Estimation of Activities in the Aqueous Solution Systems of HCl-NaCl and HCl-NiCl₂ Using the Pitzer Method[†]

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Parameterizations based on the literature activity data have been carried out for the activities of water and the solutes in the aqueous solution systems of HCl-NaCl and HCl-NiCl₂ at 298 K in terms of the Pitzer theory without explicitly considering complex formation. The single electrolyte parameters for HCl, NaCl, and NiCl₂ were determined from the osmotic coefficients for the corresponding single electrolyte solutions. Extra parameters of $\beta^{(2)}$ were included in the single electrolyte parameters for HCl and NiCl₂ to extend the applicable concentration ranges. Three kinds of activity data for the aqueous solution of HCl-NaCl, namely, the mean activity coefficients of HCl calculated by the Harned rule, those of NaCl calculated from the solubilities of NaCl, and the osmotic coefficients measured by the transpiration method, were simultaneously submitted to the weighted linear least-squares analysis to determine the mixed electrolyte parameters. Similarly, two kinds of activity data for the aqueous solution of HCl-NiCl₂, namely, the mean activity coefficients of HCl by the emf measurement and the osmotic coefficients by the transpiration method, were simultaneously employed. The χ^2 -tests of significance indicated that the Pitzer parameters obtained in this study can reproduce these activity data with no statistically significant error for both mixed solution systems. As a result, the mean activity coefficients of the solutes in these solution systems calculated by the parameters obtained in this study are in good agreement with those calculated by the McKay-Perring method.

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I. Introduction

Despite the importance of the activity concept for electrolyte solutions in hydrometallurgical studies, its use in actual experimental studies is hampered by the limitation of available activity data. The lack of an activity estimation method accurate enough even in concentrated and mixed electrolyte solutions also gives an impetus to this situation. Among some activity estimation methods proposed for concentrated and mixed electrolyte solutions⁽¹⁾⁻⁽⁴⁾, the Pitzer method seems to be the most promising owing to a recent upsurge in the use of this method to various academic fields. We have already shown the effectiveness of the Pitzer method in the prediction and analyses of the solvent extraction behavior of copper⁽⁵⁾⁻⁽⁸⁾.

Awakura *et al.*⁽⁹⁾ measured the water activities in the aqueous solution systems of HCl-MCl_x (M: Na, Ni, Cu(II), and, Fe(III)) at 298 K by the transpiration method to provide new activity data in these solution systems for which solute activities had been known only

within a limited concentration range or no activity data had been available. In the present study, we have parameterized for the activities in the aqueous solution systems of HCl-NaCl and HCl-NiCl₂ within the framework of the Pitzer theory. Here, we employed the stoichiometric approach; namely, no complex formation was explicitly considered. For determining the mixed electrolyte parameters, emf and solubility data in the literature as well as the water activity data by Awakura *et al.*⁽⁹⁾ were used, and weighted least-squares analysis was employed to obtain statistical criteria for validity of the theory. The original Pitzer method was modified to extend the applicability of this theory toward concentrated region after Filippov *et al.*⁽¹⁰⁾

II. Parameterization Procedure

1. Equations

The details of the Pitzer method have repeatedly appeared elsewhere; thus, it will not be described here. We write the expressions only for the stoichiometric osmotic coefficient, ϕ , and the stoichiometric mean activity coefficient of each solute i , $\gamma_{\pm}(i)$, in the aqueous solution system of HX-MX_x (X: a univalent anion) as:

$$\phi - 1 = \left(\sum_i m_i \right)^{-1} \{ 2If^{\phi} + 2m_H m_X (B_{HX}^{\phi} + m_X C_{HX}^{\phi}) + 2m_M m_X [B_{MX}^{\phi} + (m_X/x^{1/2})C_{MX}^{\phi}] + 2m_H m_M (\theta_{HM} + I\theta' + m_X \psi_{HMX}) \} \quad (1)$$

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$$\ln \gamma_{\pm}(\text{HX}) = f^{\gamma} + m_{\text{X}}(B_{\text{HX}} + m_{\text{X}}C_{\text{HX}}) + m_{\text{H}}(B_{\text{HX}} + m_{\text{X}}C_{\text{HX}}) + m_{\text{M}}(B_{\text{MX}} + m_{\text{X}}C_{\text{MX}} + \theta_{\text{HM}}) \\ + m_{\text{H}}m_{\text{X}}(B'_{\text{HX}} + C_{\text{HX}}) + m_{\text{M}}m_{\text{X}}(B'_{\text{MX}} + C_{\text{MX}} + \psi_{\text{HMX}}) + m_{\text{H}}m_{\text{M}}[(1/2)\psi_{\text{HMX}} + \theta'_{\text{HM}}] \quad (2)$$

$$\ln \gamma_{\pm}(\text{MX}_x) = xf^{\gamma} + 2/(1+x)m_{\text{X}}(B_{\text{MX}} + m_{\text{X}}C_{\text{MX}}) + 2x/(1+x)m_{\text{H}}(B_{\text{HX}} + m_{\text{X}}C_{\text{HX}} + x\theta_{\text{HM}}) \\ + 2x/(1+x)m_{\text{M}}(B_{\text{MX}} + m_{\text{X}}C_{\text{MX}}) + m_{\text{H}}m_{\text{X}}[xB'_{\text{HX}} + 1/(1+x)(2xC_{\text{HX}} + \psi_{\text{HMX}})] \\ + m_{\text{M}}m_{\text{X}}[xB'_{\text{MX}} + 2x/(1+x)C_{\text{MX}}] + m_{\text{H}}m_{\text{M}}[x/(1+x)\psi_{\text{HMX}} + x\theta'_{\text{HM}}] \quad (3)$$

where

$$f^{\phi} = -A_{\phi}[I^{1/2}/(1 + 1.2I^{1/2})] \quad (4)$$

$$f^{\gamma} = -A_{\phi}[I^{1/2}/(1 + 1.2I^{1/2}) + (2/1.2)\ln(1 + 1.2I^{1/2})] \quad (5)$$

$$B_{\text{NX}}^{\phi} = \beta_{\text{NX}}^{(0)} + \beta_{\text{NX}}^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta_{\text{NX}}^{(2)} \exp(-\alpha_2 I^{1/2}) \quad (6)$$

$$B_{\text{NX}} = \beta_{\text{NX}}^{(0)} + [2\beta_{\text{NX}}^{(1)}/(\alpha_1^2 I)] [1 - (1 + \alpha_1 I^{1/2}) \exp(-\alpha_1 I^{1/2})] \\ + [2\beta_{\text{NX}}^{(2)}/(\alpha_2^2 I)] [1 - (1 + \alpha_2 I^{1/2}) \exp(-\alpha_2 I^{1/2})] \quad (7)$$

