},w}^{\text{init}} \left[1 + \frac{r}{\theta_{\text{eq}} \theta_{\text{X}^-}} \right]^{-1} \\ c_{\text{H}^+}^w + c_{\text{HL}^+}^w = c_{\text{X}^-}^w + \frac{K_w^w}{c_{\text{H}^+}^w} \\ (\theta_{\text{eq}})^2 (c_{\text{H}^+}^w \theta_{\text{H}^+} + c_{\text{HL}^+}^w \theta_{\text{HL}^+}) = \frac{c_{\text{X}^-}^w}{\theta_{\text{X}^-}} + \frac{K_w}{c_{\text{H}^+}^w \theta_{\text{HO}^-}} \end{cases} \quad (23)$$

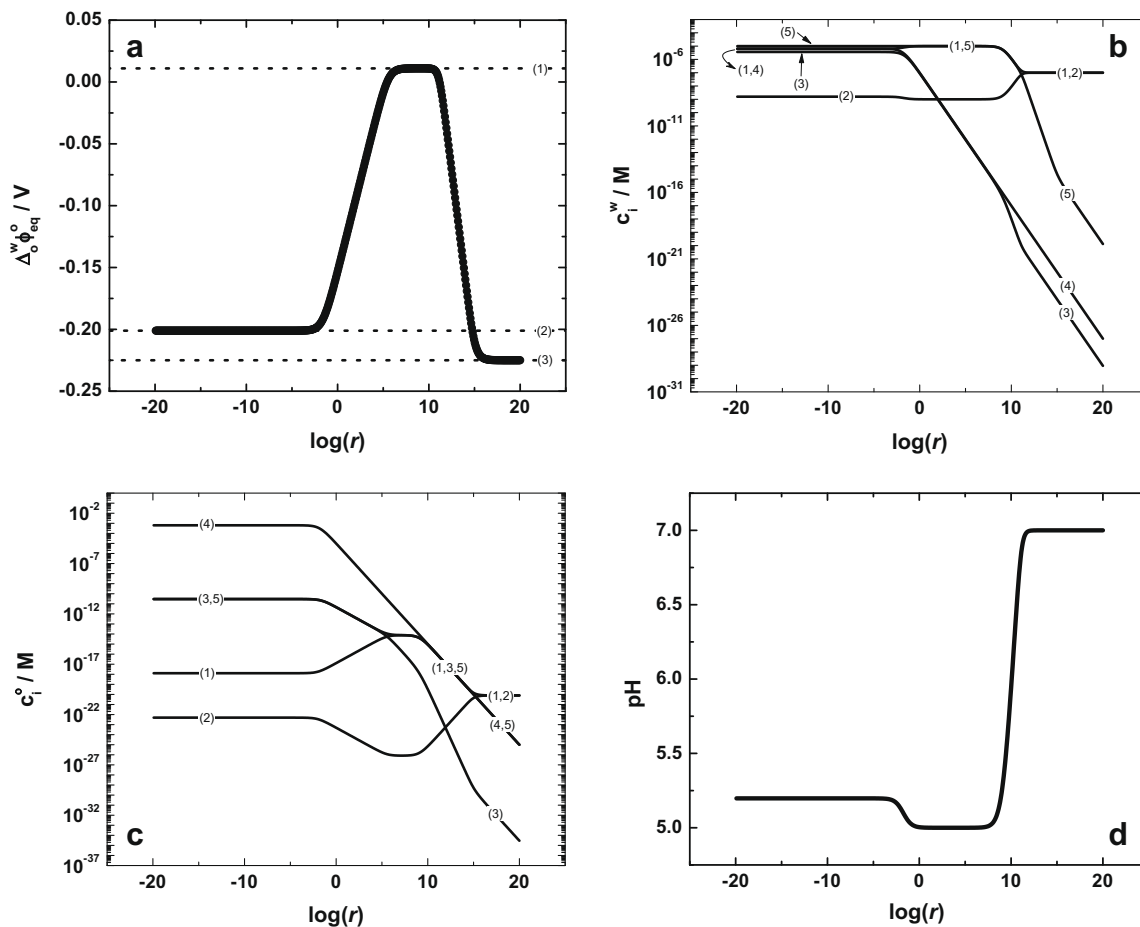


Fig. 4. Effect of the volume ratio on the distribution potential (a) and on the equilibrium concentrations of the different species in the aqueous phase (b) and organic phase (c), and pH (d). Panel (a): $\frac{1}{2} (\Delta_o^w \phi_{\text{H}^+}^o + \Delta_o^w \phi_{\text{X}^-}^o)$ (1), $\Delta_o^w \phi_{\text{eq}}^o$ value according Eq. (24) (2) and $\frac{1}{2} (\Delta_o^w \phi_{\text{H}^+}^o + \Delta_o^w \phi_{\text{HO}^-}^o)$ (3). Panels (b) and (c): $c_{\text{H}^+}^w$ (1), $c_{\text{HO}^-}^w$ (2), $c_{\text{HL}^+}^w$ (3), $c_{\text{X}^-}^w$ (4) and $c_{\text{X}^-}^o$ (5). $c_{\text{HLX},w}^{\text{init}} = 1.0 \times 10^{-5}$ M, $\log(K_{\text{D,L}}) = 2.00$, $pK_w^{\text{a,HL}^+} = 5.00$, $\Delta_o^w \phi_{\text{H}^+}^o = 0.550$ V, $\Delta_o^w \phi_{\text{HO}^-}^o = -1.00$ V, $\Delta_o^w \phi_{\text{X}^-}^o = -0.528$ V, and $\Delta_o^w \phi_{\text{HL}^+}^o = 0.100$ V. $pK_w = 14.0$.

