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Prediction of Dissociation Constants of Ammonium Ion in Artificial Seawaters and in Concentrated Sodium Chloride Solutions

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The dissociation constants of ammonium ion were determined at 25 °C by potentiometry with glass and ammonium-ion-selective electrodes in artificial seawaters at various salinities (25—45 ‰) and in concentrated sodium chloride aqueous solutions (0.72—3.2 mol kg^{-1}). The activity coefficients of ammonia in sodium chloride solutions of the same ionic strengths as those of the artificial seawaters and in the concentrated sodium chloride solutions, which were used for the theoretical estimation of the dissociation constants, were measured by a transpiration method. The dissociation constants were theoretically evaluated in terms of the ionic interaction model developed by Pitzer and co-workers, and compared with the experimental ones. The predicted dissociation constants showed a good agreement with the observed ones.

The majority of the values of thermodynamic properties such as free energy and enthalpy changes for ionic equilibria have been determined in solution containing an inert salt at a high and constant concentration.[1-3] The high electrolyte concentration is employed mainly in order to decrease the variation of the activity coefficients of the reacting species. The natural consequence is that the values of these thermodynamic properties are strongly influenced by the type and concentration of the electrolyte. Thus, the theoretical evaluation of these properties in a specified solution, or the recalculation from one ionic medium to another, is of theoretical as well as practical interest. From a theoretical point of view, the problem is reduced to estimating the effect of the ionic medium on the activity coefficients of the species participating in the ionic equilibria. The estimation of the activity coefficients of the relevant ionic species in concentrated single and mixed electrolyte solutions has been made by using various specific ion interaction theories.[4,5] Various important improvements to these theories have been made in recent years by Pitzer and coworkers.[6,7] The main point in the treatment is the consideration of short-range interactions between the species in solution through two second virial coefficient factors, $\beta^{(0)}$ and $\beta^{(1)}$, which can be a function of ionic strength. The equations derived, with various values of the β parameters along with the values of higher order electrostatic terms, give excellent fits to the experimental results up to the substantially high concentration level.

In previous works[8,9] the dissociation constant of ammonium ion, K_a,

$$NH_4^+ = H^+ + NH_3;\ K_a = [H^+][NH_3]/[NH_4^+]$$

was evaluated in $LiNO_3$, $NaNO_3$, $LiClO_4$, and $NaClO_4$ media with different concentrations (0.5—5 mol dm^{-3}) in terms of both the Brønsted-Guggenheim-Scatchard (BGS)[4,5] and the Pitzer ionic interaction models.[6,7] The predicted and observed values agreed fairly well, although in the lithium salt systems at higher concentration levels the deviations between the estimated and observed values exceeded by far the experimental uncertainties. As far as the sodium salt solutions were concerned, it was found that the values evaluated according to the Pitzer approach were in closer agreement with the observed ones than the values from the BGS approach. The Pitzer ionic interaction theory was successfully applied also to the evaluation of enthalpy changes for dissociation of ammonium ion in LiCl, NaCl, $LiNO_3$, $NaNO_3$, $LiClO_4$, and $NaClO_4$ media with different concentrations (0.5—5 mol dm^{-3}).[10]

In the present work the pK_a values for ammonium ion in artificial seawaters at salinites of 25, 30, 35, 40, and 45‰, the values at 35 and 45‰ being already reported by Khoo et al.,[11] and in the sodium chloride solutions of 0.72—3.2 mol kg^{-1} were determined at 25 °C by potentiometry with glass and ammonium-ion-selective electrodes. The activity coefficients of ammonia (γ_{NH_3}) in sodium chloride solutions at the same ionic strengths as those of the artificial seawaters and in the concentrated sodium chloride solutions were measured by a transpiration method. Since the γ_{NH_3} values in the seawaters could not be measured due to the precipitation of $Mg(OH)_2$ caused by the addition of ammonia, the experimental values for the sodium chloride solutions at the same ionic strengths must be employed. The observed pK_a values were compared with those calculated with the measured γ_{NH_3} values and the activity coefficients of H^+ and NH_4^+ evaluated in terms of the model developed by Pitzer and coworkers.

