Prediction of Dissociation Constants of Ammonium Ion in 20 Mass %
Ethanol + Water Mixed Solvent Solutions Containing Sodium Chloride

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Activity Coefficient, Pitzer’s Equations, Dissociation Constants of Ammonium Ion,
Transpiration Method, Equivalent Concentration

Dissociation constants of ammonium ion ($K_a = [H^+][NH_3]/[NH_4^+]$, where [ ] denotes the concentration) in 20 mass % ethanol + water mixtures with different concentrations of sodium chloride were determined by means of a glass electrode. The dissociation constants in p$K_a$ units (on molarity and molality bases) increase linearly with increasing ionic strength. Activity coefficients of ammonia in the ethanol + water mixtures were determined by a transpiration method. The observed dissociation constants on the molality scale were compared with those calculated from the Pitzer equations modified on the basis of the principles of corresponding states. The observed values agreed with the calculated ones almost within experimental uncertainties.

1. Introduction

In previous works [1–9] we have applied Pitzer’s ionic interaction theory [10] to the prediction of dissociation constants of ammonium ion in various 1:1 strong electrolyte aqueous solutions and compared the theoretically calculated values with the observed ones. It was found that the values calculated with the higher-order terms agreed with the observed ones within experimental uncertainties.

Recently, Ye et al. [11] have introduced modifications into the Pitzer model, which was initially designed for aqueous solutions of electrolytes, so that the model should be adapted to solutions with mixed solvents without readjusting its interaction parameters. The modification based on the principles of corresponding states was applied successfully to the calculation of the mean activity coefficients of NaBr in the mixed solvents methanol + water and ethanol + water. Since the values for the interaction parameters in Pitzer’s equations in a solvent mixture in question, which vary according to the kind and composition of the solvent [12], are not always available, the modified model will be of much use, if it is proved that the model enables equilibrium constants in mixed solvent solutions to be predicted by use of the available interaction-parameter values in aqueous solutions.

In the present work, we have applied the modified Pitzer model to the estimation of the dissociation constants of NH$_4^+$ in 20 mass % ethanol + water mixtures containing NaCl at different concentrations.

2. Experimental

Reagents. Ethanol of reagent grade, to which Linde type 4A molecular sieves had been added, was distilled twice. Reagent-grade ammonium chloride was recrystallized twice from distilled water, and the crystals thus prepared were dissolved in 20 mass % ethanol + water. The content of NH$_4$Cl in the stock solution was determined gravimetrically as AgCl. Sodium chloride of primary analytical standard quality was dried at 360 °C in an electric furnace. A sodium hydroxide solution was prepared from freshly filtered 50% NaOH and redistilled water freed from CO$_2$ by boiling.

Procedure for measurement of dissociation constant of NH$_4^+$

The dissociation constants of NH$_4^+$ ion in 20 mass % ethanol + water containing NaCl at different concentrations were measured by glass-
electrode potentiometry. The emfs were measured for the cell of the type

$$GE \mid \text{test solution} \mid \text{ref}$$

where GE denotes a glass electrode and ref the reference half-cell, e.g., in the system of 20 mass % methanol + water mixture containing \(x\) mol \(\cdot\) dm\(^{-3}\) NaCl

$$:\equiv x \text{ mol} \cdot \text{dm}^{-3} \text{NaCl in 20 mass \% EtOH+H}_2\text{O}$$

$$:x \text{ mol} \cdot \text{dm}^{-3} \text{NaCl},$$

satd. AgCl \mid AgCl–Ag. From the emf's (mV) the equilibrium hydrogen-ion concentrations were calculated according to the equation

$$E = E_0 + (59.16/\text{mV}) \log[H^+] + E_j$$

(1)

in which \(E_0\) is a constant, which was determined in situ in solutions of known hydrogen-ion concentrations. \(E_j\) is a liquid junction potential arising between the test solution and the salt bridge. \(E_j\) values, which were mainly caused by H\(^+\) and OH\(^-\) ions, were negligibly small over the \(\log[H^+]\) range from 3 to 10 in all the solutions examined. In the \(x\) mol \(\cdot\) dm\(^{-3}\) NaCl system as an example a solution with the composition of \(x\), \(y\), \(z\) mol \(\cdot\) dm\(^{-3}\) NH\(_3\)Cl, \(z\) mol \(\cdot\) dm\(^{-3}\) HCl, and \((x-y-z)\) mol \(\cdot\) dm\(^{-3}\) NaCl was titrated with an NaOH solution containing \(x\) mol \(\cdot\) dm\(^{-3}\) NaCl, while the emf's were measured.

