Activity Coefficients of HCl in the HCl + NH₄Cl + H₂O Systems at 298.15 and 313.15 K

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Using the ion-selective electrode method with a concentrated electrolyte solution added continuously, the mean activity coefficients of HCl in the HCl + NH₄Cl + H₂O system were experimentally measured at 298.15 and 313.15 K and at five molality fractions of NH₄Cl (y₂ = m₉₃/₅₉₃ + m₉₄₃/₅₉₄₃) from 0.1 to 0.9. The measurements were made by an electrochemical cell using a H glass ion-selective electrode and a chloride solid-state ion-selective electrode. It was found that the influence of NH₄⁺ on the H glass ion-selective electrode could be neglected up to 1.3 mol·kg⁻¹, and this pair of ion-selective electrodes was suitable for determining the activity coefficients of HCl in the system. A new set of Pitzer mixing parameters, correlated from the experimental results, was used to calculate the activity coefficients for HCl in the system from 293.15 to 313.15 K up to 3.0 mol·kg⁻¹.

Introduction

Aqueous electrolyte solutions play an important role in many fields, such as chemical engineering, hydrometallurgy, oceanology, geology, and environment. Determination of the mean ionic activity coefficients of electrolytes in aqueous solutions is needed for the understanding of many processes in these fields. Generally, solvent activity methods and electrochemical cell techniques are widely used in measuring the activity coefficients of electrolytes in solution. One of the traditional solvent activity methods is the isopiestic method (Robinson and Stokes, 1970), which requires good skill for the attainment of equilibrium and is time-consuming. Furthermore, it is not well-suited for aqueous solutions containing a volatile component, which may migrate and contaminate the reference solutions. Recently, with the development of ion-selective electrodes (ISEs), the electromotive force (EMF) method tends to be frequently chosen for the determination of activity coefficients of electrolytes in a solution (Butler and Roy, 1991). The activity coefficients of an electrolyte or ion in binary and ternary systems, including mixed-solvent electrolyte solutions and mixed-electrolyte aqueous solutions, have been measured during the past decades (Manohar and Ananthswamy, 1990; Reddy and Ananthswamy, 1990; Haghmetal and Vera, 1991; Sarada and Ananthswamy, 1991; Zhang et al., 1993; Marcos-Arroyo et al., 1996; Khoshkarchi and Vera, 1996; Soto-Campos et al., 1997). The rapid method of ISEs becomes a convenient tool for studying the activity coefficients. However, the possible influence of interfering ions on ISEs must be taken into consideration.

The activity coefficients of HCl in the HCl + NH₄Cl + H₂O system were measured experimentally at (293.15, 298.15, 303.15, and 308.15) K up to 3 mol·kg⁻¹ by Downes (1975), using cells containing standard hydrogen and silver–silver chloride electrodes. Zhao et al. (1992) measured the activity coefficients of HCl in the same system at 298.15 K, using cells containing H glass ISEs and silver–silver chloride electrodes, and discussed the influence of NH₄⁺ on the H glass ISE.

In this work, the Pitzer equation was chosen for data correlation, which is essential for process simulation. In the literature, the Pitzer mixing parameters for the HCl + NH₄Cl + H₂O system have been correlated at 298.15 K up to 2 mol·kg⁻¹ (Pitzer, 1991). However, the applicability of these available parameters to other temperatures and concentrations has not been established.

In this work, EMF measurements were performed for the HCl + NH₄Cl + H₂O system to study the influence of the cation NH₄⁺ on the H glass ISE; to supplement experimental data at other temperatures; and to correlate new Pitzer mixing parameters for calculating the activity coefficients of HCl in this system from 273.15 to 313.15 K up to 3 mol·kg⁻¹.

Apparatus and Chemicals

The method and apparatus used in this work have been described previously (Zhang et al., 1993). A concentrated electrolyte solution at a constant molality fraction of NH₄Cl (y₂ = m₉₃/₅₉₃ + m₉₄₃/₅₉₄₃) was added continuously into the measuring solution in order to change its ionic strength. The potential was measured using an ion meter 5 (Model PXJ-1C, China) with an internal impedance greater than 5 × 10¹³ Ω, having a resolution of about ±0.1 mV. The H glass ISE (Model 231C, China) and chloride solid-state ISE (Model 301, China) were used in the measurements. To improve the stability of the electrodes, pretreatment of ISEs was necessary. Before measuring the potential of ions, the H glass ISE was conditioned in distilled water for 1~2 h, and the chloride solid-state ISE was conditioned in a solution of NaCl for 1 h; the concentration of NaCl was about 0.1 mol·kg⁻¹. The EMF mea-
measurements were reproducible within 0.3 mV, which may cause a maximum relative deviation of activity coefficients less than 0.01.

