SALT EFFECTS ON VAPOR-LIQUID EQUILIBRIA FOR VOLATILE STRONG ELECTROLYTE-WATER SYSTEMS

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Vapor-liquid equilibria for the HCl-H2O, HCl-H2O-MgCl2 and HCl-H2O-CaCl2 systems were measured under atmospheric pressure. A new method is proposed to correlate the salt effect on vapor-liquid equilibrium for the volatile strong electrolyte-water system, and a comparison between experimental and calculated results is made for the HCl-H2O-salt and HNO3-H2O-salt systems. The new method is confirmed to be useful for correlating the salt effect on aqueous electrolyte solutions.

Introduction

There is growing interest in concentration of dilute aqueous solutions of volatile strong electrolytes. Most of these solutions, such as HCl-H2O, HNO3-H2O and HI-H2O systems, have maximum azeotropes so that it is difficult to concentrate the volatile solutes by means of a conventional distillation. When a salt is added into such systems, it may act as a separating agent in distillation. This is due to the fact that the concentration of volatile strong electrolyte in the vapor phase increases with salt content. In view of this practical importance in concentrating the volatile strong electrolyte, it is desired to obtain vapor-liquid equilibrium data and to establish an appropriate solution model which can be applied to the ternary systems composed of volatile strong electrolyte, water and salt. Vapor-liquid equilibrium data for these aqueous systems have already been reported and some correlations have been made for evaluation of the salt effect. However, the data are limited to the narrow concentration regions of volatile strong electrolyte and salt, and the correlations reported previously often give poor results for systems having a large discrepancy from ideality.

In the present study, the vapor-liquid equilibria for the HCl-H2O and HCl-H2O-salt systems were measured under atmospheric pressure. Furthermore, a new attempt is made to correlate the salt effect on the vapor-liquid equilibria for systems having a large discrepancy from ideality. The applicability of this method is examined for six ternary systems containing HCl-H2O-salt and HNO3-H2O-salt.

1. Experiment

1.1 Apparatus and procedure

The Othmer-type equilibrium still shown in Fig. 1 was used to obtain vapor-liquid equilibrium data. The volume of the still was about 500 cm³, of which about 350 cm³ was occupied by liquid phase, and that of the vapor-phase sampling cell was about 10 cm³. The pressure was controlled at 101.3 ± 0.07 kPa through the buffer tank (50,000 cm³) by manual operation and was measured by a mercury manometer. The equilibrium temperature was measured within ±0.1 K by a thermistor thermometer calibrated by a standard thermometer. After circulation for about 4 h, the equilibrium temperature was measured and samples of the liquid and vapor phases were withdrawn from the equilibrium still and the vapor-phase sampling cell to determine the compositions of both phases.

To check the consistency of the experimental apparatus, the vapor-liquid equilibrium for the HNO3-H2O system was measured under atmospheric pressure and was in good agreement with the literature data.5)
1.2 Materials
MgCl₂ and CaCl₂ used in this work were of guaranteed reagent grade from Wako Chemicals Co., of minimum purities 98%, and HCl was guaranteed reagent grade of maximum impurity 0.1% obtained from Kokusan Chemicals, Ltd. All the reagents were used without further purification. Water which was deionized and distilled was used throughout the experimental work.

1.3 Analysis
HCl in both phases was analyzed by acid-base titration with 100 mol/m³ sodium hydroxide solution. MgCl₂ and CaCl₂ were titrated with 10 mol/m³ EDTA solution. To determine the molality of each component, the density of the sample was measured at 293.2 K by use of a density meter of Antone Paar Co., Ltd. The accuracies of analysis were within 0.0002 mole fraction.

2. Vapor-Liquid Equilibrium for the HCl(1)-H₂O (2) System
The vapor-liquid equilibrium data for the HCl–H₂O system under atmospheric pressure are given in Table 1. Experimental data for the HCl–H₂O system are shown in Fig. 2 and compared with the data from the literature. At the maximum azeotropic point, the temperature was 381.7 K and the mole fraction of HCl was 0.111. The azeotropic composition is in good agreement with the values from Othmer, Lutugina and Kokovkina and Bonner et al. On the other hand, the obtained azeotropic temperature agrees well with that of Bonner et al. but deviates from those reported by Othmer and by Lutugina and Kokovkina. To determine the azeotropic temperature more precisely, the boiling points near the azeotropic point were measured by using a twin-type ebulliometer, and the maximum azeotropic temperature 381.9 K was obtained.

