Application of Pitzer's Equations to Dissociation of Ammonium Ion in Concentrated Aqueous Electrolyte Solutions. A Review

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The Pitzer approach was applied to the evaluation of dissociation constants of ammonium ion in concentrated electrolyte solutions. The calculated values showed good agreement with the observed values, provided all the higher-order terms concerned were introduced.

KEY WORDS: Pitzer's ionic interaction theory; ammonium ion; ammonia: dissociation constant; activity coefficient

1. INTRODUCTION

In previous work⁽¹⁻¹²⁾ we applied ionic interaction theories developed by Brønsted, Scatchard, and Guggenheim^(13,14) and by Pitzer⁽¹⁴⁾ to the prediction of dissociation constants and enthapies of dissociation of the ammonium ion and of ionic products of water in various concentrated electrolyte solutions and compared the theoretically evaluated values with measured data.

The present paper is concerned with the application of Pitzer's equations to the dissociation constants of ammonium ion in concentrated LiCl, NaCl, KCl, NH₄Cl, LiNO₃, NaNO₃, KNO₃, NH₄NO₃, LiClO₄, NaClO₄, LiCl-NaCl, (NH₄)₂SO₄, and Na₂SO₄ solutions. Our previous results are surveyed by re-evaluation of some of the previous data to demonstrate the validity of the Pitzer approach to the evaluation of the activity coefficients of ionic species in these concentrated electrolyte solutions.

The dissociation constant of ammonium ion $K_a(I)$ in molal units in the 1:1 electrolyte solutions listed above at ionic strength I in molal units with the exception of $(NH_4)_2SO_4$ and Na_2SO_4 is defined as

$$K_{\rm a}(I) = [{\rm H}^+][{\rm NH}_3]/[{\rm NH}_4^+],$$
 (1)

where $[\]$ denotes the molal concentration. For $(\rm NH_4)_2SO_4$ and $\rm Na_2SO_4$ solutions the dissociation constant of ammonium ion is given by

$$K_{a}(I) = ([H^{+}] + [HSO_{4}^{-}])[NH_{3}]/[NH_{4}^{+}], \quad (2)$$

which takes into account the dissociation of HSO_4^- .

The thermodynamic relationship between the dissociation constant of ammonium ion $K_a(I)$ and the activity coefficients, γ in molal units of the reacting species at ionic strength I is given by

 $pK_a(I) = pK_a + (\ln \gamma_{H^+} + \ln \gamma_{NH3} - \ln \gamma_{NH4^+})/\ln 10$ (3)

for the 1:1 electrolyte solutions and by

$$pK_{a}(I) = pK_{a} + (\ln \gamma_{H+} + \ln \gamma_{NH3} - \ln \gamma_{NH4+}) / \ln 10 - \log \{1 + (I/3) [\gamma_{HSO4-} / (K_{a + HSO4-} \gamma_{H+} \gamma_{SO4-} 2_{-})]\}$$
(4)

for the $(NH_4)_2 SO_4$ and $Na_2 SO_4^+$ solutions, where $K_a = a_{\rm H+} a_{\rm NH3} / a_{\rm NH4+}$ for the dissociation of NH₄⁺ and $K_{
m a,HSO4}$ _ = $a_{
m H+}a_{
m SO4}$ _ 2-/ $a_{
m HSO4}$ _ for the dissociation of HSO_4^- (a = activity of species indicated). The pK_a value of 9.245 at 298.15 K has been reported by Bates and Pinching⁽¹⁵⁾ and that for HSO_4^- of 1.979 at 298.15 K has been reported by Clegg et al⁽¹⁶⁾. With the known pK_a and $pK_{a,HSO4}$ – values,, Eqs.(3) and (4) permit the $pK_{a}(I)$ values to be calculated provided the activity coefficients of the species involved in the dissociations can be theoretically estimated by the Pitzer equations. Activity coefficients of neutral NH₃ have been determined by us and recently, values for Pitzer's interaction parameters of NH3 with ions have been evaluated by Clegg et al.^(17,18) from partial pressure, solubility, and partitioning data of NH₃ in electrolyte solutions.

2. PITZER'S EQUATIONS

Equations required in the present treatment were derived from Pitzer's equations in molal units for the ionic and neutral species.⁽¹⁴⁾

The logarithm of the activity coefficients γ_c for H^+ ions and NH_4^+ ions in all the electrolyte solutions MX (but not in the ammonium salt solutions), where both kinds of the ions are present in traces, is derived at 298.15 K by using

$$\ln \gamma_{\rm c} = f^{\gamma} + 2I(B_{\rm cX} + IC_{\rm cX}) + I^2(B_{\rm MX}' + C_{\rm MX})$$
$$+ I(2\theta_{\rm cM} + I\phi_{\rm cMX})$$
(5).

An analogous relationship can be written for $HSO_4^$ ions, which are also present in traces, in the $(NH_4)_2SO_4$ and Na_2SO_4 solutions. The activity coefficient γ_{NH4^+} of NH_4^+ ions in the ammonium salt solutions NH_4X can be calculated for

$$\ln \gamma_{\rm NH4-} = f^{\gamma} + 2I(B_{\rm NH4X} + IC_{\rm NH4X}) + I^2(B_{\rm NH4X}' + C_{\rm NH4X})$$
(6).

