Estimation of Activities in the Aqueous Solution Systems of HCl–CuCl₂ and HCl–FeCl₃ Using the Pitzer Method

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Parameterizations based on the literature activity data have been attempted for the activities of water and the solutes in the aqueous solution systems of HCl–CuCl₂ and HCl–FeCl₃ at 298 K in terms of the Pitzer theory without explicitly considering complex formation. The single electrolyte parameters for CuCl₂ and FeCl₃ were determined from the osmotic coefficients for the corresponding single electrolyte solutions. Extra parameters of βᵢ were included in the single electrolyte parameters for CuCl₂ and FeCl₃ to extend the applicable concentration ranges. For the aqueous solution of HCl–CuCl₂, two kinds of activity data, namely, the osmotic coefficients measured by the transpiration method and the solubilities of the copper salt, were simultaneously submitted to the weighted linear least-squares analysis to determine the mixed electrolyte parameters. The χ²-test of significance indicated that the Pitzer parameters obtained in this study can reproduce these activity data with no statistically significant error. As a result, the mean activity coefficients of the solutes in this solution system calculated by the parameters obtained in this study are in good agreement with those calculated by the McKay-Perring method. For the aqueous solution of HCl–FeCl₃, the osmotic coefficients by the transpiration method were submitted to the weighted linear least-squares analysis; however, the χ²-test of significance indicated that the Pitzer parameters obtained in this study cannot reproduce the activity data without statistically significant error. As a result, the agreement is unsatisfactory between the mean activity coefficients of the solutes in this solution system calculated by the parameters obtained in this study and those by the McKay-Perring method.

(Received December 24, 1991)

Keywords: activity coefficient, osmotic coefficient, water activity, HCl, CuCl₂, FeCl₃, Pitzer method, parameterization

I. Introduction

Pitzer’s ionic interaction theory(1) is now widely used in many academic fields as a tool for the correlation or estimation of activities in electrolyte solutions. Its use in hydrometallurgy is, however, still limited owing to the lack of mixing parameters needed in the calculation by the Pitzer method. The mixing parameters can be determined from activity data of the corresponding ternary solution system. Although such activity data have been limited so far, the recent elaborate measurements of the water activities in some hydrometallurgically important ternary electrolyte solutions at 298 K by Awakura et al.(2) have enabled parameterizations of these solution systems in terms of the Pitzer theory.

In our preceding paper(3), we have parameterized the aqueous solution systems of HCl–NaCl and HCl–NiCl₂ in terms of the Pitzer theory on the basis of the literature activity data including the water activities by Awakura et al.(2). In that study, we employed the stoichiometric approach; namely, no complex formation was explicitly considered. Satisfactory correlations were carried out up to concentrated solutions. As a continuation, this paper deals with the aqueous solution systems of HCl–CuCl₂ and HCl–FeCl₃.

II. Parameterization Procedure

1. Equations

Pitzer’s equations for the stoichiometric osmotic coefficient, φ, and the stoichiometric activity coefficient of each solute i, γₓᵢ(f), in the aqueous solution system of HX–MXₓ (X: a univalent anion) were reported in the preceding paper(3), including the extra parameters βᵢ(2) in the single electrolyte parameters after Filippov et al.(6); thus, they are not described here.

2. Evaluation of the single electrolyte parameters

Single electrolyte parameters, β₀(0), β₁(1), β₂(2), and Cₓ*, for CuCl₂ and FeCl₃ at 298 K were determined respectively from the φ values of the single CuCl₂ solutions presented by the U.S. National Bureau of Standards (NBS)(3) and the ln γₓᵢ(FeCl₃) values in the single FeCl₃ solution presented by Majima et al.(5) by the linear least-squares method assigning equal weights to the respective data. The working equations were eq. (12) in our preceding paper(5) for CuCl₂ and eq. (3) in Pitzer and Mayorga(7) for FeCl₃. A program SALS(8) was used as a least-squares program throughout this paper. The weighted least-squares method was not used because the uncertainty of each literature value was not necessarily

Footnotes:

specified in the literature.

