Dissociation Constants of Ammonium Ion and Activity Coefficients of Ammonia in Ammonium Nitrate Solutions

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Dissociation constants of NH_4^+ ion on the molality basis ($K_{a,m}$ = $[H^+][NH_3]/[NH_4^+]$) were determined at 298.15 K in aqueous NH_4NO_3 solutions at different ionic strengths (I = 0.5–10.8 mol·kg^{-1}) by means of a glass electrode. The p$K_{a,m}$ values increase gradually with increasing ionic strength. The activity coefficients of NH_3, γ_{m,NH_3}, on the molality basis in the NH_4NO_3 solutions were determined by a transpiration method and were fitted to $\ln \gamma_{m,NH_3} = -0.0416 I_m + 0.00194 I_m{}^2$ (I = 0.5–10.8 mol·kg^{-1}). The observed dissociation constants, p$K_{a,m}$, were compared with those calculated from the Pitzer equations.

The experimental investigation of ionic equilibria has usually been made in solutions containing an inert salt at a high, constant concentration for minimizing activity coefficient variations of the reacting species. The values of the thermodynamic properties such as Gibbs free energy and enthalpy changes are strongly influenced by the type and the concentration of the chosen ionic medium. Thus, the theoretical evaluation of the thermodynamic properties in a specified solution, which has not been experimentally studied or is difficult to study, is of crucial importance.

The authors (Maeda, 1986; Maeda et al., 1983, 1987, 1988, 1989, 1990, 1993) have applied Pitzer's ionic interaction theory (Pitzer, 1973, 1991) to the prediction of dissociation constants of the ammonium ion in various 1:1 electrolyte solutions and compared the theoretically evaluated values with observed ones.

The thermodynamic relationship between the dissociation constant of NH_4^+ ion, $K_{a,m}(I)$ (on the molality basis) for the reaction $NH_4^+ \rightleftharpoons H^+ + NH_3$ and the activity coefficients, γ_m, of the reacting species (on the molality basis) in electrolyte solution at ionic strength I is related by eq 1, where K_a denotes the thermodynamic dissociation

$$\mathrm{p}K_{a,m}(I) = \mathrm{p}K_a + (\ln \gamma_{m,H^+} + \ln \gamma_{m,NH_3} - \ln \gamma_{m,NH_4^+})/\ln 10 \quad (1)$$

constant of NH_4^+ in aqueous solution, *i.e.*, $K_a = a_{H^+}a_{NH_3}/a_{NH_4^+}$($a$ = activity of species indicated). The pK_a value of 9.245 at 298.15 K reported by Bates and Pinching (1949) has been used. With the known pK_a value, and empirically determined activity coefficient of NH_3, γ_{m,NH_3}, eq 1 enables the p$K_{a,m}(I)$ 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, γ_{m,H^+}, of H^+ ion, which is present in traces in NH_4NO_3 solution of ionic strength I at 298.15 K is derived from Pitzer's equations (Pitzer, 1991) as follows:

$$\ln \gamma_{m,H^+} = f^{\gamma} + 2I(B_{HNO_3} + IC_{HNO_3}) + I^2(B'_{NH_4NO_3} + C_{NH_4NO_3}) + I(2\theta_{HNH_4} + I\psi_{HNH_4NO_3}) \quad (2)$$

where

$$f^{\gamma} = -0.392[I^{1/2}/(1 + 1.2I^{1/2}) + (2/1.2)\ln(1 + 1.2I^{1/2})] \quad (3)$$

$$B_{HNO_3} = \beta^{(0)}_{HNO_3} + (\beta^{(1)}_{HNO_3}/2I)[1 - (1 + 2I^{1/2})\exp(-2I^{1/2})] \quad (4)$$

$$B'_{NH_4NO_3} = (\beta^{(1)}_{NH_4NO_3}/2I)[-1 + (1 + 2I^{1/2} + 2I)\exp(-2I^{1/2})] \quad (5)$$

and

$$C_{HNO_3} = C^{\phi}_{HNO_3}/2 \quad (6)$$

The activity coefficient of NH_4^+, γ_{m,HH_4^+}, in NH_4NO_3 solution can be calculated by

$$\ln \gamma_{m,NH_4^+} = f^{\gamma} + 2I(B_{NH_4NO_3} + IC_{NH_4NO_3}) + I^2(B'_{NH_4NO_3} + C_{NH_4NO_3}) \quad (7)$$