The experimental data were correlated by use of a method proposed by Vega and Vera, which is based on the extended Debye-Hückel law modified by Brönsted and Guggenheim. According to this method, the partial pressure of each component for volatile strong electrolyte–water system can be described by the following equations:

\[ \pi_y (x_1/x_1^0) = (x_1/x_1^0) \cdot \Gamma_1 \cdot \bar{p}_1^0 \]  
\[ \pi_y = x_2 \cdot \Gamma_2 \cdot p_2 \]  

where \( x_1 \) is the mole fraction of electrolyte in the liquid phase. In Eqs. (1) and (2), the reference fugacities for the volatile strong electrolyte and water are set equal to the partial pressure \( \bar{p}_1^0 \) at an arbitrary composition \( x_1^0 \) and to the vapor pressure of pure water \( p_2 \), respectively. In this case, the value of \( x_1^0 \) was chosen to be 0.1612 because this was close to the concentration of industrial interest. The activity coefficients, \( \Gamma_1 \) and \( \Gamma_2 \), are calculated from the following equations:

\[ \Delta T (\text{mean})^* = 1.4 \text{ K} \]  
\[ \Delta y_1 (\text{mean})^{**} = 0.0022 \]

\( * \) \( \Delta T (\text{mean}) = \sum |T (\text{cal.}) - T (\text{exp.})| / (\text{No. of data points}) \)

\( ** \) \( \Delta y_1 (\text{mean}) = \sum |y_1 (\text{cal.}) - y_1 (\text{exp.})| / (\text{No. of data points}) \)
\[
\ln \Gamma_1 = k - b_0 \ln x_1 + b_1 x_1^{-1/2} + \theta_1 x_1
\]
\[
+ \theta_2 x_1^{-1/2} + b_2 x_1^{3/2} + b_3 x_1^2
\]  
(3)

\[
\ln \Gamma_2 = b_0 x_1 + b_1 x_1^{-1/2} + b_2 x_1^{3/2} + b_3 x_1^2
\]  
(4)

where \(b_0, b_1, b_2\) and \(b_3\) are adjustable parameters, \(\theta_1 = b_0 - 2b_3, \theta_2 = b_1 - 3b_2\) and \(k\) is given by

\[
k = b_0 \ln x_1^{(y)} - b_1 (x_1^{(y)})^{-1/2} - \theta_1 x_1^{(y)} - \theta_2 (x_1^{(y)})^{1/2}
\]
\[
- b_2 (x_1^{(y)})^{3/2} - b_3 (x_1^{(y)})^2
\]  
(5)

The parameters were determined by fitting the experimental data, using the simplex search method coupled with use of Eq. (6) as an objective function.

\[
\text{O.F.} = \sum_{i=1}^{N} \left[ \left( \frac{\Gamma_{\text{exp}} - \Gamma_{\text{calc}}}{\Gamma_{\text{exp}}} \right)^2 \right] \rightarrow \text{minimum}
\]  
(6)

The calculated vapor compositions and boiling points are presented in Table 1, along with the parameters \(b_0, b_1, b_2\) and \(b_3\) in Eqs. (3), (4) and (5).

### 3. Vapor-Liquid Equilibria for Volatile Strong Electrolyte (1)–Water (2)–Salt (3) Systems

#### 3.1 Experimental results

To investigate the salt effect on a volatile strong electrolyte–water system, vapor-liquid equilibria were measured for the two ternary systems HCl–H₂O–MgCl₂ and HCl–H₂O–CaCl₂ under atmospheric pressure. The data for these systems are given in Tables 2 and 3, where \(x_1^{(y)}\) means the mole fraction of the volatile strong electrolyte in the liquid phase on salt-free basis:

\[
x_1^{(y)} = \frac{n_1}{n_1 + n_2}
\]  
(7)

#### 3.2 Correlation for the ternary system

1) Proposed method For a volatile strong electrolyte–water–salt system, the vapor-liquid equilibrium model is shown schematically in Fig. 3. In the liquid phase, it is assumed that the salt (MBₙ) dissociates perfectly; on the other hand, the volatile strong electrolyte (AB) almost completely dissociates but a very small quantity of AB exists in molecular form. The dissociation of AB in the vapor phase is appreciable only at very high temperature and is, therefore, neglected under this experimental condition. The molecules AB and H₂O in the liquid phase are in equilibrium with each component in the vapor phase. MBₙ exists only in the liquid phase because of its non-volatility.

For the system of interest, there are few data for the dissociation equilibrium constants of the volatile strong electrolytes and, therefore, the correlation method similar to that by applying Henry's law for a molecular solute of volatile weak electrolyte cannot be used. Thus an alternative method without the data for dissociation was developed. By considering the change of activity, \(\xi\), of the molecule AB caused by adding the salt, the vapor-phase composition at given liquid-phase composition was calculated.