Whitfield[12,13] estimated the pK_a values for ammonium ion in artificial seawaters and sodium chloride solutions (0.5—3 mol dm^{-3}) according to a few different ionic interation approaches, and compared them with the values reported previously. It does not seem clear whether the agreement is satisfactory especially in the sodium chloride solutions, because of the divergence of the experimental values. In his calculations the γ_{NH_3} values used for the seawaters and concentrated sodium chloride solutions were just read from a straight line drawn through the reference point at infinite dilution (ionic strength $I=0$, $\gamma_{NH_3}=1$) and the γ_{NH_3} values measured at 0.5, 1.0, and 1.5 mol dm^{-3} NaCl by Abegg and Riesenfeld[14] or a straight line drawn between the reference point at infinite dilution and the mean of the experimental values reported previously in electrolyte solutions at an ionic strength of 0.7 mol dm^{-3}.[14-16]

Experimental

Reagents. Sodium chloride of primary analytical standard quality was dried at 360 °C in an electric furnace and used without further purification. Reagent-grade ammonium chloride was recrystallized twice from water. A stock solution of ammonium chloride was analyzed gravimetrically for Cl^- as AgCl. Other salts and ammonia, of reagent quality, were used without further purification. Artificial seawaters were prepared according to Khoo et al.[11] The molal compositions of the artificial seawaters at five different salinities are shown in Table 1. The ionic strengths were calculated in the usual way with neglect of ion pairing.

Potentiometric Titration Procedures. The dissociation of ammonium ion was monitored by measuring the equilibrium hydrogen-ion and ammonium-ion concentrations with a glass electrode and an ammonium-ion-selective electrode, respectively. The emf's were measured for the cell of the type

GE, NH_4^+-ISE| test solution $\vdots\vdots$ ref

where GE and NH_4^+-ISE denote a glass electrode and an ammonium-ion-selective electrode, respectively, and ref the reference half-cell, e.g., in the artificial seawater of 35‰ salinity.

$\vdots\vdots$ 35‰ artificial seawater $\vdots\vdots$ 0.72 mol kg^{-1}
NaCl, satd. AgCl| AgCl-Ag

From the emf's the equilibrium hydrogen-ion and ammonium-ion concentrations were calculated according to the equations

$$E^{H}=E^{H}_{0}+59.16\log[H^+]+E_j, \qquad (1)$$

$$E^{NH_4}=E_0^{NH_4}+59.16\log[NH_4^+]+E_j, \qquad (2)$$

where E_0's are constants, which were determined in situ in solution of known hydrogen-ion and ammonium-ion concentrations. E_j is a liquid junction potential arising between the test solution and the salt bridge. The 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. The potentiometric titrations were performed by coulometric generation of OH^- ions.

A glass electrode of Beckman No.39314 and an ammonium-ion-selective liquid membrane electrode purchased from Denki Kagaku Keiki (DKK) were used in combination with a silver-silver chloride reference electrode prepared as recommended by Brown.[17] The emf's were measured (up to 0.1 mV) with pH meters(DKK, Ion-Meter model IOC-10). The titration cell was of the type designed by Tsukuda et al.[18] It was kept in a paraffin oil-thermostat maintained at 25.00±0.02 °C in a room thermostated at 25±1 °C. The hydroxide ions were generated by means of a coulometer (Metrohm, Coulostat E524) using the analogous cell assembly to that described by Biedermann and Ciavatta.[19] To avoid losses of ammonia the titration cell was kept tightly closed. Stirring was performed with a magnetic rod.

