

On an Expression of Extraction Constants without the Interfacial Equilibrium-Potential Differences for the Extraction of Univalent and Divalent Metal Picrates by Crown Ethers into 1,2-Dichloroethane and Nitrobenzene

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Abstract

An idea on interfacial equilibrium-potential differences ($\Delta\phi_{eq}$) which are generated for the extraction of univalent metal picrate (MPic) and divalent ones (MPic₂) by crown ethers (L) into high-polar diluents was improved. These potentials were clarified with some experimental extraction-data reported before on the M = Ag(I), Ca(II), Sr(II) and Ba(II) extraction with 18-crown-6 ether (18C6) and benzo-18C6 into 1,2-dichloroethane (DCE) and nitrobenzene (NB). Consequently, it was demonstrated that the $\Delta\phi_{eq}$ values from the extraction-experimentally obtained $\log K_{D,Pic}$ ones are in agreement with or close to those calculated from charge balance equations in many cases, where the symbol, $K_{D,Pic}$, denotes an individual distribution constant of Pic⁻ into the DCE or NB phase. Also, it was experimentally shown that extraction constants based on the overall extraction equilibria do not virtually contain the $\Delta\phi_{eq}$ terms in their functional expressions.

Keywords

Extraction Constants, Distribution Constant of a Single Ion, Interfacial Equilibrium-Potential Differences, 1,2-Dichloroethane, Nitrobenzene, Metal Picrates, Crown Ethers

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1. Introduction

Univalent and divalent metal picrates ($\text{MPic}_z, z = 1 \& 2$), such as alkali and alkaline-earth metal ones, have been extracted by crown compounds (L) into the high-polar diluents, such as 1,2-dichloroethane (DCE), dichloromethane and nitrobenzene (NB) [1]-[5]. In such high-polar diluents, an extracted ion-pair complex, MLPic_z , dissociates ML^{z+} and $z\text{Pic}^-$ [1]-[3] [6]. In introducing these component equilibria in an extraction model, an individual distribution constant ($K_{D,A}$) of $\text{Pic}^- (=A^-)$ into the diluents has been determined extraction-experimentally [1]-[3] [7]. However, in spite of the limitation of the same $K_{D,A}$ definition and the same diluents, the thus-determined $K_{D,\text{Pic}}$ values have differed from each other. For example, the $\log K_{D,\text{Pic}}$ values were -0.94 [2] for the PbPic_2 extraction with 18-crown-6 ether (18C6), -1.34 [7] for the SrPic_2 one with benzo-18C6 (B18C6) into NB, -2.4_6 [3] for the AgPic one with benzo-15-crown-5 ether, -1.89 [2] for the PbPic_2 one with 18C6 and -4.3_5 [6] for the CdPic_2 one with 18C6 into DCE. Thus, their values have changed over experimental errors with combinations of MPic_z and L.

To clarify a reason for such differences, the authors have applied the idea [8] of an interfacial potential difference ($\Delta\phi_{\text{eq}}$) at extraction equilibrium to an expression of $\log K_{D,A}$, namely $-f(\Delta\phi_{\text{eq}} - \Delta\phi_A^{0'})/2.303$ [3] [6] [7], where the negative sign being in the front of f , which denotes F/RT , comes from the electrical charge of A^- . In addition to this, extraction constants, $K_{\text{ex}\pm}$ and $K_{\text{ex}2\pm}$, have been electrochemically expressed as

$zf(\Delta\phi_{\text{eq}} - \Delta\phi_k^{0'})/2.303$ at $k = \text{ex}\pm$ and $z = 1$ and at $\text{ex}\pm, \text{ex}2\pm$ and 2 [3] [7]. Here, $\Delta\phi_A^{0'}$ and $\Delta\phi_k^{0'}$ refer to standard formal potentials for the single distribution of A^- into the diluent or organic (o or org) phase and the formal potentials for the overall equilibrium, respectively. Also, $K_{\text{ex}\pm}$ and $K_{\text{ex}2\pm}$ have been defined experimentally by extraction as $[\text{MLA}^+]_o [\text{A}^-]_o / ([\text{M}^{2+}] [\text{L}]_o [\text{A}^-]^2)$ [2] [7] or $[\text{ML}^+]_o [\text{A}^-]_o / ([\text{M}^+] [\text{L}]_o [\text{A}^-])$ [1]-[3] and $[\text{ML}^{2+}]_o [\text{A}^-]_o^2 / ([\text{M}^{2+}] [\text{L}]_o [\text{A}^-]^2)$ [7], respectively.

On the other hand, from the thermodynamic points of view, these extraction constants are resolved into $K_{D,M} (K_{D,A})^2 K_{\text{ML,org}} K_{1,\text{org}} (= K_{\text{ex}\pm})$ for $z = 2$ [7], $K_{D,M} K_{D,A} K_{\text{ML,org}}$ for 1 [3] and

$K_{D,M} (K_{D,A})^2 K_{\text{ML,org}} (= K_{\text{ex}2\pm})$ for $z = 2$ [7]. Here, the component equilibrium constants, $K_{\text{ML,org}}$ (complex formation in the o phase) and $K_{1,\text{org}}$ (1st-step ion-pair formation in the o one), do not contain the $\Delta\phi_{\text{eq}}$ terms in their expressions, because the constants are of homogeneous systems that all species relevant to the reaction are present in the single o phase [3] [7]; namely no interface is involved in these processes. Similarly, the distribution constant of M^{z+} has been expressed with $K_{D,M}$ (see Equation (3) at $z = 1$ in the Section 2.1) [3]. Therefore, since $K_{D,M}$ and $K_{D,A}$ are present in the $K_{D,M} (K_{D,A})^2$ or $K_{D,M} K_{D,A}$ term, the both terms must cancel out mutually the $\Delta\phi_{\text{eq}}$ ones. Thereby, the extraction constants virtually lose the $\Delta\phi_{\text{eq}}$ terms on their functional expressions. Thus, the above expression, such as $\log K_{\text{ex}\pm} = zf(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^{0'})/2.303$, has caused contradictions on the thermodynamic cycles [3] [7]. Furthermore, such contradictions can cause discrepancies in $\Delta\phi_k^{0'}$ between experimentally-evaluated values and theoretically-reproduced ones [7].

In the present paper, in order to solve the above two contradictions, namely the differences of $K_{D,A}$ caused by experimental conditions of extraction and the contradiction based on the thermodynamic cycles [3] [7], we proposed another expression without $\Delta\phi_{\text{eq}}$ of the extraction constants, $K_{\text{ex}\pm}$ and $K_{\text{ex}2\pm}$. In course of clarifying this expression, some experimentally-determined constants [3] [7], such as $K_{\text{ex}\pm}$, an individual distribution constant ($K_{D,\text{ML}}$) of the complex ion ML^{2+} into the NB phase and that of AgL^+ into DCE, were also reproduced by calculation. Here, the AgPic and MPic_2 ($M = \text{Ca}, \text{Sr} \& \text{Ba}$) extraction with $L = 18\text{C}6$ and/or $\text{B}18\text{C}6$ [3] [7] were employed as model systems. Also, a meaning of the $\Delta\phi_{\text{eq}}$ values [3] [7] & [8] which were calculated from the $\log K_{D,A}$ ones determined by the extraction experiments was discussed based on an electroneutrality-point of view [8] for the o phases. Moreover, the thus-obtained expressions for the extraction constants were applied to other types of extraction systems with o = DCE and NB.