A similar equation is derived for anionic SO_4^{2-} ions in the $(NH_4)_2$ SO₄ and Na₂SO₄ solutions. In the above equations

$$f^{\gamma} = -0.392[I^{1/2}/(1+1.2I^{1/2}) + (2/1.2)\ln(1+1.2I^{1/2})]$$
(7)

$$B_{cx} - \beta_{cx} + (\beta_{cx} / 2I) [1 - (1 + 2I)]$$

$$exp(-2I^{1/2})]$$
(8)

$$B_{cX}' = (\beta_{cX}^{(1)}/2I) [-1 + (1 + 2I^{1/2} + 2I) exp(-2I^{1/2})]$$
(9)

and

$$C_{\rm c} = C_{\rm cX}^{\phi} / 2\sqrt{|z_{\rm c} | z_{\rm x}|}$$

(where z = charge of ion indicated) (10)

in the systems other than the $(NH_4)_2SO_4$ system in which $C_{\rm eX}$ was expressed as

$$C_{\rm cX} = C_{\rm cX}^{(0)} + 4C_{\rm cX}^{(1)}h(2.5\sqrt{I})$$
(11)

, where $h(x) = \{6 - [6 + x(6 + 3x + x^2)\exp(-x)\} / x^4$.⁽¹⁶⁾ Values for $\beta^{(0)}, \beta^{(1)}, C^{\phi}, C^{(0)}, \text{ and } C^{(1)}$ which are constants and independent of *I* have been calculated from the activity and osmotic coefficient data for single electrolytes.⁽¹⁴⁾ These parameters used in the present paper are given in Tables 1 and 2. The higher-order terms θ_{CM} and ϕ_{CMX} are related to like-charge interaction between c and M ions and triplet

species	$\boldsymbol{\beta}^{(0)}$	$\boldsymbol{\beta}^{(1)}$	C^{ϕ}
H ⁺ Cl	0.1775	0.2945	0.00080
H^{+} NO_{3}^{-}	0.1168	0.3546	-0.00539
$\mathrm{H^{+}-ClO_{4}}$	0.1747	0.2931	0.00819
NH ⁺ ₄ Cl ⁺	0.0522	0.1918	-0.00301
$\mathrm{NH_4^+}$ $\mathrm{NO_3^-}$	-0.0154	0.1120	-0.00003
$\rm NH_4^+$ $\rm ClO_4^-$	-0.0103	-0.0194	
Li^+ Cl^-	0.1494	0.3074	0.00359
Na ⁺ Cl ⁻	0.0765	0.2664	0.00127
K ⁺ Cl ⁻	0.04835	0.2122	-0.00084
Li ⁺ NO ₃ ⁻	0.1420	0.2780	-0.00551
$Na^+ NO_3^-$	0.0068	0.1783	-0.00072
$\mathrm{K^{+}}$ $\mathrm{NO_{3}^{-}}$	-0.0816	0.0494	0.00660
${\rm Li^+}$ ${\rm ClO_4^-}$	0.1973	0.3996	0.0008
Na ⁺ ClO ₄ ⁻	0.0554	0.2755	-0.00118
Na^+ SO_4^{2-}	0.0187	1.10	0.00277
${\rm NH_{4}^{+}~SO_{4}^{2-}}$	0.0409	0.659	-0.000581
Na^+ HSO_4^-	0.0454^{b}	0.398	0
H ⁺ SO ₄ ²⁻	0.0298 ^b	0	0.0438

^{a)}Ref.14 except as noted ^bRef.24

Table 2 Ion-Ion Interaction Parameters for H_2SO_4 -(NH4) $_2SO_2$ System at 298.15 K

species	$\boldsymbol{\beta}^{\scriptscriptstyle(0)}$	$\boldsymbol{\beta}^{(1)}$	C ⁽⁰⁾	<i>C</i> ⁽¹⁾
H^+ HSO_4^{-a}	0.2959	0.4005	-0.005685	-0.4094
$H^{+} SO_{4}^{2-a}$	0.0084	0.3147	0.01019	-0.3237
NH ⁺ ₄ HSO ^{- b)}	0.0328	0.4684	0.001153	-0.3487
$\rm NH_4^+ SO_4^{2-b}$	0.0374	0.5345	-0.0002176	0.1643

^{a)}Ref.16 ^bRef.19

interactions among C, M, and X ions, respectively. In the present paper both terms were regarded as independent of *I*. The higher-order terms have been estimated from the data for mixed electrolytes,⁽¹⁴⁾ but there is a paucity of data. Thus, some of the higherorder terms associated with NH_4^+ ion interactions, which are not available in the literature, were determined by isopiestic measurements. Values for the higher-order terms θ and ϕ used in the present work are given in Table 3.

The Pitzer equation for the activity coefficient for the neutral species NH_3 in MX solutions, where the concentration of NH_3 is low enough compared to that of MX, is given by

in
$$\gamma_{\text{NH3}} = 2\lambda_{\text{NH3M}} m_{\text{M}} + 2\lambda_{\text{NH3X}} m_{\text{X}} + \xi_{\text{NH3X}} m_{\text{M}} m_{\text{X}}$$
 (12),

where λ and ξ are constants independent of *I*, and *m* denotes the molality of species indicated. Values for λ