Table 1. Molal Compositions of Artificial Seawaters at Five Salinities

Component and ionic strength I	Salinity/‰				
	25.24	30.20	35.11	40.00	44.84
NaCl	0.3041	0.3657	0.4274	0.4893	0.5514
$MgCl_2$	0.03933	0.04730	0.05527	0.06328	0.07131
Na_2SO_4	0.02086	0.02507	0.02931	0.03356	0.03780
$CaCl_2$	0.00768	0.00924	0.01079	0.01236	0.01392
KCl	0.00754	0.00907	0.01060	0.01213	0.01368
I	0.5153	0.6196	0.7241	0.8290	0.9636

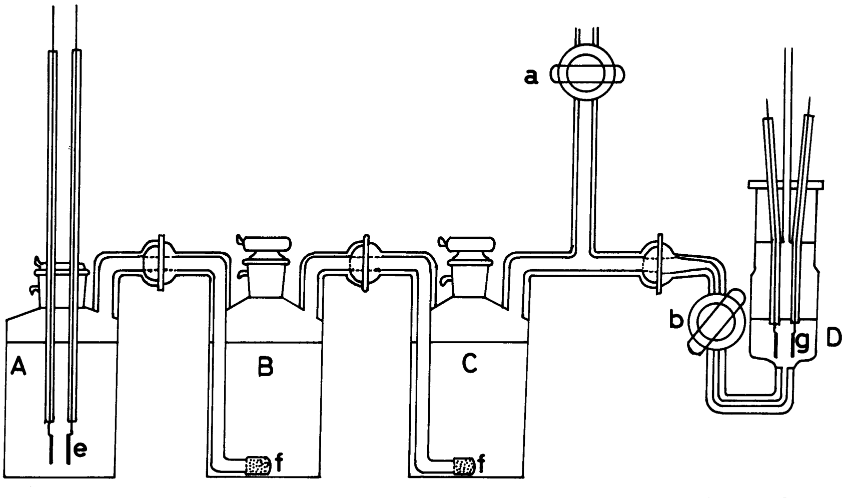

Fig. 1. Apparatus for measurement of ammonia activity. e: Platinum plates, f: sintered glass, g: platinum plates coated with platinum black.

Measurement of Activity Coefficient of Ammonia. The transpiration experiments were performed with a glass apparatus essentially similar to that used by Gaus.[20] It is schematically shown in Fig. 1. Vessel *A* was filled with a 0.5 mol dm^{-3} NaOH solution, and in vessels *B* and *C* were charged 0.4 mol dm^{-3} NH_3 solutions containing NaCl at a desired ionic strength. 10 ml of a 0.01 mol dm^{-3} HCl solution were introduced in conductivity cell *D*. The whole apparatus was immersed in a water thermostat kept at 25.00±0.01 °C. First, the detonating gas was generated 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. And then, in a condition of stopcock *a* being closed and stopcock *b* being open, the electrolysis of the detonating gas was carried out in small steps so that the NH_3 gas transpired by the "purging" gas was absorbed in the HCl solution in cell *D*, while the conductivity of the HCl solution being measured in each step. The electrolysis was carried out by means of a coulometer (Metrohm, Coulostat E524), and the conductivity measurement with an A. C. bridge (Delica, model DlS). The concentration of the NH_3 solution in vessel *C* before and after the experiment was measured by acid-base titrations to ascertain the invariance of the NH_3 concentration during the experiment.

Results and Discussion

Dissociation Constant of Ammonium Ion. The dissociation constants of ammonium ion were determined by the usual graphical and least-squares methods.[21] The ion products of H_2O in the artificial seawaters were taken from Culberson and Pytkowicz.[22] The pK_a values in the seawaters and in the sodium chloride solutions are tabulated in Table 2, together with those previously reported. The pK_a values obtained with a glass electrode and an ammonium-ion-selective electrode are in fairly good agreement with each other, although the uncertainties of the pK_a values determined with data from the ammonium-ion-selective electrode potentiometry are very large. The pK_a values increase with rising salinity and sodium chloride concentration. The pK_a value at 0.725 mol kg^{-1} NaCl is larger than the value in the 35‰ artificial seawater with the same formal ionic strength. The pK_a values at salinities of 35 and 45‰ are consistent with those reported by Khoo et al.[11]

