Activity Coefficients of Ammonia in Artificial Seawaters

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Activity coefficients of ammonia in artificial seawaters at different salinities (10 - 45 ‰) were measured at 25°C by a transpiration method. The activity coefficients (in molal units) were slightly less than unity over the measured salinity range, and increased with an increase in salinity to 35 ‰ and then decreased. The activity coefficients of ammonia in the artificial seawaters were also estimated in terms of the Pitzer theory and compared with the observed ones.

1 INTRODUCTION

The influence of electrolytes on the activity coefficients of nonelectrolytes in aqueous solutions is of both fundamental and applied interest. So far, the activity coefficients of ammonia have been measured in aqueous solutions of many salts.^{1,2)} However, the activity coefficients of ammonia in artificial seawaters do not seem to have been reported. Knowledge of the activity coefficients of ammonia in artificial seawaters is likely to be of value for the evaluation of the toxicity of ammonia in the marine environment, *e.g.* the toxic effects on marine fish. Data for the ammonia - ammonium ion equilibrium should also be indispensable

for the evaluation. Thus, recently, we have determined the dissociation constants of ammonium ion in artificial seawaters by glass-electrode potentiometry and compared the observed values with those predicted theoretically in terms of the Pitzer approach.³⁾ In the theoretical evaluation, however, due to the lack of the activity coefficients of ammonia in the artificial seawaters, we could not help employing the activity coefficients of ammonia in NaCl solutions at the same ionic strengths.

In the present work the activity coefficients of ammonia in artificial seawaters at different salinities (10 - 45 ‰) (here, salinity is defined as the weight in grams of dissolved salts in 1 kg of artificial seawaters) were measured at 25°C by a transpiration method. Since the introduction of NH_3 into the artificial seawaters caused the precipitation of $\text{Mg}(\text{OH})_2$, ammonium chloride was added so that no precipitation occurred. The activity coefficients of NH_3 in the artificial seawaters were estimated according to the Pitzer approach,^{4,5)} and

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Table 1 Molal composition of artificial seawaters at six salinities

Component and ionic strength <i>I</i>	Salinity/0/00					
	10.19	25.21	30.14	35.05	39.90	44.72
NaCl	0.1218	0.3059	0.3675	0.4296	0.4915	0.5537
MgCl ₂	0.01576	0.03956	0.04754	0.05557	0.06357	0.07162
Na ₂ SO ₄	0.00835	0.02098	0.02521	0.02946	0.03371	0.03798
CaCl ₂	0.00308	0.00776	0.00932	0.01089	0.01247	0.01404
KCl	0.00303	0.00759	0.00917	0.01066	0.01219	0.01374
<i>I</i>	0.2064	0.5184	0.6228	0.7280	0.8329	0.9384

compared with the observed ones.

2 EXPERIMENTAL

2.1 Reagents

All the reagents were of analytical grade and used without further purification.

2.2 Preparation of artificial seawaters

The artificial seawaters were prepared according to Khoo *et al.*⁶⁾ The composition of the artificial seawaters at six salinities is given in Table 1. The ionic strengths were calculated in the usual way with neglect of ion - pairing. Ammonium chloride and ammonia were introduced in the seawaters so that the concentrations of the both reagents were adjusted to 0.1 mol kg⁻¹.

2.3 Measurement of ammonia activities

The transpiration experiments were carried out with the same glass apparatus as that used in the previous works.^{3,7-9)} It is schematically shown in Fig.1. Vessel A was filled with 0.1 mol dm⁻³ NaOH solution, and vessels B and C were charged with a sample solution (one of the "artificial seawaters" containing 0.1 mol kg⁻¹ NH₄Cl and NH₃, or 0.1 mol kg⁻¹ NH₄Cl aqueous solution containing 0.1 mol kg⁻¹ NH₃). 10 cm³ of 0.001 mol dm⁻³ HCl solution

Fig.1 Apparatus for measurement of ammonia activity

e: platinum plates, f: sintered glass, g: platinum plates coated with platinum black

were introduced in conductivity cell D. The whole apparatus was immersed in a water thermostat kept at 25.00 ± 0.01°C. First, a carrier gas (mixture of H₂ and O₂) was generated by electrolysis in vessel A with stopcock *a* open and stopcock *b* closed until the empty spaces and the tubes were saturated with the NH₃ gas. Then, in a 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 NH₃ gas transpired by the carrier gas was absorbed in the HCl solution

in cell *D* with the conductivity of the HCl solution being 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 NH_3 concentration in a sample solution in vessel *C* before and after the experiment was measured by acid - base titration to ascertain the invariance of the NH_3 concentration during the experiment.

