Effect of the phase volume ratio on the equilibrium potential difference at liquid-liquid interfaces

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Two-phase liquid systems MA, H_2O(w)| MX, S(o) and MA, MX, H_2O(w)|S(o) comprising the interface between the aqueous solution (w) and an organic solvent S solution (o), and two uni-univalent electrolytes MA and MX with the common cation M^+ can serve as a simple models to study theoretically the effect of the phase volume ratio $r = V(\mathrm{w})/V(\mathrm{o})$ on the equilibrium potential difference $E = \phi(\mathrm{w})-\phi(\mathrm{o})$. Results of such study can be relevant to the fields of potentiometric and amperometric ion selective electrodes (ISE), ion extraction (IE) systems, or biological membranes, where the phase volume ratio can differ considerably from unity.

Equilibrium potential difference E can be calculated as a function of the electrolyte concentration ratio c_{MX}^0/c_{MA}^0 by combining the condition of electroneutrality for e.g. the aqueous phase w [1,2],

$$c_{M+}(\mathrm{w}) - c_{X-}(\mathrm{w}) - c_{A-}(\mathrm{w}) = 0 \qquad (1)$$

with the mass balance and the Nernst equations, respectively,

$$c_k(\mathrm{w}) + r\, c_k(\mathrm{w}) = n_k^{tot} / V(\mathrm{w}) \qquad (2)$$

$$E = E_k^{0'} + (\mathrm{R}T/z_k\mathrm{F}) \ln [c_k(\mathrm{o})/c_k(\mathrm{w})] \qquad (3)$$

where n_k^{tot} is the total number of moles of the ion k in the system, c_k is the equilibrium ion concentration, z_k is the ion charge number and $E_k^{0'}$ is the formal ion transfer potential. Figure 1 shows the effect of r on the behavior of an ISE system, where the initial ion concentrations ${}^ic_{M+}(\mathrm{w})={}^ic_{A-}(\mathrm{w})=c_{MA}^0$, ${}^ic_{M+}(\mathrm{o})={}^ic_{X-}(\mathrm{o})=c_{MX}^0$, ${}^ic_{X-}(\mathrm{w}) = {}^ic_{A-}(\mathrm{o})=0$. Figure 2 shows then the effect of r on an IE system, where both MA and MX are initially in the phase w, i.e. ${}^ic_{M+}(\mathrm{w})=c_{MA}^0+c_{MX}^0$, ${}^ic_{A-}(\mathrm{w})=c_{MA}^0$, ${}^ic_{X-}(\mathrm{w})=c_{MX}^0$, ${}^ic_{M+}(\mathrm{o})= {}^ic_{X-}(\mathrm{o}) = {}^ic_{A-}(\mathrm{o}) = 0$.

In contrast to the IE system, the effect of the phase volume ratio on the equilibrium potential difference in the ISE model is rather weak, unless the counter ions X^- and A^- differ little in their lipophilicity (or $E_k^{0'}$) from the target ion M^+. Depending on the lipophilicity of the counter ions, both the ISE and IE model exhibit the Nernstian behavior only in a limited range of the ratio c_{MX}^0/c_{MA}^0, which in the ISE model represents the ratio of the initial M^+ ion concentrations in the phase w and o. When this ratio is extremely large or small, E approaches the limiting value, which is given by the distribution potential of the excess electrolyte MA or MX, respectively, e.g. if $c_{MA}^0 >> c_{MX}^0$, $E \cong (E_{M+}^{0'}+ E_{A-}^{0'})/2$. The decline from the Nernstian behavior can complicate the determination of the ion selectivity coefficient. Qualitatively, the Nernst behavior can be observed in the potential range fulfilling $E_{A-}^{0'} << E << E_{X-}^{0'}$. Hence, in designing the ISE for a specific target ion a careful attention should be paid to the selection of the counter ions for both the aqueous and the ISE membrane phase.

References

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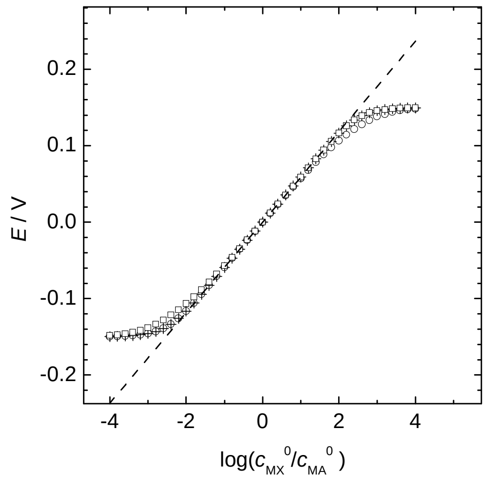

Figure 1 Equilibrium potential difference E for an ISE system vs. the logarithm of the concentration ratio c_{MX}^0/c_{MA}^0 calculated for the phase volume ratio $r = 10^{-3}$ (○), 1 (+) and 10^3 (□), and the values of the standard ion transfer potentials $E_{M+}^{0'}$= 0 V, $E_{A-}^{0'}$ = -0.3 V and $E_{X-}^{0'}$= 0.3 V. Dashed line corresponds to the ideal Nernstian behavior.

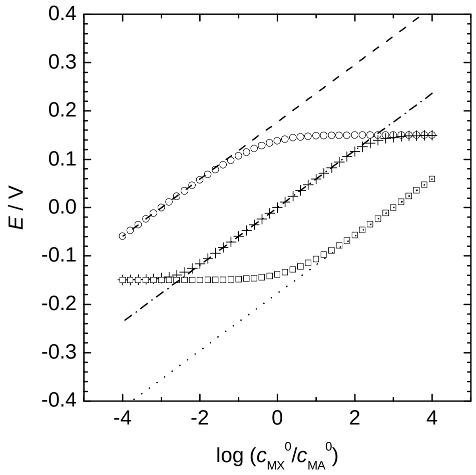

Figure 2 Equilibrium potential difference E for an IE system vs. the logarithm of the concentration ratio c_{MX}^0/c_{MA}^0 calculated for the phase volume ratio $r = 10^{-3}$ (○), 1 (+) and 10^3 (□), and the values of the standard ion transfer potentials $E_{M+}^{0'}$= 0 V, $E_{A-}^{0'}$ = -0.3 V and $E_{X-}^{0'}$= 0.3 V. Dashed line corresponds to the ideal Nernstian behavior.