Mean activity coefficients in the NaCl–NH₄HCO₃–H₂O system at 293.15–308.15 K

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Abstract

The mean activity coefficients of NaCl in the NaCl–NH₄HCO₃–H₂O system, measured by an electrochemical cell using ion-selective electrodes, were used to calculate the mean activity coefficients of NH₄HCO₃ in the system through a thermodynamic model. The measurements were made at four temperatures from 293.15 to 308.15 K up to 1.8 mol kg⁻¹, at NH₄HCO₃ molality fractions of 0.2 and 0.4. Both sets of values agree with those obtained from Pitzer equation incorporated with chemical reactions. This observation supports the applicability of the existing parameters for calculating mean activity coefficients of this system. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Activity coefficients; Ion-selective electrode; Aqueous solution; Weak electrolyte; Mixture; Data

1. Introduction

The measurement of thermodynamic properties of aqueous electrolyte solutions plays an important role in the development of thermodynamic models and process simulation. The activity coefficient is an important thermodynamic property, which has been measured by either the solvent activity methods or the electrochemical cell techniques. One of the traditional solvent activity methods is the isopiestic method [1], which is not well suited for systems containing a volatile component. Recently, with the development of ion-selective electrodes (ISE), the electromotive force (emf) method tends to be selected for the determination [2].

As far as the NaCl–NH₄HCO₃–H₂O system is concerned, activity coefficients of the electrolytes have not been reported. On the other hand, the available parameter values of Pitzer equation, in the presence of the weak electrolyte NH₄HCO₃, could be used to estimate these values. However, these parameter values...
were determined from sources other than the system under consideration. The purpose of this work is
to verify the validity of these parameter values by means of an electrochemical cell using ion-selective
electrodes (ISE).

In our previous work [3,4], the influence of the NH$_4^+$ ion was investigated in the study of the
NaCl–NH$_4$Cl–H$_2$O system [3], and the influence of the HCO$_3^-$ ion in the study of the NaCl–NaHCO$_3$–H$_2$O
system [4]. It was observed that the influence of NH$_4^+$ on the Na glass ISE was small enough to be ne-
glected, while the influence of HCO$_3^-$ on the Na glass ISE could be neglected up to 0.5 molality fraction
of HCO$_3^-$. Based on these observations it was decided to limit the molality fractions of NH$_4$HCO$_3$
below 0.5 in this investigation. As it is difficult to determine the activity coefficients of NH$_4$HCO$_3$
directly with ISEs due to the limitation of the type and properties of ISEs, a cell with the following
arrangement:

\[
\text{Na glass ISE/NaCl (}m_1\text{), NH}_4\text{HCO}_3\text{ (}m_2\text{)/Cl solid-state ISE}
\]

was adopted in this work to determine the activity coefficients of NaCl in the NaCl–NH$_4$HCO$_3$–H$_2$O sys-
tem at two lower molality fractions of NH$_4$HCO$_3$ (0.2 and 0.4), and at four temperatures (293.15, 298.15,
303.15, and 308.15 K). Subsequently, the Pitzer equation [5] incorporated with chemical reactions was
used to calculate the activity coefficients of the weak electrolyte NH$_4$HCO$_3$.

2. Apparatus and chemicals

In our previous paper [3], the ‘flow emf’ method developed by Zhang et al. [6] was improved by adding
a concentrated electrolyte solution at a constant molality fraction into the solution under investigation
and recording the measured results automatically with a personal computer. This approach was followed
in this work.

A double-walled vessel was used to contain the cell, its temperature maintained constant within ±0.1 K.
A SCHOTT-GERÄTE resistance thermometer (Model W5791 NN) with a resolution of ±0.1 K was used
to measure the temperature.

A Na glass ISE (Model 102C, Jiangsu Electroanalytical Instrument Plant, Jiangsu, PR China) and a
chloride solid-state ISE (Model 301, Jiangsu Electroanalytical Instrument Plant, Jiangsu, PR China)
were used to measure the ionic activities. In order to improve the stability of the ISEs, they were
pre-treated. The pre-treatment method was described previously [4]. The potential of the cell was mea-
sured with a SCHOTT-GERÄTE pH-meter (Model CG0841), its resolution of the emf measurements
was ±0.1 mV.