2. Theory

2.1. $\Delta\phi_{\text{eq}}$ Values Derived from Charge Balance Equations for the o Phase

(i) Case of the M(I) extraction with L. For the extraction equilibrium, $M^+ + L_o + A^- (\rightleftharpoons MLA_o) \rightleftharpoons ML_o^+ + A_o^-$, we can obtain from the extraction model (see [Appendix I](#) for more details) reported before the following charge-balance equation

$$[M^+]_o + [ML^+]_o = [A^-]_o \quad (1)$$

for the o phase. The concentrations of M^+ and A^- in the o phase were modified as

$$[M^+] \exp\left\{f\left(\Delta\phi_{\text{eq}} - \Delta\phi_M^{0'}\right)\right\} + [ML^+]_o = [A^-] \exp\left\{-f\left(\Delta\phi_{\text{eq}} - \Delta\phi_A^{0'}\right)\right\} \quad (2)$$

by using electrochemical equations [6] [8] such as

$$\Delta\phi_{\text{eq}} = \Delta\phi_M^{0'} + f^{-1} \ln\left(\frac{[M^+]_o}{[M^+]}\right) \quad (3)$$

and

$$\Delta\phi_{\text{eq}} = \Delta\phi_A^{0'} - f^{-1} \ln\left(\frac{[A^-]_o}{[A^-]}\right); \quad (4)$$

see Appendix B in ref [6] for a detailed derivation from electrochemical potentials to this equation. Here, $\Delta\phi_j^{0'}$ and $[j]_o/[j]$ denote a standard formal potential of species j ($=M(I)$, $A(-I)$ & $ML(I)$; see the introduction and section 3.3) and the individual distribution constant ($K_{D,j}$) of j between the two phases, respectively. At least, the $\Delta\phi_j^{0'}$ values are available from references for $M = Ag(I)$ [9], $Ca(II)$ [10], $Sr(II)$ [10] and $Ba(II)$ [10] and $A = Pic(-I)$ [11] into the DCE and NB phases. Additionally, the

$\log K_{D,A} \left\{ = \log\left(\frac{[A^-]_o}{[A^-]}\right) = 2.303^{-1} \ln\left(\frac{[A^-]_o}{[A^-]}\right) \right\}$ values have been determined extraction-experimentally [1]-[3] [6] [7]; see [Appendix II](#) for the $K_{D,A}$ determination. Defining as $\exp(f\Delta\phi_{\text{eq}}) = x$ and then rearranging Equation (2), we can easily obtain

$$x = \left(\sqrt{b^2 - 4ac} - b\right) / 2a (> 0) \quad (5)$$

with

$$a = [M^+] \exp\left(-f\Delta\phi_M^{0'}\right), \quad (5a)$$

$$b = [ML^+]_o \quad (5b)$$

and

$$c = -[A^-] \exp\left(f\Delta\phi_A^{0'}\right). \quad (5c)$$

Accordingly, the following equation is derived.

$$\Delta\phi_{\text{eq}} = f^{-1} \ln x = 0.05916 \log x \quad (\text{V unit at 298 K}) \quad (6)$$

Hence, if the $[M^+]$, $[ML^+]_o$ and $[A^-]$ values are determined experimentally, then we can obtain the $\Delta\phi_{\text{eq}}$ values from Equation (6) immediately; the $[ML^+]_o$ values were calculated here from the relation

$$[ML^+]_o = (K_{\text{ex}}^{\text{mix}} - K_{\text{ex}}) [M^+] [L]_o [A^-] (> 0) \quad \text{with}$$

$$K_{\text{ex}}^{\text{mix}} = \left\{ \text{total concentration of analyzed M(I) in the o phase} \right\} / \left([M^+] [L]_o [A^-] \right) \quad (\text{see [Appendix II](#) for more detail})$$

and $K_{\text{ex}} = [MLA]_o / \left([M^+] [L]_o [A^-] \right)$. The data of $[ML^+]_o \leq 0$ were neglected in a further computation.

(ii) Case of the M(II) extraction with L. Similarly, we can consider the following stepwise extraction-equilibria [6] [12] at the same time: $M^{2+} + L_o + 2A^- (\rightleftharpoons MLA_{2,o}) \rightleftharpoons MLA_o^+ + A_o^- \rightleftharpoons ML_o^{2+} + 2A_o^-$ (see [Appendix I](#)

for a basic extraction model and **Appendix II** for the $K_{D,A}$ determination). Therefore, the charge balance equation for the o phase becomes

$$2[M^{2+}]_o + 2[ML^{2+}]_o + [MLA^+]_o = [A^-]_o. \quad (7)$$

As described above, this equation was modified to [8]

$$\begin{aligned} & 2[M^{2+}] \exp\left\{2f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{M}}^{0'})\right\} + 2[ML^{2+}] \exp\left\{2f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ML}}^{0'})\right\} + [MLA^+]_o \\ & = [A^-] \exp\left\{-f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{A}}^{0'})\right\}. \end{aligned} \quad (8)$$

Defining as $\exp(f\Delta\phi_{\text{eq}}) = x$ and then rearranging Equation (8), we easily obtain the cubic equation

$$a'x^3 + b'x + c' = 0 \quad (9)$$

with

$$a' = 2[M^{2+}] \exp(-2f\Delta\phi_{\text{M}}^{0'}) + 2[ML^{2+}] \exp(-2f\Delta\phi_{\text{ML}}^{0'}), \quad (9a)$$

$$b' = [MLA^+]_o \quad (9b)$$

and

$$c' = -[A^-] \exp(f\Delta\phi_{\text{A}}^{0'}) \quad (9c)$$

We can exactly solve this equation for x based on the mathematical formula [13]. Its real solution is

$$x = \left\{-(q/2) + \sqrt{(q^2/4) + (p^3/27)}\right\}^{1/3} + \left\{-(q/2) - \sqrt{(q^2/4) + (p^3/27)}\right\}^{1/3}, \quad (10)$$

where $p = b'/a'$ and $q = c'/a'$. Therefore, we can similarly obtain the $\Delta\phi_{\text{eq}}$ value from the combination of Equations (6) and (10).

The b' values were evaluated from the relation, $r_+ \sum [MLA_N^{(2-N)+}]_o$ with $N=1$ and 2, where $r_+ = [MLA^+]_o / ([MLA^+]_o + [MLA_2]_o)$
 $(\approx (K_{\text{ex}\pm} [M^{2+}] [L]_o)^{1/2} [A^-] / \left\{ (K_{\text{ex}\pm} [M^{2+}] [L]_o)^{1/2} [A^-] + K_{\text{ex}} [M^{2+}] [L]_o [A^-]^2 \right\})$ under the condition of $[MLA^+]_o \approx [A^-]_o$ [7]). The $\sum [MLA_N^{(2-N)+}]_o$ values were directly determined by AAS measurements in the extraction experiments [2] [7] and also we were able to calculate the other values in r_+ from the experimental data [7].