From Eq. (23) after some rearrangement we obtain system of 2-non-linear equations in 2-variables ($\Delta_o^w \phi_{\text{eq}}$ and $c_{\text{H}^+}^w$).

The behaviour of the distribution potential as a function of the r values is shown in Fig. 4a. In addition, Fig. 4b and c shows the concentration profiles for all species in the aqueous and organic phase, respectively. At both, the negative and the positive extremes of $\log(r)$, $\Delta_o^w \phi_{\text{eq}}$ reaches the limiting values -0.201 and -0.225 V, respectively. The distribution potential also reaches a constant value equal to 0.011 V in the range 7.5 – 10.0 . Here, the following relation is fulfilled: $c_{\text{H}^+}^w = c_{\text{X}^-}^w$ and $c_{\text{H}^+}^o = c_{\text{X}^-}^o$. In addition, $\Delta_o^w \phi_{\text{eq}} = \frac{1}{2}(\Delta_o^w \phi_{\text{H}^+}^o + \Delta_o^w \phi_{\text{X}^-}^o)$. These behaviours can be observed in Fig. 4 b and c, where the concentration profiles for H^+ and X^- are plotted as a function of the r values.

The limiting value of $\Delta_o^w \phi_{\text{eq}}$ for $r \rightarrow 0$ can be expressed, according to Eq. (23), as:

$$\Delta_o^w \phi_{\text{eq}} = \frac{RT}{2F} \ln \left(\frac{\frac{K_w}{\theta_{\text{HO}^-} c_{\text{H}^+}^w} + \frac{c_{\text{HLX,w}}^{\text{init}}}{\theta_{\text{X}^-}}}{\theta_{\text{H}^+} c_{\text{H}^+}^w + \alpha_{\text{HL}^+} \theta_{\text{HL}^+} c_{\text{HLX,w}}^{\text{init}}} \right) \quad (24)$$

where: $\alpha_{\text{HL}^+} = \frac{c_{\text{H}^+}^w}{c_{\text{H}^+}^w + K_{\text{a,HL}^+}^w}$. The $c_{\text{H}^+}^w$ values can be calculated in all the experimental conditions according to Eq. (A3) (see Appendix A).

For high $c_{\text{HLX,w}}^{\text{init}}$, Eq. (24) presents an interesting limiting behaviour that can be expressed as follows:

$$\Delta_o^w \phi_{\text{eq}} = \frac{1}{2}(\Delta_o^w \phi_{\text{HL}^+}^o + \Delta_o^w \phi_{\text{X}^-}^o) - \frac{RT}{2F} \ln(\alpha_{\text{HL}^+}) \quad (25)$$

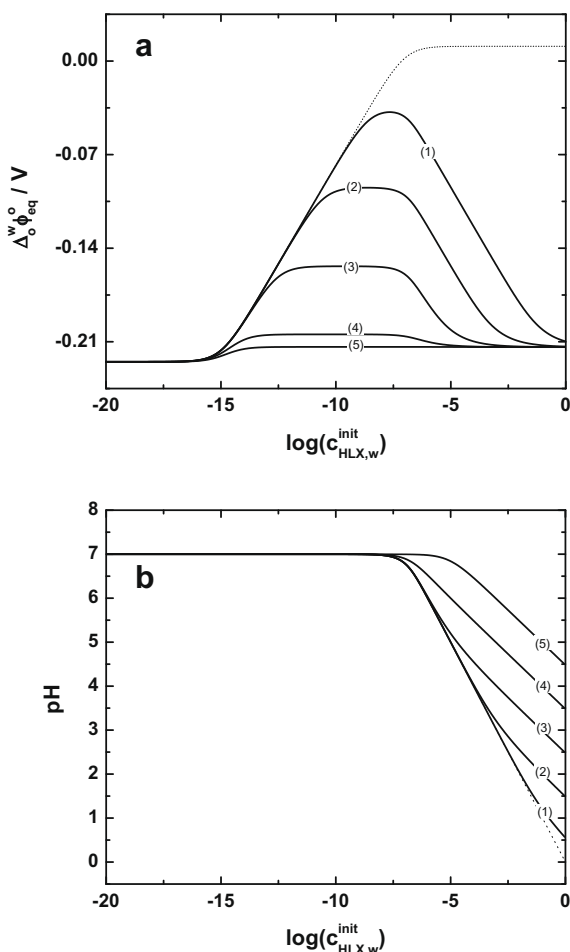


Fig. 5. Effect of the total HLX concentration on the distribution potential (a) and on the pH (b), for $r \rightarrow 0$. $pK_{\text{a,HL}^+}^w = 1.00$ (1), 3.00 (2), 5.00 (3), 7.00 (4) and 9.00 (5). Strong acid (HX) (dotted line). Other parameters as in Fig. 4.