Ammonium chloride (Guaranteed grade, purity 99.8%, YULing Chemical Plant, Shanghai) was dried in a vacuum desiccator at 0.01 kPa and 333.15 K for 4 h. The maximum error in the solvent concentration was 0.0001. The concentration of hydrochloride (Analytical Grade, Shanghai Chemical Plant, Shanghai) was determined by volume titration of hydrochloride (Analytical Grade, Shanghai Chemical Plant, Shanghai) was dried in a vacuum desiccator at 0.01 kPa and 333.15 K for 4 h. The maximum error in the solvent concentration was 0.0001. The concentration of hydrochloride was also determined by the amount of reagent grade sodium carbonate required for neutralization. When the relative deviation of its concentrations, determined by these two methods, was less than 0.2%, the average value was taken. Deionized water was prepared by redistillation in the presence of KMnO4, and its electrical conductivity was taken. Deionized water was prepared by redistillation in the presence of KMnO4, and its electrical conductivity was found to be less than 1.2 × 10⁻⁶ S·cm⁻¹. To obtain a stock solution of HCl + NH₄Cl + H₂O with a constant \( y_2 \), two binary solutions, HCl + H₂O and NH₄Cl + H₂O, were prepared by weighing.

**Calibration of ISEs**

To calibrate the behavior of electrodes, aqueous hydrochloride solutions were used to test the H glass ISE and the chloride solid-state ISE at 298.15 and 313.15 K. The cell arrangement was

\[
\text{H glass ISE} | \text{HCl (m)}, \text{H}_2\text{O}|\text{Cl solid-state ISE (A)}
\]

For 1:1 electrolyte the EMF (E) values of the cell obtained from these solutions could be represented (Butler and Roy, 1991) by

\[
E = E^0 + S \ln a = E^0 + 2S \ln(m\gamma_\pm)
\]  

(1)

where \( E \) is the potential of the cell, \( E^0 \) is the standard EMF of the cell, \( S \) is the slope of the electrodes' response to the activity of HCl. \( m \) is the molality of HCl.

When ISEs were used for determining the activity coefficients of electrolyte in binary systems, it was often found that using the theoretical value of the reversible Nernstian slope as \( S \) in eq 1 could not be justified (Bates et al., 1983). In the present study, both \( E^0 \) and \( S \) were treated as adjustable parameters. The optimization method of Simplex was used to determine the parameter values of \( E^0 \) and \( S \) when the objective function

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

(2)

reached its minimum. In eq 2, \( N \) is the number of experimental data points. \( E_{i,\text{cal}} \) was calculated by eq 1. The values of \( \gamma_\pm \) were estimated by the Pitzer equation (Pitzer, 1991) with adequate accuracy for the system HCl + H₂O. The ionic interaction parameters of pure HCl were taken from Holmes et al. (1987).

The values of \( S \) and \( E^0 \) of ISEs in the HCl + H₂O system at the two temperatures are listed in Table 1. The standard deviation between \( E_{\text{cal}} \) and \( E_{\text{exp}} \) at each temperature was found to be less than 0.15 mV, which is lower than the allowed random errors (±0.5 mV) suggested by Bates et al. (1983). The relative deviations of the experimental slopes from the Nernstian slope are less than 0.74%.