$$B'_{\text{NX}} = [2\beta_{\text{NX}}^{(1)}/(\alpha_1^2 I^2)] \{-1 + [1 + \alpha_1 I^{1/2} + (1/2)\alpha_1^2 I] \exp(-\alpha_1 I^{1/2})\} \\ + [2\beta_{\text{NX}}^{(2)}/(\alpha_2^2 I^2)] \{-1 + [1 + \alpha_2 I^{1/2} + (1/2)\alpha_2^2 I] \exp(-\alpha_2 I^{1/2})\} \quad (8)$$

$$C_{\text{NX}} = C_{\text{NX}}^{\phi} / (2|z_{\text{N}}z_{\text{X}}|^{1/2}) \quad (9)$$

$$\theta_{\text{HM}} = {}^{\text{E}}\theta_{\text{HM}}(I) + {}^{\text{S}}\theta_{\text{HM}} \quad (10)$$

$$\theta'_{\text{HM}} = {}^{\text{E}}\theta'_{\text{HM}}(I) \quad (11)$$

Here, the quantities m_i , A_{ϕ} , and I , and the prime respectively represent the molality of the ion i , the Debye-Hückel constant ($=0.392 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ for water at 298 K), ionic strength and the derivative with respect to I . The parameters of α_1 , and α_2 are constants and are 2 and $1 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$, respectively. The quantities of $\beta_{\text{NX}}^{(i)}$ (i : 0, 1, and 2) and C_{NX}^{ϕ} are single electrolyte parameters characteristic of the electrolyte NX_x , depending on temperature and pressure. In the original Pitzer method, $\beta_{\text{NX}}^{(2)}$ is zero when X is a univalent anion. In this study, however, $\beta_{\text{NX}}^{(2)}$ is not taken to be zero except for NaCl in order to extend the applicable concentration range. This modification was made after Filippov *et al.*⁽¹⁰⁾. The terms of θ_{ij} and ψ_{ijk} appear only in mixed electrolyte solutions. Here the ions of i and j have the same sign and the ion of k has the opposite sign. The term ${}^{\text{E}}\theta_{ij}(I)$ depends only on the charges of the ions i and j , and I . This term is calculated according to Pitzer *et al.*⁽¹¹⁾. When the ions i and j have the same charge, ${}^{\text{E}}\theta_{ij}(I)$ and ${}^{\text{E}}\theta_{ij}(I)'$ are zero. The terms of ${}^{\text{S}}\theta_{ij}$ and ψ_{ijk} are mixed electrolyte parameters and are constants at given temperature and pressure characteristic of the mixing, respectively, of the two ions i and j , and of the three ions i , j , and k .

2. Evaluation of the single electrolyte parameters

Pitzer's equation for the osmotic coefficient of the single NX_x solution is derived from eq. (1) as:

$$\phi - 1 = xf^{\phi} + 2x/(1+x)m_{\text{NX}}B_{\text{NX}}^{\phi} + 2x^{3/2}/(1+x)m^2C_{\text{NX}}^{\phi} \quad (12)$$

The single electrolyte parameters for HCl, NaCl, and NiCl₂ were determined by the linear least-squares method assigning equal weights to the respective data presented by the U.S. National Bureau of Standards (NBS)⁽¹²⁾⁽¹³⁾. We did not use the weighted least-squares method

because NBS did not necessarily specify the uncertainty of each literature value. A program SALS was used throughout this study as a least-squares program⁽¹⁴⁾.

3. Evaluation of the mixed electrolyte parameters

In the activity estimation for the aqueous solution system of HCl–MCl_x, the mixed electrolyte parameters of ${}^{\text{S}}\theta_{\text{HM}}$ and ψ_{HMX} should be determined from the activity data of the mixed solution and the single electrolyte parameters obtained in the preceding section. For each solution system, different kinds of data sources were simultaneously submitted to the weighted linear least-squares analysis in order to obtain consistent mixed electrolyte parameters. Three kinds of data sources were used for the aqueous solution of HCl–NaCl: (1) the $\gamma_{\pm}(\text{HCl})$ values calculated by the Harned rule⁽¹⁵⁾, where the $m(\text{HCl})$ value was set at $0.01 \text{ mol} \cdot \text{kg}^{-1}$, (2) the ϕ values calculated from the water activities⁽⁹⁾, and (3) the $\gamma_{\pm}(\text{NaCl})$ values calculated from the solubilities of NaCl^{(16)–(18)}. For the aqueous solution of HCl–NiCl₂, two kinds of data sources were used: (1) the $\gamma_{\pm}(\text{HCl})$ values measured by the emf method⁽¹⁹⁾, and (2) the ϕ values calculated from the water activities⁽⁹⁾. Here the Harned rule is written, when I is constant, as:

$$\log \gamma_{\pm}(1) = \log \gamma_{\pm}(1)_0 - \alpha(1, 2)m(2) \quad (13)$$

where the numbers in the parentheses, 1 and 2, denote the respective solutes in a ternary solution system. The suffix 0 denotes the quantity in the binary system and is used only when there is the possibility of confusion. The coefficient $\alpha(1, 2)$ is constant at given temperature and pressure when I is constant. Water activity, a_{w} , is related to ϕ as:

$$\phi = -1000 / \left[\sum_i (v(i)m(i))M_{\text{w}} \right] \ln a_{\text{w}} \quad (14)$$

where the symbol $\nu(i)$ and M_w designate the number of ions formed from the solute i and the molecular weight of water, respectively. Also, the mean activity coefficients of NaCl in the HCl solution saturated with NaCl are calculable from the following equation if the solubility product of NaCl, K_{sp} , and the solution composition are known:

$$K_{sp} = \gamma_{\pm}(\text{NaCl})_s^2 m(\text{Na}^+)_s m(\text{Cl}^-)_s \quad (15)$$

where the suffix s denotes a saturated solution. Equations used in the least-squares analysis were eqs. (1), (2), and (3) for ϕ , $\gamma_{\pm}(\text{HCl})$, and $\gamma_{\pm}(\text{NaCl})$, respectively.

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

$$w_i = 1/\sigma_i^2 \quad (16)$$

where w_i and σ_i are the weight and the standard deviation of the i th measurement, respectively. The weighted least-squares method enables us to obtain unknown parameters yielding the minimum value of the weighted residual sum of squares, S , defined as:

$$S = \sum_{i=1}^n v_i^2 w_i \quad (17)$$

where v_i and n are the difference between observed and calculated values and the number of data points, respectively.

It is known that the χ^2 -distribution with $n-m$ degrees of freedom (m is the number of unknown parameters) applies for S when the following five prerequisites are satisfied⁽¹⁴⁾: (1) the expected value of the error in the measurement is zero, (2) the variances of the errors in the measurement 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. We performed the weighted least-squares analysis for each solution system with the hypothesis that these prerequisites were satisfied, and the validity of this hypothesis for each solution system was examined by the χ^2 -test of significance.