Values for $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ}, which are constant and independent of the ionic strength I, have been calculated from the activity and osmotic coefficient data of simple electrolytes (Pitzer, 1991). The θ_{HNH_4} and $\psi_{HNH_4NO_3}$ higher-order terms are related to like-charge interaction between H^+ and NH_4^+ and triplet interactions among H^+, NH_4^+, and NO_3^-, respectively. The former term is regarded as either dependent on or independent of I, while the I dependence is usually neglected for the latter term. For the θ term, regarded as dependent on I, Yang and Pitzer (1988) have adopted an equation of the same form as eq 4:

$$\theta_{HNH_4} = \theta^{(0)}_{HNH_4} + (\theta^{(1)}_{HNH_4}/2I)[1 - (1 + 2I^{1/2}]\exp(-2I^{1/2})] \quad (8)$$

where

$$\theta^{(1)}_{HNH_4} = -\theta^{(0)}_{HNH_4}/(1 + 2/9A_{\phi}) \quad (9)$$

in which A_{ϕ} = 0.3910 at 298.15 K.

Values for $\theta^{(0)}$ and $\theta^{(1)}$ in eq 8 are constant and independent of I. Values for θ (assumed to be independent of I), $\theta^{(0)}$, $\theta^{(1)}$, and ψ have been estimated from the data of mixed electrolytes (Pitzer, 1991), but there is a paucity of data.

In our early work, calculations were made without the higher order terms θ and ψ. These values are not always available in the literature, and without them we observed large deviations between measured and calculated values, especially at high salt concentrations. These higher-order terms θ and ψ were subsequently determined by isopiestic

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measurements. It was found that the dissociation constants calculated with inclusion of the higher-order terms agree with the measurements within experimental accuracy. This suggests that the unknown θ and ψ values could be determinable by fitting the observed equilibrium constants to those calculated from Pitzer's equations.

Thus, in the preceding work (Maeda et al., 1993) the unknown higher-order parameters θ_{HNH_4}, ψ_{HNH_4Cl} and θ_{NH_4K}, ψ_{NH_4KCl} were determined on the basis of the $pK_{a,m}(I)$ values in NH_4Cl and KCl solutions, respectively, in such a way that the $pK_{a,m}(I)$ values calculated from Pitzer's equations reproduced the observed results.

The empirically determined activity coefficients of NH_3, γ_{m,NH_3}, were also used to determine the ion$-NH_3$ interaction parameters in the Pitzer equation for the neutral species (Clegg and Brimblecombe, 1989; Maeda et al., 1990; Clegg and Whitfield, 1991).

In the present work, the dissociation constants of NH_4^+ and the activity coefficients of NH_3 were determined at 298.15 K in NH_4NO_3 solutions over the wide concentration range. Then, the unknown higher-order parameters θ_{HNH_4} and $\psi_{HNH_4NO_3}$ were obtained by forcing the $pK_{a,m}$ values calculated with Pitzer's equations, fully parametrized for the system, to agree with the observed ones.

Experimental Section

Reagents. Ammonium nitrate of reagent grade was recrystallized three times from distilled water by cooling in an ice$-$salt mixture (Perrin and Armarego, 1992), and the crystals thus prepared were dissolved in distilled water. The ammonium nitrate content of the stock solution was determined as follows. The ammonia volatilized by adding (ammonia-free) KOH solution was distilled into an excess of standard H_2SO_4 solution, and the excess of the acid was titrated by a standard NaOH solution. The concentrations of NH_4NO_3 thus determined several times agreed with each other within the accuracy of 0.2%. Ammonia of reagent grade was used by dilution without further purification.