Furthermore, the boiling point for a given composition in the liquid phase was calculated by estimating the water activity of the aqueous solution containing electrolytes AB and MBₙ.

2) Calculation of vapor-phase composition by using \(\xi\). In Fig. 4 the solid and dashed lines represent \(M–y\) curves for the AB–H₂O–MBₙ and AB–H₂O systems, where \(M_1\) is the molality of AB in the liquid phase when dissociation of AB is not considered; and \(y_1\) is the mole fraction of AB in the vapor phase. When \(M_1\) at point P is equal to that at point Q, \(\xi\) is defined as the ratio of the liquid-phase activity of the molecule AB at P to that at Q. Since the vapor-phase composition at P is equal to that at R, the activity of the molecule AB at P is assumed to be equal to the activity of the molecule AB at R. By using this assumption, \(\xi\) becomes the ratio of the liquid-phase activity of the molecule AB at P to that at Q on the \(M–y\) curve of the binary system.

The dissociation equilibrium constant of AB at \(T[K]\), \(K(T)\), which is required for the calculation of \(\xi\), is given as follows:

\[
K(T) = \frac{m_{1+} m_{1-} γ_{1+} γ_{1-}}{m_1}
\]  
(8)

where \(γ_{1±}\) is the mean ionic activity coefficient of AB, and \(m_{1+}, m_{1-}, m_1\) represent the molality of cation \(A^+\), anion \(B^-\) and molecule AB in solution. In Eq. (8), the activity coefficient of the molecular form of AB is assumed to be unity because of the very low concentration of the molecule. Assuming that \(m_{1+} = m_{1-} = M_1\) for the AB–H₂O binary system because of the almost perfect dissociation of AB, \(\xi\) is approximated as follows:

\[
\xi = \frac{m_{1+}(R)}{m_{1+}(Q)} \left( \frac{M_{1+}(R)}{M_{1+}(Q)} \right)^2 \left( \frac{γ_{1+}(R)}{γ_{1+}(Q)} \right)^2
\]  
(9)

where subscripts Q, R denote the points Q, R in Fig. 4 and superscript 0 indicates salt-free binary system. From the analogy with volatile weak electrolyte, it is inferred that the dissociation equilibrium constants of volatile strong electrolytes hardly change in a narrow temperature range. Therefore, the first term in Eq. (9), \((1/K(T_R))/1/K(T_Q))\), can be assumed to be unity. Then, Eq. (9) can be reduced to

\[
\xi = \left( \frac{M_{1+}(R)}{M_{1+}(Q)} \right)^2 \left( \frac{γ_{1+}(R)}{γ_{1+}(Q)} \right)^2
\]  
(10)

By taking account of the behavior of the salt in the ternary system, the second expression for \(\xi\) is in-
Table 2. Vapor-liquid equilibrium for HCl (1)-H2O (2)-MgCl2 (3) system under atmospheric pressure

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$x_3$</th>
<th>$T$ (exp.)</th>
<th>$T$ (cal.)*</th>
<th>$y_1$ (exp.)</th>
<th>$y_1$ (cal.)*</th>
<th>$y_1$ (cal.)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0429</td>
<td>0.0211</td>
<td>379.5</td>
<td>379.4</td>
<td>0.0132</td>
<td>0.0132</td>
<td>0.0126</td>
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<tr>
<td>0.0639</td>
<td>0.0213</td>
<td>381.6</td>
<td>381.5</td>
<td>0.0459</td>
<td>0.0459</td>
<td>0.0461</td>
</tr>
<tr>
<td>0.0819</td>
<td>0.0213</td>
<td>382.4</td>
<td>382.4</td>
<td>0.1167</td>
<td>0.1161</td>
<td>0.0997</td>
</tr>
<tr>
<td>0.0902</td>
<td>0.0212</td>
<td>382.0</td>
<td>382.1</td>
<td>0.1715</td>
<td>0.1691</td>
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<tr>
<td>0.0210</td>
<td>0.0419</td>
<td>381.1</td>
<td>381.2</td>
<td>0.0143</td>
<td>0.0144</td>
<td>0.0183</td>
</tr>
<tr>
<td>0.0312</td>
<td>0.0411</td>
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<td>382.2</td>
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<td>0.0298</td>
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</tr>
<tr>
<td>0.0407</td>
<td>0.0424</td>
<td>383.3</td>
<td>383.2</td>
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</tr>
<tr>
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<td>383.1</td>
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<td>0.1774</td>
</tr>
<tr>
<td>0.0657</td>
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<td>382.2</td>
<td>0.2157</td>
<td>0.2217</td>
<td>0.2219</td>
</tr>
<tr>
<td>0.0051</td>
<td>0.0593</td>
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<td>383.8</td>
<td>0.0074</td>
<td>0.0076</td>
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</tr>
<tr>
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<td>0.0584</td>
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<td>384.1</td>
<td>0.0172</td>
<td>0.0167</td>
<td>0.0134</td>
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<tr>
<td>0.0192</td>
<td>0.0593</td>
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<td>385.2</td>
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<td>0.0489</td>
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<tr>
<td>0.0284</td>
<td>0.0588</td>
<td>385.3</td>
<td>385.3</td>
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<td>0.0965</td>
<td>0.1101</td>
</tr>
<tr>
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<td>385.1</td>
<td>385.0</td>
<td>0.1227</td>
<td>0.1235</td>
<td>0.1392</td>
</tr>
</tbody>
</table>