The values of σ were estimated in most cases by the law of propagation of errors expressed as:

$$\sigma(y)^2 = \sum_i \left(\partial y / \partial x_i \right)^2 \sigma(x_i)^2 \quad (18)$$

where

$$y = f(x_1, x_2, \dots, x_l) \quad (19)$$

Here the error of the variable x_i is independent of one

another. The detailed estimation of σ is described in Appendices A.1 and A.2. The estimation of K_{sp} is also described in Appendix A.1. For the aqueous solution of HCl-NaCl, the values of σ thus estimated ranged from: (1) 4.4×10^{-3} to 1.5×10^{-2} for $\ln \gamma_{\pm}(\text{HCl})$, (2) 1.5×10^{-2} to 0.46 for ϕ , and (3) 5.2×10^{-3} to 7.3×10^{-3} for $\ln \gamma_{\pm}(\text{NaCl})_s$. Similarly, for the aqueous solutions of HCl-NiCl₂, the values of σ were: (1) 4.2×10^{-3} throughout for $\ln \gamma_{\pm}(\text{HCl})$ and (2) from 1.9×10^{-2} to 0.37 for ϕ .

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 in ϕ , $\sigma(\phi)$, the numbers of the data points, and the concentration ranges. The value of $\beta_{\text{NaCl}}^{(2)}$ was set at zero because an excellent fit was obtained even when we did not use $\beta_{\text{NaCl}}^{(2)}$. Figures 1 and 2 show how well the parameters determined in this study reproduce the ϕ values of HCl and NiCl₂ solutions. The values calculated by the parameters determined by the other researchers without including $\beta^{(2)}$ are also shown for comparison. The NBS data⁽¹²⁾⁽¹³⁾ are represented by the circles, but some data points are not shown here for simplification. The solid, the chain, and the broken lines denote the values calculated by the parameters evaluated in this study, by Pitzer and Mayorga⁽²⁰⁾, and by Kim and Frederick⁽²¹⁾, respectively. Pitzer and Mayorga⁽²⁰⁾ evaluated the parameters from the emf data up to 6 mol·kg⁻¹ for HCl and from the ϕ values up to 2.5 mol·kg⁻¹ for NiCl₂. Kim and Frederick⁽²¹⁾ evaluated the parameters from the ϕ values up to 16 mol·kg⁻¹ for HCl and 5.5 mol·kg⁻¹ for NiCl₂.

As pointed out by Kim and Frederick⁽²¹⁾ as well as shown in Figs. 1 and 2, the ϕ and $\gamma_{\pm}$ values calculated by the parameters of Pitzer and Mayorga⁽²⁰⁾ are in good agreement with the literature values in the relatively dilute region, but considerable deviation arises in the concentrated region. On the other hand, the ϕ and $\gamma_{\pm}$ values calculated by the parameters of Kim and Frederick⁽²¹⁾ are in better agreement with the literature values in the concentrated region than those of Pitzer and Mayorga⁽²⁰⁾ but deviate considerably from the literature values in the dilute region. We confirm here that broader concentration ranges can be covered by the use of the extra parameters $\beta^{(2)}$.

Table 1 Single electrolyte parameters at 298 K.

MX	$\beta^{(0)}$ /kg·mol ⁻¹	$\beta^{(1)}$ /kg·mol ⁻¹	$\beta^{(2)}$ /kg·mol ⁻¹	C^{ϕ} /kg ² ·mol ⁻¹	$\sigma(\phi)$	Number of data points	$m(\text{MX})$ /mol·kg ⁻¹
HCl	0.2315	0.6110	-0.257	-0.00525	0.0044	39	0.001-16.000
NaCl	0.0771	0.2648	0	0.00110	0.0007	30	0.001-6.144
NiCl ₂	0.4516	2.398	-0.5896	-0.02313	0.0039	47	0.001-5.500

Fig. 1 The ϕ values in the aqueous solution of HCl at 298 K as a function of $m(\text{HCl})$. The circles denote the literature values⁽¹²⁾. The solid, chain and broken lines denote the values by the Pitzer parameters in this study, Ref. (20) and Ref. (21), respectively.

Fig. 2 The ϕ values in the aqueous solution of NiCl₂ at 298 K as a function of $m(\text{NiCl}_2)$. The circles denote the literature values⁽¹³⁾. The solid, chain and broken lines denote the values by the Pitzer parameters in this study, Ref. (20) and Ref. (21), respectively.

2. Evaluation of the mixed electrolyte parameters

(1) The aqueous solution of HCl–NaCl

We first used all the data points whose ionic strength is less than $6.31 \text{ mol} \cdot \text{kg}^{-1}$ to determine the mixed electrolyte parameters of $^S\theta_{\text{HNa}}$ and ψ_{HNaCl} (84 data points). This is in accord with the maximum ionic strength in determining the single electrolyte parameters for NaCl. As a result, the S value of 190 was obtained, far exceeding the value of $\chi^2_{0.05}(=104)$ with 82 degrees of freedom, where the suffix represents the upper-tail probability in the χ^2 -distribution (the critical χ^2 values were approximately estimated by the Wilson-Hilferty equation⁽²²⁾ throughout this paper). The examination of the normalized residuals, v_i/σ_i , showed that there were eight data points for the water activities whose absolute values of normalized residual exceed 2.8 corresponding to 99.5% coverage. These data points were omitted in the second least-squares analysis.

The mixed electrolyte parameters of $^S\theta_{\text{HNa}}$ and ψ_{HNaCl} determined in the second analysis are listed in Table 2 together with the standard deviations of the parameters, $\sigma(^S\theta)$ and $\sigma(\psi)$, the correlation coefficient between the parameters, ρ , and the value of S . The number of data points and the range of ionic strength for each data source are also included in this table.

Figures 3, 4, and 5 show the comparisons, respectively, of $\gamma_{\pm}(\text{HCl})$, a_w , and the solubility of NaCl between the experimental values and those reproduced using the mixed electrolyte parameters in Table 2 (solid lines). The blank points in these three figures denote the data used both in the first and the second analyses. The filled points in Fig. 4 denote the literature values used in the first analysis but omitted in the second analysis. The filled points in Fig. 5 denote the data not used in either analysis. The error bars at some data points in Fig. 3 designate the values of $\pm 2\sigma[\gamma_{\pm}(\text{HCl})]$. When the 2σ values are the same magnitude as or smaller than the radii of the circles, such

Table 2 Mixed electrolyte parameters for the aqueous solution of HCl–NaCl.