Table 1 Ion-Ion Interaction Parameters at 298.15 K^{a}

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n	Ē	:
4	¢)

	species	5			
i	j	k	$ heta_{ m ij}$	$oldsymbol{\psi}_{ m ijk}$	Ref.
H+	Li+	Cl-	0.015	0.000	14
H+	Na^+	Cl ~	0.036	-0.004	14
H^+	\mathbf{K}^+	$C1^-$	0.005	-0.007	14
H^+	Li^+	NO_3^{-a}			
H^+	Na ⁺	$\rm NO_3^-$	-0.011	0.0	This work
H^+	K^+	$\rm NO_3^-$	0.005	-0.015	5,22
H^+	Li +	ClO_4^-	0.015	-0.0017	14
H+	Na^+	ClO_4^-	0.036	-0.016	14
Η+	$\rm NH_4^+$	Cl ⁻	-0.0128	-0.0087	23
			-0.039	-0.0051	9
H^+	$\rm NH_4^+$	$\rm NO_3^-$	-0.065	0.011	6
$\rm NH_4^+$	Li ⁺	$C1^-$	-0.027	-0.011	10
$\rm NH_4^+$	Na^+	$C1^-$	0.0040	0.0005	7
$\rm NH_4^+$	K^+	Cl-	-0.065	0.036	9
NH_4^+	Li^+	NO3 a			
$\rm NH_4^+$	Na ⁺	$\rm NO_3^-$	-0.0166	0.0025	23
$\rm NH_4^+$	${ m K}^+$	NO_3^-	0.087	-0.048	This work
$\rm NH_4^+$	Li ⁺	ClO_{4}^{-}	-0.010	-0.0210	7
NH_4^+	Na^+	$\mathrm{ClO_4^-}$	0.059	-0.025	This work
$\rm NH_4^+$	H^+	HSO_4^-	-0.019	-0.00865	19
$\rm NH_4^+$	H^+	$\mathrm{SO_4}^{2-}$	-0.019	-0.02245	19
$\mathrm{NH_4^+}$	HSO_4^-	$\mathrm{SO_4}^{2-}$		-0.00842	19
H^+	Na+	$\mathrm{SO_4}^{2-}$	0.036	0	14
$\mathrm{NH_4^+}$	Na ⁺	$\mathrm{SO_4}^{2-}$	0	-0.0013	14
HSO_4^-	$\mathrm{SO}_4{}^{2-}$	Na^+	0	-0.0094	14

Table 3 Higher-Order Parameters θ_{ij} and ϕ_{ijk} at 298.15 K

^aSince neither θ_{HLi} and ψ_{HLiNO3} values nor θ_{NH4Li} and ψ_{NH4LiNO3} values are available in the literature, none of the values for the four terms are determinable by the fitting method.⁽⁹⁾

Table 4 Interaction Parameters for Eq.(12) for NH_3 at 298.15 K^a

species					
i	$\lambda_{i,NH3}$	i	j	$\lambda_{i, \rm NH3}$	ξ _{i, j, NH3}
NH_3	0.01472	NO_3^-		-0.01	
Li^+	-0.038	ClO_4^-		-0.056	
Na^+	0.0175	$\mathrm{SO}_4{}^{2-}$		0.140	
				0.173^{b}	
\mathbf{K}^+	0.0454	$\rm NH_4^+$	$\mathrm{SO}_4{}^{2-}$		-0.00918
					-0.0110^{b}
$\rm NH_4^+$	0.0				
Cl ⁻	0.0				

*Ref.18 except as noted b This work

and ξ in the present electrolyte solutions evaluated by Clegg and Whitfield⁽¹⁸⁾ are given in Table 4.

The Pitzer equation for the osmotic coefficient $\phi_{\rm NH4MX}$ in the mixed solution of NH₄X and MX is given by

$$b_{\rm NH4MX} - 1 = [2/(m_{\rm NH4} + m_{\rm M} + m_{\rm X})] \{If^{\,\phi} + m_{\rm NH4}m_{\rm X} \\ [B_{\rm NH4X}^{\,\phi} + (m_{\rm NH4} + m_{\rm M} + m_{\rm X})C_{\rm NH4X}^{\,\phi}] \\ + m_{\rm M}m_{\rm X}[B_{\rm MX}^{\,\phi} + (m_{\rm NH4} + m_{\rm M} + m_{\rm X})C_{\rm MX}^{\,\phi}] \\ + m_{\rm NH4}m_{\rm M}(\theta_{\rm NH4M} + m_{\rm X}\phi_{\rm NH4MX})\}$$
(13)

where

$$f^{\phi} = -0.392[I^{1/2}/(1+1.2I^{1/2})]$$
(14)

$$B_{\rm MX}^{\ \phi} = \beta_{\rm MX}^{\ (0)} + \beta_{\rm MX}^{\ (1)} \exp(-2I^{1/2}) \tag{15}$$

3. EXPERIMENTAL

3.1 Dissociation constants of NH₄⁺

The dissociation constants of NH_4^+ ion at 298.15 K in the electrolyte solutions were determined by glasselectrode potentiometry, as has been described in previous papers.^(4,10)

3.2 Activity coefficients of NH₃

Two methods were employed for these measurements. First, measurements of the partition of NH₃ between the electrolyte solution and chloroform phases were used to estimate $\gamma_{\rm NH3}$ in LiNO₃, NaNO₃, KNO₃, LiClO₄, and NaClO₄ solutions.⁽¹⁾ Second, a transpiration method, in which the NH₃ gas dissolved in an electrolyte solution was transpired by a carrier gas to an HCl solution, the change in conductivity of which was measured, was employed for the measurement of $\gamma_{\rm NH3}$ in the other electrolyte solutions. The experimental procedures have been described in detail in previous papers.^(5,6)