**Determination of the Activity Coefficients of HCl in the Ternary System**

The cell arrangement for studying the ternary system was

\[
\text{H glass ISE} | \text{HCl (m₁)}, \text{NH₄Cl (m₂)}, \text{H₂O}\text{Cl solid-state ISE (B)}
\]

It is always essential to investigate the selectivity of ISEs in a ternary study. Should any interfering ions exist, the electrochemical potential of an electrode would then be expressed (Butler and Roy, 1991) by

\[
E = E^0 + S \ln(a_1 + k_{12}a_2)
\]

(3)

where \( a_1 \) and \( a_2 \) are the activity of HCl and NH₄Cl, respectively, and \( k_{12} \) is the potentiometric selectivity coefficient of the ISE selective to H⁺ toward NH₄⁺, which acts as an interfering ion. If the interference could be neglected, then eq 1 would be suitable for representing the values of the cell EMF. In doing so, \( m \) is the mean ionic concentration in the ternary system, calculated by

\[
m = \sqrt{m_1(m_1 + m_2)}
\]

(4)

To determine the mean activity coefficients of electrolytes in ternary systems from EMF measurements with ISEs, the standard EMF of the cell (\( E^0 \)) and the electrode slope \( (S) \) must be known or determined in advance. Butler and Huston (1970) used the Nernstian slope in their calculation but determined \( E^0 \) from their experimental data, while Haghtelab and Vera (1991) determined both \( S \) and \( E^0 \) by regression of their experimental data. In this work, the same ISEs were used in cells A and B and the measured slopes deviated from the Nernstian slopes slightly. Hence, it was decided that the values of \( E^0 \) and \( S \) of cell A, regressed from the experimental data for the binary HCl + H₂O system, were also used for cell B.

If the influence of NH₄⁺ on the H glass ISE was small enough to be neglected, eq 1 could be written as

\[
\gamma_\pm = \frac{1}{m} \exp\left(-\frac{E - E^0}{2S}\right)
\]

(5)

Thus the activity coefficients of HCl could be obtained by substituting the cell EMF, \( E \), of the HCl + NH₄Cl + H₂O system in eq 5.

Using the experimentally determined cell potential values at 298.15 and 313.15 K in the system, and assuming that the influence of NH₄⁺ on the H glass ISE could be neglected, the activity coefficients of HCl obtained from eq

| T (K) | \( E^0 \) (mV) | S (mV) | SD (mV) | Nernstian slope, \( |S - S_r|/S_r \) (%) |
|-------|--------------|--------|---------|-----------------------------|
| 298.15 | 420.6        | 25.57  | 0.15    | 25.69                      | 0.47             |
| 313.15 | 423.4        | 26.78  | 0.10    | 26.98                      | 0.74             |
Influence of NH$_4$$^+$ are reported in Table 2. The validity of this assumption

\[
\text{log}(\gamma_{\text{HCl}}) = - \frac{0.5115 \sqrt{T}}{1 + 0.3291 A_1 \sqrt{T}} + A_2 l + A_3 l^{1.5} \tag{6}
\]

where $A_1$, $A_2$, and $A_3$ are the coefficients and $l$ is the ionic strength on the basis of molality. The fitted coefficients and the standard deviation of log $\gamma_{\text{HCl}}$ are reported in Table 3. The interpolated activity coefficients of HCl and those determined by Downes (1975) are listed in Table 4 for comparison. Should the influence be larger than the experimental error, the experimental values of this work ($\gamma_{\text{HCl,exp}}$) would deviate from those of Downes (1975) ($\gamma_{\text{HCl,lit}}$). Furthermore, the absolute deviations between $\gamma_{\text{HCl,exp}}$ and $\gamma_{\text{HCl,lit}}$ would increase with an increase of $y_2$. However, the deviations do not increase with the increase of $y_2$ as shown in Table 4. Meanwhile the deviations between $\gamma_{\text{HCl,exp}}$ and $\gamma_{\text{HCl,lit}}$ are all less than 0.0025 and the standard deviation

<table>
<thead>
<tr>
<th>$y_2 = 0.1$</th>
<th>$y_2 = 0.3$</th>
<th>$y_2 = 0.5$</th>
<th>$y_2 = 0.7$</th>
<th>$y_2 = 0.9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15 K</td>
<td>313.15 K</td>
<td>298.15 K</td>
<td>313.15 K</td>
<td>298.15 K</td>
</tr>
<tr>
<td>$\gamma_{\text{HCl}}$</td>
<td>$\gamma_{\text{HCl}}$</td>
<td>$\gamma_{\text{HCl}}$</td>
<td>$\gamma_{\text{HCl}}$</td>
<td>$\gamma_{\text{HCl}}$</td>
</tr>
<tr>
<td>$\sigma_{\text{HCl}}$</td>
<td>$\sigma_{\text{HCl}}$</td>
<td>$\sigma_{\text{HCl}}$</td>
<td>$\sigma_{\text{HCl}}$</td>
<td>$\sigma_{\text{HCl}}$</td>
</tr>
</tbody>
</table>