Sodium chloride (Guaranteed grade, purity ≥ 99.8%, Beijing Chemical Plant, Beijing) was dried in a
vacuum-dryer until a constant mass was reached. Ammonium bicarbonate (Guaranteed grade, purity ≥
99.8%, Beijing Chemical Plant, Beijing) was analyzed by potentiometric titration with a standard HCl
solution. The de-ionized water was prepared by re-distilling water in the presence of KMnO$_4$ and its
electrical conductivity was less than 1.2 × 10$^{-6}$ S cm$^{-1}$. The concentrated mixed-electrolyte stock solu-
tion, NaCl–NH$_4$HCO$_3$–H$_2$O, with a constant molality fraction of NH$_4$HCO$_3$ ($y_2 = m_{\text{NH}_4\text{HCO}_3}/(m_{\text{NaCl}} +$
m_{\text{NH}_4\text{HCO}_3})$), was prepared by dosing with a SCHOTT-GERÄTE multifunctional piston burette (Model
Titronic T200), which was connected to the computer and used to change the ionic strength. The maximum
dosing deviation was estimated to be ±0.15%.
Table 1
S and $E^0$ of ISEs in the NaCl–H2O system at four temperatures

| $T$ (K) | $E^0$ (mV) | S (mV) | S.D. (mV) | Nernstian slope, $S_T$ (mV) | $|S - S_T|/|S_T|$ (%) |
|---------|------------|--------|-----------|-----------------------------|-------------------|
| 293.15  | 26.22      | 24.90  | 0.22      | 25.26                       | 1.43              |
| 298.15  | 27.17      | 25.71  | 0.11      | 25.69                       | 0.08              |
| 303.15  | 28.00      | 26.36  | 0.17      | 26.12                       | 0.92              |
| 308.15  | 28.87      | 26.90  | 0.08      | 26.55                       | 1.32              |

* S.D. = $\left( \frac{1}{N-1} \sum_{i=1}^{N} (E_{i,cal} - E_{i,exp})^2 \right)^{0.5}$, where $N$ is the number of experimental data points at each temperature.

3. Determination of mean activity coefficients of NaCl in the ternary

3.1. Calibration of ISEs

The ISEs used in this work were calibrated in a NaCl–H2O solution to test their behaviors. The cell arrangement was

Na glass ISE|NaCl ($m$), H2O|Cl solid-state ISE

The emf of the ISEs are related to the mean activity coefficient $\gamma_{\pm}$ and the molality of NaCl ($m$) in the solution by

$$E = E^0 + 2S \ln(m\gamma_{\pm})$$

(1)

where $E$, $E^0$ and $S$ are the potential, the standard emf, and the slope of the cell, respectively.

Since the theoretical $S$ value (the reversible Nernstian slope) may not be justified [7], both $E^0$ and $S$ were treated first as adjustable parameters in the present study. A Simplex optimization procedure was used to determine the values of $E^0$ and $S$ with the following objective function:

$$f(x) = \sum_{i=1}^{N} (E_{i,exp} - E_{i,cal})^2$$

(2)

where $N$ is the number of experiment data points. $E_{i,cal}$ was calculated by Eq. (1). The values of $\gamma_{\pm}$ were estimated by Pitzer equation [5] in which the ionic interaction parameters of pure NaCl were taken from Peiper and Pitzer [8].

The values of $S$ and $E^0$ obtained at four temperatures are reported in Table 1. The standard deviation at each temperature is about 0.25 mV, which is less than the allowed random errors suggested by Bates et al. [7], indicating that the results are acceptable. The relative deviations of the experimental slopes from the theoretical values are less than 1.5%, which is an indication that the response of the Na glass ISE and the Cl solid-state ISE versus the ion activities in solution practically obeys the Nernst behavior.

The linear relationship of $E^0$ with $1/T$ as depicted in Fig. 1 implies that the ISEs behavior obeys the Gibbs–Helmholtz equation.

3.2. Mean activity coefficients of NaCl in the ternary

The arrangement of the cell for the ternary system was

Na glass ISE|NaCl ($m_1$), NH4HCO3 ($m_2$), H2O|Cl solid-state ISE
Fig. 1. Temperature effect on the standard emf $E^0$ for the NaCl–H$_2$O system: (●) experimental data; (—) linear fitting.

For the NaCl–NaHCO$_3$–H$_2$O system, Butler and Huston [9] observed that any concentration changes due to the removal of carbon dioxide had negligible effect on the measured activity coefficients. For the system under consideration, the amount of carbon dioxide removed was less than that in the NaCl–NaHCO$_3$–H$_2$O system at the same concentration. Hence, any concentration changes during the course of measurements due to the removal of carbon dioxide would also have a negligible effect on the measured activity coefficients.

