Dissociation Constants of Ammonium Ion and Activity Coefficients of Ammonia in Aqueous Ammonium Sulfate Solutions

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Dissociation constants of NH_4^+ ion, $K_{a,c} = cH^+_{(T)}cNH_3/cNH_4^+$, where c denotes molarity and $cH^+_{(T)} = cH^+ + cHSO_4^-$, were determined at 298.15 K in aqueous $(NH_4)_2SO_4$ solutions at different ionic strengths (I = 0.75−7.5 mol dm^{-3}) by potentiometry using a glass electrode. The $K_{a,c}$ values were converted to those on the molality basis by use of the densities of the corresponding solutions. The activity coefficients of ammonia, γ_{c,NH_3} and γ_{m,NH_3}, respectively, on the molar and molal bases, were determined by a transpiration method. The observed dissociation constants on the molality basis, p$K_{a,m}$, were compared with those calculated from the Pitzer equations.

So far, the authors (Maeda and Kato, 1995) have determined dissociation constants of ammonium ion, $K_{a,m}$ (on the molality basis) for the reaction $NH_4^+ = H^+ + NH_3$ in strong aqueous solutions of various 1:1 electrolytes such as LiCl, KCl, $LiClO_4$, $NaClO_4$, $LiNO_3$, $NaNO_3$, NH_4Cl, and NH_4NO_3 and compared them with those calculated from the Pitzer equations (Pitzer, 1991). It was found that the dissociation constants calculated with inclusion of the higher-order parameters agree with the measured values within experimental accuracy.

In the present work, the dissociation constants of NH_4^+ and the activity coefficients of NH_3 were determined at 298.15 K in aqueous solutions of 2:1 electrolyte $(NH_4)_2SO_4$ over a wide concentration range. The dissociation constants were compared with those calculated with the Pitzer equations.

Experimental Section

Reagents. Ammonium sulfate of reagent grade was crystallized twice from hot water containing 0.2% EDTA to remove metal ions and then finally from distilled water (Perrin and Armarego, 1992). The crystals thus prepared were dissolved in distilled water, and the ammonium sulfate content was determined gravimetrically as $BaSO_4$. Ammonia of reagent grade was used by dilution without further purification

Procedure for Measurement of the Dissociation Constant of NH_4^+. The dissociation constants of NH_4^+ ion in $(NH_4)_2SO_4$ solutions were measured at 298.15 K by procedures analogous to those described by Bjerrum (1957). A sample solution of $(NH_4)_2SO_4$ 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 Electronic, APB-118) with a solution of $(NH_4)_2SO_4$ at the same concentration as that of the sample solution, while the total hydrogen ion concentrations of $H^+ + HSO_4^-$ were measured by use of a combination pH glass electrode (Beckman No. 39539). Just before the titrations, the electrode had been calibrated in solutions of $(NH_4)_2SO_4$ at a given concentration containing H_2SO_4 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). Thus, the dissociation constants $K_{a,c}$ (on the molar basis) thus measured are defined by eq 1

$$K_{a,c} = cH^+_{(T)}cNH_3/cNH_4^+ \qquad (1)$$

where c stands for molarity and $cH^+_{(T)} = cH^+ + cHSO_4^-$. They could be obtained from known concentrations of $H^+ + HSO_4^-$, NH_3 (concentrations of NH_3 were decreased by dilution caused by addition of titrant), and $(NH_4)_2SO_4$.

Procedure for Measurement of the Activity Coefficient of NH_3 . These measurements were carried out with the same apparatus and procedures as those described in detail in a previous paper (Maeda and Kato, 1995).

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

I/(mol·dm^{-3})	p$K_{a,c}$	I/(mol·kg^{-1})	p$K_{a,m}$
0.75	8.77(1)	0.76	8.76(1)
1.50	8.80(1)	1.55	8.79(1)
2.25	8.70(1)	2.36	8.68(1)
3.00	8.70(1)	3.20	8.67(1)
4.50	8.74(1)	4.98	8.70(1)
6.00	8.77(1)	6.91	8.71(1)
7.50	8.82(1)	9.01	8.74(1)

[a] Numbers in parentheses are uncertainties of the least significant figure.

Results and Discussion

Dissociation Constants of NH_4^+ Ion in $(NH_4)_2SO_4$ Solutions. The observed dissociation constants of NH_4^+, $K_{a,c}(I)$ on the molarity basis at different ionic strengths I are given in Table 1, together with $K_{a,m}$ (I) values on the molality scale, into which the $K_{a,c}(I)$ values were converted by use of the measured densities of the solutions containing the salt alone.