3. Evaluation of the mixed electrolyte parameters

Mixed electrolyte parameters, \( \beta \) and \( \psi \), were determined from eqs. (1) and (3) in our preceding paper\(^8\), the literature activity data, and the single electrolyte parameters for CuCl\(_2\) and FeCl\(_3\) obtained in the preceding section. The single electrolyte parameters for HClO\(_4\) in our preceding paper\(^9\) were also used. Namely, for the aqueous solution of HCl–CuCl\(_2\), two kinds of activity data were simultaneously submitted to the weighted linear least-squares analysis in order to obtain consistent mixed electrolyte parameters: One is the \( \phi \) values calculated from the water activities, \( a_w \), by Awakura et al.\(^6\) and another is the values of \( R \), where \( R = \ln \gamma_s (\text{CuCl}_2) + (2/3) \ln a_w \) (the suffix \( s \) means a saturated solution), calculated from the solubility data by Foote\(^7\). For the aqueous solution of HCl–FeCl\(_3\), the \( \phi \) values calculated from the \( a_w \) values by Awakura et al.\(^6\) were submitted to the weighted linear least-squares analysis. Here \( a_w \) is related to \( \phi \) as:

\[
\phi = -1000 \left[ \frac{1}{\sum_i (n(i)m(i))M_i} \ln a_w \right]
\]

(1)

where the symbols \( n(i) \) and \( M_i \) designate the number of ions formed from the solute \( i \) and the molecular weight of water, respectively. Also, since the solid phase in equilibrium with the aqueous solution of HCl–CuCl\(_2\) is CuCl\(_2\)·2H\(_2\)O at least when \( m(\text{HCl}) < 17.0 \text{ mol·kg}^{-1} \), the \( R \) value is calculable from the following equation if the solubility product of CuCl\(_2\)·2H\(_2\)O, \( K_{sp} \), and the composition of the saturated solution are known:

\[
K_{sp} = \gamma_s (\text{CuCl}_2)[m(\text{Cu}^{2+})]m(\text{Cl}^-)/a_w^2
\]

(2)

Weights were assigned to the respective data according to the equation as:

\[
w_i = 1/\sigma_i^2
\]

(3)

where the symbols \( w_i \) and \( \sigma_i \) designate the weight and the standard deviation of the \( i \)th measurement. Thus, the weighted least-squares method is to minimize the \( S \) value defined as:

\[
S = \sum_i w_i \phi_i
\]

(4)

where the symbols \( \phi_i \) and \( n \) designate the difference between the observed and the calculated values and the number of data points, respectively. The weighted least-squares method was carried out with the hypothesis: (1) the expected value of the error in each measurement is zero, (2) the variances of the experimental errors are known, (3) each measurement is independent, (4) the error distribution is normal, and (5) there are model parameters reproducing the true values of measured quantities without the approximation errors. The validity of this hypothesis for each solution system was examined by the \( \chi^2 \)-test of significance, because the \( \chi^2 \)-distribution with \( n-m \) degrees of freedom (\( m \) is the number of unknown parameters) applies for \( S \) when this hypothesis is valid. The estimation of the \( \sigma(\phi) \) and \( \sigma(R) \) values are described in the Appendices A.1 and A.2, respectively. For the aqueous solution of HCl–CuCl\(_2\), the values of \( \sigma(\phi) \) and \( \sigma(R) \) ranged from 0.013 to 0.261 and from 0.027 to 0.030, respectively. For the aqueous solution of HCl–FeCl\(_3\), the value of \( \sigma(\phi) \) ranged from 9.7×10\(^{-3}\) to 0.229.

III. Results and Discussion

1. Evaluation of the single electrolyte parameters

Table 1 summarizes single electrolyte parameters determined in this study together with the standard deviations, the number of data points, and the concentration ranges. For FeCl\(_3\), the parameters without \( \beta \)\(^{(3)} \) are also listed for comparison. Solid lines in Figs. 1 and 2 respectively show the \( \phi \) values in the CuCl\(_2\) solution and the \( \psi \) (FeCl\(_3\)) values in the FeCl\(_3\) solution both calculated by the parameters including \( \beta \)\(^{(3)} \) determined in this study. The literature data are represented by the circles and some data are not shown here for simplification.

In Fig. 1, the \( \phi \) values by the parameters by Downes

![Fig. 1](image)

**Fig. 1** The \( \phi \) values in the aqueous solution of CuCl\(_2\) at 298 K as a function of \( m(\text{CuCl}_2) \). The circles denote the literature values\(^6\). The solid, chain and broken lines denote the values by the Pitzer parameters in this study, Ref. (11) and Ref. (10), respectively.