For a ternary system, the electrochemical potential of an electrode could be expressed by [2]

$$E = E^0 + S \log \left( a_1 + \sum_{j=1}^{N} k_{1,j} a_j \right)$$  \hspace{1cm} (3)

where $a_1$ is the activity of NaCl, $a_j$ the activity of interfering species, and $k_j$ is the potentiometric selectivity coefficient of ISE selective to NaCl toward other ion $j$ as interfering ion. In the present work, the values of $E^0$ and $S$ reported in Table 1 were adopted in the determination of the activity coefficients of NaCl in the ternary system. As mentioned earlier, the interference of NH$_4^+$ and HCO$_3^-$ ions on the Na glass electrode could be neglected up to 0.5 molality fraction of HCO$_3^-$. Hence, at the concentration
ranges covered in this work, Eq. (3) could be simplified to

$$\gamma_\pm = \frac{1}{m_1} \exp \left( \frac{E - E^0}{2S} \right)$$

and the mean activity coefficients of NaCl ($\gamma_\pm$) could be obtained by submitting emf of the cell, $E$, in Eq. (4). The experimental data obtained in this manner at 293.15, 298.15, 303.15 and 308.15 K, up to 1.8 mol kg$^{-1}$, and at 0.2 and 0.4 molality fractions of NH$_4$HCO$_3$ are reported in Table 2.

4. Verification of the Pitzer parameters

4.1. Chemical reactions in the liquid phase

In the liquid phase of the system under consideration, four chemical reactions are present:

$$\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) = \text{HCO}_3^-(aq) + \text{OH}^-(aq)$$

$$2\text{HCO}_3^-(aq) = \text{CO}_3^{2-}(aq) + \text{CO}_2(aq) + \text{H}_2\text{O}(l)$$

$$\text{NH}_3(aq) + \text{H}_2\text{O}(l) = \text{NH}_4^+(aq) + \text{OH}^-(aq)$$

$$\text{NH}_3(aq) + \text{HCO}_3^-(aq) = \text{NH}_2\text{COO}^-(aq) + \text{H}_2\text{O}(l)$$

The equilibrium constants for the first three reactions were calculated by the method of Johnson et al. [10]. However, for the fourth reaction, Eq. (8), it was taken from the work of Kawazuishi and Prausnitz [11]. These values are presented in Table 3.

The activity coefficients of NH$_4$CO$_3$ cannot be determined from the experimentally determined emf data directly. A suitable model with incorporation of these chemical reactions is required. In this work, the Pitzer equation was chosen for the calculation. The required parameters are available in the literature, but they were determined indirectly from other systems [8,12–17].

It should be mentioned that the Pitzer equation has been used to calculate thermodynamic properties for numerous systems [5]. However, it is desirable to verify its predictability when the parameter values were obtained indirectly. Sometimes, the parameter values should be established from the experimental data [18]. The steps taken for this purpose are as follows:

1. Establishment of the reliability of the experimentally determined activity coefficients of NaCl in the ternary system.
2. Comparison of these values with those obtained using Pitzer equation together with the parameter values available in the literature.
3. The validity of the Pitzer parameter values are confirmed if a good agreement is obtained in Step 2.

4.2. Pitzer equation

In the Pitzer equation [5], the mean activity coefficient for the electrolyte $M_{i+}X_{i-}$ in a mixture is expressed by
Table 2
Mean ionic activity coefficients of NaCl and NH₄HCO₃ in the NaCl(1)–NH₄HCO₃(2)–H₂O system

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<th>( \gamma \pm 1 ) (mol kg(^{-1}))</th>
<th>( \gamma \pm 2 ) (mol kg(^{-1}))</th>
<th>( \gamma \pm 1 ) (mol kg(^{-1}))</th>
<th>( \gamma \pm 2 ) (mol kg(^{-1}))</th>
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Table 2 (Continued)

\( T = 303.15 \text{ K}; \ y_2 = 0.2 \)

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\( T = 303.15 \text{ K}; \ y_2 = 0.4 \)

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\( T = 308.15 \text{ K}; \ y_2 = 0.2 \)

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\( T = 308.15 \text{ K}; \ y_2 = 0.4 \)