2.2. On Expressions of the Extraction Constants without $\Delta\phi_{\text{eq}}$

According to previous papers, the two of the three extraction constants have been defined as

$$\log K_{\text{ex}\pm} = f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^{0'}) / 2.303 = (f\Delta\phi_{\text{eq}} / 2.303 + \log K_{\text{ex}\pm}^S) \quad \text{for the } M^I A\text{-L extraction system [3] and}$$

$$\log K_{\text{ex}\pm} = f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}\pm}^{0'}) / 2.303 \quad \text{and} \quad \log K_{\text{ex}2\pm} = 2f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{ex}2\pm}^{0'}) / 2.303 = (2f\Delta\phi_{\text{eq}} / 2.303 + \log K_{\text{ex}2\pm}^S)$$

for the $M^{II} A_2\text{-L extraction one [7]. Here, } \log K_{\text{ex}\pm} \text{ (or } \log K_{\text{ex}2\pm}) \text{ equals } \log K_{\text{ex}\pm}^S \text{ (or } \log K_{\text{ex}2\pm}^S) \text{ at } \Delta\phi_{\text{eq}} = 0 \text{ V.}$

These two kinds of extraction constants contain the $\Delta\phi_{\text{eq}}$ terms as parameters in their functional expressions [3] [7]. On the other hand, $\log K_{\text{ex}}$ has been expressed as $-f\Delta\phi_{\text{ex}}^{0'} / 2.303$ or $-2f\Delta\phi_{\text{ex}}^{0'} / 2.303$ without $\Delta\phi_{\text{eq}}$ and spontaneously became an expression electrochemically-standardized at $\Delta\phi_{\text{eq}} = 0 \text{ V}$ [3] [7].

In the above functions, some contradictions have been observed in the former cases: see Appendix in ref. [7]. As an example similar to that described in the introduction, the relation,

$\log K_{\text{ex}} - \log K_{\text{ex}\pm} = \log K_{2,\text{org}} \left\{ = \log \left(\frac{[\text{MLA}_2]_o}{[\text{MLA}^+]_o [\text{A}^-]_o} \right) \right\}$, must give a function without $\Delta\phi_{\text{eq}}$, because the resulting component equilibrium-constant $K_{2,\text{org}}$ does not relate with $\Delta\phi_{\text{eq}}$ [7]; namely $K_{2,\text{org}}$ and K_{ex} are the constants at $\Delta\phi_{\text{eq}} = 0 \text{ V}$. However, using the above definition [3] [7], the same term, $\log K_{\text{ex}} - \log K_{\text{ex}\pm}$, becomes $\log K_{\text{ex}}^{\text{S}} - \log K_{\text{ex}\pm}^{\text{S}} = -f\Delta\phi_{\text{eq}}/2.303$ and then the $\Delta\phi_{\text{eq}}$ term does not disappear, where

$\log K_{\text{ex}}^{\text{S}} (= \log K_{\text{ex}}) = -2f\Delta\phi_{\text{ex}}^{0'}/2.303$ and $\log K_{\text{ex}\pm}^{\text{S}} = -2f\Delta\phi_{\text{ex}\pm}^0/2.303$. The same is also true of the result of $\log K_{\text{ex}\pm} - \log K_{\text{ex}2\pm} = (\log K_{\text{ex}\pm}^{\text{S}} - \log K_{\text{ex}2\pm}^{\text{S}} - f\Delta\phi_{\text{eq}}/2.303) = \log K_{1,\text{org}}$ which is defined as

$\log \left(\frac{[\text{MLA}^+]_o}{[\text{ML}^{2+}]_o [\text{A}^-]_o} \right)$. These two facts obviously have the contradiction with respect to $\Delta\phi_{\text{eq}}$.

In order to cancel such contradictions, we assume here that the two extraction constants are functions without $\Delta\phi_{\text{eq}}$, as well as that of K_{ex} [3] [7]. Accordingly, the constants are defined as

$$\log K_{\text{ex}\pm} = \log K_{\text{ex}\pm}^{\text{S}} = -f\Delta\phi_{\text{ex}\pm}^0/2.303 \quad (11)$$

and

$$\log K_{\text{ex}2\pm} = \log K_{\text{ex}2\pm}^{\text{S}} = -2f\Delta\phi_{\text{ex}2\pm}^0/2.303. \quad (12)$$

That is, by our traditional sense, it is proposed here that complicated equilibrium constants, such as K_{ex} , $K_{\text{ex}\pm}$ and $K_{\text{ex}2\pm}$, do not contain the $\Delta\phi_{\text{eq}}$ terms in their functions. This means that these constants are ordinarily defined without $\Delta\phi_{\text{eq}}$ or under the condition of $\Delta\phi_{\text{eq}} = 0 \text{ V}$ and thereby are electrochemically-standardized as $K_{\text{ex}\pm}^{\text{S}}$ and $K_{\text{ex}2\pm}^{\text{S}}$ [3] [7]. **Table 1** lists new (or traditional) expressions of such extraction constants composed of some component equilibrium constants based on thermodynamic cycles.

The relations in **Table 1** shows that the individual distribution process of A^- [12] cancels out that of a cation [14], such as M^+ , R_4N^+ , M^{2+} and ML^{2+} , in $\Delta\phi_{\text{eq}}$. As an example, the thermodynamic relation for M(II)

$$\log K_{\text{ex}\pm} = \log K_{\text{D},\text{M}} + 2\log K_{\text{D},\text{A}} + \log K_{\text{ML},\text{org}} + \log K_{1,\text{org}} \quad (13)$$

can be rearranged into

$$\begin{aligned} -f\Delta\phi_{\text{ex}\pm}^0/2.303 &= 2f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{M}}^{0'}) - 2f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{A}}^{0'}) - 2f\Delta\phi_{\text{ML},\text{org}}^0/2.303 - f\Delta\phi_{1,\text{org}}^0/2.303 \\ &= -2f\Delta\phi_{\text{M}}^{0'} + 2f\Delta\phi_{\text{A}}^{0'} - 2f\Delta\phi_{\text{ML},\text{org}}^0/2.303 - f\Delta\phi_{1,\text{org}}^0/2.303. \end{aligned} \quad (14)$$

Table 1. Relations between $K_{\text{ex}\pm}$ or $K_{\text{ex}2\pm}$ and its component equilibrium constants and their corresponding $\Delta\phi_k^{0'}$ values^a.