$^S\theta/\text{kg} \cdot \text{mol}^{-1}$	0.0369
$\psi/\text{kg}^2 \cdot \text{mol}^{-2}$	−0.0038
$\sigma(^S\theta)/\text{kg} \cdot \text{mol}^{-1}$	0.0021
$\sigma(\psi)/\text{kg}^2 \cdot \text{mol}^{-2}$	0.0005
ρ	−0.9562
S	91.4
Number of data points for each data source	8 for Ref. (15) 53 for Ref. (9) 15 for Refs. (16)–(18)
$I(\text{minimum})/\text{mol} \cdot \text{kg}^{-1}$	0.11 and 6.01 for Ref. (15)
and $I(\text{maximum})/\text{mol} \cdot \text{kg}^{-1}$ for each data source	0.20 and 6.31 for Ref. (9) 6.05 and 6.20 for Refs. (16)–(18)

Fig. 3 The $\gamma_{\pm}(\text{HCl})$ values in the aqueous solution of HCl–NaCl at 298 K as a function of $m(\text{NaCl})$. The $m(\text{HCl})$ value is $0.01 \text{ mol} \cdot \text{kg}^{-1}$ throughout. The circles, solid line, and error bars denote the values calculated by the Harned rule⁽¹⁵⁾, the values calculated by the Pitzer parameters evaluated in this study, and the values of $\pm 2\sigma$ in the circles, respectively.

Fig. 4 The a_w values in the aqueous solution of HCl–NaCl at 298 K as a function of $m(\text{NaCl})$. The blank and filled points denote the literature values⁽⁹⁾ respectively used and not used in the evaluation of the mixed electrolyte parameters. The solid lines and numbers in the figure denote the values calculated by the Pitzer parameters in this study and the values of $m(\text{HCl})/m(\text{NaCl})$, respectively.

Fig. 5 Solubilities of NaCl in the aqueous solution of HCl–NaCl at 298 K. The circles, squares, and triangles respectively denote the solubilities reported in Refs. (16), (17), and (18). The blank and the filled points denote the values used and not used in the evaluation of the mixed electrolyte parameters, respectively. The solid line denotes the values calculated by the Pitzer parameters in this study.

error bars are not shown in Fig. 3. The calculated values are in good agreement with the blank points in these three figures without significant systematic deviation. The deviations of most filled points from the calculated values in Fig. 4 are evidently greater than those of the blank points. It is likely that the data points in the region where the a_w values are less than 0.88 have standard deviations larger than that estimated in Appendix A.1. Since it is difficult to quantitatively estimate these uncertainties, our treatment that some data points in this region were omitted in the least-squares analysis would be justified.

For 74 degrees of freedom in the second analysis, the approximate values of $\chi^2_{0.95}$ and $\chi^2_{0.05}$ are 55.2 and 95.1,

respectively. Since the value of S lies between these two values, our hypothesis cannot be rejected. Although the S value exceeds the value of $\chi^2_{0.10}$ ($=90.0$) by 1.4, this was probably caused by the underestimate of $\sigma(a_w)$ in the low a_w region as stated above.

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

It is notable that good agreement is obtained also in the region concentrated in HCl in Fig. 5 despite a bold extrapolation. Zemaitis *et al.*⁽²³⁾ also reported that such an extrapolation is effective for calculating the solubilities of NaCl in HCl solutions by the single and the mixed electrolyte parameters given respectively by Pitzer and Mayorga⁽²⁰⁾ and Pitzer and Kim.⁽²⁴⁾

Briefly, this is because the higher HCl concentration causes a smaller error in $m(\text{NaCl})_s$. Namely, the solubilities of NaCl in HCl solution decrease toward zero with the increasing $m(\text{HCl})$ values as shown by the literature data in Fig. 5. Equation (15) indicates that there are two factors which reduce the solubilities of NaCl in HCl solutions: One is the increase in $m(\text{HCl})_s$, and another is the increase in $\gamma_{\pm}(\text{NaCl})_s$. The latter is ascribed mainly to the hydration of H^+ and Cl^- and confirmed by the actual calculation; namely, the values of $\gamma_{\pm}(\text{NaCl})_s$ when the $m(\text{HCl})_s$ values are 5, 10, and 15 $\text{mol}\cdot\text{kg}^{-1}$ are respectively calculated to be 1.93, 4.74, and 6.78 by eq. (15) and the solubility data⁽¹⁸⁾. From eq. (15), the partial derivative of $m(\text{NaCl})_s$ with respect to $\gamma_{\pm}(\text{NaCl})_s$ is derived as:

$$\frac{\partial m(\text{NaCl})_s}{\partial \gamma_{\pm}(\text{NaCl})_s} = -4K_{sp} / \{ \gamma_{\pm}(\text{NaCl})_s^3 [m(\text{HCl})_s^2 + 4K_{sp} / \gamma_{\pm}(\text{NaCl})_s^2]^{1/2} \} \quad (20)$$

This equation indicates that the simultaneous increase in $m(\text{HCl})_s$ and $\gamma_{\pm}(\text{NaCl})_s$ results in a decrease in the absolute value of this partial derivative value. Actually, these partial derivative values when the $m(\text{HCl})_s$ values are 5, 10, and 15 $\text{mol}\cdot\text{kg}^{-1}$ are -2.61 , -0.14 , and $-0.03 \text{ mol}\cdot\text{kg}^{-1}$, respectively. Further, the relative error of $\pm 5\%$ in the value of $\gamma_{\pm}(\text{NaCl})_s$ when the $m(\text{HCl})_s$ values are 5, 10, and 15 $\text{mol}\cdot\text{kg}^{-1}$ respectively causes the errors in the $m(\text{NaCl})_s$ values of ∓ 0.252 , ∓ 0.033 , and $\mp 0.011 \text{ mol}\cdot\text{kg}^{-1}$ (the double signs in same order). Therefore, a bold extrapolation as performed in this study and in Zemaitis *et al.*⁽²³⁾ tends to be tolerated as far as the solubility estimation in this solution system is concerned.

(2) The aqueous solution of HCl–NiCl₂

We submitted all the data points of Khoo *et al.*⁽¹⁹⁾ and Awakura *et al.*⁽⁹⁾ to determine the mixed electrolyte parameters of $^S\theta_{\text{HNi}}$ and ψ_{HNiCl_2} , because the maximum ionic strength among these data is less than those in the determination of the single electrolyte parameters for HCl and NiCl₂.

The mixed electrolyte parameters of $^S\theta_{\text{HNi}}$ and ψ_{HNiCl_2} , thus determined are listed in Table 3 together with the values of $\sigma(^S\theta)$, $\sigma(\psi)$, ρ , and S . The number of data points and the range of ionic strength for each data

Table 3 Mixed electrolyte parameters for the aqueous solution of HCl-NiCl₂.