Moreover, for $r \rightarrow \infty$, it can be clearly seen that Eq. (23) can be rewritten as: $\Delta_o^w \phi_{\text{eq}} = \frac{1}{2}(\Delta_o^w \phi_{\text{H}^+}^o + \Delta_o^w \phi_{\text{HO}^-}^o)$.

In addition, Fig. 4d shows the change of the pH as a function of the $\log(r)$ values. For $r \rightarrow 0$, the pH value is determined by the dissociation of HL^+ species and can be estimated from the acid–base equilibrium at the homogeneous aqueous phase (see Appendix A). For $r \rightarrow \infty$, the pH reaches a constant value equal to 7.00. This behaviour derives from the dilution of the HL^+ and L species due to their partition to the organic phase (see Fig. 4b and c).

Fig. 5 shows the distribution potential (Fig. 5a) and the pH (Fig. 5b) values as a function of the total HLX concentration, for $r \rightarrow 0$. When $c_{\text{HLX,w}}^{\text{init}} \rightarrow 0$, the pH is equal to 7.00 and $\Delta_o^w \phi_{\text{eq}} = \frac{1}{2}(\Delta_o^w \phi_{\text{H}^+}^o + \Delta_o^w \phi_{\text{HO}^-}^o)$, since the aqueous phase can be considered as pure water. When $c_{\text{HLX,w}}^{\text{init}} \rightarrow \infty$, $\Delta_o^w \phi_{\text{eq}}$ reaches a constant value equal to $\frac{1}{2}(\Delta_o^w \phi_{\text{HL}^+}^o + \Delta_o^w \phi_{\text{X}^-}^o)$ and the pH values depend on the $pK_{\text{a,HL}^+}^w$ (Fig. 5b). The $\Delta_o^w \phi_{\text{eq}}$ limiting value is reached for lower r values as $pK_{\text{a,HL}^+}^w$ increases, because for high $pK_{\text{a,HL}^+}^w$ values, HL^+ is the prevailing species in the aqueous phase. When HL^+ and X^- are the predominant species in the aqueous phase, this system is equivalent to the system studied in Section 3.1 for the completely dissociated electrolyte solutions. In contrast, when $c_{\text{HLX,w}}^{\text{init}} \rightarrow \infty$, and considering that HLX is a strong acid, the $\Delta_o^w \phi_{\text{eq}}$ reaches a constant value equal to $\frac{1}{2}(\Delta_o^w \phi_{\text{H}^+}^o + \Delta_o^w \phi_{\text{X}^-}^o)$ (see dotted lines in Fig. 5).

Since the weak base distribution in the system is also defined by the partition equilibrium of the neutral species, we analyze the effect of different partition constant values on the system behaviour (Fig. 6). An increase in the volume ratio produces an increase in the amount of neutral species in the organic phase. As expected, this partition process is enhanced when the partition coefficient increases. As a consequence, the interval of r values in which $\Delta_o^w \phi_{\text{eq}}$ remains constant depends on the $K_{\text{D,L}}$ values, i.e., $\Delta_o^w \phi_{\text{eq}} = -0.21$ V for $\log(K_{\text{D,L}}) = 5.0$ and $\log(r) < -6.0$, and for $\log(K_{\text{D,L}}) = -5.0$ and $\log(r) < 4.0$ (see Fig. 6 and Eq. (25)).

Additionally, the distribution potential reaches a constant value equal to $\frac{1}{2}(\Delta_o^w \phi_{\text{H}^+}^o + \Delta_o^w \phi_{\text{X}^-}^o)$, only for high coefficient partition constants. In such cases, the following relation is fulfilled: $c_{\text{H}^+}^w = c_{\text{X}^-}^w$ and $c_{\text{H}^+}^o = c_{\text{X}^-}^o$. This behaviour can be explained considering that HL^+ totally dissociates due to the partition of L.

Finally, with the incorporation in the model of the following reduced variable, $\Xi = K_{\text{a,HL}^+}^w \cdot K_{\text{D,L}}$, we can obtain an interval of r values, where the distribution potential is the same.

According to the definition of Ξ and to Eq. (23), the total weak base concentration can be expressed as:

$$c_{\text{HLX,w}}^{\text{init}} = c_{\text{HL}^+}^w \left[1 + r \theta_{\text{eq}} \theta_{\text{HL}^+} \frac{\Xi}{c_{\text{H}^+}^w} \left(\frac{1}{K_{\text{D,L}}} + r \right) \right] \quad (26)$$

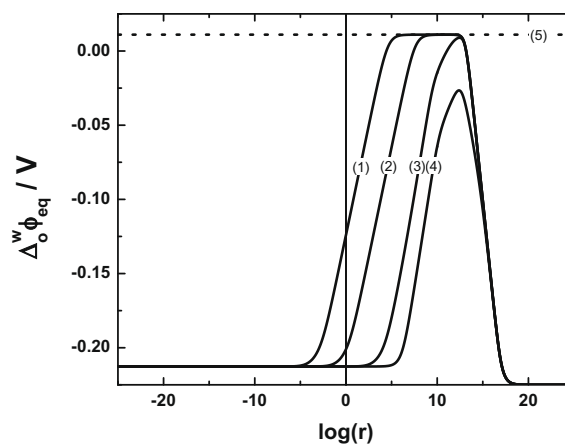


Fig. 6. Effect of the volume ratio on the distribution potential for different partition coefficients. $\log(K_{\text{D,L}}) = 5.00$ (1), 2.00 (2), -2.00 (3) and -5.00 (4). $\frac{1}{2}(\Delta_o^w \phi_{\text{H}^+}^o + \Delta_o^w \phi_{\text{X}^-}^o)$ (5). $c_{\text{HLX,w}}^{\text{init}} = 1.0 \times 10^{-3}$ M. Other parameters as in Fig. 4.