Activity Coefficient of Ammonia. The experimental plots of the conductivities κ against the quantities of electricity passed (for generation of the detonating gas) Q in salt-free and 3.2 mol kg^{-1} NaCl solutions are illustrated in Fig. 2. The amount of electricity passed Q_e for the transpiration of NH_3 needed to neutralize 10 ml of a 0.01 mol dm^{-3} HCl solution was calculated from the point of the slope change. The activity coefficients of ammonia γ_{NH_3} in the sodium chloride solutions with different concentrations were determined by the use of Q_e values and ammonia concentrations C_{NH_3} (in molal units) according to Eq. 3 on the assumption that the γ_{NH_3} value in a salt-free solution be unity.

$$\gamma_{NH_3} = (Q_e^0/Q_e)\times(C^0_{NH_3}/C_{NH_3}) \qquad (3)$$

where the superscript 0 is for a salt-free solution. The values of C_{NH_3} and $C^0_{NH_3}$ were adjusted practically equal to each other. The γ_{NH_3} values determined in the sodium chloride solutions of different ionic strengths are given in Table 3. It is seen that the γ_{NH_3} values increase with increasing sodium chloride concentration.

The γ_{NH_3} values in the artificial seawaters could not be determined due to the precipitation of $Mg(OH)_2$ caused by the addition of NH_3. Thus, the adequacy of the employment of the γ_{NH_3} value in the sodium chloride solution for the seawater at the same ionic strength was examined with reference to the artificial seawater at 35‰ salinity. It was suggested in the previous paper[8] that the activity coefficient of ammonia is strongly influenced by the extent of polarization of water molecules coordinated to cations. Accordingly, the Mg^{2+} ions in the artificial seawater of 35‰ salinity were replaced by the Li^+ ions which have the analogous surface charge density to that of the Mg^{2+} ions, with the ionic strength being kept at 0.725 mol kg^{-1}. The γ_{NH_3} value measured in the "artificial seawater" containing Li^+ ions was found to be 1.021, which is smaller than the value (1.057) in the 0.725 mol kg^{-1}

Table 2. Comparison between Observed and Estimated Dissociation Constants of Ammonium Ion in Artificial Seawaters and Sodium Chloride Solutions at 25 °C (pK_a values in molal units) The Numbers in Parentheses are the Uncertainties of the Last Decimal Place

Solution	Salinity/‰ and ionic strength/mol kg^{-1}	Obsd					Est
		Present work GE	Present work NH_4^+-ISE	Khoo et al.[11]	Fouad[26]	Whitfield[12]	
Artificial seawater	25.24	9.30(1)	9.29(3)				9.316
	30.26	9.33(1)	9.34(3)				9.329
	35.11	9.35(1)	9.33(3)	9.354[a)]			9.343
	40.00	9.38(1)	9.37(3)				9.357
	44.84	9.39(1)	9.40(3)	9.374[b)]			9.371
NaCl solution	0.725	9.41(1)	9.44(3)				9.372
	1.022	9.44(1)	9.45(3)		9.56	9.51	9.417
	2.087	9.60(2)			9.71	9.66	9.578
	3.202	9.77(2)			9.89	9.80	9.739

a) At 35.00‰. b) At 44.55‰.