<table>
<thead>
<tr>
<th>MX</th>
<th>( \beta^{(3)} ) / kg·mol(^{-1})</th>
<th>( \beta^{(1)} ) / kg·mol(^{-1})</th>
<th>( \beta^{(2)} ) / kg·mol(^{-1})</th>
<th>( C^\phi ) / kg·mol(^{-1})</th>
<th>( \sigma )</th>
<th>Number of data points</th>
<th>( m(\text{MX}) ) / mol·kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl(_2)</td>
<td>0.1496</td>
<td>0.1301</td>
<td>0.8516</td>
<td>-0.00759</td>
<td>0.0050</td>
<td>48</td>
<td>0.001–0.75</td>
</tr>
<tr>
<td>FeCl(_3)</td>
<td>0.3606</td>
<td>6.099</td>
<td>1.314</td>
<td>-0.01626</td>
<td>0.0097</td>
<td>20</td>
<td>0.2–4.0</td>
</tr>
<tr>
<td>FeCl(_3)</td>
<td>0.4383</td>
<td>9.196</td>
<td></td>
<td>-0.02702</td>
<td>0.0301</td>
<td>20</td>
<td>0.2–4.0</td>
</tr>
</tbody>
</table>
and Pitzer\(^{(10)}\) denoted by the chain lines agree well with the literature data up to 2 mol·kg\(^{-1}\) but significantly deviate downward in the more concentrated region. The fit of the values by the parameters without \(\beta^{(5)}\) by Kim and Frederick\(^{(1)}\) denoted by the broken lines is not satisfactory over the entire region. The \(\phi\) values by the parameters evaluated in this study are in good agreement with the literature values over the entire region.

In Fig. 2, broken lines denote the values calculated by the parameters without \(\beta^{(2)}\) in Table 1. As shown by Fig. 2 as well as by the standard deviations in Table 1, the agreement of the \(\chi_{\text{FeCl}_3}\) values by the parameters with \(\beta^{(2)}\) to the literature values is better than that without \(\beta^{(2)}\).

Consequently, broader concentration ranges can be covered by using the extra parameters \(\beta^{(2)}\) in accord with our preceding paper\(^{(3)}\).

### 2. Evaluation of the mixed electrolyte parameters

#### (1) The aqueous solution of HCl–CuCl\(_2\)

We first used all the data points whose ionic strength is less than 16.3 mol·kg\(^{-1}\) in accord with the maximum ionic strength in the evaluation of the single electrolyte parameters for HCl. The \(S\) value of 116 (45 degrees of freedom) was obtained, and this value far exceeds the value of \(\chi_{0.05}^2(=58.1)\), where the suffix represents the upper-tail probability in the \(\chi^2\)-distribution (the critical \(\chi^2\) values were approximately estimated by the Wilson-Hilferty equation\(^{(10)}\) throughout this paper). The examination of the normalized residuals, \(v_i/\sigma_i\), showed that there were three data points for \(a_w\) whose absolute values of normalized residuals were larger than 2.8 corresponding to 99.5% coverage. Thus, in accord with our preceding paper\(^{(19)}\), these data points were omitted in the second least-squares analysis.

The mixed electrolyte parameters of \(\psi_{\text{HCl}}\) and \(\psi_{\text{CuCl}_2}\) determined in the second analysis are listed in Table 2 together with the standard deviations of the parameters, the correlation coefficient between the parameters, \(\rho\), and the value of \(S\). Also, for each data source, the number of data points and the range of ionic strength are listed in Table 2. Figures 3 and 4 show the comparisons, respectively, of \(a_w\) and the solubility of CuCl\(_2\) between experimental values and those reproduced using the single and the mixed electrolyte parameters evaluated in this study (solid lines). Blank points in these two figures denote the data used both in the first and the second analyses. Filled points in Fig. 3 denote the data used in the first analysis but omitted in the second analysis. The filled circle in Fig. 4 denotes the average value of the three literature values\(^{(49,90,90)}\). The calculated values are in good agreement with the blank points in these two figures without significant systematic deviation. The deviations of filled points from the calculated values in Fig. 3 are evidently greater than those of the blank points. Thus, our treatment that the data denoted by the filled points in Fig. 3 were omitted in the least-squares analysis would be justified.

For 42 degrees of freedom in the second analysis, the values of \(\chi_{0.05}^2\) and \(\chi_{0.10}^2\) are 30.8 and 54.1, respectively.