$\Delta T$ (mean)* = 0.096 K

$\Delta y_1$ (mean)* = 0.0011

$\Delta y_1$ (mean)** = 0.0118

* Calculated by the present method.

** Calculated by the Hala method.

Table 3. Vapor-liquid equilibrium for HCl (1)-H2O (2)-CaCl2 (3) system under atmospheric pressure

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$x_3$</th>
<th>$T$ (exp.)</th>
<th>$T$ (cal.)*</th>
<th>$y_1$ (exp.)</th>
<th>$y_1$ (cal.)*</th>
<th>$y_1$ (cal.)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0320</td>
<td>0.0206</td>
<td>377.9</td>
<td>378.0</td>
<td>0.0072</td>
<td>0.0069</td>
<td>0.0071</td>
</tr>
<tr>
<td>0.0432</td>
<td>0.0210</td>
<td>379.2</td>
<td>379.2</td>
<td>0.0137</td>
<td>0.0143</td>
<td>0.0154</td>
</tr>
<tr>
<td>0.0729</td>
<td>0.0206</td>
<td>382.0</td>
<td>382.1</td>
<td>0.0625</td>
<td>0.0654</td>
<td>0.0625</td>
</tr>
<tr>
<td>0.0818</td>
<td>0.0205</td>
<td>382.3</td>
<td>382.5</td>
<td>0.0968</td>
<td>0.0982</td>
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</tr>
<tr>
<td>0.0980</td>
<td>0.0206</td>
<td>381.5</td>
<td>382.1</td>
<td>0.2030</td>
<td>0.1988</td>
<td>0.1522</td>
</tr>
<tr>
<td>0.0160</td>
<td>0.0416</td>
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<td>380.3</td>
<td>0.0080</td>
<td>0.0076</td>
<td>0.0065</td>
</tr>
<tr>
<td>0.0304</td>
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<td>382.0</td>
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<td>0.0290</td>
</tr>
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<td>0.0490</td>
<td>0.0411</td>
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<td>383.5</td>
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<td>0.0397</td>
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<tr>
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<td>385.2</td>
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<td>0.0169</td>
<td>0.0674</td>
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<td>385.6</td>
<td>0.0525</td>
<td>0.0532</td>
<td>0.0562</td>
</tr>
</tbody>
</table>

$\Delta T$ (mean)* = 0.22 K

$\Delta y_1$ (mean)* = 0.0035

$\Delta y_1$ (mean)** = 0.0131

* Calculated by the present method.

** Calculated by the Hala method.

Fig. 3. Vapor-liquid equilibrium model for AB-H2O-MB$_n$ system.

introduced. When MB$_n$ is added into the liquid phase and Eq. (8) is considered, $\xi$ is given as follows:

$$\xi = \frac{m_1(q)}{m_1(0)} = \frac{1}{K(T)} m_1^{s} \cdot \frac{m_1^{s} \cdot \left( \frac{1}{1 (T)} \frac{1}{1 (T)} \right)^2}{m_1^{0} \cdot 0.001 + (T^{10})}$$

where superscript $s$ denotes the AB-H2O-MB$_n$ system. In Eq. (11), the decrease in number of ions A$^+$ and B$^-$ owing to formation of molecule AB by salt addition is assumed to be negligible in the solution.
The first term, \((1/K(T^*)/1/K(T^0))\), represents the small change of \(K\) on account of boiling point elevation by salt addition and can be assumed to be unity. Then, Eq. (11) is reduced to the following expression:

\[ \xi = \frac{m_1^a}{m_1^m} \cdot \left( \frac{\gamma_{\pm 1}(p)}{\gamma_{\pm 1}(0)} \right)^2 \]  