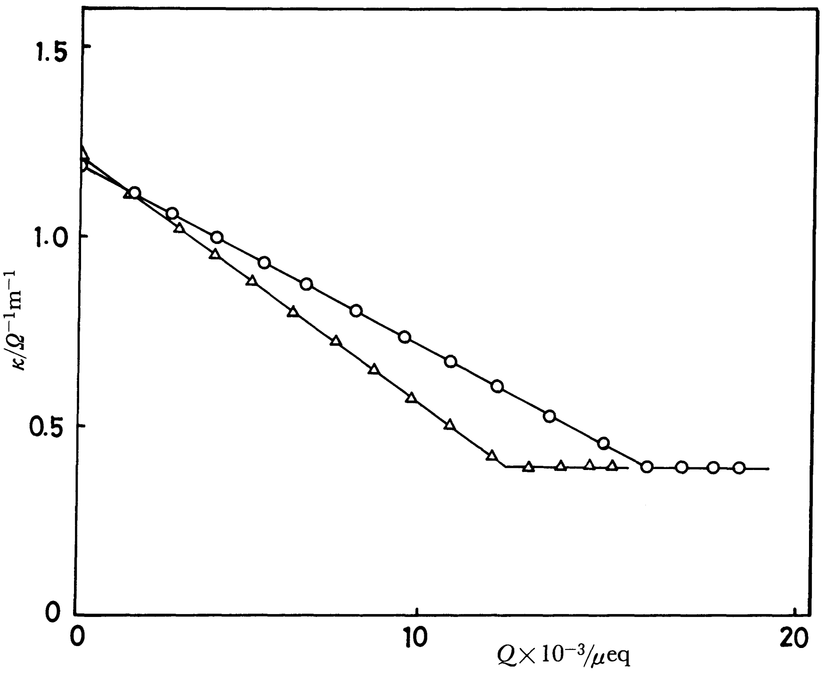

Fig. 2. Plot of conductivity κ against quantity of electricity Q. ○: Salt-free solution, △: 3.202 mol kg^{-1} NaCl solution.

Table 3. Activity Coefficients of Ammonia γ_{NH_3} at 25 °C in Sodium Chloride Solutions with Different Ionic Strengths (in molal units)

Ionic strength/mol kg^{-1}	γ_{NH_3}
0.516	1.040
0.621	1.048
0.725	1.057
0.829	1.066
0.966	1.077
1.022	1.076
2.087	1.158
3.202	1.228

NaCl solution at the same ionic strength as that of the seawater at 35‰. If this is true in the real artificial seawater of 35‰ salinity, the theoretical pK_a value is lowered by 0.025 units compared with the value calculated by use of the γ_{NH_3} value (1.057) in the 0.725 mol kg^{-1} NaCl solution. However, since the concentration of the Li$^+$ ions in the "artificial seawater" is 2.5 times larger than that of the Mg^{2+} ions in the artificial seawater at 35‰, the adoption of 1.021 as the γ_{NH_3} value in the 35‰ artificial seawater would lead to an underestimation of the theoretical pK_a value. In conclusion, it may be said that the use of the γ_{NH_3} values obtained in the NaCl solutions at the same ionic strengths as those of the artificial seawaters is unlikely to introduce an error of more than 0.02 units into the calculation of the pK_a values in the artificial seawaters.

Prediction of p*K*a Values. The relation between the dissociation constant of ammonium ion, $K_a(I)$, and the activity coefficients of the relevant species in solution of ionic strength I is represented by Eq.4.

$$pK_a(I) = pK_a(0) + (\ln \gamma_{H^+} + \ln \gamma_{NH_3} - \ln \gamma_{NH_4^+})/2.303 \quad (4)$$

where pK_a(0) denotes the dissociation constant in a salt-free solution. The pK_a(0) value =9.245 reported by Bates and Pinching[23] was accepted in the present calculations. As is evident from Eq. 4, since the pK_a(0) value is available and the γ_{NH_3} values have been measured in the preceeding section, the present problem is reduced to the estimation of the γ values of H$^+$ and NH$_4^+$ ions in the solution at ionic strength I. For these calculations the Pitzer ionic interaction approach[6,7] was employed. The trace activity coefficients of the ionic components of unit charge, H$^+$ and NH$_4^+$, in the solution containing cations c's and anions a's of ionic strength I can be determined from Pitzer's equations which can be expressed in the ionic form.[24]

$$\begin{aligned}\ln \gamma_{M^+} = {} & f^\gamma + \sum_c \sum_a m_c m_a B'_{ca} + \sum\sum_{c<c'} m_c m_{c'} \theta'_{cc'} + \\ & \sum\sum_{a<a'} m_a m_{a'} \theta'_{aa'} + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \\ & \sum_c m_c (2\theta_{Mc} + \sum_a m_a \psi_{Mca}) + \sum\sum_{a<a'} m_a m_{a'} \psi_{aa'M} + \\ & \sum_c \sum_a m_c m_a C_{ca} \end{aligned} \quad (5)$$