3.3 Isopiestic Measurement

The measurements of osmotic coefficients of NH_4X -MX mixtures used an apparatus similar to that employed by Kirgintsev and Luk'yanov⁽²⁰⁾ and Michimoto *et al.*⁽²¹⁾ Details about the experimental procedures have been described in a previous paper.⁽⁶⁾

4. EXPERIMENTAL RESULTS

4.1 Dissociation Constants of NH₄⁺

The dissociation constants as $pK_a(I)$ are plotted in Fig.1 as a function of I. The plots of the $(NH_4)_2SO_4$ and Na_2SO_4 systems are shown in Figs.2 and 3, respectively. The $pK_a(I)$ values increase generally with increasing ionic strength in the electrolyte solutions excepting the sulfate solutions in which,



Fig.1 Plots of observed $pK_a(I)$ values vs. ionic strength I in (\bigcirc) LiCl, (\bigcirc) NaCl, (\bigcirc) KCl, (\bigcirc) NH₄Cl, (\triangle) LiNO₃, (\triangle) NaNO₃, (\triangle) KNO₃, (\triangle) NH₄NO₃, (\triangle) NH₄NO₃, (\diamondsuit) LiClO₄, and (\diamondsuit) NaClO₄, solutions. (\bigoplus) thermodynamic pK_a value of 9.245. Data at I less than 0.5 mol kg⁻¹ are not plotted for simplicity.



Fig.3 Comparison of the $pK_a(I)$ values measured in Na₂SO₄ with those calculated with the Pitzer equations:filled symbol:thermodynamic pK_a value of 9.245;open symbol:observed;solid line:calculated with $\gamma_{\rm NH3}$ values from the Pitzer equation Eq.(12) by use of the parameter values in Table 4.

 pK_a decrease abruptly with an increase in ionic strength and then, slightly increase. pK_a in the sodium chloride and perchlorate solutions depend most strongly on the ionic strength, while the dependence of



Fig.2 Comparison of the $pK_a(I)$ values measured in $(NH_4)_2 SO_4$ with those calculated with the Pitzer equations:filled sysmbol:thermodynamic pK_a value of 9.245; open symbol:observed; solid line: calculated with γ_{NH3} values from the Pitzer equation Eq.(12) by use of the parameter values in Table 4; broken line: calculated with observed γ_{NH3} values



Fig.4 Plots of observed $\ln \gamma_{\text{NH3}}$ values vs, ionic strength *I* in LiCl, NaCl, KCl, and NH₄Cl solutions. The straight lines were calculated according to Eq.(12) by use of the parameter values in Table 4.

the values on the ionic strength in the ammonium chloride and nitrate solutions is the weakest and practically the same with each other.



Fig.5 Plots of observed $\ln \gamma_{\rm NH3}$ values vs. ionic strength *I* in LiNO₃, NaNO₃, KNO₃, and NH₄NO₃ solutions. The straight lines were calculated according to Eq.(12) by use of the parameter values in Table 4.

4.2 Activity Coefficients of NH₃

Log $\gamma_{\rm NH3}$, (in molal units) in LiNO₃, NaNO₃, KNO₃, LiClO₄, and NaClO₄ measured by the partition method and in the other electrolyte solutions measured by the transpiration method are plotted as a function of ionic strength *I* in Figs.4-6.

4.3 Higher-Order Terms Pertinent to NH₄⁺ interactions

The $\theta_{\rm NH4M}$ and $\phi_{\rm NH4MX}$ (where MX = LiCl, NaCl, and $LiClO_4$) values were determined by use of the osmotic coefficients $\phi_{\rm NH4MX}$ of the $\rm NH_4X\text{-}MX$ solutions. As was described in Section 2, rearrangement of Eq.(13) reveals that $\theta_{\rm NH4M} + m_{\rm X} \phi_{\rm NH4MX}$ can be plotted as a function of $m_{\rm X}$. The values for $\theta_{\rm NH4M}$ and $\phi_{\rm NH4MX}$ are obtained from the intercept and slope of the straight line, respectively. The $\theta_{\rm NH4M}$ and $\phi_{\rm NH4MX}$ values thus obtained in the NH₄Cl- LiCl, NH₄ClO₄-LiClO₄, and NH₄Cl-NaCl systems⁽⁶⁻⁸⁾ are listed in Table 3. The $\theta_{\rm NH4Li}$ value of -0.027 determined in the NH₄Cl-LiCl system is not identical with the corresponding value of -0.010 determined in the NH₄ClO₄-LiClO₄ system perhaps for the following reason. Due to the low solubility of NH_4ClO_4 the measurements in the NH_4ClO_4 -LiClO₄ system covered only limited and moderate ionic strengths between 1.4 and 1.9, where the contributions from the $heta_{
m NH4Li}$ and $\phi_{
m NH4LiClO4}$ terms to the



Fig.6 Plots of observed $\ln \gamma_{\rm NH3}$ values vs. ionic strength *I* in LiClO₄, NaClO₄, and $(\rm NH_4)_2SO_4$ solutions. The solid lines were calculated according to Eq.(12) by use of the parameter values in Table 4. The brocken line was calculated according to Eq.(12) by use of the parameter values $\lambda_{\rm NH3, SO4} = -0.173$ and $\xi_{\rm NH3, NH4+, SO4} = -0.0110$ estimated in the present work, the values being also given in Table 4.

osmotic coefficient $\phi_{\text{NH4LiCIO4}}$ may be rather small. Thus, the θ_{NH4Li} value obtained in the NH₄ClO₄-LiClO₄ system from the linear plot as the intercept may not be as accurate as the corresponding value in the NH₄ Cl-LiCl system, where the concentrations of NH₄Cl and LiCl were kept high and varied over a wide range.