Overall equilibrium & Its cycle ^b	Relation
$\text{M}^+ + \text{L}_o + \text{A}^- \rightleftharpoons \text{ML}_o^+ + \text{A}_o^-$	(a) $\log K_{\text{ex}\pm} = \log K_{\text{D},\text{M}} + \log K_{\text{D},\text{A}} + \log K_{\text{ML},\text{org}}$
(a) $K_{\text{ex}\pm} = K_{\text{D},\text{M}} K_{\text{D},\text{A}} K_{\text{ML},\text{org}}$ ^c	or $\Delta\phi_{\text{ex}\pm}^0/2.303 = \Delta\phi_{\text{M}}^{0'} - \Delta\phi_{\text{A}}^{0'} + \Delta\phi_{\text{ML},\text{org}}^0/2.303$
(b) $K_{\text{ex}\pm} = K_{\text{D},\text{ML}} K_{\text{D},\text{A}} K_{\text{ML}}/K_{\text{D},\text{L}}$	(b) $\log K_{\text{ex}\pm} = \log K_{\text{D},\text{ML}} + \log K_{\text{D},\text{A}} + \log K_{\text{ML}} - \log K_{\text{D},\text{L}}$ or $\Delta\phi_{\text{ex}\pm}^0/2.303 = \Delta\phi_{\text{ML}}^0/2.303 - \Delta\phi_{\text{A}}^{0'} + \Delta\phi_{\text{ML},\text{w}}^0/2.303 - \Delta\phi_{\text{L}}^{0'}$
$\text{M}^{2+} + \text{L}_o + 2\text{A}^- \rightleftharpoons \text{ML}_o^{2+} + \text{A}_o^-$	(c) $\log K_{\text{ex}\pm} = \log K_{\text{D},\text{M}} + 2\log K_{\text{D},\text{A}} + \log K_{\text{ML},\text{org}} + \log K_{1,\text{org}}$ or $\Delta\phi_{\text{ex}\pm}^0/2.303 = 2\Delta\phi_{\text{M}}^{0'} - 2\Delta\phi_{\text{A}}^{0'} + 2\Delta\phi_{\text{ML},\text{org}}^0/2.303 + \Delta\phi_{1,\text{org}}^0/2.303$
(c) $K_{\text{ex}\pm} = K_{\text{D},\text{M}} (K_{\text{D},\text{A}})^2 K_{\text{ML},\text{org}} K_{1,\text{org}}$ ^d	(d) $\log K_{\text{ex}\pm} = \log K_{\text{D},\text{ML}} + 2\log K_{\text{D},\text{A}} + \log K_{\text{ML}} + \log K_{1,\text{org}} - \log K_{\text{D},\text{L}}$ or $\Delta\phi_{\text{ex}\pm}^0/2.303 = 2\Delta\phi_{\text{ML}}^0/2.303 - 2\Delta\phi_{\text{A}}^{0'} + 2\Delta\phi_{\text{ML},\text{w}}^0/2.303 + \Delta\phi_{1,\text{org}}^0/2.303 - \Delta\phi_{\text{L}}^{0'}$
(d) $K_{\text{ex}\pm} = K_{\text{D},\text{ML}} (K_{\text{D},\text{A}})^2 K_{\text{ML}} K_{1,\text{org}}/K_{\text{D},\text{L}}$ ^d	(e) $\log K_{\text{ex}2\pm} = \log K_{\text{D},\text{M}} + 2\log K_{\text{D},\text{A}} + \log K_{\text{ML},\text{org}}$ or $\Delta\phi_{\text{ex}2\pm}^0/2.303 = \Delta\phi_{\text{M}}^{0'} - \Delta\phi_{\text{A}}^{0'} + \Delta\phi_{\text{ML},\text{org}}^0/2.303$
$\text{M}^{2+} + \text{L}_o + 2\text{A}^- \rightleftharpoons \text{ML}_o^{2+} + 2\text{A}_o^-$	(f) $\log K_{\text{ex}2\pm} = \log K_{\text{D},\text{ML}} + 2\log K_{\text{D},\text{A}} + \log K_{\text{ML}} - \log K_{\text{D},\text{L}}$ or $2\Delta\phi_{\text{ex}2\pm}^0/2.303 = 2\Delta\phi_{\text{ML}}^0/2.303 - 2\Delta\phi_{\text{A}}^{0'} + 2\Delta\phi_{\text{ML},\text{w}}^0/2.303 - \Delta\phi_{\text{L}}^{0'}$
(e) $K_{\text{ex}2\pm} = K_{\text{D},\text{M}} (K_{\text{D},\text{A}})^2 K_{\text{ML},\text{org}}$ ^d	
(f) $K_{\text{ex}2\pm} = K_{\text{D},\text{ML}} (K_{\text{D},\text{A}})^2 K_{\text{ML}}/K_{\text{D},\text{L}}$	

^a $k = \text{ex}\pm, \text{ex}2\pm, \text{ML}, \text{org}, \text{ML}, \text{w}, \& 1, \text{org}$, where the symbol “w” shows a water phase; ^bThermodynamic cycle; ^cRef. [3]; ^dRef. [7].

Therefore, the relation (c) in **Table 1** is immediately obtained. From Equations (2) and (8), one should obviously see that $\Delta\phi_{\text{eq}}$ of $K_{\text{D,M}}$ equals that of $K_{\text{D,A}}$ in the extraction system of Equation (13). Also, we can rewrite Equation (13) to

$$\log K_{\text{ex}\pm} = \log K_{\text{D,M}}^{\text{S}} + 2 \log K_{\text{D,A}}^{\text{S}} + \log K_{\text{ML,org}} + \log K_{\text{l,org}} = \log K_{\text{ex}\pm}^{\text{S}} \quad (13a)$$

Consequently, Equation (14) or (13) does not contain the $\Delta\phi_{\text{eq}}$ term and is virtually expressed with only the standard formal potentials (at $\Delta\phi_{\text{eq}} = 0 \text{ V}$) as Equation (13a). The thermodynamic relations are also satisfied with the expressions such as Equations (11) and (12). The same is true of the other relations in **Table 1**.

3. Results and Discussion

3.1. On a Meaning of $\Delta\phi_{\text{eq}}$ Estimated from $\log K_{\text{D,A}}$

Table 2(a) lists fundamental data [3] for the extraction of AgPic by B18C6 into DCE. The $\Delta\phi_{\text{eq}}$ values were calculated from Equation (4) and the experimental $\log K_{\text{D,Pic}}$ values in **Table 2(a)**.

Here, $f\Delta\phi_{\text{Pic}}^0 / 2.303 (= \Delta\phi_{\text{Pic}}^0 / 0.05916 = \log K_{\text{D,Pic}}^{\text{S}}) = -1.01_1$ [11] at 298 K was employed in the calculation.

Table 2. (a) Fundamental data for the extraction of AgPic by B18C6 into DCE at 298 K; (b) Evaluated $\Delta\phi_{\text{eq}}$ values; (c) Reproduced $\log K_{\text{ex}\pm}$ values; (d) Evaluated $\log K_{\text{D,AgL}}^{\text{S}}$ and reproduced $\log K_{\text{D,AgL}}$ values.

(a)						
Data no.	$\log K_{\text{ex}}$	$\log K_{\text{ex}\pm}$	$\log K_{\text{D,A}}$	$\log K_{\text{ML,DCE}}^{\text{a}}$ ($I_{\text{DCE}}^{\text{c}}/10^{-5}$)	$\log K_{\text{l,DCE}}^{\text{b}}$	$\log K_{\text{D,ML}}$
1A ^d	5.55	$0.17 \pm 0.03, -0.5_1$	-2.70	5.68^{f} (0.64)	$5.38^{\text{e}}, 6.0_5$	3.05^{f}
1B ^g	5.17 ± 0.01	0.25 ± 0.09	-2.33 ± 0.03	5.76 (0.40)	4.92	2.76
1C ^g	5.336 ± 0.004	$0.5_1 \pm 0.1_0$	-2.60 ± 0.05	6.03 (1.1)	4.82	3.3
2 ^g	5.07 ± 0.01	-0.13 ± 0.09	-1.68 ± 0.02	5.38 (0.55)	5.20	1.73

(b)				
	Data no. 1A	1B	1C	2
$\Delta\phi_{\text{eq}}^{(\text{P1})} / \text{V}$	0.10	0.078	0.094	0.040
$\Delta\phi_{\text{eq,av}}^{(\text{P2})} / \text{V}$	$0.09_3 \pm 0.01_3$	$0.07_4 \pm 0.01_2$	$0.08_9 \pm 0.01_2$	0.040 ± 0.005

(c)				
	Data no. 1A	1B	1C	2
$\log K_{\text{ex}\pm}^{(\text{K5})}$ *	0.17	0.25	0.52	-0.13

(d)				
	Data no. 1A	1B	1C	2
$\log K_{\text{D,AgL}}^{\text{S(K6)}} *$	1.36	1.44	1.7	1.06
$\log K_{\text{D,AgL}}^{(\text{K7})} \text{ §}$	2.94	2.70	3.2	1.74

* $\log K_{\text{ex}\pm}^{(\text{K5})} = \log K_{\text{D,Ag}}^{\text{S}} + \log K_{\text{D,Pic}}^{\text{S}} + \log K_{\text{AgL,DCE}}^{(\text{Table 2(a)})}$.
 § $\log K_{\text{D,AgL}}^{(\text{K7})} = \Delta\phi_{\text{eq,av}}^{(\text{P2})} / 0.05916 + \log K_{\text{D,AgL}}^{\text{S(K6)}}$.