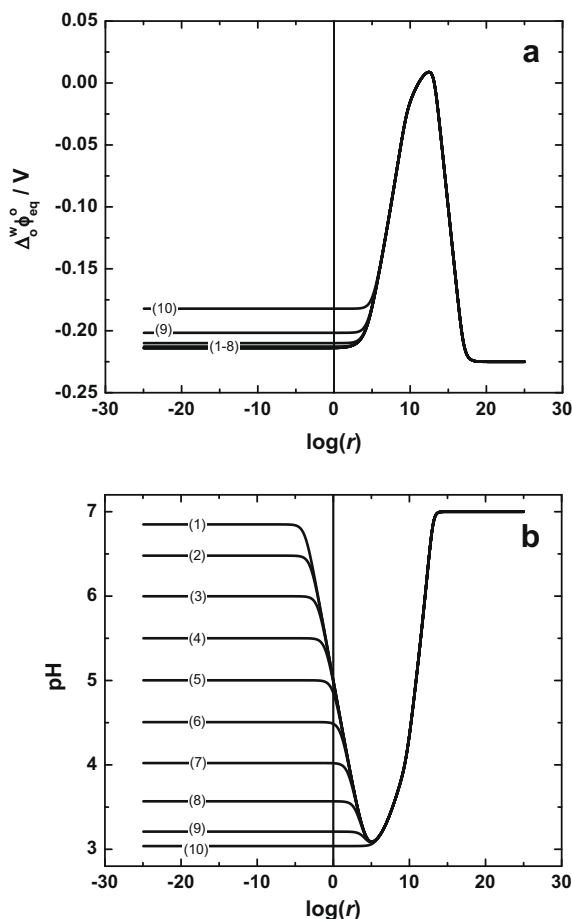


Fig. 7. Effect of the volume ratio on the distribution potential for $\log(\Xi) = \log(K_{D,L}) - pK_{a,HL^+}^w = -7.00$, $pK_{a,HL^+}^w = 11.0$ (1), 10.0 (2), 9.00 (3), 8.00 (4), 7.00 (5), 6.00 (6), 5.00 (7), 4.00 (8), 3.00 (9) and 2.00 (10). $c_{HLX,w}^{init} = 1.0 \times 10^{-3}$ M. Other parameters as in Fig. 4.

It is remarkable that, for $r \gg (K_{D,L})^{-1}$, the total weak base distribution and distribution potential in the system are only dependent on Ξ . This approach can be extended to all systems that contain a weak base, i.e., a base electrolyte in both phases and aqueous buffer solution.

The distribution potential and pH behaviours obtained for $\log(\Xi) = -7.00$ and $\Delta_0^w \phi_{HL^+}^0 = 0.10$ V are shown in Fig. 7. In this approach, we consider that the product of Ξ and $(K_{a,HL^+}^o)^{-1}$ is a constant value.

The $\Delta_0^w \phi_{eq}$ behaviour is defined by two different processes: the acid–base dissociation and the partition equilibrium. A given reduced variable Ξ value implies a constant dissociation degree of HL^+ for different pK_{a,HL^+}^w values.

3.3. Ion-pair formation

The ion-pair formation process is negligible only in solvents with a high dielectric constant [8]. In this section, ion-pair formation in the organic phase is taken into account for the prediction of the distribution potential behaviour. Two different systems with ion-pair formation in the organic phase are examined: completely dissociated electrolytes (Section 3.3.1.) and weak bases (Section 3.3.2.).

3.3.1. Distribution of completely dissociated electrolytes

First, we consider a two-phase system composed of a completely dissociated electrolyte MX in the aqueous phase. In the organic phase, the ion-pair formation of MX is considered.

According to Eqs. (13) and (14), the system of equations to be solved is as follows:

$$\begin{cases} c_{M^+}^w = c_{MX,w}^{init} \left\{ 1 + r \left[\theta_{eq} \theta_{M^+} + K_{MX}^o c_{X^-}^w \frac{\theta_{M^+}}{\theta_{X^-}} \right] \right\}^{-1} \\ c_{MX,w}^{init} = c_{X^-}^w \left\{ 1 + r \left[\frac{1}{\theta_{eq} \theta_{X^-}} + K_{MX}^o c_{M^+}^w \frac{\theta_{M^+}}{\theta_{X^-}} \right] \right\} \\ c_{M^+}^w + c_{H^+}^w = c_{X^-}^w + \frac{K_w}{c_{H^+}^w} \\ (\theta_{eq})^2 (c_{M^+}^w \theta_{M^+} + c_{H^+}^w \theta_{H^+}) = \frac{c_{X^-}^w}{\theta_{X^-}} + \frac{K_w}{c_{H^+}^w \theta_{HO^-}} \end{cases} \quad (27)$$

From Eq. (27) after some rearrangement we obtain system of 3-non-linear equations in 3-variables ($\Delta_0^w \phi_{eq}$, $c_{H^+}^w$ and $c_{X^-}^w$).