5. DISCUSSION

5.1 Activity Coefficients of Ammonia

In the evaluation of the $\gamma_{\rm NH3}$ values by the partition method it is assumed that the chloroform phase is immiscible with the aqueous phase. However, there is a possibility that water may be dissolved in effect in the chloroform phase so that the dissolved water has an appreciable influence on the activity of NH₃ in the organic phase and thus on the activity of NH₃ in the electrolyte solution. Thus, the $\gamma_{\rm NH3}$ values in LiClO₄ solutions were measured also by the transpiration method and compared with those measured by the partition method. It was found that $\gamma_{\rm NH3}$ in the LiClO₄ solutions determined by both methods agreed with each other within experimental uncertainties.⁽³⁾ These results indicate that $\gamma_{\rm NH3}$ in the other electrolyte solutions determined by the partition method are

reasonable.

In $\gamma_{\rm NH3}$ in the various electrolyte concentrations were calculated according to Eq.12 using parameter values in Table 4⁽¹⁸⁾ and compared with the observed values in Figs.4-6. It is apparent that the agreement is rather good except for the sodium salt and $(\rm NH_4)_2SO_4$ systems. It has been pointed out by Clegg and Brimblecombe⁽¹⁷⁾ that $\lambda_{NH3 Na+}$ (0.034) calculated with the activity coefficients for NH₃ in NaNO₃ and NaClO₄ media measured by us is high compared to that from salt solubility data reported by other investigators. On the assumption of $\lambda_{NH3,NH4^+} = 0$, which was made by Clegg and Brimblecombe, $\lambda_{NH3,SO42-}$ and $\xi_{\rm NH3, NH4-, SO42-}$ were calculated to be 0.173 and -0.0110, respectively, with our data in the $(NH_4)_2SO_4$ solutions.⁽¹¹⁾ The absolute values calculated in the present work are larger compared to those ($\lambda_{\text{NH3,SO4 2-}}\!=\!0.138$ and $\xi_{\text{NH3,NH4}-,\text{SO4}2-} = -0.00918$) evaluated by Clegg and Brimblecombe. The discrepancy will be referred to in the evaluation of pK_a in the $(NH_4)_2SO_4$ solutions in Section 5.2.

5.2 Comparison of the observed Dissociation Constants with Those Calculated with Pitzer Equations

The calculations of $pK_a(I)$ in the various electrolyte solutions were carried out using Pitzer's equations described in Section 2.

5.2.1 Calculation of Dissociation Constants without Higher-Order Terms

Since higher-order terms in electrolyte solutions are not always available, first, the $pK_a(I)$ values in the various electrolyte solutions were calculated without them and compared with the observed values in Tables 5-15. It is clear that the estimated and observed values are roughly in agreement in the sodium salt and KCl solutions. Large discrepancies are observed in the other salt solutions especially at high molalities, indicating the higher-order terms cannot be neglected. The agreement in the sodium salt and KCl media may be the result of either the negligibly small contributions from the higher-order terms or a fortuitous cancellation of their contributions.

Table	5	Values of	f p $K_{\rm a}$ (in M	(lolal)	Observ	ed and
		Estimated	at 298.1	15 K	in Aq	ueous	Lithium
		Chloride	Solut	tions	wit	h I	Different
		Concentra	tions				

concn of		e	est
LiCl/mol kg ⁻¹	obsdª	with ^b	without ^b
1.022	9.39(1)	9.39	9.35
2.086	9.51(1)	9.50	9.41
3.197	9.66(1)	9.67	9.50
4.360	9.85(2)	9.84	9.59
5.582	10.08(2)	10.06	9.71

^aThe numbers in parentheses are uncertainties of the least significant figure. ^bWith and without higher-order terms $\theta_{\rm HLi} = 0.015$, $\phi_{\rm HLiCl} = 0.000$, $\theta_{\rm NH4Li} = -0.027$, and $\phi_{\rm NH4LiCl} = -0.011$.

Table 6Values of pK_a (in Molal) Observed and
Estimated at 298.15 K in Aqueous Sodium
Chloride Solutions with Different
Concentrations

concn of		e	est
NaCl/mol kg ⁻¹	obsd*	with ^b	without ^b
0.506	9.35(1)	9.35	9.34
0.725	9.41(1)	9.39	9.37
1.022	9.44(1)	9.44	9.42
2.087	9.60(2)	9.63	9.58
3.202	9.80(1)	9.81	9.74
4.373	10.01(2)	10.01	9.92
5.609	10.22(2)	10.20	10.11

^aThe numbers in parentheses are uncertainties of the least significant figure. ^bWith and without higher-order terms $\theta_{\rm HNa} = 0.036$, $\phi_{\rm HNaCl} = -0.004$, $\theta_{\rm NH4Na} = 0.004$, and $\phi_{\rm NH4NaCl} = 0.0005$.