(12)

Combining Eq. (10) with Eq. (12) and rewriting for \(M_{1(r)}\) gives

\[ M_{1(r)} = M_{1(Q)} \cdot \left( \frac{m_1^a}{m_1^m} \right)^{1/2} \cdot \frac{\gamma_{\pm 1}(p)}{\gamma_{\pm 1}(0)} \]  

(13)

When \(M_{1(r)}\) is calculated by Eq. (13), \(y_{1(r)}\) for the ternary system can be determined by using \(M-y\) data for the AB-H\(_2\)O binary system as shown in Fig. 4.

In calculation of \(M_{1(r)}\) from Eq. (13), the second term, \(m_1^a/m_1^m\), is approximated by

\[ \left( \frac{m_1^a}{m_1^m} \right)^{1/2} = \left( \frac{M_1 + nM_3}{M_1} \right)^{1/2} \]  

(14)

where \(n\) and \(M_3\) represent the valency of the cation \(M^{n+}\) and molality of \(MB_n\), respectively.

The value of \(\gamma_{\pm 1}(r)\) in the third term can be calculated as follows\(^2\):

\[ \gamma_{\pm 1}^0 = \gamma_{\pm 1}^0(p) \cdot \left( \frac{M_1}{\bar{p}_1} \right)^{1/2} \]  

(15)

where \(\gamma_{\pm 1}^0(p)\) is the mean ionic activity coefficient of electrolyte AB at the system temperature in an arbitrary reference molality \(M_1^0\); \(\bar{p}_1\) is the partial pressure of AB at the temperature of the system in molality \(M_1\); and \(\bar{p}_1^0\) is that in molality \(M_1^0\). In Eq. (15), the value of \(\bar{p}_1\) in a given molality of AB and temperature is calculated by the following equation of Antoine type:

\[ \log \bar{p}_1(kPa) = A(M_1) + \frac{B(M_1)}{T + C} \]  

(16)

where the parameters \(A(M_1)\) and \(B(M_1)\) are a function of the molality of AB (see Appendix 1).

The value of \(\gamma_{\pm 1}(r)\) can be computed by using Harned’s rule\(^1\) which has often been used to describe the mean ionic activity coefficient in concentrated mixed electrolyte solution. Using the rule, the expression for \(\gamma_{\pm 1}^0\) is written as follows:

\[ \log \gamma_{\pm 1}^0 = \frac{1}{T} \sum I_k \ln \left( \frac{\bar{p}_1^0(k)}{\bar{p}_1^0} \right) \]  

(20)

where \(\bar{p}_1^0(k)\) is the partial pressure of water in the solution containing only the electrolyte \(k\) at the same ionic strength and temperature as in the ternary mixture; \(I_k\) shows the total ionic strength in the ternary mixture; and \(I_k\) is the ionic strength of the electrolyte \(k\) in the ternary mixture. In this equation, \(\bar{p}_1^0(k)\) is determined by using the method shown in Appendix 1. Finally, the boiling point temperature can be calculated from Eq. (18) coupled with Eqs. (19) and (20).

3.3 Correlated results

The vapor-phase compositions for the AB-H\(_2\)O–MB\(_n\) system were calculated by using Eqs. (13)–(17) and \(M-y\) data for the AB-H\(_2\)O system.

In Eq. (15), the arbitrary molality of the reference state, \(M_1^0\), was chosen as 4 mol/kg of the volatile strong electrolyte for both the HCl–H\(_2\)O–salt and HNO\(_3–H_2\)O–salt systems (HCl–H\(_2\)O–salt system is abbreviated below as HCl system and HNO\(_3–H_2\)O–salt as HNO\(_3\) system). Then \(\gamma_{\pm 1}^0\) and \(\bar{p}_1^0\) were 1.138, 1.138 Pa for the isobaric HCl system under atmospheric pressure; 1.772, 2.666 Pa for the isothermal HCl system at 298.2 K; 1.080, 772.3 Pa for the isobaric HNO\(_3\) system under atmospheric pressure; and 1.100, 1.333 Pa for the isothermal HNO\(_3\) system at 298.2 K, respectively (see Appendix 2). The parameters \(A(M_1)\) and \(B(M_1)\) in Eq. (16) are given in...
Table 4. Parameters in Eq. (21)