${}^s\theta/\text{kg}\cdot\text{mol}^{-1}$	0.1029
$\psi/\text{kg}^2\cdot\text{mol}^{-2}$	-0.0111
$\sigma({}^s\theta)/\text{kg}\cdot\text{mol}^{-1}$	0.0043
$\sigma(\psi)/\text{kg}^2\cdot\text{mol}^{-2}$	0.0025
ρ	-0.8357
S	50.9
Number of data points for each data source	25 for Ref. (19) 43 for Ref. (9)
$I(\text{minimum})/\text{mol}\cdot\text{kg}^{-1}$ and $I(\text{maximum})/\text{mol}\cdot\text{kg}^{-1}$ for each data source	0.10 and 3.00 for Ref. (19) 0.40 and 8.52 for Ref. (9)

source are also included in this table. Figures 6 and 7 show the comparisons, respectively, of $\gamma_{\pm}(\text{HCl})$ and a_w between experimental values and those reproduced using the mixed electrolyte parameters in Table 3 (solid lines). These figures exhibit that the calculated values are in good agreement with the blank points without significant systematic deviation. In Fig. 6, the comparisons when the I values are 0.5 and 1 mol·kg⁻¹ are not drawn for simplification but show the same tendency.

For 66 degrees of freedom in the analysis, the values of $\chi^2_{0.95}$ and $\chi^2_{0.05}$ are 48.3 and 86.0, respectively; thus, since the value of S lies between these two values, our hypothesis cannot be rejected. Although the S value is less than the value of $\chi^2_{0.90}$ (=51.8) by 0.9, this would be explained by the uncertainties in the estimation of the experimental errors.

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

3. Estimation of the mean activity coefficients of solutes

Majima *et al.*⁽²⁵⁾ tabulated the mean activity coefficients of solutes in various ternary solution systems calculated from the water activities measured by them using the method of McKay and Perring⁽²⁶⁾. The broken lines in Figs. 8-11 are smooth curves drawn through a part of their mean activity coefficients of the solutes in the aqueous solution systems of HCl-NaCl and HCl-NiCl₂. The $\gamma_{\pm}$ values calculated by the Pitzer method with the parameters evaluated in this study are also shown as solid lines in these figures. Here error bars at some points designate the values of $\pm 2\sigma(\gamma_{\pm})$ estimated by the following equation⁽¹⁴⁾:

$$\sigma(\ln \gamma_{\pm})^2 = G({}^s\theta)^2 \sigma({}^s\theta)^2 + G(\psi)^2 \sigma(\psi)^2 + 2G({}^s\theta)G(\psi)\rho\sigma({}^s\theta)\sigma(\psi) \quad (21)$$

where

$$G(x) = \partial \ln \gamma_{\pm} / \partial x \quad (22)$$

Here the symbol x is ${}^s\theta$ or ψ .

The $\gamma_{\pm}$ values calculated by the Pitzer method in Figs. 8-11 are at least in qualitative agreement with those by

Fig. 6 The $\gamma_{\pm}$ values in the aqueous solution of HCl-NiCl₂ at 298 K as a function of the ionic strength fraction of NiCl₂, $\gamma(\text{NiCl}_2)$ ($=3m(\text{NiCl}_2)/[m(\text{HCl})+3m(\text{NiCl}_2)]$). The blank circles, solid lines and numbers in the figure, denote the values by Khoo *et al.*⁽¹⁹⁾, the values calculated by the Pitzer parameters in this study, and the values of $I/\text{mol}\cdot\text{kg}^{-1}$, respectively.

Fig. 7 The a_w values in the aqueous solution of HCl-NiCl₂ at 298 K as a function of $m(\text{NiCl}_2)$. The blank points denote the literature values⁽⁹⁾ used in the evaluation of the mixed electrolyte parameters. The solid lines and numbers in the figure, denote the values calculated by the Pitzer parameters in this study and the values of $m(\text{HCl})/m(\text{NiCl}_2)$, respectively.

the McKay-Perring method. Nevertheless, there are small deviations which cannot be explained only by the uncertainties in the $\gamma_{\pm}$ values calculated by the Pitzer method. For example, the $\gamma_{\pm}(\text{NaCl})$ value by the McKay-Perring method in Fig. 9 is 4.1% larger than that by the Pitzer method when $m(\text{HCl})=2.0 \text{ mol}\cdot\text{kg}^{-1}$ and $m(\text{NaCl})=0.2 \text{ mol}\cdot\text{kg}^{-1}$. Also, the $\gamma_{\pm}(\text{HCl})$ value by the Pitzer method in Fig. 10 is 5.0% larger than that by the McKay-Perring method when $m(\text{HCl})=0.2 \text{ mol}\cdot\text{kg}^{-1}$ and $m(\text{NiCl}_2)$

Fig. 8 The $\gamma_{\pm}(\text{HCl})$ values in the aqueous solution of HCl-NaCl at 298 K as a function of $m(\text{NaCl})$. The broken and solid lines denote the values calculated respectively by the McKay-Perring method⁽²⁵⁾ and by the Pitzer method with the parameters evaluated in this study. The error bars and numbers in the figure, denote the values of $\pm 2\sigma$ in the $\gamma_{\pm}$ values by the Pitzer method and the values of $m(\text{HCl})/\text{mol}\cdot\text{kg}^{-1}$, respectively.

Fig. 9 The $\gamma_{\pm}(\text{NaCl})$ values in the aqueous solution of HCl-NaCl at 298 K as a function of $m(\text{HCl})$. The broken and solid lines denote the values calculated respectively by the McKay-Perring method⁽²⁵⁾ and by the Pitzer method with the parameters evaluated in this study. The error bars and numbers in the figure denote the values of $\pm 2\sigma$ in the $\gamma_{\pm}$ values by the Pitzer method and the values of $m(\text{NaCl})/\text{mol}\cdot\text{kg}^{-1}$, respectively.

$= 2.0 \text{ mol}\cdot\text{kg}^{-1}$. We will discuss below the reasons for these deviations.

Apart from the uncertainties in the measurement, the following points can be considered as sources of the errors in the $\gamma_{\pm}$ values calculated by the McKay-Perring

Fig. 10 The $\gamma_{\pm}(\text{HCl})$ values in the aqueous solution of HCl-NiCl₂ at 298 K as a function of $m(\text{NiCl}_2)$. The broken and solid lines denote the values calculated respectively by the McKay-Perring method⁽²⁵⁾ and by the Pitzer method with the parameters evaluated in this study. The error bars and numbers in the figure respectively denote the values of $\pm 2\sigma$ in the $\gamma_{\pm}$ values by the Pitzer method and the values of $m(\text{HCl})/\text{mol}\cdot\text{kg}^{-1}$.

method:

(1) The McKay-Perring method needs the values of $\gamma_{\pm}$ and a_w for the corresponding single electrolyte solutions. Majima *et al.*⁽²⁵⁾ seemingly used the values compiled by Robinson and Stokes⁽²⁷⁾ (RS); whereas, we used the NBS values for determining the single electrolyte parameters. Slight deviations are sometimes seen between the values in these two data sources. For example, for the single HCl solution, when $m(\text{HCl})$ is $1.0 \text{ mol}\cdot\text{kg}^{-1}$, the a_w and $\gamma_{\pm}$ values by RS are respectively $3 \times 10^{-3}\%$ and 0.25% less than those by NBS. Further, for the single NiCl₂ solution, when $m(\text{NiCl}_2)$ is $1.0 \text{ mol}\cdot\text{kg}^{-1}$, the a_w value by RS is 2.0% larger than that by NBS, whereas the $\gamma_{\pm}$ value by RS is 3.3% less than that by NBS. These deviations slightly affect the $\gamma_{\pm}$ values in the mixed electrolyte solutions calculated by the McKay-Perring method.