Table 7Values of pK_a (in Molal) Observed and
Estimated at 298.15 K in Aqueous Potassium
Chloride Solutions with Different
Concentrations

conen of			est
KCl/mol kg ⁻¹	obsd*	with ^b	without ^b
0.1	9.37	9.27	9.27
0.2	9.37	9.30	9.28
0.5	9.38	9.37	9.34
1.0	9.46	9.47	9.42
1.03	9.47(1)	9.48	9.42
1.58	9.56(1)	9.57	9.50
2.0	9.62	9.63	9.57
2.72	9.71(1)	9.70	9.68
3.0	9.74	9.73	9.73

^aThe numbers in parentheses are uncertainties of the least significant figure. ^bWith and without higher-order terms $\theta_{\rm HK} = 0.005$, $\phi_{\rm HKCl} = -0.007$, $\theta_{\rm NH4K} = -0.065$, and $\phi_{\rm NH4KCl} = 0.036$.

Table	8	Values	of	$\mathbf{p}K$	C _a (i	n	Mo	lal)	Obse	rved	and
		Estimat	ed	at	298.	.15	Κ	in	Aque	ous	Am-
		monium	ı C	hloi	ride	\mathbf{Sc}	oluti	ons	with	Diff	erent
		Concent	rat	ions	3						

concn of			est	
NH ₄ Cl/mol kg ⁻¹	obsd*	with ^b	with ^c	without ^d
0.512	9.28(1)	9.30	9.29	9.31
1.054	9.35(1)	9.36	9.34	9.38
1.611	9.41(1)	9.42	9.39	9.45
2.201	9.45(1)	9.47	9.43	9.52
2.821	9.50(1)	9.53	9.48	9.59
3.475	9.54(1)	9.58	9.53	9.67
4.162	9.57(1)	9.64	9.58	9.76
4.887	9.62(1)	9.70	9.63	9.85
5.670	9.67(1)	9.76	9.69	9.95
6.480	9.72(1)	9.82	9.74	10.05

^aThe numbers in parentheses are uncertainties of the least significant figure. ^{bc,d} With and without^d higherorder terms; ^b $\theta_{\text{HNH4}} = -0.0128$ and $\phi_{\text{HNH4CI}} = -0.0087$ in Ref.20, ^c $\theta_{\text{HNH4}} = -0.039$, and $\phi_{\text{HNH4CI}} = -0.0051$ in Ref.9 evaluated by the fitting method.

Table 9Values of pK_a (in Molal) Observed and
Estimated at 298.15 K in Aqueous Lithium
Nitrate Solutions with Different
Concentrations

concn of		est
LiNO ₃ /mol kg ⁻¹	obsdª	without ^b
0.508	9.29(2)	9.32
1.033	9.37(1)	9.38
2.132	9.53(1)	9.49
3.307	9.69(1)	9.58
4.570	9.84(2)	9.66
5.922	10.01	9.75

^aThe numbers in parentheses are uncertainties of the least significant figure. ^bWithout higher-order terms due to the lack of their values, which were not determinable by the fitting method.

Table 10Values of pKa (in Molal) Observed and
Estimated at 298.15 K in Aqueous Sodium
Nitrate
Solutions with Different
Concentrations

concn of			est
NaNO ₃ /mol kg ⁻¹	obsd*	with ^b	without ^b
0.508	9.33(1)	9.35	9.35
1.033	9.43(1)	9.44	9.44
1.575	9.52(1)	9.53	9.52
2.137	9.60(1)	9.60	9.60
2.725	$9.69(1)^{\circ}$	9.69	9.68
3.322	9.78(1)	9.77	9.76
3.957	$9.86(1)^{\circ}$	9.86	9.86
4.603	9.94(2)	9.95	9.95
5.297	$10.03(1)^{\circ}$	10.04	10.04
6.002	10.12(2)	10.12	10.13

^aThe numbers in parentheses are uncertainties of the least significant figure. ^bWith and without higher-order terms $\theta_{\rm HNa} = -0.011$, $\phi_{\rm HNaNO3} = 0.0$, $\theta_{\rm NH4Na} = -0.0166$, and $\phi_{\rm NH4NaNO3} = 0.0025$. ^cMeasured in the present work.

Table 11Values of pK_a (in Molal) Observed and
Estimated at 298.15 K in Aqueous Potassium
Nitrate
Solutions with Different
Concentrations

concn of		est		
$\mathrm{KNO}_3/\mathrm{mol}\ \mathrm{kg}^{-1}$	obsd*	with ^{b}	without ^b	
0.512	9.32(1)	9.32	9.35	
1.045	9.36(1)	9.39	9.45	
1.602	9.47(1)	9.47	9.55	
2.186	9.55(1)	9.56	9.64	
2.799	9.64(1)	9.64	9.73	
3.446	9.73(1)	9.74	9.81	

^aThe numbers in parentheses are uncertainties of the least significant figure. ^bWith and without higher-order terms $\theta_{\rm HK} = 0.005$, $\phi_{\rm HKNO3} = -0.015$, $\theta_{\rm NH4K} = 0.087$, and $\phi_{\rm NH4KNO3} = -0.048$.

Table 12Values of pKa (in Molal) Observed and
Estimated at 298.15 K in Aqueous
Ammonium Nitrate Solutions with Different
Concentrations

concn of		(est
$\rm NH_4NO_3/mol~kg^{-1}$	obsd*	with ^b	without ^b
0.51	9.29(1)	9.32	9.34
1.06	9.35(1)	9.36	9.41
1.63	9.40(1)	9.39	9.47
2.22	9.45(1)	9.42	9.52
2.85	9.50(1)	9.45	9.57
3.54	9.54(1)	9.49	9.63
4.24	9.59(1)	9.53	9.68
5.01	9.64(1)	9.58	9.74
5.83	9.68(1)	9.63	9.80
6.70	9.73(1)	9.70	9.86
7.62	9.76(1)	9.77	9.92
8.61	9.81(1)	9.86	9.99
9.66	9.88(1)	9.96	10.06
10.82	9.91(1)	10.09	10.13

^aThe numbers in parentheses are uncertainties of the least significant figure. ^bWith and without higher-order terms $\theta_{\text{HNH4}} = -0.065$, and $\phi_{\text{HNH4NO3}} = 0.011$.