A glass electrode of DKK (Tokyo) No. 5100 was used in combination with a silver-silver chloride reference electrode. The emf's were measured (up to 0.1 mV) with a pH meter (DKK, Ion-Meter model COM-30). The titration cell was of the type designed by Tsukuda et al. [14]. This was kept in a water thermostat maintained at \((25.00 \pm 0.01)\) °C in a room thermostated at \((25 \pm 1)\) °C. To avoid losses of ammonia the titration cell was tightly closed. Stirring of the test solutions was carried out with a magnetic rod.

**Procedure for measurement of activity coefficient of NH\(_3\)**

The activity coefficients of NH\(_3\) were measured by a transpiration method. The measurements were carried out with the same apparatus and procedures as those described in detail in the previous papers [5,9] except that vessels B and C shown in Fig. 1 in the previous papers contained a 20 mass % EtOH + \(H_2O\) mixed solution with the composition of, say, \(x\) mol \(\cdot\) dm\(^{-3}\) NaCl and 0.2 mol \(\cdot\) dm\(^{-3}\) NH\(_3\).

### 3. Results and Discussion

**Dissociation constants of ammonium ion in 20 mass \% ethanol + water mixtures**

The observed dissociation constants of NH\(_4^+\) ion, \(K_{a,m}(I)\) on the molarity basis at different ionic strengths are given in Table I, together with \(K_{a,c}(I)\) values on the molality basis, into which the \(K_{a,c}(I)\) values were converted by use of the measured densities of the solutions containing the salt alone. Both the \(pK_{a,c}\) and \(pK_{a,m}\) values increase linearly with increasing ionic strength.

**Table I. Values of \(pK_{a,c}\) at 298.15 K in 20 mass \% ethanol + water solvent solutions containing sodium chloride at different ionic strengths (on molarity and molality bases)**

<table>
<thead>
<tr>
<th>(c/(\text{mol} \cdot \text{dm}^{-3}))</th>
<th>(\gamma_c,\text{NH}_3)</th>
<th>(pK_{a,c}(I))</th>
<th>(m/\text{mol} \cdot \text{kg}^{-1})</th>
<th>(pK_{a,m}(I))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.500</td>
<td>0.9877(5)</td>
<td>9.11(1)</td>
<td>0.522</td>
<td>9.09(1)</td>
</tr>
<tr>
<td>1.000</td>
<td>1.0078(5)</td>
<td>9.23(1)</td>
<td>1.053</td>
<td>9.21(1)</td>
</tr>
<tr>
<td>1.500</td>
<td>1.0269(5)</td>
<td>9.33(1)</td>
<td>1.597</td>
<td>9.31(1)</td>
</tr>
<tr>
<td>2.000</td>
<td>1.0451(5)</td>
<td>9.42(1)</td>
<td>2.155</td>
<td>9.39(1)</td>
</tr>
<tr>
<td>2.500</td>
<td>1.0639(5)</td>
<td>9.51(1)</td>
<td>2.724</td>
<td>9.47(1)</td>
</tr>
<tr>
<td>3.000</td>
<td>1.0833(5)</td>
<td>9.63(1)</td>
<td>3.304</td>
<td>9.59(1)</td>
</tr>
</tbody>
</table>

\(\gamma_c,\text{NH}_3\) values in parenthesis are uncertainties of the least significant figure; \(\gamma_m,\text{NH}_3\) denotes the densities of the solutions containing the salt alone.

**Activity coefficients of ammonia in 20 mass \% ethanol + water mixtures**

The observed activity coefficients of NH\(_3\), \(\gamma_c,\text{NH}_3\) on the molarity scale are given in Table II, together with \(\gamma_m,\text{NH}_3\) values on the molality scale, into which the \(\gamma_c,\text{NH}_3\) values were converted by use of the measured densities of the solutions containing the salt alone. The observed values rise with ionic strength.