Procedure for Measurement of the Dissociation Constant of NH_4^+. Dissociation constants of NH_4^+ in NH_4NO_3 solutions were determined at 298.15 K by procedures analogous to those described by Bjerrum (1957). A sample solution of NH_4NO_3 at a given concentration containing ammonia was prepared. The ammonia concentration in that solution was determined by acid$-$base titrations (Bromocresol Purple as indicator) in a room thermostated at 298.15 ± 1 K. A known volume of the sample solution was transferred into a titration vessel, which was then kept in a water thermostat maintained at 298.15 ± 0.01 K in a room thermostated at 298.15 ± 1 K. The sample solution was titrated from an automatic piston buret (Kyoto Electronics, APB-118) with a solution of NH_4NO_3 at the same concentration as that of the sample solution, while the hydrogen ion concentrations were measured by use of a combination pH glass electrode (Beckman No. 39539). The electrode was calibrated in solutions of NH_4NO_3 at a given concentration containing HNO_3 of known concentrations. Emf values of the combination electrode were measured up to 0.01 mV with a pH meter (DKK Corp. Model COM-30). The titration vessel was kept tightly closed so that losses of ammonia were avoided. Thus, the dissociation constants could be obtained from known concentrations of H^+, NH_3 (concentrations of NH_3 were decreased by dilution caused by addition of titrant), and NH_4NO_3.

Procedure for Measurement of the Activity Coefficient of NH_3. The activity coefficients of NH_3 in NH_4NO_3 solutions were determined with essentially the same glass apparatus as that used previously (Maeda et al., 1988). It is schematically shown in Figure 1. Vessel A was filled with a 0.5 mol·dm^{-3} NaOH solution, and vessels B and C were charged with 0.2 mol·dm^{-3} NH_3 solutions containing NH_4NO_3 at a desired ionic strength. A 0.005 mol·dm^{-3} HCl solution (10 mL) was introduced into conductivity cell D. The whole apparatus was immersed in a water thermostat kept at 298.15 ± 0.01 K. First, a carrier gas (mixture of H_2 and O_2) was generated by electrolysis in vessel A with stopcock a open and stopcock b closed until the empty spaces in the vessels and the tubes were saturated with the NH_3 gas. Then, under the condition of stopcock a being closed and stopcock b being open, the electrolysis for the generation of the carrier gas was carried out in small steps so that the NH_3 gas transpired by the carrier gas was absorbed into the HCl solution in cell D, while the conductivity of the HCl solution was measured in each step. The electrolysis was carried out by means of a coulometer (Metrohm, E524) and the conductivity measurement with an ac bridge (Delica Model D1S). The concentration of the NH_3 solution in vessel C before and after the experiment was measured by acid$-$base titrations to confirm the invariance of the NH_3 concentration during the experiment.

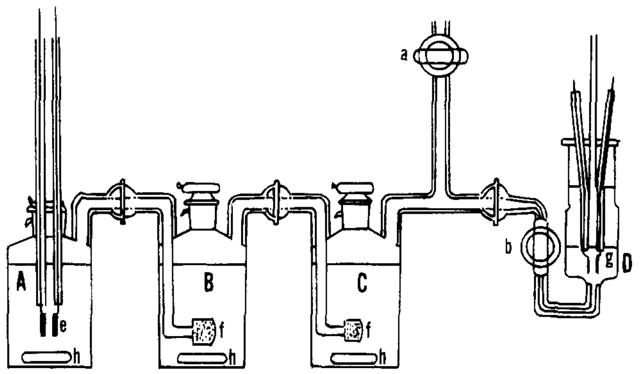

Figure 1. Glass apparatus for measurement of ammonia activity: (e) platinum plates; (f) sintered glass; (g) platinum plates coated with platinum black; (h) magnetic rod.

An improved procedure in this experiment is that the solutions in vessels A$-$C were stirred with magnetic rods. The stirring, which had not been carried out in the previous works, resulted in better reproducibility.