where M$^+$ denotes H$^+$ and NH$_4^+$, and m the concentration (in molal units) of the ion represented by the subscript,

$$\begin{aligned} f^\gamma = {} & -A_\phi[I^{1/2}/(1+1.2\,I^{1/2}) \\ & + (2/1.2)\ln(1+1.2\,I^{1/2})] \end{aligned} \quad (6)$$

with A_ϕ=0.392 at 25 °C,

$$B_{Ma} = \beta_{Ma}^{(0)} + (\beta_{Ma}^{(1)}/2I)\,[1-\exp(-2\,I^{1/2})(1+2\,I^{1/2})] \quad (7)$$

$$B'_{ca} = (\beta_{ca}^{(1)}/2\,I^2)[-1+\exp(-2\,I^{1/2})(1+2\,I^{1/2}+2\,I)] \quad (8a)$$

Table 4. Single Electrolyte Parameters in Pitzer's Equations at 25 °C

Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}
H	Cl	0.1775	0.2945		0.00080
H	SO_4	0.0027	0		0.0416
NH_4	Cl	0.0522	0.1918		−0.00301
NH_4	SO_4	0.0409	0.659		−0.00116
Na	Cl	0.07650	0.2664		0.00127
Na	SO_4	0.01958	1.1130		0.00497
K	Cl	0.04835	0.2122		−0.00084
K	SO_4	0.04995	0.7793		0
Mg	Cl	0.35235	1.6815		0.00519
Mg	SO_4	0.22100	3.3430	−37.25	0.025
Ca	Cl	0.31590	1.6140		−0.00034
Ca	SO_4	0.20000	2.650	−57.70	0

$$B'_{\mathrm{ca}} = (\beta_{\mathrm{ca}}^{(1)}/I^2)(2/1.96)[-1+\exp(-1.4I^{1/2})(1+1.4I^{1/2}+0.98I)] + (\beta_{\mathrm{ca}}^{(2)}/I^2)(1/72)[-1+\exp(-12I^{1/2}) \times (1+12I^{1/2}+72I)] \tag{8b}$$

$$Z = \sum_{\mathrm{i}} m_{\mathrm{i}} |z_{\mathrm{i}}| \tag{9}$$

z_{i} being the charge of ion i,

$$C_{\mathrm{ca}} = C_{\mathrm{ca}}^{\phi}/2|z_{\mathrm{c}}z_{\mathrm{a}}|^{1/2}. \tag{10}$$

Equation 8a is for 1-1 and 1-2 electrolytes and Eq. 8b for higher valence types such as 2-2 electrolytes. The θ and θ' terms are related to like charge interactions, and the ψ term accounts for triplet ion interactions.

The values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} used in the calculations[7] are listed in Table 4. The calculations were made without the higher order terms θ, θ', and ψ, the contributions of which are usually small,[25] because their values for all the ions are not available. A comparison between the measured pK_a values and ones estimated using Pitzer's equations is shown in Table 2. It is seen that the values observed and those predicted in the present work are in good agreement each other in almost all the solutions. The pK_a values in the sodium chloride solutions measured in the present work are in closest agreement with the theoretically estimated values.

In view of the previous[8–10]and present results, it may be said that the ionic interaction model developed by Pitzer and coworkers is adequately applied to estimate free energy and enthalpy changes both in concentrated single electrolyte solutions and in mixed electrolyte solutions as complex as seawaters. However, the large discrepancies between the observed and estimated pK_a values occurred at higher ionic strengths in the lithium salts solutions.[8,9] This may be ascribed to the fact that the higher order terms θ, θ' and ψ for binary mixtures NH_4A-LiA with a common anion A(A=NO_3 or ClO_4), the contributions of which might unexpectedly be too large to be neglected, were omitted in the calculations because of their unavailableness. Thus, it may be necessary to measure the higher order terms in order to predict the values of the thermodynamic properties more accurately. With the intention to make clear this point, isopiestic measurements of NH_4A-LiA(A=NO_3 or ClO_4) are in progress.

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