(2) Majima *et al.*⁽²⁵⁾ approximated the equi- a_w lines to the following corrected Zdanovskii rule proposed by Kirgintsev and Luk'yanov⁽²⁸⁾:

$$m(1)/M(1) + m(2)/M(2) + bm(1)m(2)/[m(1) + m(2)] = 1 \quad (23)$$

where $M(i)$ is the value of $m(i)$ in an aqueous solution containing only solute i with the same a_w value as the ternary mixed solution, and b is the correction parameter as a function of a_w . When b is zero, eq. (23) reduces to the Zdanovskii rule⁽²⁹⁾. Mikhailov⁽³⁰⁾ pointed out on the basis of the theoretical consideration that, for mixtures of electrolytes of the same valence type, the value of b is zero in

Fig. 11 The $\gamma_{\pm}(\text{NiCl}_2)$ values in the aqueous solution of HCl–NiCl₂ at 298 K as a function of $m(\text{HCl})$. The broken and solid lines denote the values calculated respectively by the McKay-Perring method⁽²⁵⁾ and by the Pitzer method with the parameters evaluated in this study. The error bars and numbers in the figure respectively denote the values of $\pm 2\sigma$ in the $\gamma_{\pm}$ values by the Pitzer method and the values of $m(\text{NiCl}_2)/\text{mol} \cdot \text{kg}^{-1}$.

the region where the limiting Debye-Hückel law holds. The value of b for the aqueous solution of HCl–NaCl in Awakura *et al.*⁽⁹⁾ is, however, not zero in very dilute solution as a result of a linear extrapolation from the region where the limiting Debye-Hückel law does not hold.

(3) For the aqueous solution of HCl–NiCl₂, Awakura *et al.*⁽⁹⁾ performed a numerical integration of b with respect to $\ln a_w$ to calculate the mean activity coefficients by the McKay-Perring method. According to the theoretical consideration by Mikhailov⁽³⁰⁾, for mixtures of electrolytes of different valence types, the value of b is nonzero and positive in the region where the limiting Debye-Hückel law holds and tends toward infinity at very low concentrations. It is, however, very difficult to experimentally obtain the accurate value of b in the very dilute region.

(4) The fitting of the corrected Zdanovskii rule to the equi- a_w lines can contain small errors owing to the empirical nature of this rule.

(5) Interpolations needed in the construction of equi- a_w lines and in the tabulation of the $\gamma_{\pm}$ values can also contain small errors.

Although the quantitative evaluation of the errors in the $\gamma_{\pm}$ values as a result of the above points is very difficult, it is conceivable that the deviations beyond the uncertainties in the Pitzer method found in some cases in Figs. 8–11 can be explained by some of these points when we consider that the tendency of these deviations is the same as those in the previous observations. Namely, Awakura *et al.*⁽³¹⁾ compared the $\gamma_{\pm}(\text{H}_2\text{SO}_4)$ values in the aqueous solution of $\text{H}_2\text{SO}_4\text{--}M_x(\text{SO}_4)_y$ (M : Li, Na, and Mg) calculated by the McKay-Perring method with those

determined by the emf measurements and found that the deviations exceeded 10% when $m(M_x(\text{SO}_4)_y)$ was $0.1 \text{ mol} \cdot \text{kg}^{-1}$ while the agreement was very good when $m(M_x(\text{SO}_4)_y)$ was $1.0 \text{ mol} \cdot \text{kg}^{-1}$. Also, Majima and Awakura⁽³²⁾ compared the $\gamma_{\pm}(\text{Fe}_2(\text{SO}_4)_3)$ values in the aqueous solution of $\text{H}_2\text{SO}_4\text{--}\text{Fe}_2(\text{SO}_4)_3$ calculated by the McKay-Perring method with those calculated by the Gibbs-Duhem method. Their comparative figure shows that the agreement in the concentrated region is much better than that in the dilute region. The deviations in the present comparison also appear in the relatively dilute region.

Furthermore, the $\gamma_{\pm}$ values can be examined from another viewpoint. Namely, the mean activity coefficients of the solutes in a mixed electrolyte solution are interconnected by a cross-derivative relation as:

$$v(1)[\partial \log \gamma_{\pm}(1)/\partial m(2)] = v(2)[\partial \log \gamma_{\pm}(2)/\partial m(1)] \quad (24)$$

As emphasized by Pitzer⁽³³⁾, the Pitzer method analytically satisfy eq. (24). This is a logical outcome of the Pitzer theory because this theory is based on the single equation expressing the excess Gibbs energy and other equations such as eqs. (1), (2), and (3) were derived by thermodynamic relations. Even when the mean activity coefficients calculated by the Pitzer method contain any error, this cross-derivative relation is satisfied as long as the same parameters are used. Also, the McKay-Perring method analytically satisfies eq. (24) as long as the a_w value for the solution containing only solute 1 with composition $M(1)$ is equal to that for the solution containing only solute 2 with composition $M(2)$.

To examine this numerically, the values of both sides of eq. (24) based on the Pitzer method and the McKay-Perring method were calculated by the procedure described in Appendix A.3 at some solution compositions and are shown in Tables 4 and 5. Here the quantities, A , B , and δ are given by the equations as:

$$A = v(\text{HCl})[\partial \log \gamma_{\pm}(\text{HCl})/\partial m(\text{MCl}_x)] \quad (25)$$

$$B = v(\text{MCl}_x)[\partial \log \gamma_{\pm}(\text{MCl}_x)/\partial m(\text{HCl})] \quad (26)$$

$$\delta = A - B \quad (27)$$

Here M is Na or Ni. In Tables 4 and 5, the symbol **a** designates that the $\gamma_{\pm}$ values were taken from Majima *et al.*⁽²⁵⁾ In this data source, significant figures are to three decimal places and the increments in m range from 0.1 to $0.5 \text{ mol} \cdot \text{kg}^{-1}$ depending on the composition. The symbol **b** designates that the $\gamma_{\pm}$ values with the same significant figures and the variable increments in m as those of method **a** were calculated by the Pitzer method. The symbol **c** designates that the $\gamma_{\pm}$ values with significant figures to six decimal places and the increment in m of $0.02 \text{ mol} \cdot \text{kg}^{-1}$ were calculated by the Pitzer method. As shown by method **c**, we confirm that the $\gamma_{\pm}$ values calculated by the Pitzer method satisfy the cross-derivative relation. On the other hand, the nonzero values of δ in method **a** in most solution compositions cannot be wholly explained by the error introduced by the truncation and the variable increments larger than

Table 4 The cross-derivative relation in the aqueous solution of HCl–NaCl.