![Figure 3](image3.png)

**Fig. 3** The \(a_w\) values in the aqueous solution of HCl–CuCl\(_2\) at 298 K as a function of \(m(\text{CuCl}_2)\). The blank and the filled points denote the literature values\(^{(10)}\) used and not used in the evaluation of the mixed electrolyte parameters, respectively. The solid lines and numbers in the figure denote the values calculated by the Pitzer parameters in this study and the values of \(m(\text{HCl})/m(\text{CuCl}_2)\), respectively.
Since the value of $S$ lies between these two values, our hypothesis cannot be rejected.

Consequently, there is no statistical reason for suspecting the validity of the Pitzer model for this solution system.

(2) The aqueous solution of HCl–FeCl$_3$

First, all the data points by Awakura et al.$^{(1)}$ were submitted to the least-squares analysis to determine the mixed electrolyte parameters of $\theta_{HF}$ and $\psi_{HF}$, because the maximum ionic strength among these data is less than those in the determination of single electrolyte parameters for HCl and FeCl$_3$. The $S$ value obtained here was 167 (43 degrees of freedom), far exceeding the value of $\chi^2_{0.05}(=59.3)$. Since there were seven data points whose normalized residuals are larger than 2.8. Thus, these data were omitted in the second least-squares analysis in accord with our preceding paper.$^{(10)}$

The second analysis yielded the results in Table 3, showing the values of $\theta_{HF}$, $\psi_{HF}$, $\sigma(\theta_{HF})$, $\sigma(\psi_{HF})$, $\rho$, and $S$ together with the number of data points and the range of ionic strength. Again the $S$ value exceeds the value of $\chi^2_{0.05}(=51.0)$ with 36 degrees of freedom.

Figure 5 shows the comparison of $a_w$ between experimental values and those reproduced using the mixed electrolyte parameters in Table 3 (solid lines). Here the blank points denote the data used in the first and the second analysis, and the filled points denote the data used only in the first analysis. It is likely that there is a systematic deviation in the $a_w$ range of 0.9–1.0; namely, the calculated values are always lower than the literature values in this region.

Consequently, our hypothesis for this solution system should be rejected at present. This is probably caused by the inappropriateness of the item (5) in our hypothesis. The reason for this will be discussed in the next section.

3. Estimation of the mean activity coefficients of solutes

Majima et al.$^{(13)}$ tabulated the mean activity coefficients of solutes in the solution systems of HCl–CuCl$_2$ and HCl–FeCl$_3$ calculated by the McKay-Perring method$^{(15)}$ from the water activities measured by them. The broken lines in Figs. 6–9 are smooth curves drawn through a part of their mean activity coefficients. The mean activity coefficients calculated by the Pitzer method (eqs. (2) and (3) in our preceding paper$^{(10)}$ with the parameters evaluated in this study are also shown by the solid lines in these figures. Here error bars at some points designate $\pm 2\sigma(\gamma_{x})$ estimated on the basis of the values of $\sigma(\theta)$, $\sigma(\psi)$, and $\rho$ in Tables 3 and 4 by eqs. (21) and (22) in the preceding paper$^{(10)}$.

(1) The aqueous solution of HCl–CuCl$_2$

Deviations between the solid and the broken lines are seen in Fig. 7 when $m$(HCl)$=0$ mol·kg$^{-1}$. This deviation

\begin{table}[h]
\centering
\begin{tabular}{l|l}
\hline
Parameter & Value  \\
\hline
$\theta$/kg·mol$^{-1}$ & -0.0666 \\
$\psi$/kg$^{-2}$·mol$^{-1}$ & 0.00162 \\
$\sigma(\theta)$/kg·mol$^{-1}$ & 0.0335 \\
$\sigma(\psi)$/kg$^{-2}$·mol$^{-1}$ & 0.0031 \\
$\rho$ & -0.9674 \\
$S$ & 67.5 \\
Number of data points & 45 for Ref. (2) \\
$I$(minimum)/mol·kg$^{-1}$ and $I$(maximum)/mol·kg$^{-1}$ & 0.50 and 12.29 for Ref. (2) \\
\hline
\end{tabular}
\end{table}
is due to the difference in the data source for the $\gamma_\pm$(CuCl$_2$) values in the single CuCl$_2$ solution. Namely, the McKay-Perring method needs the values of $a_\omega$ and $\gamma_\pm$ in the corresponding single electrolyte solutions. Majima et al.$^{8(13)}$ used the data presented by Robinson and Stokes$^{15}$ (RS), whereas we used the data critically evaluated by NBS$^{5}$ to evaluate the single electrolyte parameters. A considerable deviation is found between the values of RS and NBS. For example, when $m$(CuCl$_2$) = 1 mol·kg$^{-1}$, the values of $a_\omega$ and $\gamma_\pm$(CuCl$_2$) are respectively 0.966 and 0.419 in RS and 0.9500 and 0.4046 in NBS. In this example, the values of RS are larger than those of NBS by 1.7% for $a_\omega$ and 3.6% for $\gamma_\pm$. Thus, the
deviation found in Fig. 7 when \( m(\text{HCl}) = 0 \text{ mol} \cdot \text{kg}^{-1} \) reflects the difference in the \( \gamma_z(\text{CuCl}_2) \) values in the single CuCl\(_2\) solution. Further, the differences in the \( a_x \) values as well as in the \( \gamma_z(\text{CuCl}_2) \) values in the single CuCl\(_2\) solution affect the \( \gamma_z(\text{CuCl}_2) \) values in the mixed solution. This effect is discussed as follows:

