On the definition of distribution equilibrium potentials in the distribution systems with simple salts

Abstract
A deviation in the definition of distribution equilibrium potential between electrochemical and extraction-chemical phenomena was discussed and examined quantitatively.

Keywords: distribution equilibrium potential, inner potential, Nernst equation, conditional distribution constant, distribution ratio, distribution of simple salts

Introduction
In electrochemistry and analytical chemistry, the following equations have been employed.\(^1,2\)

\[
E = E^0 - (RT / zF) \ln \left( \frac{C_{g}^*}{C_{o}^*} \right)
\]  

\[
\text{Emf} = \text{constant} + (0.05916) \log \left[ M^I X \right] \text{ at } 298K ,
\]

\[
\Delta \phi_{i/2} = \Delta \phi_{M} + \left( \frac{RT}{zF} \right) \ln \left[ \left( 1 + \frac{\xi \beta_{i}^*}{\beta_{M}^*} \right) \frac{C_{o}^*}{C_{g}^*} \right],
\]

And

\[
E_j = A \left( \frac{RT}{F} \right) \ln \left[ \left( \frac{1}{2} \right) C(\alpha) \right] 
\]

With

\[
A = \left[ \xi [\xi u / z] \left[ C(\beta) - C(\alpha) \right] \right] / \left[ \xi [\xi u [C(\beta) - C(\alpha)] \right]
\]

These Equations 1,2,3, & 4 shown so-called the Nernst equation for the electrode reaction O\(+z\)e\(\rightarrow\)R, a calibration curve based on potentiometric measurements with ISE\(^2\), a polarographic half-wave potential for a facilitated ion transfer across liquid/liquid interfaces,\(^2\) and the Henderson equation\(^1\) for a liquid junction potential, respectively. The concentrations \(C_{g}^*\), \(C_{o}^*\), \([M^I X]\), \(C_{\beta}^*\), and \(C(\alpha)\) in the equations denote bulk total concentrations of their ions (or salts). That is, they do not reflect net concentrations of individual ions (or ion pairs) in the bulk phase. In this opinion, we pointed a deviation in the definition of distribution equilibrium potential between electrochemical and extraction-chemical phenomena was discussed and examined quantitatively.

Discussion
For example, considering the mass balances in the MCI aqueous solutions relevant to the above equations, the concentrations in Equation 2 to 4 must be more-precisely expressed by using the equilibrium concentrations as

\[
[\text{MCI}] = [M^+] + [\text{MCI}] = [Cl^-] + [\text{MCI}] ,
\]

\[
dep = (RT / \cdot K_{D_0} \cdot 5) \times c^*_{M} = [M^+] + [\text{MCI}] ,
\]

And

\[
C(\alpha) = [M^+] (\alpha) + [\text{MCI}] (\alpha)
\]

When dilute solutions are used for their experiments, the [MCI] and [MCI](\alpha) (the concentration for the \(\alpha\) phase at equilibrium) terms can be generally neglected. The same expression as those in Equation (2A) to (4A) essentially holds for \(C_{g}^*\) and \(C_{o}^*\) in Equation 1. So, the \(C_{g}^*, C_{o}^*, [M^I X], C_{M}^*, \) and \(C(\alpha)\) terms do not necessarily equivalent to the ionic strength (\(i\)) for the phase. Accordingly, the \(E, \text{emf}, \Delta \phi_{i/2}\), and \(E_i\) values are defined as fundamentally the difference between inner potentials (\(\phi\)) for the two phases, such as the phases with liquid/solid, and liquid/liquid interfaces.\(^1,2\) Namely, Equation 1 to 4 describe the differences \(\Delta \phi\) in overall energy between the two phases.

On the other hand, in extraction and distribution systems, a conditional distribution constant (\(K_{D_0}\)) of a single ion (\(i\)) between the two bulk phases has been defined as the ratio of the concentrations (or activities) of the individual \(i\) with DEP at equilibrium,\(^1,3,4\) and a standard distribution constant (\(K_{D_0}^{\text{S}}\)) at DEP=0V.\(^1,4\) It is

\[
K_{D_0} = \frac{[i}_{\text{org}} / [i] = K_{D_0}^{\text{S}} \exp \left[ (zF / RT) \Delta \phi \right]
\]

And this modified form is

\[
dep = (RT / \cdot F) \cdot \ln \left[ K_{D_0} \cdot \ln K_{D_0}^{\text{S}} \right]
\]

Here, \(z\) denotes the formal charge \(z\) with the sign of the ion. In Equation (5) or (5A), the \(K_{D_0}^{\text{S}}\) value contains only the amount of an ionic component, such as \(i=M^+\) or \(Cl\). These facts indicate that with the difference \(\Delta \phi\) of only the individual \(M^+\) or \(Cl\) is expressed Equation (5A), while Equation 1 to 4 are done with the \(\Delta \phi\) of the mixture of \(M^+\), \(Cl\), and \(MCI\). This means that the electrochemical definition for \(E, \text{emf}, \Delta \phi_{i/2}\), and \(E_i\) can slightly deviate from the dep definition based on the experimental \(K_{D_0}^{\text{S}}\) values.\(^1,3,4\) Of course, the
energetic states of the phases may influence the $K_{D,i}$ determination in the extraction experiments.