$m(\text{HCl})/\text{mol} \cdot \text{kg}^{-1}$	$m(\text{NaCl})/\text{mol} \cdot \text{kg}^{-1}$	$A/10^{-2} \text{ kg} \cdot \text{mol}^{-1}$			$B/10^{-2} \text{ kg} \cdot \text{mol}^{-1}$			$\delta/10^{-2} \text{ kg} \cdot \text{mol}^{-1}$		
		a*	b*	c*	a	b	c	a	b	c
0.2	0.2	−3.5	−4.6	−4.946	−6.2	−5.1	−4.949	2.7	0.5	0.003
0.2	1.0	8.7	11.3	11.148	11.5	11.0	11.145	−2.8	0.3	0.003
0.2	1.8	13.7	15.2	15.404	15.7	15.1	15.406	−2.0	0.1	−0.002
1.0	0.2	10.9	10.9	10.977	14.5	11.1	10.977	−3.6	−0.2	0.000
1.0	1.0	14.5	15.3	15.494	17.2	15.3	15.496	−2.7	0.0	−0.002
1.0	1.8	16.9	17.5	17.653	19.2	17.5	17.656	−2.3	0.0	−0.003
1.8	0.2	14.8	15.2	15.582	17.6	15.7	15.582	−2.8	−0.5	0.000

* The meanings of **a**, **b**, and **c** are described in the text.

Table 5 The cross-derivative relation in the aqueous solution of HCl–NiCl₂.

$m(\text{HCl})/\text{mol} \cdot \text{kg}^{-1}$	$m(\text{NiCl}_2)/\text{mol} \cdot \text{kg}^{-1}$	$A/10^{-2} \text{ kg} \cdot \text{mol}^{-1}$			$B/10^{-2} \text{ kg} \cdot \text{mol}^{-1}$			$\delta/10^{-2} \text{ kg} \cdot \text{mol}^{-1}$		
		a*	b*	c*	a	b	c	a	b	c
0.2	0.2	12.2	9.2	8.471	20.5	8.0	8.477	−8.3	1.2	−0.006
0.2	1.0	38.3	44.5	44.537	44.7	44.1	44.538	−6.4	0.4	−0.001
0.2	1.8	47.9	49.9	49.886	49.8	50.0	49.877	−1.9	−0.1	0.009
1.0	0.2	25.9	30.8	30.444	34.6	30.7	30.436	−8.7	0.1	0.008
1.0	1.0	43.2	47.2	47.298	47.1	46.8	47.302	−3.9	0.4	−0.004
2.0	0.2	34.3	41.5	41.499	38.7	41.4	41.492	−4.4	0.1	0.007
2.0	1.0	49.3	48.7	48.583	47.9	48.6	48.577	1.4	0.1	0.006
3.0	0.2	40.9	46.1	46.139	41.0	46.3	46.147	0.1	−0.2	−0.008

* The meanings of **a**, **b**, and **c** are described in the text.

that in method **c**, because the absolute values of δ by method **a** are much larger than those by the method **b**. This suggests that at least the third decimal places in the $\gamma_{\pm}$ values by the McKay-Perring method contain a certain magnitude of errors.

To summarize, the uncertainties in the $\gamma_{\pm}$ values by the McKay-Perring method should be recognized despite the careful measurement and data treatment. This is due to the experimental uncertainties inevitable in the transpiration method and the computational difficulties inherent in the McKay-Perring method. In the $\gamma_{\pm}$ values for the present solution systems by the Pitzer method, uncertainties are brought about only as a result of experimental uncertainties, because the a_w values are reproduced within experimental uncertainties and eqs. (2) and (3) are thermodynamically consistent with eq. (1). Therefore, it is thought that the uncertainties in the $\gamma_{\pm}$ values by the McKay-Perring method are at least of the same magnitude as or probably larger than those by the Pitzer method. In this sense, the deviations between the mean activity coefficients calculated by the Pitzer method and those by the McKay-Perring method are acceptable.

IV. Conclusions

Parameterizations for the activities of water and the solutes in the aqueous solution systems of HCl–NaCl and HCl–NiCl₂ at 298 K have been made 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 $\beta^{(2)}$ in the single electrolyte parameters for HCl and NiCl₂ extends

the applicable concentration ranges.

(2) From the literature activity data including salt solubilities and the water activities, the mixed electrolyte parameters have been determined by the weighted linear least-squares method without statistically significant error.

(3) Mean activity coefficients of the solutes in both solution systems calculated by the parameters obtained in this study are in good agreement with those calculated by the McKay-Perring method.

Appendices

A.1 Evaluation of experimental errors in the aqueous solution of HCl–NaCl

(1) Mean activity coefficients of HCl

According to the description by Harned and Owen⁽¹⁵⁾, the value of $\sigma[\alpha(\text{HCl}, \text{NaCl})]$ was assumed to be $1 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$. From Table 1, the standard deviation of the calculated values of ϕ for the single HCl solution from the literature values is 4.4×10^{-3} . The Gibbs-Duhem equation in the single HCl solution leads to the following relation on condition that $m(\text{HCl})_0$ is constant:

$$d \ln \gamma_{\pm}(\text{HCl})_0 = d\phi_0 \quad (\text{A1})$$

Thus, the $\sigma[\ln \gamma_{\pm}(\text{HCl})_0]$ value was assumed to be 4.4×10^{-3} . Consequently, eqs. (13) and (18) lead to the expression for $\sigma[\ln \gamma_{\pm}(\text{HCl})]$ as:

$$\begin{aligned} \sigma[\ln \gamma_{\pm}(\text{HCl})]^2 = & (\ln 10)^2 m(\text{NaCl})^2 \sigma[\alpha(\text{HCl}, \text{NaCl})]^2 \\ & + \sigma[\ln \gamma_{\pm}(\text{HCl})_0]^2 \end{aligned} \quad (\text{A2})$$

(2) Osmotic coefficients

Awakura *et al.*⁽⁹⁾ repeatedly measured the vapor pressure of pure water at 298 K by the transpiration method. The relative standard deviation of a_w was calculated from their results by the equation as:

$$100\sigma(a_w)/a_w = 100 \left[\sum_i^n (p_{w,i} - \bar{p}_w)^2 / (n-1) \right]^{1/2} / \bar{p}_w \quad (\text{A3})$$