Dissociation Constants of Ammonium Ion in Ammonium Nitrate Solutions. The observed dissociation constants of NH_4^+ ion, $K_a(I)$ (on both concentration and molality bases), in NH_4NO_3 solutions at different ionic strengths I are given in Table 1. The $pK_{a,c}$ value of 9.50 in 2 mol·dm^{-3} NH_4NO_3 is consistent with the value of 9.50 reported by Spike (1953). As is the case in other 1:1 electrolyte solutions, $pK_{a,c}$ values in the NH_4NO_3 system increase almost linearly with increasing ionic strength. It is found that the pK_a values in the NH_4NO_3 system increase to the least extent with increasing ionic strength, compared with those in other electrolytes such as lithium, sodium, and potassium salts reported previously. An exception is the NH_4Cl system, in which the dependence of the pK_a values on the ionic strength is similar to the present results within experimental uncertainties.

Activity Coefficients of Ammonia in Ammonium Nitrate Solutions. The experimental plots of the conductivities κ against the quantities of electricity passed (for generation of the carrier gas) Q in salt-free and 10.8 mol kg^{-1} NH_4NO_3 solutions are illustrated in Figure 2. The amount of electricity passed Q_e for the transpiration of NH_3 required to neutralize 10.00 mL of a 0.005 mol·dm^{-3} HCl

Table 1. Values of p$K_a(I)$ at 298.15 K in Ammonium Nitrate Solutions with Different Concentrations (on Molar and Molal Bases)[a]

c/(mol·dm^{-3})	p$K_{a,c}(I)$	m/(mol·kg^{-1})	p$K_{a,m}(I)$
0.50	9.30(1)	0.51	9.29(1)
1.00	9.37(1)	1.06	9.35(1)
1.50	9.44(1)	1.62	9.40(1)
2.00	9.50(1)	2.22	9.45(1)
2.50	9.56(1)	2.85	9.50(1)
3.00	9.61(1)	3.54	9.54(1)
3.50	9.67(1)	4.23	9.59(1)
4.00	9.74(1)	5.01	9.64(1)
4.50	9.79(1)	5.83	9.68(1)
5.00	9.86(1)	6.70	9.73(1)
5.50	9.91(1)	7.62	9.76(1)
6.00	9.97(1)	8.61	9.81(1)
6.50	10.05(1)	9.66	9.88(1)
7.00	10.10(1)	10.82	9.91(1)

[a] Numbers in parentheses are uncertainties of the least significant figure. Values of $K_{a,c}$ were converted into those on the molality scale by use of the measured densities of the solutions containing the salt alone.

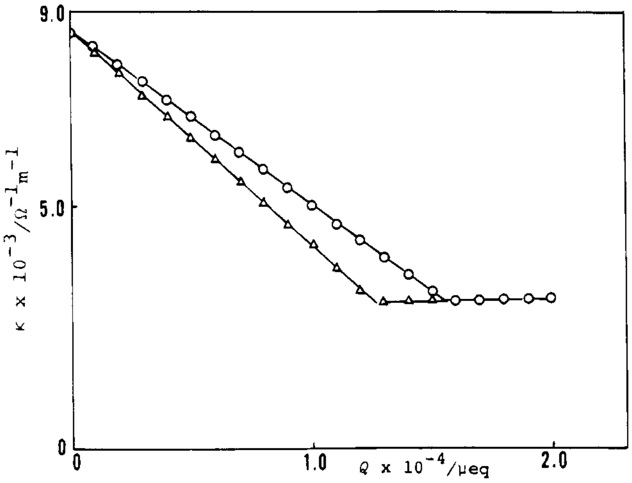

Figure 2. Conductivity κ versus amount of electricity Q: (○) salt-free solution, (△) 10.81 mol·kg^{-1} NH_4NO_3 solution.

solution was calculated from the point of the slope change. The activity coefficients γ_{m,NH_3} in the NH_4NO_3 solutions with different concentrations were determined by use of Q_e values and ammonia concentrations m_{NH_3} (molality basis) according to

$$\gamma_{m,NH_3} = (Q_e^0/Q_e)(m_{NH_3}^0/m_{NH_3}) \qquad (10)$$

on the assumption that the γ_{m,NH_3} value in a salt-free solution is unity. The superscript 0 is for the salt-free solution. The values of $m_{NH_3}^0$ and m_{NH_3} were adjusted to be practically equal.