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<td>0.18</td>
<td>0.27</td>
<td>0.564</td>
<td>0.57</td>
<td>0.634</td>
<td>0.474</td>
<td>0.59</td>
</tr>
</tbody>
</table>
Table 3
Equilibrium constants of Eqs. (5)–(8) and their standard deviations between \( \ln \gamma_{\exp} \) and \( \ln \gamma_{\text{cal}} \) of NaCl in the NaCl(1)–NH\(_4\)HCO\(_3\)(2)–H\(_2\)O system at each temperature

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>293.15</th>
<th>298.15</th>
<th>303.15</th>
<th>308.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \ln K_1 )</td>
<td>−8.7243</td>
<td>−8.4419</td>
<td>−8.1675</td>
<td>−7.9006</td>
</tr>
<tr>
<td>( \ln K_3 )</td>
<td>−10.9787</td>
<td>−10.9467</td>
<td>−10.9230</td>
<td>−10.9070</td>
</tr>
<tr>
<td>( \ln K_4 )</td>
<td>0.8669</td>
<td>0.7896</td>
<td>0.7145</td>
<td>0.6416</td>
</tr>
<tr>
<td>( \text{S.D.}_{\ln \gamma} )</td>
<td>0.0047</td>
<td>0.0039</td>
<td>0.0050</td>
<td>0.0074</td>
</tr>
</tbody>
</table>

\( \text{S.D.} = \left( \frac{1}{N-1} \sum_{i=1}^{N} (\ln \gamma_{\text{cal}} - \ln \gamma_{\exp})^2 \right)^{0.5} \), where \( N \) is the number of experimental data points at each temperature.

\[
\ln \gamma_{\pm, MX} = |Z_M Z_X| \left( f^\gamma + \sum_c \sum_a m_c m_a B_{ca}^c \right) + \left( \frac{V_M}{V} \right) \sum_a m_a \left[ 2B_{Ma} + ZC_{Ma} + 2 \left( \frac{v_X}{v_M} \right) \Phi_{Xa} \right] \\
+ \left( \frac{V_M}{V} \right) \sum_c m_c \left[ 2B_{cx} + ZC_{cx} + 2 \left( \frac{v_M}{v_X} \right) \Phi_{Mc} \right] \\
+ \sum_c \sum_a m_c m_a v^{-1} \left[ 2v_M Z_M C_{ca} + v_M v_M c + v_X \psi_{caX} \right] \\
+ \sum_c \sum_{c' < c} m_c m_{c'} \left( \frac{V_X}{V} \right) \psi_{cc'X} + \sum_a \sum_{a < a'} m_a m_{a'} \left( \frac{V_M}{V} \right) \psi_{Ma'X} 
\]

where \( c \) and \( c' \) represent various cations, and \( a \) and \( a' \), various anions. \( Z_M \) and \( Z_X \) represent the ion charges for cations and anions, respectively. The ion numbers of an electrolyte are indicated by \( V^+ \) and \( V^- \). The \( B \) and \( C \) terms can be evaluated empirically from data on binary system, while the \( \Phi \) and \( \psi \) terms arise only for mixed solutions and can best be determined from common ion mixtures. The quantity \( f^\gamma \) and other terms are expressed as follows:

\[
f^\gamma = -A_{\phi} \left[ \frac{I^{1/2}}{1 + b I^{1/2}} + \left( \frac{2}{b} \right) \ln(1 + b I^{1/2}) \right] 
\]

\[
B_{ca} = \beta_{ca}^{(0)} + \beta_{ca}^{(1)} \left( \frac{2}{\alpha^2 I} \right) \left[ 1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2}) \right] 
\]

\[
C_{ca} = \frac{1}{\eta} C^\phi |Z_M Z_X|^{1/2} 
\]

\[
\Phi_{ij} = \theta_{ij} 
\]

\[
B_{ca}' = -\beta_{ca}^{(1)} \left( \frac{2}{\alpha^2 I} \right) \left[ 1 - \left( 1 + \alpha I^{1/2} + \frac{\alpha^2 I}{2} \right) \exp(-\alpha I^{1/2}) \right] 
\]

\[
Z = \sum_i m_i |Z_i| 
\]
Table 4
Ion-interaction parameters for the NaCl–NH₄HCO₃–H₂O system