where $\gamma_{\text{HCl,exp}}$ and $\gamma_{\text{HCl,lit}}$ is only 0.0015. A comparison of the activity coefficients of HCl determined in this work with those reported by Downes (1975) is depicted in Figure 1, indicating that both sets are in good agreement over the whole concentration range of this work. In other words, the influence of the cation NH$_4$$^+$ on the H glass ISE was small enough to be neglected up to 1.3 mol-kg$^{-1}$. Therefore, it may be concluded that the pair of ISEs used in this work is suitable for determining the activity coefficients of HCl in the ternary system up to 1.3 mol-kg$^{-1}$, and the experimental activity coefficients of HCl obtained by eq 5 are reasonable and accurate.

It should be mentioned that Zhao et al. (1992) reported that the influence of the cation NH$_4$$^+$ on the H glass ISE could not be neglected. It is most likely that this was due to the different ISEs used in their work.

Generally, the concentration of some species may vary with time in a dynamic process. It is essential to know the
Table 4. Comparison of the Experimental Activity Coefficients of HCl (\(\gamma_{\pm,\text{exp}}\)) with Those Reported by Downes (1975) (\(\gamma_{\pm,\text{lit}}\)) at 298.15 K

<table>
<thead>
<tr>
<th>(y_2)</th>
<th>(\gamma_{\pm,\text{exp}})</th>
<th>(\gamma_{\pm,\text{lit}})</th>
<th>(\gamma_{\pm,\text{exp}} - \gamma_{\pm,\text{lit}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.7552</td>
<td>0.7528</td>
<td>0.0024</td>
</tr>
<tr>
<td>0.3</td>
<td>0.7989</td>
<td>0.7976</td>
<td>0.0013</td>
</tr>
<tr>
<td>0.5</td>
<td>0.7408</td>
<td>0.7401</td>
<td>0.0007</td>
</tr>
<tr>
<td>0.7</td>
<td>0.7738</td>
<td>0.7718</td>
<td>0.0020</td>
</tr>
<tr>
<td>0.9</td>
<td>0.7291</td>
<td>0.7285</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

The activity coefficients of HCl in the HCl + NH₄Cl + H₂O System at 298.15 K up to 2.0 mol·kg⁻¹ are presented. The predicted results were then compared with the values reported by Downes (1975) and Zhao et al. (1992) and those determined using the existing Pitzer mixing parameters (case 1 in Table 5). The parameters of pure HCl and NH₄Cl were taken from Pitzer (1991). The predicted results were then compared with the values reported by Downes (1975) and Zhao et al. (1992) and with those obtained in this work. The resulting deviations of \(\ln \gamma_{\pm}\) are presented in Table 6 (case 1). The distribution of \((\ln \gamma_{\pm,\text{exp}} - \ln \gamma_{\pm,\text{cal}})\) obtained from the comparison is depicted in Figure 2. It is obvious from the results shown in Table 6 for case 1 that the existing Pitzer mixing parameters cannot be used to calculate the activity coefficients up to 3.0 mol·kg⁻¹. This further confirms that the existing Pitzer mixing parameters are only suitable for calculating activity coefficients up to 2.0 mol·kg⁻¹ (Pitzer, 1991). It appears that there is a need to obtain a new set of values for the Pitzer mixing parameters to extend its applicability to ionic strengths greater than 2.0 mol·kg⁻¹ for the HCl + NH₄Cl + H₂O system.

In this work the experimental activity coefficients of Downs (1975) and Zhao et al. (1992) and those determined in this work at 298.15 K were used to evaluate the Pitzer mixing parameters by the least-squares method, using the objective function

\[
f(x) = \ln \gamma_{\pm,\text{exp}} - \ln \gamma_{\pm,\text{cal}}
\]

In the correlation, the ionic interaction parameters of pure HCl were taken from Holmes et al. (1987). The ionic interaction parameters of pure NH₄Cl were taken from Thiessen and Simonson (1990). The new parameter values thus obtained are reported in Table 5 (case 2). The values of \((\ln \gamma_{\pm,\text{exp}} - \ln \gamma_{\pm,\text{cal}})\) obtained from using the new set of parameter values are also depicted in Figure 2 (case 2). It is obvious that the deviations are much reduced when the new set of values was used.