Also, we estimated $\Delta\phi_{\text{eq,av}}$ from Equation (6) with Equation (5), where $\Delta\phi_{\text{eq,av}}$ denotes an average value for each run.

The both values, expressed as $\Delta\phi_{\text{eq}}^{(\text{P1})}$ & $\Delta\phi_{\text{eq,av}}^{(\text{P2})}$ in **Table 2(b)**, agreed well within experimental errors.

Average I values of the extraction systems in **Table 2(a)** were $0.0036 \text{ mol}\cdot\text{dm}^{-3}$ for the no. 1A [3], 0.0028 for 1B, 0.0027 for 1C and 0.097 for 2; I denotes the ionic strength of the water phase in the extraction. Except for the data no. 2, we can handle other three data on the average, because experimental conditions [3] of the data are essentially the same (see the footnote g in **Table 2(a)** for no. 2). So the following values were obtained at 298 K and $L = \text{B18C6}$: $\log K_{\text{ex}\pm} = 0.31 \pm 0.14$ and $\log K_{\text{D,Pic}} = -2.54 \pm 0.07$;

$\log K_{\text{AgL,DCE}} \left\{ = \log \left(\frac{[\text{AgL}^+]_{\text{DCE}}}{[\text{Ag}^+]_{\text{DCE}} [\text{L}]_{\text{DCE}}} \right) \right\} = 5.71 \pm 0.2_3$ in the I_{DCE} range of $(0.40 - 1.1) \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ (see the data in **Table 2(a)**) and $\log K_{\text{L,DCE}} \left\{ = \log \left(\frac{[\text{AgLPic}]_{\text{DCE}}}{[\text{AgL}^+]_{\text{DCE}} [\text{Pic}^-]_{\text{DCE}}} \right) \right\} = 5.0_8 \pm 0.2_2$ in the same I_{DCE} range. The symbol, I_{DCE} , refers to the average ionic strength of the DCE phase; the same is true of I_{NB} (see **Table 3**).

Table 3(a) summarizes the fundamental data [7] for the extraction of MPic_2 ($M = \text{Ca, Sr \& Ba}$) by 18C6 and B18C6 into NB.

The $\Delta\phi_{\text{eq}}$ values were calculated from Equation (4) with the $\log K_{\text{D,Pic}}$ values in **Table 3(a)** and the $\Delta\phi_{\text{Pic}}^0 / 0.05916 (= \log K_{\text{D,Pic}}^S) = 0.05$ [11] ones reported previously. From Equation (6) with Equation (10), the $\Delta\phi_{\text{eq,av}}$ values were estimated in the same manner. The above findings are listed in **Table 3(b)**.

For the 18C6 extraction systems, the $\Delta\phi_{\text{eq}}^{(\text{P3})}$ values obtained from Equation (4) are close to the $\Delta\phi_{\text{eq,av}}^{(\text{P4})}$ ones from Equation (6) with Equation (10). On the other hand, the former values are larger than the latter ones for the B18C6 extraction systems.

Except for the $\Delta\phi_{\text{eq}}^{(\text{P3})}$ and $\Delta\phi_{\text{eq,av}}^{(\text{P4})}$ values of the B18C6 systems, the above results indicate that the interfacial equilibrium-potential differences, $\Delta\phi_{\text{eq}}$, based on Equation (4) are essentially the same as those based on Equation (6). The differences between $\Delta\phi_{\text{eq}}^{(\text{P3})}$ and $\Delta\phi_{\text{eq,av}}^{(\text{P4})}$ for the B18C6 systems can be due to those in the charge balance equation between extraction experiments (see **Appendix II**) and electrochemical (or theoretical) treatments, namely $[\text{MLPic}^+]_{\text{NB}} \approx [\text{Pic}^-]_{\text{NB}}$ [7] and Equation (7) or (8). In other words, the condition of $2[\text{M}^{2+}]_{\text{NB}} + 2[\text{ML}^{2+}]_{\text{NB}} \ll [\text{MLPic}^+]_{\text{NB}}$ cannot be satisfied in the B18C6 systems. For example, an average value of $2[\text{BaL}^{2+}]_{\text{NB}} / [\text{BaLPic}^+]_{\text{NB}}$ was 0.1_2 for $L = \text{B18C6}$, while that was 0.02_9 for 18C6; these values were the maximum of the B18C6- and 18C6-M(II) extraction systems. Practically, the $\Delta\phi_{\text{eq,av}}^{(\text{P4})}$ values based on Equation (7) or (8) must be more accurate than the $\Delta\phi_{\text{eq}}^{(\text{P3})}$ ones.

On the basis of the above facts, $\Delta\phi_{\text{eq}}^{(\text{P1})} = \Delta\phi_{\text{eq,av}}^{(\text{P2})}$ and $\Delta\phi_{\text{eq}}^{(\text{P3})} \geq \Delta\phi_{\text{eq,av}}^{(\text{P4})}$, we see that the $\Delta\phi_{\text{eq}}$ value obtained from the distribution process of $\text{A}^- \rightleftharpoons \text{A}_o^-$ is essentially equivalent to that from the combined process of $\text{M}^+ \rightleftharpoons \text{M}_o^+$ and $\text{ML}^+ \rightleftharpoons \text{ML}_o^+$ [8] {see Equations (1) & (2)} or $\text{M}^{2+} \rightleftharpoons \text{M}_o^{2+}$, $\text{MLA}^+ \rightleftharpoons \text{MLA}_o^+$ and $\text{ML}^{2+} \rightleftharpoons \text{ML}_o^{2+}$ {see Equations (7) & (8)} into $o = \text{DCE}$ and NB.

3.2. Experimental Proof of $K_{\text{ex}\pm}$ and $K_{\text{ex}2\pm}$ without $\Delta\phi_{\text{eq}}$

We obtained the $\log K_{\text{ex}\pm}$ values of the AgPic extraction with B18C6 into DCE from the relation (a) in **Table 1** with $\log K_{\text{D,Ag}}^S = -4.502$ [9] ($= -\Delta\phi_{\text{Ag}}^0 / 0.05916$ [3]), $\log K_{\text{D,Pic}}^S = -1.01_1$ [11] (into DCE) and the corresponding $\log K_{\text{ML,DCE}}$ value in **Table 2(a)**. These values, expressed as $\log K_{\text{ex}\pm}^{(\text{K5})}$ below, are in good agreement with those listed in **Table 2(a)**.

The $K_{\text{D,AgL}}$ calculation can be an indirect proof of $K_{\text{ex}\pm}$ without $\Delta\phi_{\text{eq}}$. First, the $\log K_{\text{D,AgL}}$ values (namely $\log K_{\text{D,AgL}}^S$ ones) standardized at $\Delta\phi_{\text{eq}} = 0 \text{ V}$ for $L = \text{B18C6}$ were calculated from the modified form, $\log K_{\text{D,AgL}}^S = \log K_{\text{ex}\pm} - \log K_{\text{D,Pic}}^S - \log K_{\text{AgL}} + \log K_{\text{D,L}}$, of the relation (b) in **Table 1**. The obtained values are

shown as $K_{D,AgL}^{S(K6)}$ in **Table 2(d)**. In this calculation, we employed $\log K_{D,Pic}^S = -1.01_1$ [11] (into DCE), $\log K_{AgL} = \left\{ \log \left(\frac{[AgL^+]}{[Ag^+][L]} \right) \right\} = 1.83$ [15] (in water), $\log K_{D,B18C6} = \left\{ \log \left(\frac{[B18C6]_{DCE}}{[B18C6]} \right) \right\} = 2.009$ [16] at 298 K.