**Table II. Activity coefficients of ammonia, \(\gamma_c\) at 298.15 K in 20 mass \% ethanol + water solvent solutions containing sodium chloride at different ionic strengths**

<table>
<thead>
<tr>
<th>(c/(\text{mol} \cdot \text{dm}^{-3}))</th>
<th>(\gamma_c)</th>
<th>(m/\text{mol} \cdot \text{kg}^{-1})</th>
<th>(\gamma_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.500</td>
<td>1.110(5)</td>
<td>0.522</td>
<td>1.064(5)</td>
</tr>
<tr>
<td>1.000</td>
<td>1.137(5)</td>
<td>1.053</td>
<td>1.080(5)</td>
</tr>
<tr>
<td>1.500</td>
<td>1.168(7)</td>
<td>1.597</td>
<td>1.097(7)</td>
</tr>
<tr>
<td>2.000</td>
<td>1.192(10)</td>
<td>2.155</td>
<td>1.106(10)</td>
</tr>
<tr>
<td>2.500</td>
<td>1.235(8)</td>
<td>2.724</td>
<td>1.133(8)</td>
</tr>
<tr>
<td>3.000</td>
<td>1.271(5)</td>
<td>3.304</td>
<td>1.154(5)</td>
</tr>
</tbody>
</table>

\(\gamma_c\) values in parenthesis are uncertainties of the least significant figure.
Comparison of the observed dissociation constants with those calculated with the modified Pitzer model

The thermodynamic relationship between the dissociation constant of NH$_4^+$ ion, $K_{a,m}(I)$ (on the molality basis) and the activity coefficients, $\gamma_{m}$, of the reacting species (on the molality basis) in electrolyte solution at ionic strength $I$ is related by eq. (1), where $K_a$ stands for the thermodynamic dissociation constant of NH$_4^+$ in 20 mass % ethanol + water mixture. The $pK_a$ value of 9.00 at 298.15

$$pK_{a,m}(I) = pK_a + (\ln \gamma_{m,H^+} + \ln \gamma_{m,NH_3} - \ln \gamma_{m,NH_4^+})/\ln 10 \quad (1)$$

$K_{[15]}$ has been used. With the known $pK_a$ value, and empirically determined activity coefficient of NH$_3$, $\gamma_{m,NH_3}$, eq. (1) enables the $pK_{a,m}(I)$ values to be calculated, provided that the activity coefficients of H$^+$ and NH$_4^+$ ions can be theoretically estimated by, for example, the Pitzer equation for the ionic species.

The activity coefficient, $\gamma_{m,M^+}$, of the monovalent cation M$^+$ (M=H$^+$ and NH$_4^+$), which is present in traces in a 20 mass % ethanol + water at ionic strength $I$ of NaCl at 298.15 K is derived from Pitzer's equations [10] as follows:

$$\ln \gamma_{m,M^+} = f'_m + 2I(B_{M^+} + IC_{M^+}) + I^2(B'_{M^+} + C_{M^+})$$

where

$$f'_m = -A_\phi[I^{1/2}/(1+1.2I^{1/2}) + (2/1.2)\ln(1+1.2I^{1/2})] \quad (3)$$

in which $A_\phi = (1/3)(2\pi N_0/1000)^{1/2}(e^2/k_BT)^{3/2}$ with $N_0$ Avogadro's number, $Q$ the density of water, $e$ the electronic charge, $k$ Boltzmann's constant, and $D$ the dielectric constant or the relative permittivity of water.

$$B_{M^+} = \beta_{M^+}^{(0)} + (\beta_{M^+}^{(1)}/2I) [1 - \exp(-2I^{1/2})/(1+2I^{1/2})] \quad (4)$$

$$B'_{M^+} = (\beta_{M^+}^{(1)}/2I^2) [1 + \exp(-2I^{1/2})/(1+2I^{1/2} + 2I)] \quad (5)$$

$$C_{M^+} = C_{M^+}^{(2)}/2 \quad (6)$$

According to Ye et al. [11], the modification has been carried out as follows. The modification consists of using the experimental density of the mixed solvent, and an equivalent dielectric coefficient calculated from a linear law with respect to