The γ_{m,NH_3} values are given in Table 2, together with γ_{c,NH_3} values. The γ_{m,NH_3} values are expressed as $\ln \gamma_{m,NH_3} = -0.01416 I_m + 0.00194 I_m{}^2$. The following equation is derived for the γ_{m,NH_3} value in NH_4NO_3 solution from the Pitzer equation for the neutral species at a low concentration (Pitzer and Silvester, 1976; Pitzer, 1991):

$$\ln \gamma_{m,NH_3} = 2m_{NH_4NO_3}(\lambda_{NH_3NH4} + \lambda_{NH_3NO_3}) + 3(m_{NH_4NO_3})^2(\mu_{NH_3NH_4NH_4} + 2\mu_{NH_3NH_4NO_3} + \mu_{NH_3NO_3NO_3}) \qquad (11)$$

where λ and μ represent doublet and triplet ion interaction parameters with NH_3, respectively, and are independent of ionic strength I. Thus, it is obvious that the first virial terms $\lambda_{NH_3NH_4} + \lambda_{NH_3NO_3} = -0.0208$ and the second virial terms $\mu_{NH_3NH_4NH_4} + 2\mu_{NH_3NH_4NO_3} + \mu_{NH_3NO_3NO_3} = 0.000\,647$. The value for the first virial terms obtained in the present work is in good agreement with the value of -0.0165 calculated by Clegg and Brimblecombe (1989) on the basis of the NH_3 partitioning data in NH_4NO_3 solutions up to 1 mol·dm^{-3} measured at 293.15 K by Dawson and McCrae (1901). It was found that the second virial terms cannot be neglected in the NH_4NO_3 solutions at high ionic strengths I.

Table 2. Activity Coefficients of Ammonia, γ, at 298.15 K in Ammonium Nitrate Solutions[a]

c/(mol·dm^{-3})	γ_c	m/(mol·kg^{-1})	γ_m
0.50	1.004(4)	0.51	0.979(4)
1.00	0.997(5)	1.06	0.977(5)
2.00	1.010(2)	2.22	0.911(2)
3.00	1.017(4)	3.54	0.867(4)
4.00	1.071(10)	5.01	0.855(10)
5.00	1.116(10)	6.70	0.834(10)
6.00	1.190(5)	8.61	0.829(5)
7.00	1.224(1)	10.82	0.786(1)

[a] Numbers in parentheses are uncertainties of the least significant figure. Values of γ_c were converted into those of γ_m by use of the measured densities of the solutions containing the salt alone.

Evaluation of Higher-Order Terms θ_{HNH_4} and $\psi_{HNH_4NO_3}$ in the Pitzer Equation. Equation 12 is derived from the difference between the observed p$K_{a,m}(I)$ values and the values calculated with $\beta^{(0)}$, $\beta^{(0)}$, and C^{ϕ}, but with $\theta_{HNH_4} = \psi_{HNH_4NO_3} = 0$ according to the Pitzer equations (eqs 2–7). θ_{HNH_4} is regarded as either dependent on or independent of I. For θ_{HNH_4} dependent on I, eq 8 is adopted. Equation 8 is introduced into eq 12 so that the right-hand side of eq 12 is expressed with $\theta_{HNH_4}^{(0)}$ and $\psi_{HNH_4NO_3}$ terms. Values for θ_{HNH_4} or $\theta_{HNH_4}^{(0)}$ and $\psi_{HNH_4NO_3}$ were obtained by solution of normal equations at different I and p$K_{a,m}(I)$ values according to eq 12. The $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} values for HNO_3 and NH_4NO_3 were taken from Kim and Frederick (1988). The value for $\theta_{HNH_4}^{(1)}$ was obtained, with the known $\theta_{HNH_4}^{(0)}$ value, from eq 9. The values obtained are $\theta_{HNH_4} = -0.06_5$ and $\psi_{HNH_4NO_3} = 0.01_1$, and $\theta_{HNH_4}^{(0)} = -0.07_9$, $\theta_{HNH_4}^{(1)} = 0.05_1$, and $\psi_{HNH_4NO_3} = 0.01_4$. The θ_{HNH_4} and $\theta_{HNH_4}^{(0)}$ values obtained in the NH_4NO_3 system are larger in absolute value than the corresponding ones (-0.03_9 an -0.03_8) determined in the NH_4Cl system (Maeda et al., 1993).