Next, the $\log K_{D,AgL}$ values were reproduced by using the equation,

$\log K_{D,AgL} = \left\{ \log \left(\frac{[AgL^+]_o}{[AgL^+]} \right) \right\} = \Delta\phi_{eq}/0.05916 + \log K_{D,AgL}^S$ at 298 K (see Appendix in ref. [3] for its detailed derivation), with the calculated $\log K_{D,AgL}^{S(K6)}$ values and the $\Delta\phi_{eq,av}^{(P2)}$ ones. These $\log K_{D,AgL}^{S(K7)}$ values in **Table 2(d)** are in good accordance with the values listed in **Table 2(a)**. Thus the $\log K_{D,AgL}$ values can be well reproduced. From the results of $K_{ex\pm}^{(K5)}$ & $K_{D,AgL}^{(K7)}$ at least, we can see that Equation (11) is valid for the Ag Pic-B18C6 extraction system.

Moreover, an average $\log K_{D,AgL}^S$ value for all the $\log K_{D,AgL}^{S(K6)}$ ones was $1.3_9 \pm 0.2_3$. From this value and the $\Delta\phi_{eq}^{(P1)}$ ones, we calculated the $\log K_{D,AgL}$ values again, using the above relation [3]. The value obtained from $\Delta\phi_{eq}^{(P1)}$ of no. 1C was under-estimated by $|0.3|$ and that of no. 2 was over-estimated by the same, compared to those in **Table 2(a)** or of $\log K_{D,AgL}^{(K7)}$. On the other hand, the $\log K_{D,AgL}$ values ($= 3.1$ & 2.7 , respectively) of nos. 1A and 1B were close to those in **Table 2(a)**.

The $\log K_{ex\pm}$ values for the M(II)-B18C6 extraction into NB were calculated from the relation (c) in **Table 1**.

These $\log K_{ex\pm}^{(K8)}$ values are in accordance with the values in **Table 3(a)**; the $\log K_{ex\pm}$ values in **Table 3(a)** have been determined by the procedure [2] [7] described in **Appendix II**. This accordance indicates that Equation (11) without $\Delta\phi_{eq}$ is satisfied. In this calculation, $\log K_{D,Ca}^S = -11.80$, $\log K_{D,Sr}^S = -11.56$, $\log K_{D,Ba}^S = -10.82$ [10], $\log K_{CaL,NB} = 11.2$, $\log K_{SrL,NB} = 13.1$, $\log K_{BaL,NB} = 13.4$ for $L = 18C6$ [17], $\log K_{CaL,NB} = 9.43$, $\log K_{SrL,NB} = 11.1$ and $\log K_{BaL,NB} = 11.6$ for $L = B18C6$ [17] were employed. Also, the $\log K_{D,M}$ values were calculated from the modified form of Equation (3), $\log K_{D,M} = 2\Delta\phi_{eq}/0.05916 + \log K_{D,M}^S$, with the $\Delta\phi_{eq}^{(P3)}$ values, where the $\log K_{D,Pic} = \left\{ \Delta\phi_{eq}^{(P3)}/0.05916 + 0.05 \right\}$ values in **Table 3(a)** corresponding to them were employed accordingly.

The following discussion is similar to that from $K_{D,AgL}^S$ to $K_{D,AgL}$ at $L = B18C6$ (**Table 2(d)**). The $\log K_{D,ML}^S$ values at M(II) were calculated from a modified form, $\log K_{D,ML}^S = \log K_{ex2\pm} - 2\log K_{D,A}^S - \log K_{ML} + \log K_{D,L}$, of the relation (f) in **Table 1**. Here, the adopted $\log K_{ML} = \left\{ \log \left(\frac{[ML^{2+}]}{[M^{2+}][L]} \right) \right\}$, in water at 298 K} values were 0.48 for the Ca-18C6 [18] and -B18C6 [19] systems, 2.72 [20] for Sr-18C6, 3.87 [20] for Ba-18C6, 2.41 [15] for Sr-B18C6 and 2.90 [13] for Ba-B18C6. Also, $\log K_{D,Pic}^S = 0.05$ [11] (into NB), $\log K_{D,18C6} = -1.00$ [21] and $\log K_{D,B18C6} = 1.57$ [17] (into NB) at 298 K were used for calculation. Furthermore, from the assumption in the section 2.2, we employed the $\log K_{ex2\pm}$ values [12] which have been reported before and their values virtually correspond to the ones standardized at $\Delta\phi_{eq} = 0$ V (see **Table 3(a)**).

The calculated $\log K_{D,ML}^{S(K9)}$ values are listed in **Table 3(d)**. These values agreed well with those [17] previously-reported by the ion-transfer polarographic measurements, except for the Ba-18C6 and -B18C6 systems. This fact indirectly indicates that Equation (12) is satisfied. For the Ba-18C6 and -B18C6 systems, -2.6 for the former and -0.8 for the latter have been reported [17].

As similar to $\log K_{D,AgL}^{(K7)}$ in **Table 2(d)**, the calculation of $\log K_{D,ML}$ becomes the indirect proof of $\log K_{ex2\pm}$ without $\Delta\phi_{eq}$. Then, the $\log K_{D,ML}$ values at 298 K were estimated from the $\log K_{D,ML}^{S(K9)}$ ones and the equation, $\log K_{D,ML} = \left\{ 2f \left(\Delta\phi_{eq} - \Delta\phi_{ML}^0 \right) / 2.303 \right\} = 2\Delta\phi_{eq}/0.05916 + \log K_{D,ML}^S$ [7]; the $\Delta\phi_{eq}^{(P3)}$ values were used here.

The thus-calculated $\log K_{D,ML}^{(K10)}$ values were close to the values listed in **Table 3(a)**; the experimental $\log K_{D,ML}$ values in **Table 3(a)** have been calculated from the relation (d) in **Table 1** [7]. This fact indicates that Equation (12) satisfies indirectly the thermodynamic cycle of (f).

Table 3. (a) Fundamental data for the extraction of MPic₂ (M = Ca, Sr& Ba) by L into NB at 298 K.^a; (b) Evaluated $\Delta\phi_{\text{eq}}$ values; (c) Reproduced $\log K_{\text{ex}\pm}$ values; (d) Evaluated $\log K_{\text{D,ML}}^{\text{S}}$ and reproduced $\log K_{\text{D,ML}}$ values.

(a)

L	M	$\log K_{\text{ex}\pm}$	$\log K_{\text{D,A}}$	$\log K_{1,\text{NB}} (I_{\text{NB}}^{\text{b}}/10^{-4})$	$\log K_{\text{D,ML}}$	$\log K_{\text{ex}2\pm}^{\text{c}}$
18C6	Ca	5.44	-1.43	5.9 (8.9)	0.8 ₈	-0.5
	Sr	6.9 ₂	-0.98	5.3 (4.8)	-0.1 ₇	1.6
	Ba	7.3 ₅	-0.69	4.9 (5.9)	-0.9 ₉	2.7 ^d
B18C6	Ca	2.7 ₁	-1.92	5.0 (6.9)	2.6 ₂	-2.3
	Sr	4.34	-1.34	4.7 (2.3)	1.4 ₄	-0.4
	Ba	5.0 ₁	-1.17	4.1 (2.1)	1.6 ₁	0.9 ^d

^aRef. [7]; ^bUnit: mol dm⁻³; ^c $\log K_{\text{ex}\pm}^{\text{S}}$ values: see ref [12]; ^dValues re-calculated from the data in ref [12].