By the way, the distribution ratio ($D$) has been defined as

$$D = c_{\text{org}}/c_i = [M^+]/[M]_{\text{org}} + [MX]/[MX]_{\text{org}}$$ \hspace{1cm} (6)

In the simple MX distribution systems, the symbols $c_i$ and $c_{\text{org}}$ denote the total concentrations of the species with M(I) {or X(−I)} in the water and org phases, respectively.

Equation (6) can be rearranged as $D=\pm$:

$$\left[\frac{[M]}{[M]^+}\right]_{\text{org}} \times \left(1 + K_{MX,\text{org}} \frac{[X]^+}{[M]^+}\right)/\left(1 + K_{MX}[X]^{-}\right)$$ \hspace{1cm} (6A)

With $K_{MX,\text{org}}$

$$org = \frac{[MX]}{[M]^+} \times \frac{[X]^+}{[M]^+}$$

Using Equation (5) with the charge balance relations

$$[M]^+ = [X]^+ = I$$

Equation (6A) also becomes

$$D = \left(1 + K_{MX,\text{org}}[1 + K_{+}, I]\right)/\left(1 + K_{MX}I\right)$$ \hspace{1cm} (6B)

With $r = \left(1 + K_{MX,\text{org}}[1 + K_{+}, I]\right)/\left(1 + K_{MX}I\right)$

Moreover, assuming that $D^S = r'K_{D,S}^S$ at DEP=0, the following equation can be derived from Equations (5) & (6B):

$$D = D^S \exp\{3.9F/RT\}$$ \hspace{1cm} (7)

This equation is very similar to the above electrochemical expression, because the $c_i$ and $c_{\text{org}}$ terms are equivalent with the expression of $C_i$, $C_{\text{org}}$, $[MX]$, $c_i^*$, and $C(\alpha)$. That is, the dep values calculated from $D$, based on Equation (7), approach to the definition corresponding to $E$, $\text{emf}$, $\alpha_{DEP}$, and $E_i$. Also, the use of $D$ is not in conflict with the above electrochemical definitions.

Table 1 summarizes some experimental $K_{D,\pm}$ and $D$ values, in the MX distribution into several diluents, where the relation $K_{D,\pm} = K_{D,o}$ holds. The plot of log $K_{D,\pm}$ versus log $D$ listed in Table 1 yielded $K_{D,\pm} = 0.98 \pm 0.04 \log D – 0.10 \pm 0.13$ at the correlation coefficient of 0.996. This regression line show that the log $K_{D,\pm}$ values are proportional to the log $D$ ones, namely log $K_{D,\pm}$ = log $D$ – log $r$ (see Equation (6B)). In other words, this fact indicates that $K_{D,\pm}$ is a function of $D$ and $r$. When the $r$ value is approximately equal to unity, we can immediately obtain $D$ & $K_{D,\pm}$ which equals $K_{D,o}$. The intercept ($\log r = 0.1$) of the regression line shows the possibility that the evaluated $r$ values equal unity within the calculation error ($\pm 0.1$).

<table>
<thead>
<tr>
<th>Diluent</th>
<th>MX</th>
<th>$\log K_{D,\pm}$</th>
<th>Log D</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Nitrobenzene</td>
<td>NaMnO</td>
<td>$-3.17$</td>
<td>$-3.17$</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>NaPic</td>
<td>$-2.62$</td>
<td>$-2.61$</td>
<td></td>
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<tr>
<td></td>
<td>(CH$_3$)$_2$NPic</td>
<td>$0.053$</td>
<td>$0.07$</td>
<td></td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>NaMnO</td>
<td>$-4.7$</td>
<td>$-4.72$</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>NaPic</td>
<td>$-3.55$</td>
<td>$-3.58$</td>
<td></td>
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<tr>
<td></td>
<td>(CH$_3$)$_2$NPic</td>
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<td>$-0.90$</td>
<td></td>
</tr>
<tr>
<td>o-Dichlorobenzene</td>
<td>LiPic</td>
<td>$-5.3 \pm 0.3$</td>
<td>$-5.5 \pm 0.1$</td>
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</tr>
<tr>
<td></td>
<td>NaPic</td>
<td>$-4.8 \pm 0.4$</td>
<td>$-4.53 \pm 0.04$</td>
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</tr>
<tr>
<td></td>
<td>KPic</td>
<td>$3.9 \pm 0.3$</td>
<td>$-3.6 \pm 0.1$</td>
<td></td>
</tr>
</tbody>
</table>

1 MPic: picrate. The relation $K_{D,\pm} = K_{D,o} = K_{D,X}$ holds in the present distribution systems.

**Conclusion**

Consequently, the DEP in Equations (5) and (5A) satisfies the electrochemical definition in the case of $r=1$. At the same time, the definition for $C_i^*$, $[MX]^*$, and $C(\alpha)$ is reflected in indirectly the $K_{D,\pm}$ values through the D ones. A similar discussion will be also needed for the more-complicated extraction systems, with various extracting reagents.

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None

**Conflicts of interest**

The author declares that there are no conflicts of interest.