Table 13Values of pK_a (in Molal) Observed and
Estimated at 298.15 K in Aqueous Lithium
Perchlorate Solutions with Different
Concentrations

concn of		est		
LiClO ₄ /mol kg ⁻¹	obsd*	with ^b	without ^b	
0.512	9.34(1)	9.35	9.34	
1.049	9.44(1)	9.44	9.41	
1.583	9.52(1)	9.51	9.46	
2.202	9.63(1)	9.63	9.54	
3.481	9.84(1)	9.83	9.66	

"The numbers in parentheses are uncertainties of the least significant figure. ^bWith and without higher-order terms $\theta_{\text{HLi}} = -0.015$, and $\phi_{\text{HLiCIO4}} = -0.0017$, $\theta_{\text{NH4Li}} = -0.010$, and $\phi_{\text{NH4LiCIO4}} = -0.0210$.

concn of		est		
$\underline{\text{NaClO}_4/\text{mol kg}^{-1}}$	obsd*	with ^b	without ^b	
0.512	9.34(1)	9.36	9.37	
1.046	9.46(1)	9.48	9.49	
1.614	9.56(1)	9.57	9.59	
2.205	9.67(1)	9.66	9.69	
2.822	9.77(1)°	9.77	9.79	
3.486	9.89(1)	9.89	9.91	
4.174	10.03(1)°	10.02	10.03	
4.919	10.16(1)	10.17	10.17	

Table 14Values of pK_a (in Molal) Observed and
Estimated at 298.15 K in Aqueous Sodium
Perchlorate Solutions with Different
Concentrations

^aThe numbers in parentheses are uncertainties of the least significant figure. ^bWith and without higher-order terms $\theta_{\rm HNa} = 0.036$, $\phi_{\rm HNaClO4} = -0.016$, $\theta_{\rm NH4Na} = 0.059$, and $\phi_{\rm NH4NaClO4} = -0.025$. ^cmeasured in the present work.

Table 15Values of $pK_a(I)$ (in Molal) Observed and
Estimated at 298.15 K in Aqueous LiCl-NaCl
Mixed
Solutions with Different
Concentrations

concn of	concn of			est
LiCl/mol kg ⁻¹	NaCl/mol kg ⁻¹	obsdª	with ^{b}	without ^b
0.744	2.478	9.77(1)	9.76	9.67
1.051	2.196	9.74(1)	9.73	9.63
1.600	1.600	9.70(1)	9.71	9.59
1.817	1.428	9.70(1)	9.70	9.58
2.430	0.807	9.69(1)	9.70	9.55

^aThe numbers in parentheses are uncertainties of the least significant figure. ^bWith and without higher-order terms $\theta_{\rm HLi} = 0.015$, $\phi_{\rm HLiCl} = 0.000$, $\theta_{\rm NH4Li} = -0.027$, $\phi_{\rm NH4LiCl} = -0.011$, $\theta_{\rm HNa} = 0.036$, $\phi_{\rm HNaCl} = -0.004$, $\theta_{\rm NH4Na} = 0.004$, and $\phi_{\rm NH4NaCl} = 0.0005$.

 Table 16 Values of pK_a(I) (in Molal) Observed and Estimated at 298.15 K in Aqueous Ammonium Sulfate Solutions with Different Ionic Strengths

$I/\mathrm{mol}~\mathrm{kg}^{-1}$	obsd*	est^{\flat}	est°
0.76	8.76(1)	8.73	8.74
1.55	8.79(1)	8.69	8.70
2.36	8.68(1)	8.67	8.70
3.20	8.67(1)	8.67	8.71
4.98	8.70(1)	8.69	8.73
6.91	8.71(1)	8.70	8.76
9.01	8.74(1)	8.72	8.79

"The numbers in parentheses are uncertainties of the least significant figure. ^bEstimated with observed $\gamma_{\rm NH3}$ "Estimated with $\gamma_{\rm NH3}$ calculated using Eq.(12)

E S S	stimate ulfate trongth	ed at 298.15 Solutions	K in with	Aqueous 3 Different	Sodium Ionic
I/mol k	rength rg ⁻¹	obsdª		est	

Table 17 Values of $pK_a(I)$ (in Molal) Observed and

I/mol kg	obsd"	est
0.21	8.89(1)	8.85
0.32	8.77(1)	8.79
0.75	8.76(1)	8.74
1.06	8.74(1)	8.74
1.52	8.74(1)	8.75
1.83	8.76(1)	8.76
2.14	8.76(1)	8.77
2.45	8.77(1)	8.80
2.78	8.77(1)	8.81
3.09	8.83(1)	8.83
3.26	8.82(1)	8.84
3.41	8.84(1)	8.85
3.72	8.84(1)	8.86

"The numbers in parentheses are uncertainties of the least significant figure.