<table>
<thead>
<tr>
<th>System</th>
<th>( c_0 )</th>
<th>( c_1 )</th>
<th>( c_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl-H_2O-MgCl_2</td>
<td>( 4.78283 \times 10^{-2} )</td>
<td>( -4.99503 \times 10^{-3} )</td>
<td>( 1.58483 \times 10^{-4} )</td>
</tr>
<tr>
<td>HCl-H_2O-CaCl_2</td>
<td>( -1.10973 \times 10^{-2} )</td>
<td>( 7.29943 \times 10^{-3} )</td>
<td>( -4.02762 \times 10^{-4} )</td>
</tr>
<tr>
<td>HCl-H_2O-KCl</td>
<td>0.25462</td>
<td>( -4.68074 \times 10^{-2} )</td>
<td>2.99308 \times 10^{-3}</td>
</tr>
<tr>
<td>HNO_3-H_2O-Mg(NO_3)_2</td>
<td>( -2.62271 \times 10^{-2} )</td>
<td>( 8.73303 \times 10^{-4} )</td>
<td>( -5.24208 \times 10^{-5} )</td>
</tr>
<tr>
<td>HNO_3-H_2O-Ca(NO_3)_2*</td>
<td>( -3.49672 \times 10^{-2} )</td>
<td>( -4.26234 \times 10^{-3} )</td>
<td>( 7.41779 \times 10^{-5} )</td>
</tr>
<tr>
<td>HNO_3-H_2O-KNO_3</td>
<td>0.33163</td>
<td>( -2.82413 \times 10^{-2} )</td>
<td>6.54995 \times 10^{-4}</td>
</tr>
</tbody>
</table>

* In this system, the values of \( a_1 \) were fitted by use of the following equation because of high ionic strength:

\[
a_1 = c_0 + c_1 I_t + c_2 I_t^2 + c_3 I_t + c_4 I_t^3
\]

where \( c_3 \) and \( c_4 \) are \( -1.09426 \times 10^{-3} \) and \( 6.66934 \times 10^{-5} \), respectively.

Table 5. Correlated results by use of the present and Hála methods

<table>
<thead>
<tr>
<th>System</th>
<th>Experimental condition</th>
<th>Ionic strength range [mol/kg]</th>
<th>( y_1 \times 100 )</th>
<th>Error ( T[K] )</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl-H_2O-MgCl_2</td>
<td>101.3 kPa</td>
<td>6.24-12.50</td>
<td>0.11</td>
<td>0.10</td>
<td>This work</td>
</tr>
<tr>
<td>HCl-H_2O-CaCl_2</td>
<td>101.3 kPa</td>
<td>5.45-13.20</td>
<td>0.35</td>
<td>0.22</td>
<td>This work</td>
</tr>
<tr>
<td>HCl-H_2O-KCl</td>
<td>298.2 K</td>
<td>5.76-12.46</td>
<td>0.15</td>
<td>1.75</td>
<td>(19)</td>
</tr>
<tr>
<td>HNO_3-H_2O-Mg(NO_3)_2</td>
<td>101.3 kPa</td>
<td>10.30-25.30</td>
<td>0.92</td>
<td>1.92</td>
<td>(17)</td>
</tr>
<tr>
<td>HNO_3-H_2O-Ca(NO_3)_2</td>
<td>101.3 kPa</td>
<td>13.56-32.36</td>
<td>0.87</td>
<td>2.28</td>
<td>(17)</td>
</tr>
<tr>
<td>HNO_3-H_2O-KNO_3</td>
<td>298.2 K</td>
<td>17.09-26.25</td>
<td>0.28</td>
<td>0.24</td>
<td>(6)</td>
</tr>
</tbody>
</table>

In Eq. (17), \( a_1 \) is available in the literature for several ternary electrolyte solutions. However, most values of \( a_1 \) are reported only to about 5 mol/kg in total ionic strength and so there are no data for this parameter under this experimental condition. For this reason, \( a_1 \) was determined from a few ternary \( M-y \) data for every system. The value of \( a_1 \) was determined by the following method: (1) obtain \( M_1(R) \) by using both binary and ternary \( M-y \) data as shown in Fig. 4, and (2) calculate \( a_1 \) from Eqs. (13)-(17). Furthermore, to compute \( a_1 \) in a wide range of total ionic strength, these values were fitted to the following empirical equation by the least-squares method:

\[
a_1 = c_0 + c_1 I_t + c_2 I_t^2
\]

where \( c_0 \), \( c_1 \), \( c_2 \) are parameters and \( I_t \) is total ionic strength. The parameters are given in Table 4.