The \( \gamma_z(\text{CuCl}_2) \) in the aqueous HCl(1)-CuCl\(_2\)(2) solution is written in terms of the McKay-Perring theory as:

\[
\gamma_z(2) = I_z(2)M(2)(v(2)^e)^2 \left\{ \frac{[v(1) + v(2)]}{m(v(1) + v(2))} \right\}
\]

where

\[
\Delta = -\left( \frac{1000v(2)}{M_v v(1)^2} \right) \int_0^{a_w} \frac{b d \ln a_w}{a_w}
\]

\[
y(i) = m(i)/m
\]

\[
m = m(1) + m(2)
\]

Here the quantities \( I_z(i) \) and \( M(i) \) respectively designate the \( \gamma_z \) and the \( m(i) \) for an aqueous solution containing the solute alone with the same \( a_w \) value as that in the ternary solution. The quantity \( b \) designates the correction parameter in the corrected Zdanovskii rule. The \( \gamma_z(\text{HCl}) \) is obtained by interchanging 1 and 2 in the parentheses in eqs. (5) and (6). The difference between the \( I_z \) values of RS and NBS is negligible for \( I_z(\text{HCl}) \), whereas that for \( I_z(\text{CuCl}_2) \) is not as stated earlier; namely,

\[
I_z(\text{CuCl}_2, \text{RS}) > I_z(\text{CuCl}_2, \text{NBS})
\]

Further, the earlier-stated difference between the \( a_w \) values in the single CuCl\(_2\) solution of RS and NBS causes the difference between the \( M(\text{CuCl}_2) \) values; namely, since the \( a_w \) values in the single CuCl\(_2\) solution decrease with the increase in \( m(\text{CuCl}_2) \) and the \( a_w \) values by RS are larger than those by NBS,

\[
M(\text{CuCl}_3, \text{RS}) > M(\text{CuCl}_3, \text{NBS})
\]

although the difference between the \( M(\text{HCl}) \) values is negligible. Inequality (10) and the inspection of equi-\( a_w \) lines for this solution system presented by Awakura et al.\(^{(2)}\) lead to the inequality as:

\[
0 > b(\text{RS}) > b(\text{NBS})
\]

Equations (5)–(8) and ineqs. (9)–(11) lead to the inequality as:

\[
\gamma_z(\text{CuCl}_2, \text{RS}) > \gamma_z(\text{CuCl}_2, \text{NBS})
\]

Also, eqs. (5)–(8) and ineq. (11) yield:

\[
\gamma_z(\text{HCl}, \text{RS}) > \gamma_z(\text{HCl}, \text{NBS})
\]

though the difference between both sides in ineq. (13) is thought to be much less than that in ineq. (12).

Ultimately, considerable deviation between the \( \gamma_z(\text{CuCl}_2) \) values in Fig. 7 by the McKay-Perring method and the Pitzer method would be reduced if the NBS data were used. Also, very slight deviation between the \( \gamma_z(\text{HCl}) \) values by the McKay-Perring method and the Pitzer method in Fig. 6 would be reduced if so.