5.2.2 Calculation of Dissociation Constants with All the Needed Higher-Order Terms

The $pK_a(I)$ in LiCl, NaCl, LiClO₄, NH₄Cl and LiCl-NaCl media were calculated by introduction of all the needed higher-order terms ; the need for these terms was determined by the accuracy of reproduction of the observed $pK_a(I)$. Besides θ_{HM} and ψ_{HMX} (where MX=LiCl, NaCl, and LiClO₄) values, which are available in the literature (Table 3), $\theta_{\rm NH4M}$ and $\psi_{\rm NH4MX}$ required for LiCl, NaCl and LiClO₄ media (which are not available in the literature) were determined from isopiestic measurements⁽⁶⁻⁸⁾. Only θ_{HNH4} and ψ_{HNH4Cl} , which are found in the literature (Table 3), are introduced for the NH₄Cl system. The $pK_a(I)$ values in LiCl, NaCl, LiClO₄, NH₄Cl, and LiCl-NaCl media calculated with all the needed higher-order terms are compared with the observed values in Tables 5, 6, 13, 8, and 15, respectively. It is clear that for the LiCl, NaCl, LiClO₄, and LiCl-NaCl systems, the values calculated with all the needed higher-order terms agree with the measured data within the experimental uncertainties.

The large deviations especially at high molality levels in the NH₄Cl system will be discussed below in Section 5.2.3.

The calculations of $pK_a(I)$ values in the $(NH_4)_2SO_4$ solutions were carried out using the extended Pitzer equations derived by Clegg et al.,⁽¹⁶⁾

using the ion-ion interaction parameter values in Tables 2 and 3 and the $\gamma_{\rm NH3}$ experimentally determined. The p $K_{\rm a}(I)$ values thus calculated are compared with the observed data in Table 16 and in Fig.2. It is obvious that there are discrepancies beyond the experimental uncertainties. As a second estimation of p $K_{\rm a}(I)$, $\gamma_{\rm NH3}$ calculated according to Eq.(12) using the parameters in Table 4 were employed. The $\gamma_{\rm NH3}$ obtained are illustrated in Fig.2 and also given in Table 16. It is clear that the agreement is satisfactory. These findings suggest that $\gamma_{\rm NH3}$ determined directly in the (NH₄)₂SO₄ solutions are larger than the true values. However, the measurements were repeated a few times and had a good reproducibility, so that the reason for the discrepancy is not clear at present.

 $pK_a(I)$ calculated in the Na₂SO₄ system are compared with the measured data in Table 17 and in Fig.3. It may be said that the agreement is rather good, although some data exceed the experimental uncertainties.

5.2.3 Estimation of Unknown Higher-Order Terms

Since $\theta_{\rm HK}$ and $\phi_{\rm HKCl}$ for KCl, $\theta_{\rm NH4Na}$ and $\phi_{\rm NH4NaNO3}$ for NaNO₃, $\theta_{\rm HK}$ and $\phi_{\rm HKNO3}$ for KNO₃, and $\theta_{\rm HNa}$ and $\phi_{\rm HNaClO4}$ for NaClO₄ medium are available in the literature (Table 3), their unknown counterparts, e.g., for $\theta_{\rm HNH4}$ and $\phi_{\rm HNH4NO3}$ for the NH₄NO₃ medium are estimated by the fitting method.⁽⁹⁾

Equation 16 is derived from the difference between the observed $pK_a(I)$ and the values calculated with $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} but with θ_{HNH4} and $\phi_{\text{HNH4NO3}}=0$, e.g., in the NH4NO3 system, according to the Pitzer equations described in Section 2

$$[pK_{a}(I)(calc) - pK_{a}(I)(obsd)] \ln 10/I$$

= $2\theta_{\text{NH4K}} + I\phi_{\text{NH4KCl}}$ (16).

The quantity on the left-hand side of Eq.(16) was calculated as a function of I for each system by use of the relevant parameters in Tables 1 and 3 and the observed $pK_a(I)$, the data at low I values, where uncertainties may be magnified, being discarded. As expected from Eq.(16), plots of $2\theta + I\phi$ vs. I gave a straight line for each system. Values for θ and ϕ obtained from the intercept and the slope are given in Table 3. $pK_a(I)$ for KCl, NaNO₃, KNO₃, and NaClO₄ systems calculated with all the necessary high-order parameters are compared with the observed ones in Tables 7, 10, 11, and 14, respectively. The agreement is good in all the systems examined.

As was described for the NH₄Cl system in Section 5.2.2, the good agreement between the observed and calculated pK_a values at molalities less than 3 was observed, while large deviations occurred at the higher molalities. The behavior may be attributed to the fact that $heta_{ ext{HNH4}}$ and $\phi_{ ext{HNH4Cl}}$ in Table 3 have been determined for activity data for HCl in the HCl-NH4Cl aqueous system up to 3 mol kg^{-1} .⁽²³⁾ Therefore, the higher-order parameters may give poorer agreement beyond 3 mol kg⁻¹. The higher-order parameters were evaluated over the NH₄Cl concentration range of 0.5- 6.5 mol kg^{-1} using Eq.(16). The parameter thus evaluated are given in Table 3, and the $pK_a(I)$ calculated with the new parameter are compared with the observed values in Table 8. The agreement is almost within the experimental uncertainties over the whole molality range examined.

These results indicate that the $pK_a(I)$ values can be predicted with high accuracy even in concentrated salt solutions, if all the higher-order terms concerned are introduced. However, there is a paucity of higherorder parameter data. Thus, the fitting procedures may be a convenient means for the practical evaluation of higher-order parameters.

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