(b)

	18C6 extraction system			B18C6 extraction system		
	M = Ca	Sr	Ba	M = Ca	Sr	Ba
$\Delta\phi_{\text{eq}}^{(\text{P}3)}/V$	0.088	0.061	0.044	0.12	0.082	0.072
$\Delta\phi_{\text{eq,av}}^{(\text{P}4)}/V$	0.080 ± 0.008	0.051 ± 0.008	0.036 ± 0.006	0.097 ± 0.008	0.059 ± 0.008	0.04 ₂ ± 0.01 ₀

(c)

	18C6 extraction system			B18C6 extraction system		
	M = Ca	Sr	Ba	M = Ca	Sr	Ba
$\log K_{\text{ex}\pm}^{(\text{K}8) \text{ }^{\ast}}$	5.4	7.0	7.6	2.7	4.4	5.3

^{\ast} $\log K_{\text{ex}\pm}^{(\text{K}8)} = \{2\Delta\phi_{\text{eq}}^{(\text{P}3)}/0.05916 + \log K_{\text{D,M}}^{\text{S}} [10]\} + 2\log K_{\text{D,A}}^{(\text{Table 3(a)})} - \log K_{\text{ML,org}} [17] + \log K_{\text{I,org}}^{(\text{Table 3(a)})}$.

(d)

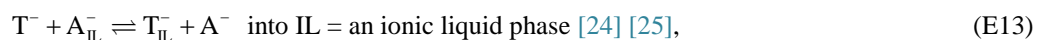
	L = 18C6			B18C6		
	M = Ca	Sr	Ba	M = Ca	Sr	Ba
$\log K_{\text{D,ML}}^{\text{S(K}9) \text{ }^{\ast}}$	-2.1	-2.2	-2.3	-1.3	-1.3	-0.5
$\log K_{\text{D,ML}}^{(\text{K}10) \text{ }^{\S}}$	0.9	-0.1	-0.8	2.7	1.5	1.9

^{\ast} $\log K_{\text{D,ML}}^{\text{S(K}9)} = \log K_{\text{ex}\pm}^{\text{S}} [12] - 2\log K_{\text{D,A}}^{\text{S}} - \log K_{\text{ML}} [13][15] \& [18] - [20] + \log K_{\text{D,L}} [17][21]$. ^{\S} $\log K_{\text{D,ML}}^{(\text{K}10)} = 2\Delta\phi_{\text{eq}}^{(\text{P}3)}/0.05916 + \log K_{\text{D,ML}}^{\text{S(K}9)}$.

The above calculation results for the AgPic and MPic₂ extraction with L indicate that the assumption of Equations (11) and (12) without $\Delta\phi_{\text{eq}}$ is essentially valid. In other words, the overall extraction constants, $K_{\text{ex}\pm}$ and $K_{\text{ex}2\pm}$, must be expressed rationally as functions without $\Delta\phi_{\text{eq}}$.

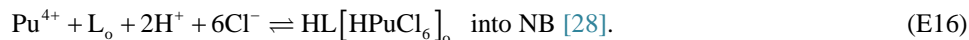
3.3. For Applications to Other Extraction Systems

The above handling based on **Table 1** can be also applied to the practical extraction equilibria of





and



As examples, thermodynamic points of view suggest the following cycles for the above equilibria:

$$K_{\text{ex}} = K_{\text{D,M}} K_{\text{D,A}}, \quad (\text{E11c})$$

$$K_{\text{ex}} = K_{\text{D,C}} K_{\text{D,A}} K_{\text{CA,DCE}} \text{ at } \text{C}^+ = \text{R}_4\text{N}^+, \quad (\text{E12c})$$

$$K_{\text{ex,IE}'} = K_{\text{D,T}} / K_{\text{D,A}}, \quad (\text{E13c})$$

$$K_{\text{ex}} = K_{\text{D,H}} K_{\text{D,AuCl}_4} K_{\text{HL,DCE}} K_{\text{I,DCE}} \quad (\text{E14c})$$

with $K_{\text{HL,DCE}} = \frac{[\text{HL}^+]_{\text{DCE}}}{([\text{H}^+]_{\text{DCE}} [\text{L}]_{\text{DCE}})}$ and $K_{\text{I,DCE}} = \frac{[\text{HLAuCl}_4]_{\text{DCE}}}{([\text{HL}^+]_{\text{DCE}} [\text{AuCl}_4^-]_{\text{DCE}})}$,

$$K_{\text{ex}} = K_{\text{D,Pb}} (K_{\text{D,SCN}})^2 K_{\text{PbL,NB}} K_{\text{I,NB}} K_{\text{2,NB}} \quad (\text{E15c})$$

and

$$K_{\text{ex}} = (K_{\text{D,H}})^2 K_{\text{D,Pu}} (K_{\text{D,Cl}})^6 K_{\text{HL,NB}} \beta_{6,\text{NB}} K_{\text{HPuCl}_6,\text{NB}} K_{\text{I,NB}} \quad (\text{E16c})$$

with $\beta_{6,\text{NB}} = \frac{[\text{PuCl}_6^{2-}]_{\text{NB}}}{([\text{Pu}^{4+}]_{\text{NB}} ([\text{Cl}^-]_{\text{NB}})^6)}$, $K_{\text{HPuCl}_6,\text{NB}} = \frac{[\text{HPuCl}_6^-]_{\text{NB}}}{([\text{H}^+]_{\text{NB}} [\text{PuCl}_6^{2-}]_{\text{NB}})}$ and $K_{\text{I,NB}} = \frac{[\text{HL}^+ \text{HPuCl}_6^-]_{\text{NB}}}{([\text{HL}^+]_{\text{NB}} [\text{HPuCl}_6^-]_{\text{NB}})}$, respectively. Similarly, only the $K_{\text{D},j}$ values are expressed as functions with the $\Delta\phi_{\text{eq}}$ ones.

The relation, $\log K_{\text{ex}} = \log K_{\text{D,M}} + \log K_{\text{D,A}}$, for the process (E11) can be arranged into

$\log K_{\text{D,M}} + \log K_{\text{D,A}} \left\{ = f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{M}}^{0'}) / 2.303 - f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{A}}^{0'}) / 2.303 \right\} = \log K_{\text{D,M}}^{\text{S}} + \log K_{\text{D,A}}^{\text{S}}$. This does not contradict the fact [14] that the determination of $K_{\text{ex}} (= [\text{M}^+]_{\text{NB}} [\text{A}^-]_{\text{NB}} / [\text{M}^+] [\text{A}^-])$ by solvent extraction experiments gives $K_{\text{D,M}}^{\text{S}}$ and $K_{\text{D,A}}^{\text{S}}$, when either $K_{\text{D,M}}$ or $K_{\text{D,A}}$ was standardized at $\Delta\phi_{\text{eq}} = 0\text{V}$ which is based on the $\text{Ph}_4\text{As}^+\text{BPh}_4^-$ assumption [14] [29] & [30]. Also, $K_{\text{D,C}}$ cancels out $K_{\text{D,A}}$ in (E12c):

$\log K_{\text{D,C}} + \log K_{\text{D,A}} \left\{ = f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{C}}^{0'}) / 2.303 - f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{A}}^{0'}) / 2.303 \right\} = \log K_{\text{D,C}}^{\text{S}} + \log K_{\text{D,A}}^{\text{S}}$. For $\text{C}^+ = (\text{C}_4\text{H}_9)_4\text{N}^+$ and $\text{A}^- = \text{Pic}^-$, the $(\log K_{\text{D,C}}^{\text{S}} + \log K_{\text{D,A}}^{\text{S}})$ value becomes 2.66 ($= \log K_{\text{ex}} - \log K_{\text{CA,DCE}}$ [22]) and accordingly we have obtained the $\log K_{\text{D,C}}^{\text{S}}$ value at 298 K from the experimental $\log K_{\text{D,A}}^{\text{S}}$ one [11].