The computational difficulty inherent in the McKay-Perring method as detailed in our preceding paper\(^{(3)}\) constitutes another point which has to be taken into account in discussing the reason for the deviation of the \( \gamma_z \) values. This situation can be viewed, though indirectly, by the examination of the cross-derivative relation. For the ternary solution of HCl(1)–MCl\(_2\)(2)–H\(_2\)O, we define \( A, B, \) and \( \delta \) as:

\[
A = v(1) [\partial \log \gamma_z(1)/\partial m(2)]
\]

\[
B = v(2) [\partial \log \gamma_z(2)/\partial m(1)]
\]

\[
\delta = A - B
\]

Thus, the cross-derivative relation requires that \( \delta = 0 \). Analytically, the Pitzer method and the McKay-Perring method satisfy this relation.

To examine this numerically, the values of \( A, B, \) and \( \delta \) were calculated at some compositions in the aqueous solution of HCl–CuCl\(_2\) according to the procedure described in the Appendix in our preceding paper\(^{(3)}\). The result is summarized in Table 4. Here the symbol \( a \) designates that the mean activity coefficients were taken from Majima and Awakura\(^{(3)}\). In this data source, significant figures are down to three decimal places and the variable increments range from 0.1 to 0.5 mol·kg\(^{-1}\) depending on the composition. The symbol \( b \) designates that the mean activity coefficients with the same significant figures and the variable increments as those of the method \( a \) were calculated by the Pitzer method. The symbol \( c \) designates that the mean activity coefficients with the significant

<table>
<thead>
<tr>
<th>( m(\text{HCl})/ \text{mol} \cdot \text{kg}^{-1} )</th>
<th>( m(\text{CuCl}_2)/ \text{mol} \cdot \text{kg}^{-1} )</th>
<th>( A/10^{-2} \text{ kg} \cdot \text{mol}^{-1} )</th>
<th>( B/10^{-2} \text{ kg} \cdot \text{mol}^{-1} )</th>
<th>( \delta/10^{-2} \text{ kg} \cdot \text{mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>( b )</td>
<td>( c )</td>
<td>( a )</td>
<td>( b )</td>
</tr>
<tr>
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<td>14.2</td>
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</tr>
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<td>0.2</td>
<td>18.1</td>
<td>19.4</td>
<td>19.445</td>
</tr>
</tbody>
</table>

* The meanings of \( a, b, \) and \( c \) are described in the text.
figures down to six decimal places and a variable increment of 0.02 mol·kg⁻¹ were calculated by the Pitzer method. As shown by method c, the mean activity coefficients calculated by the Pitzer method are confirmed to satisfy the cross-derivative relation. On the other hand, the nonzero values of δ in method a cannot be wholly explained by the error introduced by the truncation and a variable increment larger than that in method c, because most absolute values of δ by method a are much larger than those by method b. This suggests that at least the third decimal places in the γ± values by the McKay-Perring method contain a certain magnitude of errors.

Therefore, the uncertainties in the γ± values by the McKay-Perring method should be recognized owing to the experimental uncertainties and computational difficulty which are inevitable respectively in the transpiration method and the McKay-Perring method. In the Pitzer method, experimental uncertainties affect the accuracy of the γ± values, but, owing to the use of thermodynamically consistent equations for φ and γ±, the computational difficulty is removed when the aα values are reproduced within experimental uncertainties. Thus, even if the γ± values were calculated on the basis of the NBS data, the uncertainties in the γ± values by the McKay-Perring method would be at least the same magnitude as or probably larger than those by the Pitzer method. Consequently, when we take into account the difference in the data source and the uncertainties in the γ± values by the Pitzer method and the McKay-Perring method, the deviation between the mean activity coefficients of the solutes in the solution system of HCl-CuCl₂ calculated by the Pitzer method and those by the McKay-Perring method is acceptable.

Haung also parameterized for the aqueous solution of HCl-CuCl₂ in terms of the Pitzer theory on a stoichiometric basis using the water activity data by Awakura et al. and concluded that the Pitzer theory can predict the thermodynamic properties for this solution system. Haung's procedure is different from ours in four points: In his paper, (1) the single electrolyte parameters for HCl without β(2) as well as the mixed electrolyte parameters were simultaneously determined from the water activity data of the ternary solution, (2) the effect of the term β in the Pitzer equations was not considered, (3) the single electrolyte parameters for CuCl₂ given by Filippov were used (but, there are discrepancies in the values of Cα and of the parameter α₂ in the Pitzer's equations between the two papers), and (4) the experimental uncertainties were not considered. Considering these differences, we refrain from comparing the Pitzer parameters obtained in this study with those by Haung. However, our result that the Pitzer theory on the stoichiometric basis reliably calculates the activities of water and solutes in this solution system is in accord with Haung’s conclusion.