$$[pK_{a,m}(I)(calc) - pK_{a,m}(I)(obs)](\ln 10)/I = 2\theta_{HNH_4} + I\psi_{HNH_4NO_3} \qquad (12)$$

The p$K_{a,m}(I)$ values calculated with and without the higher-order terms are compared with the observed ones in Table 3.

In our previous works (Maeda et al., 1988, 1989, 1990), we determined from isopiestic measurements unknown θ_{HNH_4} and ψ_{NH_4NX} (NX = LiCl, NaCl, and $LiClO_4$) values pertinent to interactions between $NH_4{}^+$ ions and these salts. The p$K_{a,m}(I)$ values calculated with all the required higher-order terms (θ_{HN}, ψ_{HNX} (available in the literature) and θ_{NH_4N}, ψ_{NH_4NX}) agreed with the data measured in those electrolyte solutions within experimental accuracy (±0.01–0.02). The good agreement suggested that the values, for example, for θ_{NH_4N} and ψ_{NH_4NX}, which are not available in the literature, are determinable by fitting observed p$K_{a,m}(I)$ values to those calculated according to eqs 1–7, provided that the θ_{HN} and ψ_{HNX} values are known. Thus, this procedure was applied to the calculations of θ_{NH_4K} and ψ_{NH_4KCl} values in KCl solutions and of θ_{HNH_4} and ψ_{HNH_4Cl} values in NH_4Cl solutions. The calculated θ and ψ values

Table 3. Values for p$K_{\mathrm{a},m}$ Observed and Estimated at 298.15 K in NH_4NO_3 Solutions

		p$K_{\mathrm{a},m}(I)$ estimated		
m/(mol·kg^{-1})	obsd	without[a]	with[b]	with[c]
0.51	9.29	9.34	9.32	9.32
1.06	9.35	9.41	9.36	9.36
1.63	9.40	9.47	9.39	9.39
2.22	9.45	9.52	9.42	9.42
2.85	9.50	9.57	9.45	9.44
3.54	9.54	9.63	9.49	9.48
4.24	9.59	9.68	9.53	9.51
5.01	9.64	9.74	9.58	9.56
5.83	9.68	9.80	9.63	9.62
6.70	9.73	9.86	9.70	9.68
7.62	9.76	9.92	9.77	9.76
8.61	9.81	9.99	9.86	9.85
9.66	9.88	10.06	9.96	9.96
10.82	9.91	10.13	10.09	10.10

[a] Values calculated without $\theta_{\mathrm{HNH_4}}$ and $\psi_{\mathrm{HNH_4NO_3}}$. [b] Values calculated with $\theta_{\mathrm{HNH_4}} = -0.065$ and $\psi_{\mathrm{HNH_4NO_3}} = 0.011$. [c] Values calculated with $\theta^{(0)}_{\mathrm{HNH_4}} = 0.079$, $\theta^{(1)}_{\mathrm{HNH_4}} = 0.051$, and $\psi_{\mathrm{HNH_4NO_3}} = 0.014$.

reproduced the measured p$K_{\mathrm{a},m}(I)$ values within experimental accuracy (±0.01–0.02) in both systems.

On the other hand, as is apparent from Table 3, the discrepancies between the measured and calculated p$K_{\mathrm{a},m}(I)$ values exceed by far the experimental accuracy (±0.01). The reason for the large discrepancies is not clear at the present stage of investigation.

Literature Cited

Bates, R. G.; Pinching, G. D. Acidic Dissociation Constant of Ammonium Ion at 0 to 50 °C, and the Base Strength of Ammonia. *J. Res. Natl. Bur. Stand. (U.S.)* **1949**, *42*, 419–430.