<table>
<thead>
<tr>
<th></th>
<th>NaOH</th>
<th>Na₂CO₃</th>
<th>NaHCO₃</th>
<th>NaCl</th>
<th>(NH₄)₂CO₃</th>
<th>NH₄HCO₃</th>
<th>NH₄Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta^{(0)}$ (kg mol⁻¹)</td>
<td>0.0864ᵇ</td>
<td>0.0362ᶜ</td>
<td>0.028ᶜ</td>
<td>0.0765ᵇ</td>
<td>0.1288ᵈ</td>
<td>−0.038ᵈ</td>
<td>0.0522ᵇ</td>
</tr>
<tr>
<td>$\beta^{(1)}$ (kg mol⁻¹)</td>
<td>0.253ᵇ</td>
<td>1.51ᶜ</td>
<td>0.044ᶜ</td>
<td>0.2664ᵇ</td>
<td>1.433ᵈ</td>
<td>0.007ᶜ</td>
<td>0.1918ᵇ</td>
</tr>
<tr>
<td>$C^\gamma$ (kg mol⁻²)</td>
<td>0.0044ᶠ</td>
<td>0.0052ᶜ</td>
<td>0</td>
<td>0.0012⁷ᵇ</td>
<td>0.0005ᵈ</td>
<td>0</td>
<td>−0.003⁰ᵇ</td>
</tr>
<tr>
<td>$10^3\delta\beta^{(0)/}\delta T$ (kg mol⁻¹ K⁻¹)</td>
<td>0.7⁷</td>
<td>1.7⁹ᶜ</td>
<td>1.0⁰ᶜ</td>
<td>0.715⁹ᵈ</td>
<td>1.1ᵈ</td>
<td>−12.6ᶜ</td>
<td>0.579⁴ᵈ</td>
</tr>
<tr>
<td>$10^3\delta\beta^{(1)/}\delta T$ (kg mol⁻¹ K⁻¹)</td>
<td>0.13⁴ᶠ</td>
<td>2.0⁵ᶜ</td>
<td>1.1⁰ᶜ</td>
<td>0.70⁰⁵ᶠ</td>
<td>4.3⁶ᵈ</td>
<td>−1.7⁵ᶜ</td>
<td>1.0⁷¹ᶠ</td>
</tr>
<tr>
<td>$10^3\delta C^\gamma/\delta T$ (kg² mol⁻² K⁻¹)</td>
<td>−0.189⁴ᶠ</td>
<td>0</td>
<td>0</td>
<td>−0.10⁵⁴ᵈ</td>
<td>0</td>
<td>0</td>
<td>−0.05⁶ᶠ</td>
</tr>
<tr>
<td>$10^3\delta^2\beta^{(0)/}\delta T^2$ (kg mol⁻¹ K⁻²)</td>
<td>−2.0⁰ᶜ</td>
<td>−4.2²ᶜ</td>
<td>−2.6ᵈ</td>
<td>−1.4⁹⁸ᶠ</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$10^3\delta^2\beta^{(1)/}\delta T^2$ (kg mol⁻¹ K⁻²)</td>
<td>−2.1ᶜ</td>
<td>−16.8ᶜ</td>
<td>−4.3ᶜ</td>
<td>0.2¹⁴³ᶠ</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$10^3\delta^2 C^\gamma/\delta T^2$ (kg² mol⁻² K⁻²)</td>
<td>0.2⁹ᶜ</td>
<td>0</td>
<td>0</td>
<td>0.1⁴⁵⁴⁰ˢ</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

ᵃ [14] $\theta_{\text{ClOH}} = −0.050$ kg mol⁻¹, $\psi_{\text{Na,ClOH}} = −0.006$ kg² mol⁻².
ᵇ [12].
ᶜ [8] $\theta_{\text{HCO₃,Cl}} = 0.0359$ kg mol⁻¹, $\theta_{\text{ClO₂,Cl}} = −0.053$ kg mol⁻¹, $\psi_{\text{Na,NaCl,Cl}} = −0.0143$ kg² mol⁻².
ᵈ [17].
ᵉ [16].
ᶠ [13].
ᵍ [15].

\[ \nu = \nu^+ + \nu^- \] (16)
\[ I = \frac{1}{2} \sum_i m_i Z_i^2 \] (17)

The values of the empirical parameters $b$ and $a$ are 1.2 and 2.0 kg⁻¹/² mol⁻¹/², respectively [5]. $A_0$ was obtained from the work of Pitzer [5]. $\theta$ represents the difference in the interaction of unlike ions with charges of the same sign from an appropriate average for like ions.