(2) The aqueous solution of HCl–FeCl₃
The cross-derivative relation was again examined only for the γ± values calculated by the McKay-Perring method according to the same procedure as in the HCl-CuCl₂ aqueous solution system (Table 5). Since the magnitude of the δ values is the same as that in Table 4, the uncertainties in the γ± values by the McKay-Perring method cannot be neglected. However, satisfactory agreement between the γ± values by the McKay-Perring method and the Pitzer method cannot be expected, because the Pitzer method failed to reproduce the aα values within the experimental uncertainties. Actually, the deviations in Figs. 8 and 9, especially when m(HCl) = 0.2 mol·kg⁻¹ for Fig. 8 and m(FeCl₃) = 0.2 mol·kg⁻¹ for Fig. 9, are so large that these deviations cannot be explained only by the uncertainties in the γ± values by the Pitzer method and the McKay-Perring method.

The failure of the Pitzer method in the aqueous HCl–FeCl₃ solution system seems to be closely related to the degree of association. For many solution systems where the association is negligible or weak, it is known that the Pitzer model is successfully applied using stoichiometric coefficients, because the chemical interactions can be incorporated in the ion interaction; conversely, for a strongly associated solution system, the Pitzer model for stoichiometric coefficients is unsuccessful. Instead, the free coefficients would be favored, although the calculation becomes complicated and cumbersome. Figure 10

| Table 5 The cross-derivative relation in the aqueous solution of HCl–FeCl₃ (the method a²). |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| m(HCl)/ mol·kg⁻¹ | m(FeCl₃)/ mol·kg⁻¹ | A/ 10⁻² mol·kg⁻¹ | B/ 10⁻² kg·mol⁻¹ | δ/ 10⁻³ kg·mol⁻¹ |
| 0.2             | 0.2             | -108.5          | -103.6          | -4.9            |
| 0.2             | 1.0             | -8.2            | 1.1             | -9.3            |
| 0.2             | 2.0             | 42.2            | 41.9            | 0.3             |
| 1.0             | 0.2             | -19.0           | -13.5           | -5.5            |
| 1.0             | 1.0             | 14.5            | 20.7            | -6.2            |
| 1.0             | 2.0             | 38.6            | 28.1            | 10.5            |
| 2.0             | 0.2             | 15.1            | 20.2            | -5.1            |
| 2.0             | 1.0             | 30.1            | 27.8            | 2.3             |
| 2.0             | 2.0             | 48.1            | 24.4            | 23.7            |
| 4.0             | 0.2             | 46.1            | 35.5            | 10.6            |
| 4.0             | 1.0             | 57.9            | 30.9            | 27.0            |

* The meaning of a is described in the text.
exemplifies the average ligand numbers of the metal ions M\(^{m+}\) (M\(^{m+}\): Ni\(^{2+}\), Cu\(^{2+}\), and Fe\(^{3+}\)) in the aqueous solution of HCl–MCl, at 298 K as a function of the HCl concentration, C(HCl), when the metal chloride concentration is 0.2 mol·dm\(^{-3}\). Here the average ligand numbers, \(\bar{n}\), were approximately calculated using the stability constants of chloride complexes at zero ionic strength at 298 K\(^{10}\) and assuming that the free activity coefficients of all the species are unity. This figure shows that the \(\bar{n}\) values for Fe\(^{3+}\) are the largest among those for the three ions. Thus, it is conceivable that stoichiometric coefficient approach in the Pitzer method for the aqueous solution of HCl–FeCl\(_3\) is not appropriate.

IV. Conclusions

Parameterizations for the activities of water and the solutes in the aqueous solution system of HCl–CuCl\(_2\) and HCl–FeCl\(_3\) at 298 K have been attempted in terms of the Pitzer theory without explicitly considering complex formation. The results are summarized as follows:

1. The inclusion of the extra parameters of \(\beta^{(0)}\) as single electrolyte parameters for CuCl\(_2\) and FeCl\(_3\) extends the applicable concentration ranges.

2. For the aqueous solution of HCl–CuCl\(_2\), the mixed electrolyte parameters were determined from the literature activity data including salt solubilities and the water activities by the weighted linear least-squares method without statistically significant error. As a result, the mean activity coefficients of the solutes in this solution system calculated by the parameters obtained in this study are in good agreement with those calculated by the McKay-Perring method.