the weight fraction. An equivalent temperature, $T'$ is also calculated in the sense of corresponding states; this equivalent temperature expresses the equality of the reduced temperature between the equivalent aqueous solution and the initial solution

$$T' = (T/T_{cm})T_c \quad (7)$$

and an equivalent concentration $m' = m(\rho_{H_2O}/\rho_{mix})$, since the Debye-Hückel model was established from the distribution of ions in the aqueous solution. For the binary interaction part, an equivalent concentration defined by eq. (8) was introduced on

$$m' = m(\rho_{H_2O}/\rho_{mix})(D_{H_2O}/D_{mix}) \quad (8)$$

the assumption that the ionization of electrolytes and the interaction energy depend directly on the distribution of ions in the solution and the dielectric constant $D$ of the solvent. The same assumption was also applied to the ternary interaction part in the present work, whose contributions are usually small. Since the Debye-Hückel factors for H$^+$ and NH$_4^+$ are the same, it is apparent that they offset each other in eq. (1). Thus, fortunately it is not necessary to calculate the equivalent temperature, in which an unknown fitting parameter $k_{ij}$ is included, in the theoretical estimation of $pK_a$ values. Ionic strengths in molal units for the binary and ternary interaction parts were converted to equivalent ones, $I'$, according to eq. (8) with $\rho_{H_2O} = 0.99707$, $\rho_{mix} = 0.9664$ [16], $D_{H_2O} = 78.30$ [17], and $D_{mix} = 67.1$ [15]. Binary [18] and ternary

<table>
<thead>
<tr>
<th>System</th>
<th>$\theta$</th>
<th>$\varphi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl–NaCl$^a$</td>
<td>0.0368</td>
<td>-0.0033</td>
</tr>
<tr>
<td>NH$_4$Cl–NaCl$^b$</td>
<td>0.0040</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

$^a$ Ref. [19]; $^b$ Ref. [6].

<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion</th>
<th>$\beta^{(0)}$</th>
<th>$\beta^{(1)}$</th>
<th>$C^\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Cl</td>
<td>0.20332</td>
<td>-0.01668</td>
<td>-0.00372</td>
</tr>
<tr>
<td>Na</td>
<td>Cl</td>
<td>0.07722</td>
<td>0.25183</td>
<td>0.00106</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>Cl</td>
<td>0.05191</td>
<td>0.17937</td>
<td>-0.00301</td>
</tr>
</tbody>
</table>

Table III. Single electrolyte parameters in Pitzer's equations at 298.15 K.

Table IV. Higher-order parameters for mixtures with a common ion in Pitzer's equations at 298.15.
interaction parameters in aqueous solution involved in the theoretical estimation are given in Tables III and IV, respectively.

Values for $pK_a(I)$ were calculated according to eqs (1–8). The calculated values are compared with the observed ones in Table V. It can be said that the observed values are in agreement with the calculated ones within experimental uncertainties, if it is realized that the activity coefficients of ammonia experimentally determined have also their own uncertainties that originate from several experimental procedures. This means that the assumption of eq. (8) holds in the present system. However, it is not clear yet whether the applicability of eq. (8) is universal or fortuitous, since there is a paucity of data for the dissociation of $\text{NH}_4^+$ ion in mixed solvent solutions.

Table V. Values for $pK_{a,m}$ observed and estimated at 298.15 K in 20 mass % ethanol + water solvent solutions containing sodium chloride at different equivalent ionic strengths $\Gamma$.

<table>
<thead>
<tr>
<th>$\Gamma$ (mol·kg$^{-1}$)</th>
<th>obsd</th>
<th>est</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.628</td>
<td>9.09</td>
<td>9.09</td>
</tr>
<tr>
<td>1.258</td>
<td>9.21</td>
<td>9.18</td>
</tr>
<tr>
<td>1.923</td>
<td>9.31</td>
<td>9.28</td>
</tr>
<tr>
<td>2.595</td>
<td>9.39</td>
<td>9.37</td>
</tr>
<tr>
<td>3.280</td>
<td>9.47</td>
<td>9.49</td>
</tr>
<tr>
<td>3.978</td>
<td>9.59</td>
<td>9.59</td>
</tr>
</tbody>
</table>