3 RESULTS AND DISCUSSION

3.1 Activity coefficient of ammonia

Fig.2 Plot of conductivity κ against quantity of electricity Q for $0.1 \text{ mol kg}^{-1} \text{ NH}_4\text{Cl}$ aqueous solution

Experimental plots of the conductivities κ against the quantities of electricity passed Q (for generation of the carrier gas) in $0.1 \text{ mol kg}^{-1} \text{ NH}_4\text{Cl}$ aqueous solution containing $0.1 \text{ mol kg}^{-1} \text{ NH}_3$, which is taken as a standard in the evaluation of the activity coefficients of ammonia in the artificial seawaters, are illustrated in Fig.2. The similar plots were obtained for the "artificial seawaters" containing $0.1 \text{ mol kg}^{-1} \text{ NH}_4\text{Cl}$ and NH_3 .

The amount of electricity passed Q_e for the transpiration of NH_3 needed to neutralize 10 cm^3 of a $0.001 \text{ mol dm}^{-3} \text{ HCl}$ solution was calculated from the slope change. As was the case in the evaluation of the activity coefficients of ammonia in various electrolyte solutions,^{3,7-9)} the activity coefficients of ammonia, γ_{NH_3} , in the artificial seawaters with the composition given in Table 1 were evaluated according to Eq. (1) by use of the Q_e values and the ammonia concentrations C_{NH_3} (in molal units) in $0.1 \text{ mol kg}^{-1} \text{ NH}_4\text{Cl}$ aqueous solution and in the "artificial seawaters" containing $0.1 \text{ mol kg}^{-1} \text{ NH}_4\text{Cl}$. Equation (1) means that the subtraction of contributions due to $\text{NH}_3 - \text{NH}_4\text{Cl}$ and $\text{NH}_3 - \text{NH}_3$ interactions, which are observed in $0.1 \text{ mol kg}^{-1} \text{ NH}_4\text{Cl}$ aqueous solution containing $0.1 \text{ mol kg}^{-1} \text{ NH}_3$, from the activity coefficients of ammonia in the "artificial seawaters" containing $0.1 \text{ mol kg}^{-1} \text{ NH}_4\text{Cl}$ and NH_3 leads to the activity coefficients of ammonia, γ_{NH_3} , in the artificial seawaters.

$$\gamma_{\text{NH}_3} = (Q_e^0 / Q_e) (C_{\text{NH}_3}^0 / C_{\text{NH}_3}) \quad (1)$$

in which the superscript 0 is for $0.1 \text{ mol kg}^{-1} \text{ NH}_4\text{Cl}$ aqueous solution of $0.1 \text{ mol kg}^{-1} \text{ NH}_3$.

The γ_{NH_3} values in the artificial seawaters thus³⁾ determined are tabulated in Table 2. Evidently the γ_{NH_3} values in the artificial seawaters are less than unity over the measured salinity range, and increase with increasing salinity to 35 ‰ and then decrease. The γ_{NH_3} values in the artificial seawaters are much smaller than those in the NaCl solutions with the same ionic strengths as those in the artificial seawaters, i.e., the values in the NaCl solutions are larger than unity, and in-

Table 2 Activity coefficients of ammonia γ_{NH_3} (in molal units) at 25°C observed and estimated in artificial seawaters with different salinities (ionic strengths) and those observed in sodium chloride solutions with different ionic strengths^{3),*)}

Salinity/0/00(ionic strength)	γ_{NH_3}		Ionic strength of NaCl	γ_{NH_3}
	Obsd	Est		
10.19(0.2064)	0.978 ₆	1.00 ₀		
25.21(0.5184)	0.981 ₄	1.00 ₁	0.516	1.04 ₀
30.14(0.6228)	0.984 ₆	1.00 ₁	0.621	1.04 ₈
35.05(0.7280)	0.987 ₇	1.00 ₁	0.725	1.05 ₇
39.90(0.8329)	0.978 ₄	1.00 ₁	0.829	1.06 ₆
44.72(0.9384)	0.971 ₇	1.00 ₂	0.966	1.07 ₇

*) The ionic strengths in the NaCl solutions are not strictly in agreement with those in the artificial seawaters.

crease with increasing NaCl concentration.