Table 5. Pitzer Mixing Parameters for the HCl + NH₄Cl + H₂O System at 298.15 K

<table>
<thead>
<tr>
<th>case</th>
<th>(\theta)</th>
<th>(\psi)</th>
<th>(l_{\text{max}})</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.019</td>
<td>0.0</td>
<td>2.0</td>
<td>Pitzer (1991)</td>
</tr>
<tr>
<td>2</td>
<td>-0.007941</td>
<td>-0.01100</td>
<td>3.0</td>
<td>this work</td>
</tr>
</tbody>
</table>

The Pitzer equation (Pitzer, 1991) has been used to calculate the thermodynamic properties for numerous systems. The Pitzer mixing parameters are available for the HCl + NH₄Cl + H₂O system at 298.15 K up to 2.0 mol·kg⁻¹ (Pitzer, 1991). However, the applicability of these values to other temperatures and concentrations is still unknown. The activity coefficients of HCl in the HCl + NH₄Cl + H₂O system at 298.15 K were predicted in this work using the existing Pitzer mixing parameters (case 1 in Table 5). The parameters of pure HCl and NH₄Cl were taken from Pitzer (1991). The predicted results were then compared with the values reported by Downes (1975) and Zhao et al. (1992) and with those obtained in this work. The resulting deviations of \(\ln \gamma_{\pm}\) are presented in Table 6 (case 1). The distribution of \((\ln \gamma_{\pm,\text{exp}} - \ln \gamma_{\pm,\text{cal}})\) obtained from the comparison is depicted in Figure 2. It is obvious from the results shown in Table 6 for case 1 that the existing Pitzer mixing parameters cannot be used to calculate the activity coefficients up to 3.0 mol·kg⁻¹. This further confirms that the existing Pitzer mixing parameters are only suitable for calculating activity coefficients up to 2.0 mol·kg⁻¹ (Pitzer, 1991). It appears that there is a need to obtain a new set of values for the Pitzer mixing parameters to extend its applicability to ionic strengths greater than 2.0 mol·kg⁻¹ for the HCl + NH₄Cl + H₂O system.

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Table 6. Comparison of Deviations Obtained at Various Temperatures, Using Two Sets of the Pitzer Mixing Parameters (\(\theta\) and \(\psi\)) for the HCl + NH₄Cl + H₂O System

<table>
<thead>
<tr>
<th>case</th>
<th>(l_{\text{max}})</th>
<th>(\sigma^a)</th>
<th>(l_{\text{max}})</th>
<th>(\sigma)</th>
<th>(l_{\text{max}})</th>
<th>(\sigma)</th>
<th>(l_{\text{max}})</th>
<th>(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>0.0015</td>
<td>3</td>
<td>0.0014</td>
<td>3</td>
<td>0.0017</td>
<td>3</td>
<td>0.0016</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0.0015</td>
<td>3</td>
<td>0.0014</td>
<td>3</td>
<td>0.0017</td>
<td>3</td>
<td>0.0016</td>
</tr>
</tbody>
</table>

\[\sigma = \left(\frac{1}{N} \sum_{i=1}^{N} (\ln \gamma_{\pm,\text{exp}} - \ln \gamma_{\pm,\text{cal}})^2\right)^{0.5}\]

\[N = \text{number of experimental data points at each temperature.} \]

1. This further confirms that the existing Pitzer mixing parameters are only suitable for calculating activity coefficients up to 2.0 mol·kg⁻¹ (Pitzer, 1991). It appears that there is a need to obtain a new set of values for the Pitzer mixing parameters to extend its applicability to ionic strengths greater than 2.0 mol·kg⁻¹ for the HCl + NH₄Cl + H₂O system.

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Received for review May 19, 1999. Accepted September 21, 1999. The authors thank the National Natural Science Foundation of P. R. China (No. 29376244), the National Natural Science Foundation of Jiangsu Province of P. R. China (BK97124), the outstanding young teacher Foundation of Education Ministry of P. R. China, the Alexander-von-Humboldt Foundation of Germany for financial support, and the outstanding youth of National Natural Science Foundation.

J E 990139T