When this system is solved without taking into account the water autoprotolysis process ($c_{H^+}^w = c_{HO^-}^w = 0$), the limiting behaviour of the distribution potential is the same as that reported by Kakiuchi [8]. The solution of Eq. (27) for $r \rightarrow 0$ or $r \rightarrow \infty$ takes the following form: $\Delta_0^w \phi_{eq} = \frac{1}{2} (\Delta_0^w \phi_{M^+}^0 + \Delta_0^w \phi_{X^-}^0)$. Thus, $\Delta_0^w \phi_{eq}$ depends neither on r nor on $c_{MX,w}^{init}$ or K_{MX}^o values.

When water autoprotolysis is considered (Eq. (12)), the $\Delta_0^w \phi_{eq}$ depends on the $c_{MX,w}^{init}$ values, for $r \rightarrow 0$. In this limit the solution of Eq. (27) takes the form of Eq. (18) (see Section 3.1). For $r \rightarrow \infty$, $\Delta_0^w \phi_{eq} = \frac{1}{2} (\Delta_0^w \phi_{H^+}^0 + \Delta_0^w \phi_{HO^-}^0)$.

In what follows, we consider a two-phase system composed of two completely dissociated electrolytes, MX and OY, in the aqueous and organic phase, respectively. Ion-pair formation of MY and OX in the organic phase is also considered.

According to Eqs. (13) and (14), the system of equations to be solved is the following:

$$\begin{cases} c_{M^+}^w = c_{MX,w}^{init} \left[1 + r \left(\theta_{eq} \theta_{M^+} + K_{MY}^o c_{Y^-}^w \frac{\theta_{M^+}}{\theta_{Y^-}} \right) \right]^{-1} \\ c_{O^+}^w = r c_{OY,o}^{init} \left[1 + r \left(\theta_{eq} \theta_{O^+} + K_{OX}^o c_{X^-}^w \frac{\theta_{O^+}}{\theta_{X^-}} \right) \right]^{-1} \\ c_{MX,w}^{init} = c_{X^-}^w \left\{ 1 + r \left[\frac{1}{\theta_{eq} \theta_{X^-}} + K_{OX}^o c_{M^+}^w \frac{\theta_{O^+}}{\theta_{X^-}} \right] \right\} \\ r c_{OY,o}^{init} = c_{Y^-}^w \left\{ 1 + r \left[\frac{1}{\theta_{eq} \theta_{Y^-}} + K_{MY}^o c_{M^+}^w \frac{\theta_{M^+}}{\theta_{Y^-}} \right] \right\} \\ c_{M^+}^w + c_{O^+}^w + c_{H^+}^w = c_{X^-}^w + c_{Y^-}^w + \frac{K_w}{c_{H^+}^w} \\ (\theta_{eq})^2 (c_{M^+}^w \theta_{M^+} + c_{O^+}^w \theta_{O^+} + c_{H^+}^w \theta_{H^+}) = \frac{c_{X^-}^w}{\theta_{X^-}} + \frac{c_{Y^-}^w}{\theta_{Y^-}} + \frac{K_w}{c_{H^+}^w \theta_{HO^-}} \end{cases} \quad (28)$$

From Eq. (28) after some rearrangement we obtain system of 4-non-linear equations in 4-variables ($\Delta_0^w \phi_{eq}$, $c_{H^+}^w$, $c_{Y^-}^w$ and $c_{X^-}^w$).

For $r \rightarrow 0$, the solution of Eq. (28) takes the form of Eq. (18) (see Section 3.1). For $r \rightarrow \infty$, the ion-pair formation in the organic phase is negligible since $c_{X^-}^w \rightarrow 0$ and $c_{M^+}^w \rightarrow 0$ (see line (5) in Fig. 8). The distribution potential depends on the $c_{OY,o}^{init}$ values. The limiting behaviour of the distribution potential can be obtained from Eq. (20) (see Section 3.1). Hence, the limiting behaviour of $\Delta_0^w \phi_{eq}$ depends neither on r nor on ion-pair constant formation. A similar analysis can be performed for $r \rightarrow 0$.

The behaviour of the distribution potential as a function of $\log(r)$ is shown in Fig. 8. In this figure different systems are compared: (1) $K_{OX}^o = K_{MY}^o = 0$; (2) $K_{OX}^o = 0$ and $\log(K_{MY}^o) = 10.0$; (3) $\log(K_{OX}^o) = 5.0$ and $K_{MY}^o = 0$ and (4) $\log(K_{OX}^o) = 5.0$ and $\log(K_{MY}^o) = 10.0$. In general, a change in the distribution potential behaviour occurs for $0 < \log(r) < 17$. In this range, the $\Delta_0^w \phi_{eq}$ value of system (2) presents a marked shift to lower values compared to system (1). Despite the fact that the maximal ion-pair concentration in the organic phase is in the order of 10^{-11} M as shown in Fig. 8, the change in the distribution potential is about 150 mV. In addition, for system (3) the value of distribution potential for $0 < \log(r) < 17$ is higher than that in the absence of ion-pair formation (system (1)). The same trend is observed when comparing system (4) with system (2).