Although the values of these parameters could be generated from the experimental activity coefficients of NaCl in the ternary system, and then used to calculate the activity coefficients of NH₄HCO₃, the existing parameter values were used to calculate the activity coefficients of NaCl for the reason mentioned above. These parameter values are summarized in Table 4.

It should be mentioned that for the subsystem of NaCl–NH₄Cl–H₂O another set of parameters was correlated from solubility data in order to calculate activity coefficients of saturated solutions up to 373.15 K [19]. However, for the system considered the temperature and concentration are not high, and these correlated parameters were not used in this work.

Using the existing Pitzer parameters of Table 4 incorporated with the chemical reactions, the mean activity coefficients of NaCl were calculated at 298.15 K and compared with the experimental values obtained in this work in Table 3. In addition, the deviations at 298.15 K between the experimental and calculated values of the activity coefficients of NaCl in the ternary at $y_2 = 0.2$ and 0.4 are depicted in Fig. 2. In all cases, the standard deviations are less than 0.008, indicating that the existing parameter values are adequate to estimate the activity coefficients for the electrolyte components in the ternary system. The calculated mean activity coefficients of NH₄HCO₃ are also presented in Table 2.

It was observed in a previous paper [4] that when the real molality of HCO₃⁻ was less than 0.5, the influence of interfering ions could be neglected. For this reason, the equilibrium compositions of real species were further checked and found to be with the limit mentioned.
Fig. 2. Deviations between $\ln \gamma_{\text{exp}}$ and $\ln \gamma_{\text{cal}}$ of NaCl in the NaCl–NH₄HCO₃–H₂O system as a function of ionic strength at 298.15 K: (+) deviations at 0.2 molality fraction of NH₄HCO₃; (△) deviations at 0.4 molality fraction of NH₄HCO₃.

5. Conclusion

The mean activity coefficients of NaCl in the NaCl–NH₄HCO₃–H₂O system were determined by using a cell composed of Na glass ISE/NaCl ($m_1$), NH₄HCO₃ ($m_2$)/Cl solid-state ISE, at NH₄HCO₃ molality fractions of 0.2 and 0.4, at temperatures from 293.15 to 308.15 K, and up to 1.8 mol kg⁻¹. These experimentally determined values were used successfully to verify the validity of the parameter values available in the literature for calculating activity coefficients by means of Pitzer equation incorporated with chemical reactions. The mean activity coefficients of NH₄HCO₃ in the system were then obtained by means of these parameter values.

**List of symbols**

- $a$: activity in Eq. (3)
- $A_\phi$: Debye–Hückel parameter for osmotic coefficient in Eq. (10)
- $b$: empirical parameter of Pitzer equation in Eq. (10)
- $B$: parameter of Pitzer equation in Eqs. (9) and (11)
- $C$: parameter of Pitzer equation in Eqs. (9) and (12)
- $C^{\phi}$: Pitzer mixing parameter in Eq. (12)
- $E$: potential of the cell
- $E^0$: standard emf of the cell
$f'$ parameter of Pitzer equation in Eq. (9)
$I$ ionic strength on molality scale
$k_{i,j}$ the potentiometric selectivity coefficient of ISE selective toward Na$^+$ to other ions as interfering ions
$K$ equilibrium constant in Eqs. (5)–(8)
$m$ molality of species (mol kg$^{-1}$)
$N$ the number of experiment data points
$S$ slope of the cell
$S_T$ Nernstian slope
$T$ thermodynamic temperature (K)
$y$ molality fraction of NH$_4$HCO$_3$
$y^*$ real molality fraction of NH$_4$HCO$_3$
$Z$ charge number of ionic species

**Greek letters**

$\alpha$ empirical parameter of Pitzer equation in Eq. (11)
$\beta^{(0)}, \beta^{(1)}$ Pitzer interaction parameter of pure species in Eq. (11)
$\phi$ parameter of Pitzer equation in Eq. (9)
$\gamma^{\pm}$ mean ionic activity coefficient on molality scale
$v$ stoichiometric number in Eq. (9)
$\theta$ Pitzer mixing parameters in Eq. (13)
$\psi$ Pitzer mixing parameters in Eq. (9)

**Subscripts**

$a, a'$ anions
$c, c'$ cations
$\text{cal}$ calculation value
$\text{exp}$ experimental value
$M$ cation of an electrolyte
$X$ anion of an electrolyte

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**References**