The fact that the γ_{NH_3} values in the artificial seawaters are much smaller than those in the NaCl solutions may be ascribed mainly to the difference in hydration extent between Na^+ and Mg^{2+} ions. The Mg^{2+} ion may be more strongly hydrated than the Na^+ ion, because the former has a smaller ionic radius and a higher electric charge than the latter. Thus, the coordinated water molecules to the Mg^{2+} ion are more strongly oriented with their protons outward and the attraction between these protons and ammonia molecules may then be stronger, which could lead to the lower activity coefficients in the artificial seawaters than in the NaCl solutions. The increase of the γ_{NH_3} values with increasing NaCl concentration in the NaCl solutions may be explained on the basis of the competition of the following two phenomena (a) and (b). The rise in NaCl concentration may bring about (a) the increase in interaction between protons in water molecules coordinated to Na^+ ions

and ammonia molecules, which should result in the reduction of the γ_{NH_3} values, and (b) the decrease of the so-called free water, in which ammonia molecules should be dissolved, due to the hydration of Na^+ ions, which should lead to the enhancement of the γ_{NH_3} value. Thus, it may be said that the increase of the γ_{NH_3} values in the NaCl solutions is ascribed to the fortuitous superiority of the phenomenon (b) over (a) in extent.

3.2 Comparison between observed and estimated γ_{NH_3} values in artificial seawaters

Table 3 Interaction parameters for NH_3 in Pitzer equation

Ion i	$\lambda_{\text{NH}_3 i}$	$\mu_{\text{NH}_3 i \text{Cl}}$
Na^+	0.0175	
K^+	0.0454	
Mg^{2+}	-0.21	
Ca^{2+}	-0.081	-0.00134
Cl^-	0 (defined)	
SO_4^{2-}	0.140	

In Pitzer's model¹⁰⁾ the equation for the activity coefficient of ammonia in the mixed electrolyte solution is given by Eq. (2)

$$\ln \gamma_{\text{NH}_3} = 2 \sum_c m_c \lambda_{\text{NH}_3 c} + 2 \sum_a m_a \lambda_{\text{NH}_3 a} + \sum_{i,j} 3 \sum_c m_i m_j \mu_{\text{NH}_3 ij} \quad (2)$$

where λ and μ are second and third virial coefficients for ion - NH_3 interactions, respectively, which are independent of ionic strength. m_i and m_j are molalities of species i and j , and the subscripts c and a represent cations and anions, respectively.

Recently, Clegg and Brimblecombe²⁾ have calculated the values for $\lambda_{\text{NH}_3 c}$, $\lambda_{\text{NH}_3 a}$, and $\mu_{\text{NH}_3 ij}$ by using partial pressure, salt solubility, and partitioning data for aqueous electrolyte solutions containing NH_3 . The γ_{NH_3} values in the artificial seawaters were estimated according to Eq. (2) by use of their λ and μ values given in Table 3. The results are listed in Table 2, together with the observed ones for comparison. The estimated γ_{NH_3} values are obviously close to unity with indication of slight increase with salinity. This tendency differs from that in the observed γ_{NH_3} values. The discrepancy may be ascribed partly to the fact that for want of the μ data, as is apparent from Table 3, the theoretical calculations have been made with almost no μ value.

In conclusion, it may be said that the γ_{NH_3} values in the artificial seawaters are slightly less than unity over the mea-

sured salinity range (10 - 45 ‰), and increase with increasing salinity up to 35 ‰ and then decrease, and that the employment of γ_{NH_3} values in NaCl solutions as those in artificial seawaters which have the same ionic strengths as the NaCl solutions will lead to inaccurate results.

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