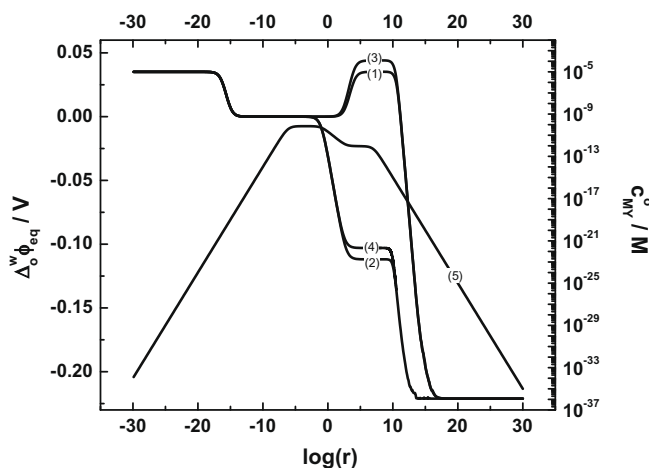


Fig. 8. Effect of the volume ratio on the distribution potential for different ion-pair formation constants. $K_{OX}^o = K_{MY}^o = 0$ (1); $K_{OX}^o = 0$ and $\log(K_{MY}^o) = 10.0$ (2); $\log(K_{OX}^o) = 5.0$ and $K_{MY}^o = 0$ (3); and $\log(K_{OX}^o) = 5.0$ and $\log(K_{MY}^o) = 10.0$ (4). Line (5) represents the c_{MV}^o in the organic phase for system (2). $c_{MX,w}^{init} = 1.0 \times 10^{-5}$ M, $c_{OY,o}^{init} = 1.0 \times 10^{-5}$ M, $\Delta_o^w \phi_{H^+} = 0.550$ V, $\Delta_o^w \phi_{HO^-} = -1.00$ V, $\Delta_o^w \phi_{M^+} = 0.600$ V, $\Delta_o^w \phi_{X^-} = -0.528$ V, $\Delta_o^w \phi_{O^+} = -0.364$ V and $\Delta_o^w \phi_{Y^-} = 0.364$ V. $pK_w = 14.0$.

3.3.2. Distribution of weak bases

We now consider a two-phase system composed of completely dissociated electrolytes MX and HLX in the aqueous phase and OY in the organic phase. The ion-pair formation of HLY in the organic phase is considered.

According to Eqs. (13) and (14), the system of equations to be solved is the following:

$$\begin{cases} c_{HL^+}^w = c_{HLX,w}^{init} \left[1 + r\theta_{eq}\theta_{HL^+} + \frac{K_{a,HL^+}^w}{c_{H^+}^w} (1 + rK_{D,L}) + rK_{HLY}^o c_{Y^-}^w \frac{\theta_{HL^+}}{\theta_{Y^-}} \right]^{-1} \\ c_{M^+}^w = c_{MX,w}^{init} [1 + r\theta_{eq}\theta_{M^+}]^{-1} \\ c_{O^+}^w = r c_{OY,o}^{init} [1 + r\theta_{eq}\theta_{O^+}]^{-1} \\ c_{X^-}^w = (c_{HLX,w}^{init} + c_{MX,w}^{init}) \left[1 + \frac{r}{\theta_{eq}\theta_{X^-}} \right]^{-1} \\ r c_{OY,o}^{init} = c_{Y^-}^w \left[1 + \frac{r}{\theta_{eq}\theta_{Y^-}} + rK_{HLY}^o c_{HL^+}^w \frac{\theta_{HL^+}}{\theta_{Y^-}} \right] \\ c_{H^+}^w + c_{M^+}^w + c_{HL^+}^w + c_{O^+}^w = c_{X^-}^w + c_{Y^-}^w + \frac{K_w}{c_{H^+}^w} \\ (\theta_{eq})^2 (c_{H^+}^w \theta_{H^+} + c_{M^+}^w \theta_{M^+} + c_{HL^+}^w \theta_{HL^+} + c_{O^+}^w \theta_{O^+}) \\ = \frac{c_{X^-}^w}{\theta_{X^-}} + \frac{c_{Y^-}^w}{\theta_{Y^-}} + \frac{K_w}{c_{H^+}^w \theta_{HO^-}} \end{cases} \quad (29)$$

From Eq. (29) after some rearrangement we obtain system of 3-non-linear equations in 3-variables ($\Delta_o^w \phi_{eq}$, $c_{H^+}^w$ and $c_{Y^-}^w$).