3. For the aqueous solution of HCl–FeCl\(_3\), the mixed electrolyte parameters were determined from the water activity data in the literature by the weighted linear least-squares method; however, the fit was associated with statistically significant error. As a result, the agreement is unsatisfactory between the mean activity coefficients of the solutes in this solution system calculated by the parameters obtained in this study and by the McKay-Perring method.

Appendices

A.1 Evaluation of the \(\sigma(\phi)\) values

Relative standard deviations of the \(a_\phi\) values in the mixed solutions were assumed to be 0.33% in accord with our preceding paper\(^{19}\), and the \(\sigma(\phi)\) values were calculated on the basis of the law of propagation of error neglecting the effects of the uncertainties in \(m\). Although we should not expect the values of \(\sigma\) in a mixed electrolyte solution to be less than those in the corresponding single electrolyte solutions, the \(\sigma(\phi)\) value thus calculated was less than that in the single FeCl\(_3\) solution (=9.7 × 10\(^{-3}\)) only when \(m(\text{HCl})=2.01\text{ mol·kg}^{-1}\) and \(m(\text{FeCl}_3)=4.03\text{ mol·kg}^{-1}\). Namely, since the Gibbs-Duhem equation indicates that \(\sigma(\phi)\) is equal to \(\sigma(\ln \gamma_x)\) in the single electrolyte solution, the \(\sigma(\phi)\) value for the single FeCl\(_3\) solution is 9.7 × 10\(^{-3}\) from Table 1. Therefore, the value of \(\sigma(\phi)\) in this solution composition was assumed to be 9.7 × 10\(^{-3}\).

A.2 Evaluation of the \(\sigma(R)\) values

\(K_\phi\) in the single CuCl\(_2\) solution is expressed as:

\[
\ln K_{\phi} = 3 \ln \gamma_x(\text{Cl}^\text{Cl}_2), \quad 3 \ln m(\text{CuCl}_2), \quad 2 \ln a_{\text{Cu}_2}\quad\quad (A1)
\]

where the suffix 0 means the binary system and is used only in this section to avoid confusion. Thus, \(\sigma(\ln K_{\phi})\) is written on the basis of the law of propagation of error as:

\[
\sigma(\ln K_{\phi})^2 = 9 \sigma(\ln \gamma_x(\text{Cl}^\text{Cl}_2), \quad 9 \sigma(\ln m(\text{CuCl}_2), \quad 4 \sigma(\ln a_{\text{Cu}_2})^2 \quad\quad (A2)
\]

Three literature values for CuCl\(_2\) solubility in the single CuCl\(_2\) solution at 298 K\(^{10,19,19}\) were averaged and the values of 5.708 mol·kg\(^{-1}\) and 0.036 mol·kg\(^{-1}\) were obtained as \(m(\text{CuCl}_2),\) and \(\sigma(m(\text{CuCl}_2))\) respectively. The value of \(\sigma(\ln \gamma_x(\text{CuCl}_2),\) was assumed to be 0.024, because the difference of the value of \(\ln \gamma_x(\text{CuCl}_2)\) by NBS from that calculated by the Pitzer method amounts to 0.024 when \(m(\text{CuCl}_2)=5.75\text{ mol·kg}^{-1}\). Similarly, the value of \(\gamma_x(\text{CuCl}_2),\) was calculated by the Pitzer method using the value of \(m(\text{CuCl}_2),\) obtained above. Consequently, the values of \(\ln K_{\phi}\) and \(\sigma(\ln K_{\phi})\) were calculated to be 4.43 and 0.08, respectively.

In the aqueous solution of HCl–CuCl\(_2\), the law of propagation of error leads to the expression for \(\sigma(R),\) which indicates that we need the values of \(\sigma(\ln K_{\phi}),\) \(\sigma(\ln (\text{HCl}))\), and \(\sigma(m(\text{CuCl}_2))\) as well as \(m(\text{HCl}),\) and \(m(\text{CuCl}_2),\) to estimate \(\sigma(R).\) The value of \(\sigma(\ln K_{\phi})\) is 0.08 as estimated in the preceding paragraph. When the molality in the literature has three significant figures, the relative standard deviation of this molality was assumed to be 2%. When the molality in the literature has four significant figures, the relative standard deviation was assumed to be the same magnitude as that when \(m(\text{HCl})=0\text{ mol·kg}^{-1}\), namely, 0.63% (=100\% \(m(\text{CuCl}_2)/m(\text{CuCl}_2))\).

REFERENCES