Similarly, $K_{\text{D,T}}$ cancels out $K_{\text{D,A}}$ in (E13c), where T^- denotes another anion. That is,

$\log K_{\text{D,T}} - \log K_{\text{D,A}} \left\{ = -f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{T}}^{0'}) / 2.303 + f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{A}}^{0'}) / 2.303 \right\} = \log K_{\text{D,T}}^{\text{S}} - \log K_{\text{D,A}}^{\text{S}}$. For the overall equilibria, (E14) & (E15), one can handle them in the same manner as that described above for the AgPic and MPic_2 extraction with L , respectively.

We can easily see that the $K_{\text{D,H}}$ and $K_{\text{D,Pu}}$ values cancel out the $K_{\text{D,Cl}}$ one in (E16c). That is,

$2 \log K_{\text{D,H}} + \log K_{\text{D,Pu}} + 6 \log K_{\text{D,Cl}}$ equals

$2 \cdot f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{H}}^{0'}) / 2.303 + 4 \cdot f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{Pu}}^{0'}) / 2.303 - 6 \cdot f(\Delta\phi_{\text{eq}} - \Delta\phi_{\text{Cl}}^{0'}) / 2.303$ and then becomes

$2 \log K_{\text{D,H}}^{\text{S}} + \log K_{\text{D,Pu}}^{\text{S}} + 6 \log K_{\text{D,Cl}}^{\text{S}}$. We found the $\Delta\phi_{\text{PuO}_2}^{0'}$ value $\{ = -(0.05916/2) \log \left(\frac{[\text{PuO}_2^{2+}]_{\text{NB}}}{[\text{PuO}_2^{2+}]} \right)$

= 0.035 V [29] at 298 K), but were not able to find the $\Delta\phi_{pu}^{0'}$ value in references.

4. Conclusion

It was demonstrated that the $\Delta\phi_{eq}$ values calculated from the experimental $\log K_{D,Pic}$ ones are in agreement with or close to those more-accurately done from the charge balance equations for the species with M(I) in the DCE phase and with M(II) in the NB one, except for some cases. This demonstration indicates that the plots of $\log K_{ex}^{mix}$ versus $-\log\left(\left[M^+\right][L]_o\left[A^-\right]^{z-1}\right)$, described in **Appendix II** with $z = 1$ & 2, yield the practical $K_{D,A}$ values and then the first-approximated $\Delta\phi_{eq}$ ones. These results will give an answer to how one explain the differences in $K_{D,A}$ among extraction experiments of various MA or MA₂ by various L. Also, we clarified that the assumption of Equations (11) and (12) is valid for the AgPic and MPic₂ extraction with 18C6 and/or B18C6. This eliminated the contradictions [3] [7] due to $\Delta\phi_{eq}$ from the thermodynamic cycles. Moreover, the present work indicates a possibility that the proposed handling can be applied to various extraction systems with neutral ligands at least.

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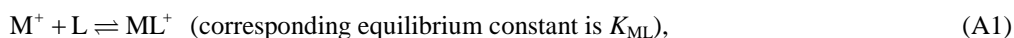
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Appendix I

The basic extraction model [1] [3] [31] for the case (i) is as follows.



and



Consequently, these component equilibria yield those of $M^+ \rightleftharpoons M_o^+$ ($K_{D,M}$), $ML^+ \rightleftharpoons ML_o^+$ ($K_{D,ML}$), $L \rightleftharpoons L_o$ ($K_{D,L}$) and $A^- \rightleftharpoons A_o^-$ ($K_{D,A}$). An extraction of HPic, $H^+ + Pic^- \rightleftharpoons HPic_o$ ($K_{ex,HPic}$), was added in the [Pic⁻] calculation. The distribution [31] of AgPic(=MA) into the DCE phase was neglected in this study; its constant was not available from references.

The case (ii) [2] [6] [7] was



and



where the distribution of MPic⁺(=MA⁺) into the NB phase was neglected; their constants were not available from references. Similarly, some equilibria, such as $M^{2+} \rightleftharpoons M_o^{2+}$ ($K_{D,M}$), $ML^{2+} \rightleftharpoons ML_o^{2+}$ ($K_{D,ML}$) and $L \rightleftharpoons L_o$, can be given from the above component equilibria and the $K_{ex,HPic}$ value was included in the calculation.

The both models, (i) & (ii), do not contain supporting electrolytes in the o phases. This point is a large difference from corresponding electrochemical measurements [29] [30].

Appendix II

The $K_{D,A}$ values have been determined extraction-experimentally using the following equations [1]-[3] [6] [7].

$$\log K_{\text{ex}}^{\text{mix}} = \log \left(\sum \left[\text{MLA}_N^{(z-N)+} \right]_o / \left[\text{M}^{z+} \right] \left[\text{L} \right]_o \left[\text{A}^- \right]^z \right) \quad (\text{A15})$$

$$\approx \log \left\{ K_{\text{ex}} + K_{D,A} / \left(\left[\text{M}^{z+} \right] \left[\text{L} \right]_o \left[\text{A}^- \right]^{z-1} \right) \right\} \quad (\text{A16})$$

for $N=0,1$ at $z=1$ (the case of M^+) or for $N=1,2$ at $z=2$ (that of M^{2+}). Hence, the plots of $\log K_{\text{ex}}^{\text{mix}}$ versus $-\log \left(\left[\text{M}^+ \right] \left[\text{L} \right]_o \right)$ [1] [3] and versus $-\log \left(\left[\text{M}^{2+} \right] \left[\text{L} \right]_o \left[\text{A}^- \right] \right)$ [2] [6] [7] based on Equation (A16) give the $K_{D,A}$ value with the K_{ex} ones for the MA- and MA₂-L extraction systems, respectively. Here, the $\sum \left[\text{MLA}_N^{(z-N)+} \right]_o$ values are determined by AAS measurements and then the $\left[\text{M}^{z+} \right]$, $\left[\text{L} \right]_o$ and $\left[\text{A}^- \right]$ values are calculated by a successive approximation [1]-[3] [6] [7]. The following mass-balance equations have been employed for the approximation: $\left[\text{ML}^+ \right]_o \approx \left[\text{A}^- \right]_o$ [1] [3] against Equation (1) and $\left[\text{MLA}^+ \right]_o \approx \left[\text{A}^- \right]_o$ [2] [6] [7] against Equation (7) (see the Section 3.1).

Similarly, the $K_{\text{ex}\pm}$ values have been evaluated from the other arranged form of Equation (A15),

$$\log K_{\text{ex}}^{\text{mix}} \approx \log \left\{ K_{\text{ex}} + \left(K_{\text{ex}\pm} / \left(\left[\text{M}^{z+} \right] \left[\text{L} \right]_o \left[\text{A}^- \right]^z \right)^{1/2} \right) \right\} \quad (\text{A17})$$

for $N=0,1$ at $z=1$ or for 1, 2 at 2 [3] [7].