The behaviour of the distribution potential as a function of r is shown in Fig. 9. The change of the ion-pair concentration in the organic phase, c_{HLY}^o , for $\log(K_{HLY}^o) = 3.00$ is also shown. The effect of the ion-pair formation on the distribution potential is maximal for $-6 < \log(r) < 8$. In this interval, the dissociation of the protonated species, HL^+ , takes place. It should be noted that the minimal distribution potential value, $\Delta_o^w \phi_{eq, min}$, decreases when the ion-pair constant formation increases; i.e., for $\log(K_{HLY}^o) = 3.00$, $\Delta_o^w \phi_{eq, min} = -0.069$ V and $\log(K_{HLY}^o) = 5.00$, $\Delta_o^w \phi_{eq, min} = -0.11$ V. In the same figure, the $\Delta_o^w \phi_{eq}$ for the system without ion-pair formation is shown.

The ion-pair concentration formed in the organic phase presents a maximal value equal to 0.14 mM at $\log(r)$ close to -4.5 . At high $\log(r)$ values, the ion-pair concentration decreases and the distribution potential is $\frac{1}{2}(\Delta_o^w \phi_{M^+} + \Delta_o^w \phi_{X^-})$. At both, the nega-

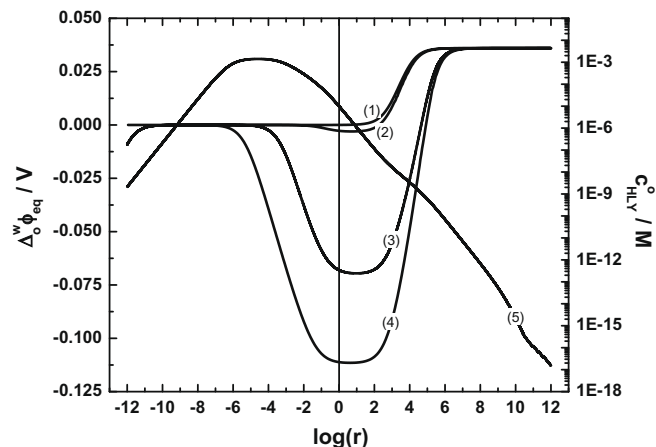


Fig. 9. Effect of the volume ratio on the distribution potential for different ion-pair formation constants. In all lines: $c_{MX,w}^{init} = 1.0$ M and $c_{OY,o}^{init} = 1.0$ M. $c_{HLX,w}^{init} = 0.0$ M and $K_{HLY}^o = 0.0$ (1); $c_{HLX,w}^{init} = 1.0 \times 10^{-4}$ M and $K_{HLY}^o = 0.0$ (2); $c_{HLX,w}^{init} = 1.0 \times 10^{-4}$ M and $\log(K_{HLY}^o) = 3.0$ (3); and $c_{HLX,w}^{init} = 1.0 \times 10^{-4}$ M and $\log(K_{HLY}^o) = 5.0$ (4). Line (5) represents the c_{HLY}^o in the organic phase for system (3). $\log(K_{D,L}) = 2.00$, $pK_{a,HL^+} = 5.00$, $\Delta_o^w \phi_{H^+} = 0.550$ V, $\Delta_o^w \phi_{HO^-} = -1.00$ V, $\Delta_o^w \phi_{M^+} = 0.600$ V, $\Delta_o^w \phi_{X^-} = -0.528$ V, $\Delta_o^w \phi_{O^+} = -0.364$ V, $\Delta_o^w \phi_{Y^-} = 0.364$ V and $\Delta_o^w \phi_{HL^+} = 0.100$ V. $pK_w = 14.0$.

tive and the positive extremes of $\log(r)$, the ion-pair concentration decreases because $c_{Y^-}^w \rightarrow 0$ or $c_{HL^+}^w \rightarrow 0$, respectively (*vide infra*).

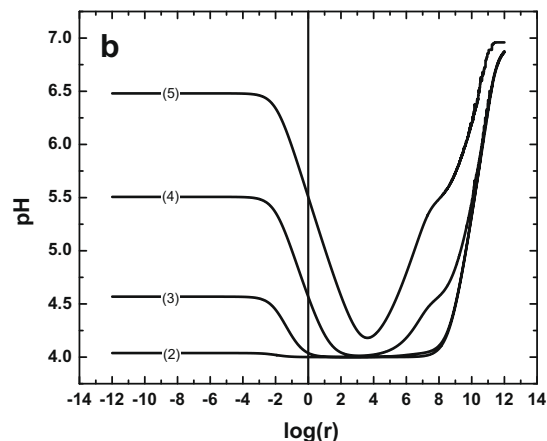
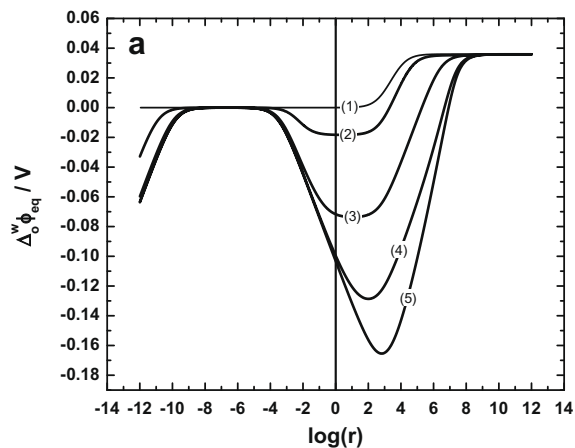


Fig. 10. Effect of the volume ratio on the distribution potential (a) and on pH (b) for different pK_{a,HL^+} . In all lines: $c_{MX,w}^{init} = 1.0$ M and $c_{OY,o}^{init} = 1.0$ M. $c_{HLX,w}^{init} = 0.0$ M (1); $c_{HLX,w}^{init} = 1.0 \times 10^{-4}$ M: $pK_{a,HL^+} = 3.00$ (2); 5.00 (3); 7.00 (4); and 9.00 (5). $\log(K_{HLY}^o) = 3.0$. Other parameters as in Fig. 9.