Here the left side defines the relative standard deviation of a_w , $p_{w,i}$ is the vapor pressure of pure water in the i th measurement, $\bar{p}_w$ is an average value of $p_{w,i}$, and n is the number of measurement. The calculation showed that the relative standard deviations of a_w were 0.32% (measured using dehydrating agents) and 0.34% (measured using a mixture of dry ice and methanol). It is likely that the effect of the presence of HCl on $\sigma(a_w)$ is negligible, because Majima *et al.*⁽³⁴⁾ observed that the difference between water vapor pressure for the single HCl solution measured by the transpiration method and the literature values was less than 1% over the HCl molalities ranging from 0 to 6 mol·kg⁻¹. Thus, it would be appropriate to take the relative standard deviation of a_w to be 0.33%. This relative standard deviation includes the uncertainties in the measurement itself and in the temperature. In order to estimate the value of $\sigma(\phi)$ for the aqueous solution system of HCl–NaCl, therefore, the effects of $\sigma[m(\text{HCl})]$ and $\sigma[m(\text{NaCl})]$ should also be considered. Accordingly, the values of $\sigma[m(\text{HCl})]$ and $\sigma[m(\text{NaCl})]$ were estimated from the significant figures; however, the effects of $\sigma[m(\text{HCl})]$ and $\sigma[m(\text{NaCl})]$ on $\sigma(\phi)$ were found to be much less than that of $\sigma(a_w)$. Thus, the effects of $\sigma[m(\text{HCl})]$ and $\sigma[m(\text{NaCl})]$ were neglected in the estimation of $\sigma(\phi)$. Consequently, the expression for $\sigma(\phi)$ can be expressed on the basis of eqs. (14) and (18) as:

$$\begin{aligned} \sigma(\phi)^2 &= (\partial\phi / \partial a_w)^2 \sigma(a_w)^2 \\ &= [1000 / \sum_i (\nu(i)m(i))M_w a_w]^2 \sigma(a_w)^2 \end{aligned} \quad (\text{A4})$$

(3) Mean activity coefficients of NaCl

K_{sp} in the single NaCl solution is expressed as:

$$\ln K_{sp} = 2 \ln \gamma_{\pm}(\text{NaCl})_{s,0} + 2 \ln m(\text{NaCl})_{s,0} \quad (\text{A5})$$

Thus, $\sigma(\ln K_{sp})$ is written as:

$$\begin{aligned} \sigma(\ln K_{sp})^2 &= 4\sigma[\ln \gamma_{\pm}(\text{NaCl})_{s,0}]^2 \\ &\quad + 4\sigma[m(\text{NaCl})_{s,0}]^2 / m(\text{NaCl})_{s,0}^2 \end{aligned} \quad (\text{A6})$$

Six literature values for NaCl solubility in single NaCl solution at 298 K^{(16)–(18)(35)(36)} were averaged, and the values of 6.158 mol·kg⁻¹ and 8×10^{-3} mol·kg⁻¹ were obtained as $m(\text{NaCl})_{s,0}$ and $\sigma[m(\text{NaCl})_{s,0}]$, respectively. The value of $\sigma[\ln \gamma_{\pm}(\text{NaCl})_{s,0}]$ was assumed to be 5×10^{-3} , because the difference in the value of $\ln \gamma_{\pm}(\text{NaCl})_0$ given in the literature from that calculated by the Pitzer method is 5×10^{-3} when $m(\text{NaCl})_0 = 6$ mol·kg⁻¹. The values of $\gamma_{\pm}(\text{NaCl})_{s,0}$ were calculated by the Pitzer method using the value of $m(\text{NaCl})_{s,0}$ obtained above. Consequently,

the values of $\ln K_{sp}$ and $\sigma(\ln K_{sp})$ were respectively calculated to be 3.64 and 0.01.

In the aqueous solution of HCl–NaCl, eqs. (15) and (18) lead to the expression for $\sigma[\ln \gamma_{\pm}(\text{NaCl})_s]$. This expression indicates that we need the values of $\sigma(\ln K_{sp})$, $\sigma[m(\text{HCl})_s]$, and $\sigma[m(\text{NaCl})_s]$ as well as $m(\text{HCl})_s$ and $m(\text{NaCl})_s$ to estimate $\sigma[\ln \gamma_{\pm}(\text{NaCl})_s]$. The value of $\sigma(\ln K_{sp})$ is 0.01 as estimated in the preceding paragraph. When the molality in the literature has three or four significant figures, the relative standard deviation of this molality was assumed to be 2 or 0.2%, respectively.

A.2 Evaluation of experimental errors in the aqueous solution of HCl–NiCl₂

(1) Mean activity coefficients of HCl

The standard deviation between the values of $\gamma_{\pm}(\text{HCl})$ in the single HCl solutions by Khoo *et al.*⁽¹⁹⁾ and those calculated by the Pitzer method using the parameters in Table 1 was calculated to be 4.3×10^{-3} . Error estimation based on eq. (18) taking into account the uncertainties of the emf measurement and the solute molalities of the mixed solution in Khoo *et al.*⁽¹⁹⁾ gave lower values of $\sigma[\ln \gamma_{\pm}(\text{HCl})]$ ($=1 \times 10^{-3}$) than 4.3×10^{-3} . Thus, the value of $\sigma[\ln \gamma_{\pm}(\text{HCl})]$ was assumed to be 4.3×10^{-3} .

(2) Osmotic coefficients

For the same reason as that for the aqueous solution of HCl–NaCl, the value of $\sigma(\phi)$ was estimated by eq. (A4) using the value of 0.33% as a relative standard deviation of a_w .

A.3 Computational procedure for the cross-derivatives

The computational procedure for the value of $\partial \log \gamma_{\pm}(\text{HCl}) / \partial m(\text{MCl}_x)$ at a solution composition where $m(\text{HCl}) = m(\text{HCl})_a$ and $m(\text{MCl}_x) = m(\text{MCl}_x)_a$ is: (1) take consecutive five $\gamma_{\pm}(\text{HCl})$ values as a function of $m(\text{MCl}_x)$ on condition that $m(\text{HCl}) = m(\text{HCl})_a$ so that the $\gamma_{\pm}(\text{HCl})$ value when $m(\text{MCl}_x) = m(\text{MCl}_x)_a$ should be placed in the middle, (2) this data set is submitted to the linear least-squares analysis to obtain the coefficients c_i of the third order polynomial as:

$$\log \gamma_{\pm}(\text{HCl}) = \sum_{i=0}^3 c_i m(\text{MCl}_x)^i \quad (\text{A7})$$

(3) Thus, the partial derivative is expressed by the equation as:

$$\partial \log \gamma_{\pm}(\text{HCl}) / \partial m(\text{MCl}_x) = \sum_{i=1}^3 i c_i m(\text{MCl}_x)^{i-1} \quad (\text{A8})$$

The partial derivative value at the given composition is calculated by substituting $m(\text{MCl}_x)_a$ for $m(\text{MCl}_x)$ on the right side of eq. (A·8). The partial derivative value of $\log \gamma_{\pm}(\text{MCl}_x)$ with respect to $m(\text{HCl})$ at this composition can be calculated by interchanging HCl and MCl_x throughout this procedure.

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