Conclusion

Experimental data were obtained for the vapor-liquid equilibria for the HCl-H_2O and HCl-H_2O-salt systems under atmospheric pressure. Furthermore, a new method was proposed to correlate the salt effect on vapor-liquid equilibrium for the volatile strong electrolyte-water system and the applicability of the proposed method was examined by comparison with the Hála method for six ternary systems HCl-H_2O-salt and HNO_3-H_2O-salt. The Hála method gives good correlated results for aqueous systems containing monovalent cation of the salt, but it gives poor results for systems containing divalent cation. The proposed method was confirmed to be useful in agreement with the experimental results. The correlated results by the present method were compared with those by the Hála method, which has frequently been used to correlate the vapor-phase composition for the multicomponent system containing electrolytes but cannot be used to calculate the boiling point. For the systems in the presence of a salt having monovalent cation, both the present and the Hála methods yield approximately the same deviation between observed and correlated vapor-phase compositions. However, for the systems in the presence of a salt having divalent cation, the results calculated by the present method show better agreement with the experiments than those by the Hála method.
Table A-1. Parameters in Eq. (A-2)

<table>
<thead>
<tr>
<th>System</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O–MgCl$_2$</td>
<td>7.09562</td>
<td>$-5.42893 \times 10^{-2}$</td>
<td>$2.50527 \times 10^{-2}$</td>
<td>$-4.02686 \times 10^{-3}$</td>
</tr>
<tr>
<td>H$_2$O–CaCl$_2$</td>
<td>7.09453</td>
<td>$-2.84935 \times 10^{-2}$</td>
<td>$-2.76703 \times 10^{-3}$</td>
<td>$1.48604 \times 10^{-3}$</td>
</tr>
<tr>
<td>H$_2$O–Mg(NO$_3$)$_2$</td>
<td>7.09654</td>
<td>$-4.26886 \times 10^{-2}$</td>
<td>$1.52113 \times 10^{-2}$</td>
<td>$-3.04790 \times 10^{-3}$</td>
</tr>
<tr>
<td>H$_2$O–Ca(NO$_3$)$_2$</td>
<td>7.09767</td>
<td>$-3.64237 \times 10^{-3}$</td>
<td>$-7.75681 \times 10^{-3}$</td>
<td>$6.73888 \times 10^{-4}$</td>
</tr>
<tr>
<td>H$_2$O–HCl</td>
<td>7.53695</td>
<td>$-1.03550 \times 10^{-1}$</td>
<td>$8.17180 \times 10^{-3}$</td>
<td>$-2.02166 \times 10^{-4}$</td>
</tr>
<tr>
<td>H$_2$O–HNO$_3$</td>
<td>6.67929</td>
<td>$-7.49844 \times 10^{-2}$</td>
<td>$3.03998 \times 10^{-2}$</td>
<td>$-1.13366 \times 10^{-3}$</td>
</tr>
<tr>
<td>HCl–H$_2$O</td>
<td>9.55704</td>
<td>$1.26769 \times 10^{-1}$</td>
<td>$-4.02686 \times 10^{-3}$</td>
<td>$1.48604 \times 10^{-3}$</td>
</tr>
<tr>
<td>HNO$_3$–H$_2$O</td>
<td>7.49844</td>
<td>$-1.28598 \times 10^{-2}$</td>
<td>$7.56629 \times 10^{-2}$</td>
<td>$-3.17776 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

The parameters are those for the partial pressure of the first component of the system.

Table A-2. Parameters in Eq. (A-3)

<table>
<thead>
<tr>
<th>System</th>
<th>$B_0$</th>
<th>$B_1$</th>
<th>$B_2$</th>
<th>$B_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O–MgCl$_2$</td>
<td>$-1670.05$</td>
<td>$10.5198$</td>
<td>$-9.38085$</td>
<td>$1.07931$</td>
</tr>
<tr>
<td>H$_2$O–CaCl$_2$</td>
<td>$-1669.84$</td>
<td>$3.76316$</td>
<td>$-1.45301$</td>
<td>$-4.17236 \times 10^{-1}$</td>
</tr>
<tr>
<td>H$_2$O–Mg(NO$_3$)$_2$</td>
<td>$-1670.38$</td>
<td>$6.63978$</td>
<td>$-6.43427$</td>
<td>$9.40113 \times 10^{-1}$</td>
</tr>
<tr>
<td>H$_2$O–Ca(NO$_3$)$_2$</td>
<td>$-1670.53$</td>
<td>$-5.76007$</td>
<td>$2.36871$</td>
<td>$-2.71730 \times 10^{-1}$</td>
</tr>
<tr>
<td>H$_2$O–HCl</td>
<td>$-1820.87$</td>
<td>$30.5400$</td>
<td>$-33.4818$</td>
<td>$9.49961 \times 10^{-2}$</td>
</tr>
<tr>
<td>H$_2$O–HNO$_3$</td>
<td>$-1529.15$</td>
<td>$-33.4818$</td>
<td>$1.19920$</td>
<td>$-1.34501 \times 10^{-2}$</td>
</tr>
<tr>
<td>HCl–H$_2$O</td>
<td>$-286.710$</td>
<td>$-18.7777$</td>
<td>$-2.64012$</td>
<td>$6.32745 \times 10^{-2}$</td>
</tr>
<tr>
<td>HNO$_3$–H$_2$O</td>
<td>$-3779.23$</td>
<td>$286.710$</td>
<td>$7.56629 \times 10^{-2}$</td>
<td>$3.17776 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

