

On two kinds of equilibrium constants in an extraction system: does an interfacial equilibrium potential control the equilibrium constant?

Abstract

Two kinds of equilibrium constants were discussed based on a thermodynamic cycle of overall extraction equilibrium. Consequently, it was clarified that the individual distribution constants of cation and anion into an organic (o) phase is controlled by an equilibrium potential at the water/o solution interface.

Keywords: individual distribution constant, interfacial equilibrium potential, two kinds of equilibrium constants, extraction constant, dissociation of extracted ion pair

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Abbreviations: O: Organic; Org: organic;

Introduction

An extraction constant with the dissociation of the ML^+A^- ion pair has been defined as

$$K_{ex\pm} = \left[ML^+ \right]_o \left[A^- \right]_o / \left(\left[M^+ \right]_o \left[L \right]_o \left[A^- \right]_o \right) \quad (1)$$

in a molar concentration unit.^{1,2} where M^+ , L, and A^- refer to a univalent metal ion, a ligand such as crown ethers, and a pairing anion as picrate and permanganate ions, respectively. This equation corresponds to the overall extraction equilibrium, $M^+ + L_o + A^- ML_o^+ + A^-_o$ ^{1,2} and is expressed by the product of

$$K_{M/ML} \left(= \left[ML^+ \right]_o / \left[M^+ \right]_o \left[L \right]_o \right) \text{ with } K_{D,A} \left(= \left[A^- \right]_o / \left[A^- \right]_o \right)^1$$

$$K_{ex\pm} = K_{M/ML} \times K_{D,A} \quad (2)$$

at given values of ionic strength. The constants, $K_{M/ML}$ ($= K_{D,M} \times K_{ML,org}$) and $K_{D,A}$, are the functions of an interfacial equilibrium-potential difference ($\Delta\phi_{eq}$)^{3,4} as follows:

$$\log K_{M/ML} = (F / 2.303RT) (\Delta\phi_{eq} - \Delta\phi_M^{0'}) + \log K_{ML,org} \quad (3)$$

with

$$(F / 2.303RT) (\Delta\phi_{eq} - \Delta\phi_M^{0'}) = \log K_{D,M} \quad (3a)$$

$$\log K_{D,A} = -(F / 2.303RT) (\Delta\phi_{eq} - \Delta\phi_A^{0'})^5 \quad (4)$$

The symbols, $K_{D,M}$, $K_{D,A}$, $K_{ML,org}$, $\Delta\phi_M^{0'}$, and $\Delta\phi_A^{0'}$, in Eqs. (3)-(4) denote the individual distribution constant, $\left[M^+ \right]_o / \left[M^+ \right]_o$, of M^+ into an o phase, that of A^- into the o phase, the complex formation constant, $\left[ML^+ \right]_o / \left[M^+ \right]_o \left[L \right]_o$, for ML^+ in the o phase ($\Delta\phi_{eq} = 0$ V because of the reaction in the homogeneous phase), a standard formal potential for the M^+ transfer across the water/o solution interface, and that for A^- across the interface, respectively.^{3,4,6}

Combinations of the experimental $K_{M/ML}$ and $K_{D,A}$ values are infinite in the variation of $\Delta\phi_{eq}$. On the other hand, the combination

of the $K_{M/ML}^s$ and $K_{D,A}^s$ values which are defined as the $K_{M/ML}$

and $K_{D,A}$ ones at $\Delta\phi_{eq} = 0$ V is only one. However, their products, Eq. (2), have to equal with each other by a compensation of the two $\Delta\phi_{eq}$ terms between Eqs. (3) and (4).^{4,6}

Also, Eq. (3) is showing us an interesting fact in an equilibrium condition of the extraction system. For example, the $\log K_{M/ML}$ value is not generally equal to the $\log K_{M/ML}^s$ one. This reason is because the $K_{M/ML}^s$ value is of the condition of $\Delta\phi_{eq} = 0$ V, while the $K_{M/ML}$ ones are of that of certain $\Delta\phi_{eq}$ values. The latter value (or also $K_{D,A}$) becomes a constant only under the condition that all the P, T and $\Delta\phi_{eq}$ values are fixed. That is, there are two kinds of equilibrium constants, $K_{M/ML} (P, T, \Delta\phi_{eq} = \text{constant})$ and $K_{M/ML}^s (P, T = \text{constant})$ or $K_{ML,org}$, in the extraction system.

Moreover, this means that zero of the $E_{ex\pm}$ or $\Delta G_{ex\pm}$ value, which corresponds to the overall extraction system of Eq. (1) and is related with $-zFE_{ex\pm}^0 = -RT \ln K_{ex\pm} (= \Delta G_{ex\pm}^0)$ at $E_{ex\pm} = 0$ V, is not necessarily agreeable to zero of the $\Delta\phi_{eq}$ value at the water/o solution interface. In other words, the condition of

$$E_{ex\pm} = \Delta\phi_{eq,M} + (-\Delta\phi_{eq,A}) = 0 \text{ V} \quad (5)$$

Should be satisfied at the extraction equilibrium.^{3,4,6} That is, the relation, $\Delta\phi_{eq,M} = \Delta\phi_{eq,A} = \Delta\phi_{eq}$, holds in the extraction system.^{3,4,6} Here, the symbols, $\Delta\phi_{eq,M}$ and $\Delta\phi_{eq,A}$, denote the $\Delta\phi_{eq}$ value evaluated from the $K_{D,M}$ and $K_{D,A}$ ones, respectively; the front sign of $\Delta\phi_{eq,A}$ in Eq. (5) shows the formal charge of A^- with the sign.⁵

Conclusion

Consequently, we can see that the two kinds of equilibrium constants, $K_{ML,org}(P,T)$ and $K_{M/ML}(P,T,\Delta\phi_{eq})$, are present in an extraction system at the same time. With respect to this fact, $\Delta\phi_{eq}$ controls magnitudes of $K_{M/ML}$ and $K_{D,A}$ at least.

Acknowledgment

None.

Conflict of Interest

None.

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