Activity Coefficients of Ammonia in Ammonium Sulfate Solutions. The observed activity coefficients of NH_3 (on the molarity basis) are given in Table 2, together with those on the molality basis, into which the γ_c values were converted by use of the measured densities of the solutions containing the salt alone. The observed γ_m values as a function of the molal concentration of $(NH_4)_2SO_4$ were inset for comparison in a figure (Figure 14) drawn by Clegg and Brimblecombe (1989), in which data from a few

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Table 2. Activity Coefficients of Ammonia, γ, at 298.15 K in Ammonium Sulfate Solutions with Different Ionic Strengths (on Molar and Molal Bases)[a]

I/(mol·dm^{-3})	γ_c	I/(mol·kg^{-1})	γ_m
0.75	1.11(1)	0.76	1.09(1)
1.50	1.23(1)	1.55	1.19(1)
2.25	1.36(1)	2.36	1.29(1)
3.00	1.51(1)	3.20	1.41(1)
4.50	1.84(1)	4.98	1.67(1)
6.00	2.23(1)	6.91	1.97(1)
7.50	2.68(1)	9.01	2.31(1)

[a] Numbers in parentheses are uncertainties of the least significant figure.

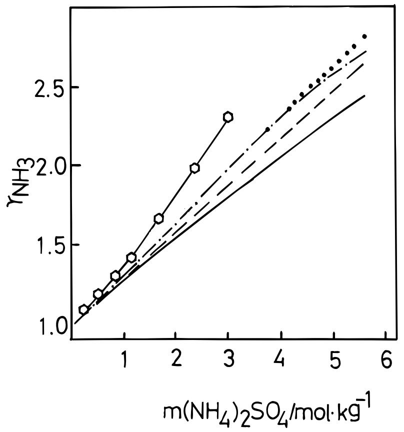

Figure 1. Comparison of calulated values of γ_{m,NH_3} at 298.15 K in $(NH_4)_2SO_4$ dilute with respect to NH_3 with those determined in the present work. (···, i) from data of Gaus; (—·—, ii) estimated using in the Pitzer model; (- - -, iii) from data of Dawson and McCrae; (—, iv) from data of Benoit; estimates (i) and (iii) were carried out by Benoit; (—○—, v) data obtained in the present work.

investigators had been plotted. They are illustrated in Figure 1. It is apparent that the observed values are significantly larger than those reported previously.

Comparison of the Observed Dissociation Constants with Those Calculated with Pitzer Equations. The thermodynamic relationship between the dissociation constant of NH_4^+ ion, $K_{a,m}(I)$ (defined by eq 1 on the molality basis), 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 2 in consideration of the dissociation of HSO_4^-

$$pK_{a,m}(I) = pK_a + (\ln \gamma_{m,H^+} + \ln \gamma_{m,NH_3} - \ln \gamma_{m,NH_4^+})/\ln 10 - \log\{1 + (I/3)[\gamma_{m,HSO_4^-}/(K_{a,HSO_4^-}\gamma_{m,H^+}\gamma_{m,SO_4^{2-}})]\} \quad (2)$$

where $K_a = a_{H^+}a_{NH_3}/a_{NH_4^+}$ for the dissociation of NH_4^+ and $K_{a,HSO_4^-} = a_{H^+}a_{SO_4^{2-}}/a_{HSO_4^-}$ for the dissociation of HSO_4^- (a = activity of species indicated). The pK_a value of 9.245 at 298.15 K reported by Bates and Pinching (1949) and the pK_{a,HSO_4^-} value = 1.979 at 298.15 K reported by Clegg et al. (1994) have been used. With the known pK_a and pK_{a,HSO_4^-} values, and empirically determined activity coefficients of NH_3, γ_{m,NH_3}, eq 1 enables the p$K_{a,HSO_4^-}(I)$ values and thus the p$K_{a,m}(I)$ values to be calculated provided that the activity coefficients of the cations and the anions involved in the dissociation reactions can be theoretically estimated by the Pitzer equations for ionic species.

The calculations of p$K_{a,m}(I)$ values were carried out according to the extended Pitzer equations derived by Clegg et al. (1994).

Table 3. Ion–Ion Interaction Parameters

species		$\beta^{(0)}$	$\beta^{(1)}$	$C^{(0)}$	$C^{(1)}$
H^+	HSO_4^- [a]	0.2959	0.4005	−0.005 658	−0.4094
H^+	SO_4^{2-} [a]	0.0084	0.3147	0.010 19	−0.3237
NH_4^+	HSO_4^- [b]	0.0328	0.4684	0.001 153	−0.3487
NH_4^+	SO_4^{2-} [b]	0.0374	0.5345	−0.000 217 6	0.1643

[a] Clegg et al. (1994). [b] Clegg et al. (1996).