When the water autoprotolysis is considered (Eq. (12)), the lower limit of $\Delta_o^w \phi_{eq}$ depends on the $c_{HLX,w}^{init}$, $c_{MX,w}^{init}$ and the pK_{a,HL^+}^w values. The $\Delta_o^w \phi_{eq}$ limiting value for $r \rightarrow 0$ according to Eq. (29) can be expressed as follows:

$$\Delta_o^w \phi_{eq} = \frac{RT}{2F} \ln \left[\frac{\frac{K_w}{\theta_{HO^-} c_{H^+}^w} + \frac{(c_{HLX,w}^{init} + c_{MX,w}^{init})}{\theta_{X^-}}}{(\theta_{H^+} c_{H^+}^w + \theta_{M^+} c_{MX,w}^{init} + \alpha_{HL^+} \theta_{HL^+} c_{HLX,w}^{init})} \right] \quad (30)$$

where $\alpha_{HL^+} = \frac{c_{H^+}^w}{c_{H^+}^w + K_{a,HL^+}^w}$. The $c_{H^+}^w$ values can be calculated in all the experimental conditions according to Eq. (A3) (see Appendix A). On the other hand, as $r \rightarrow \infty$, the $c_{HL^+}^w$ value vanishes and therefore, the ion-pair formation in the organic phase is negligible. For this reason, the distribution potential only depends on the total concentration of the electrolyte in the organic phase. In this limit, $\Delta_o^w \phi_{eq}$ is described by Eq. (20) (Section 3.1).

In summary, the ion-pair formation in the organic phase is controlled by the concentration of HL^+ in the aqueous phase and the concentration of Y^- in the organic phase. In the limiting cases, one of these concentrations vanishes (for $r \rightarrow 0$, $c_Y^o \rightarrow 0$ or for $r \rightarrow \infty$, $c_{HL^+}^w \rightarrow 0$). As a consequence, the ion-pair formation in the organic phase is negligible. Therefore, the distribution potential at the limiting r values is independent of the ion-pair formation.

Due to the fact that the dissociation of HL^+ modifies the behaviour of the distribution potential at $\log(r)$ close to zero, in Fig. 10a the change of the $\Delta_o^w \phi_{eq}$ for different acid dissociation constant values of HL^+ are shown. In general, when the acid dissociation constant increases, the $\log(r)$ value where $\Delta_o^w \phi_{eq}$ is minimal increases. This is a consequence of the amount of HL^+ present in the aqueous phase. The change of the pH values as a function of the volume ratio is shown in Fig. 10b. The effect of the acid dissociation of HL^+ is clearly seen in this figure. For $\log(r) > -2.00$, the pH decreases due to the partition of the neutral species, L, at the organic phase.

4. Conclusion

The effect of the volume ratio on the partition of ionic components and on the distribution potential established between two immiscible phases has been theoretically examined. The consequences of the presence of weak bases and the effect of water autoprotolysis on the distribution potential are exhaustively analyzed. The principal results of this work are the effect of the water autoprotolysis, in particular at $r \rightarrow \infty$, and the marked effect of the dissociation of the protonated weak base, on the distribution potential. In the case of completely dissociated electrolytes that do not exhibit acid–base activity, the pH value can be different from $\sqrt{K_w}$ for $r \rightarrow \infty$ (see Eq. (22)). In this sense, the results presented here are of fundamental importance for gaining further understanding of the basic properties of the partition of weak bases, with direct application in drug partitions, and in the theoretical treatments of ion-selective electrodes and of liquid extraction.

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Appendix A

In this appendix, the general equations are developed for obtaining the aqueous proton concentration of the analyzed systems in the lower limiting case ($r \rightarrow 0$).

Considering the dissociation of the monoprotic acid (HL^+) and the water hydrolysis the following full equation can be expressed as:

$$(c_{H^+}^w)^3 + a(c_{H^+}^w)^2 + bc_{H^+}^w + c = 0 \quad (A1)$$

where

$$\begin{aligned} a &= K_{a,HL^+}^w \\ b &= -(K_{a,HL^+}^w c_{HLX}^{init} + K_w) \\ c &= -K_w K_{a,HL^+}^w \end{aligned} \quad (A2)$$

The aqueous proton concentration is given by the following analytical equation:

$$c_{H^+}^w = -2\sqrt{Q} \cos\left(\frac{\theta + 2\pi}{3}\right) - \frac{a}{3} \quad (A3)$$

where:

$$Q = \frac{a^2 - 3b}{9}, \quad R = \frac{2a^3 - 9ab + 27c}{54} \quad \text{and} \quad \cos(\theta) = \left(\frac{R}{\sqrt{Q^3}}\right) [12].$$

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