Bjerrum, J. *Metal Ammine Formation in Aqueous Solution Theory of the Reversible Step Reactions*; P. Haase and Son: Copenhagen, 1957.

Clegg, S. L.; Brimblecombe, P. Solubility of Ammonia in Pure Aqueous and Multicomponent Solutions. *J. Phys. Chem.* **1989**, *93*, 7237–7248.

Clegg, S. L.; Whitfield, M. Activity Coefficients in Natural Waters. In *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC: Boca Raton, FL, 1991; Chapter 6.

Dawson, H. M.; MacCrae, J. Metal-Ammonia Compounds in Aqueous Solution. Part II. The absorptive Powers of Dilute Solutions of Salts of the Alkali Metals. *J. Chem. Soc.* **1901**, *79*, 493–511.

Kim, H.-T.; Frederick, W. J., Jr. Evaluation of Pitzer Ion Interaction Parameters of Aqueouis Electrolytes at 25 °C. 1. Single Salt Parameters. *J. Chem. Eng. Data* **1988**, *33*, 177–184.

Maeda, M. Estimation of Medium Effect on Enthalpy Changes for Ionization of Water and Ammonium Ion in Aqueous Solution. *J. Phys. Chem.* **1986**, *90*, 1134–1137.

Maeda, M.; Nakagawa, G.; Biedermann, G. Estimation of Medium Effect on Dissociation Constants of Ammonium Ion and Formation Constants of Silver(I)-Ammine Complexes in Aqueous Solution. *J. Phys. Chem.* **1983**, *87*, 121–125.

Maeda, M.; Hayashi, M.; Ikeda, S.; Kinjo, Y.; Ito, K. Prediction of Dissociation Constants of Ammonium Ion in Artificial Seawaters and in Concentrated Sodium Chloride Solutions. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2047–2052.

Maeda, M.; Ikedo, H.; Masuda, H.; Kinjo, Y.; Ito, K. Prediction of Dissociation Constants of Ammonium Ion in Aqueous Lithium Chloride Solutions in Terms of the Pitzer Approach. *J. Phys. Chem.* **1988**, *92*, 6404–6407.

Maeda, M.; Hisada, O.; Kinjo, Y.; Ito, K. Application of Pitzer's Equations to Dissociation Constants of Ammonium Ion in Lithium Chloride-Sodium Chloride Mixtures. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2555–2562.

Maeda, M.; Kinjo, Y.; Hisada, O.; Ito, K. Evaluation of Dissociation Constants of Ammonium Ion in Lithium Perchlorate and Lithium Chloride-Sodium Chloride Mixed Solutions. *J. Solution Chem.* **1990**, *19*, 1019–1027.

Maeda, M.; Furuhashi, H.; Ikami, J. Evaluation of Dissociation Constants of Ammonium Ion in Aqueous Ammonium Chloride and Potassium Chloride and of Pertinent Higher-Order Parameters according to the Pitzer Approach. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3371–3374.

Perrin, D. D.; Armarego, L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, 1992.

Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **1973**, *77*, 268–277.

Pitzer, K. S. Ion Interaction Approach: Theory and Data Correlation. In *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC: Boca Raton, FL, 1991; Chapter 3 and references cited therein.

Pitzer, K. S.; Silvester, L. F. Thermodynamics of Electrolytes. VI. Weak Electrolytes Including H_3PO_4. *J. Solution Chem.* **1976**, *5*, 269–278.

Spike, C. G. Thesis, University of Michigan, Ann Arbor, MI, 1953 (cited from *Stability Constants*, Special Supplement No. 17; compiled by Sillén, L. G.; Martell, A. E.; The Chemical Society: London, 1964).

Yang, J.-Z.; Pitzer, K. S. Thermodynamics of Electrolyte Mixtures. Activity and Osmotic Coefficients consistent with the Higher-Order Limiting Law for Symmetrical Mixing. *J. Solution Chem.* **1988**, *17*, 909–924.

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