Table 4. Mixture Parameters θ_{ij} and Ψ_{ijk}[a] Involving NH_4^+

species			
j	k	$\theta_{NH_4\,j}$	$\Psi_{NH_4\,jk}$
H^+	HSO_4^-	−0.019	−0.008 65
H^+	SO_4^{2-}	−0.019	−0.022 45
HSO_4^-	SO_4^{2-}		−0.008 42

[a] Clegg et al. (1996).

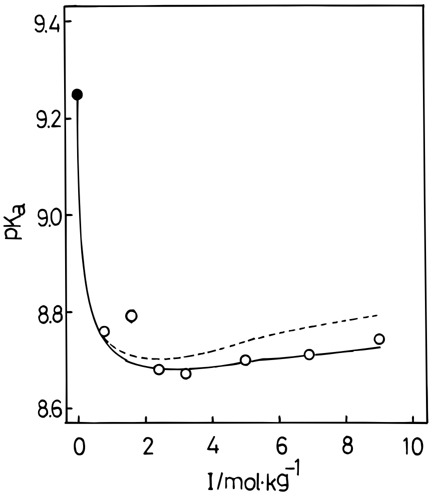

Figure 2. Comparison of the observed p$K_{a,m}(I)$ values with those calculated with the Pitzer equations: ●, thermodynamic pK_a value of 9.245; ○, observed in the present work; —, calculated with γ_{m,NH_3} values from the Pitzer mode; - - - calculated with γ_{m,NH_3} values observed in the present work.

The parameter values for $\beta^{(0)}$, $\beta^{(1)}$, $C^{(0)}$, $C^{(1)}$, θ, and Ψ pertaining to the dissociation of NH_4^+ and HSO_4^- are tabulated in Tables 3 (Clegg et al., 1994, 1996) and 4 (Clegg et al., 1996).

The p$K_{a,m}(I)$ values thus calculated are compared with the observed ones in Figure 2. It is obvious that discrepancies beyond experimental uncertainties occur between the observed and calculated values. Next, as a second estimation of the p$K_{a,m}(I)$ values, the γ_{m,NH_3} values evaluated by the Pitzer model (Clegg and Brimblecombe,1989) were employed. The Pitzer equation for neutral species NH_3 for the present system of NH_3, NH_4^+, and SO_4^{2-} is given by eq 3.

$$\ln \gamma_{NH_3} = 2\lambda_{NH_3,NH_3}m_{NH_3} + 3\mu_{NH_3,NH_3,NH_3}m_{NH_3}^{\ 2} + 2\lambda_{NH_3,NH_4^+}m_{NH_4^+} + 2\lambda_{NH_3,SO_4^{2-}}m_{SO_4^{2-}} + \xi_{NH_3,NH_4^+,SO_4^{2-}}m_{NH_4^+}m_{SO_4^{2-}} \quad (3)$$

The ion-neutral parameters in salt solutions have been determined by Clegg and Brimblecombe (1989) from available experimental measurements of equilibrium pNH$_3$, salt solubilities in aqueous NH_3, and NH_3 partitioning between salt solutions and $CHCl_3$. The values for the interaction parameters relevant to the present system are given in Table 5(Clegg and Whitfield,1991). The p$K_{a,m}$ values estimated with the γ_{m,NH_3} values (corresponding to line ii

Table 5. Interaction Parameters for NH_3[a]

species *i, j*	$\lambda_{NH_3,i}$	$\mu_{NH_3,NH_3,i}$	$\zeta_{NH_3,i,j}$
NH_3	0.014 78	0.0	
NH_4^+	0.0	−0.000 75	
SO_4^{2-}	0.138	0.0	
NH_4^+, SO_4^{2-}			−0.009 18

[a] Clegg and Whitfield (1991).

in Figure 1) calculated according to eq 3 are illustrated in Figure 2. It is apparent that the agreement between the observed and calculated p$K_{a,m}$ values is satisfactory. These findings suggest that the γ_{m,NH_3} values determined directly in $(NH_4)_2SO_4$ solutions were estimated to be larger than the true values. However, in view of the fact that the γ_{m,NH_3} value in a given $(NH_4)_2SO_4$ solution, the measurements of which were repeated a few times, had a reproducibility, the reason for the discrepancy is not clear at the present stage of investigation.

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