The parameters are those for the partial pressure of the first component of the system.

Appendix 1

The partial pressures of volatile strong electrolyte and water over the aqueous electrolyte solution were correlated to the molality of electrolyte, $M$, by an equation of Antoine type:

$$\log p_i(kPa) = A(M) + \frac{B(M)}{T+C}$$

where $C$ is $-45.107$ for the system containing MgCl$_2$, CaCl$_2$, Mg(NO$_3$)$_2$ or Ca(NO$_3$)$_2$; and is $-43.2$ for the system containing HCl or HNO$_3$. The parameters in Eqs. (A-2) and (A-3) are given in Tables A-1 and A-2, respectively.

Appendix 2

The reason why $M^{1/2}$ was chosen as 4 mol/kg is that the literature data for dependence on the temperature of $y_i^{1/2}$ are available to 4 mol/kg for HCl and this concentration is close to the concentration under the experimental condition. For an isobaric system $y_i^{1/2}$ and $\beta_i^{1/2}$ change with boiling point, but the changes of $y_i^{1/2}$ and $(\beta_i/\beta_i^{1/2})^{1/2}$ were small in the range of temperature of these experiments and so, to simplify, $y_i^{1/2}$ and $\beta_i^{1/2}$ were assumed to be equal to those at 383.2 K for the HCl system and at 393.2 K for the HNO$_3$ system. The value of $y_i^{1/2}$ for HCl at 383.2 K was determined by the method suggested by Vega and Vera; on the other hand, $y_i^{1/2}$ for HNO$_3$ is not available at various temperatures and so was assumed to be equal to $y_i^{1/2}$ for HCl at 393.2 K. (When Eq. (21) is used for calculation of $a_i$, the difference in $y_i^{1/2}$ doesn't affect the correlated results of the vapor-phase composition and boiling point.)

Acknowledgment

The authors wish to thank Professor I. Yamada of Nagoya Institute of Technology for his helpful advice regarding the present study.

Nomenclature

$A, B, C$ = constants of Antoine equation
$a_i$ = activity of component $i$
$b_0, b_1, b_2, b_3$ = parameters in Eqs. (3), (4) and (5)
$c_0, c_1, c_2$ = parameters in Eq. (21)
$I$ = ionic strength in unit of molality
$K$ = dissociation equilibrium constant
$M_i$ = molality of component $i$ when dissociation is not considered
$m_i$ = molality of component $i$
$N$ = number of data points
$n$ = valency of cation of salt
$n_i$ = number of moles of component $i$
$\rho_i$ = partial pressure of component $i$
$\rho_2$ = vapor pressure of pure water
$T$ = temperature
$x_i$ = mole fraction of component $i$ in liquid phase
$x_i'$ = mole fraction of component $i$ in liquid phase on salt-free basis
$\gamma_i$ = mole fraction of component $i$ in vapor phase
$\alpha_i$ = ternary parameter of component $i$ in Harned's rule
$\Gamma_i$ = activity coefficient of component $i$
$\gamma_i^{1/2}$ = mean ionic activity coefficient of electrolytic component $i$
$\xi$ = ratio of activity of undissociated strong electrolyte for volatile strong electrolyte–water–salt system to that for volatile strong electrolyte–water system
$\pi$ = total pressure
\( P, Q, R \) = position in Fig. 4

1 = volatile strong electrolyte

2 = water

3 = salt

+ = cation

- = anion

\( 0 \) = volatile strong electrolyte-water system

\( r \) = reference state

\( s \) = volatile strong electrolyte-water-salt system

**Literature Cited**


*(A part of this paper was presented at the 14th Autumn Meeting of The Society of Chemical Engineers, Japan, at Yokohama, October, 1980.)*