Estimation of Setchenow Coefficients of Ammonia in Aqueous Salt Solutions

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1 INTRODUCTION

The activity coefficient γ and solubility S of a nonelectrolyte in an aqueous salt solution at a low salt concentration have been empirically found to be expressed as a function of the salt concentration c in molar units(1,2).

$$\log \gamma/\gamma_0 = \log S_0/S = k_s c \quad (1)$$

where γ_0 , to which unity is usually assigned, and S_0 are for a salt-free solution, and the proportionality factor k_s , which concerns the ion-nonelectrolyte interaction, is known as the Setchenow(salting) coefficient and has a characteristic value for a given salt-nonelectrolyte pair. A positive value of k_s corresponds to salting-out, and if k_s is negative, salting-in is observed.

So far, a number of theories have been developed for the prediction of the k_s values for nonpolar nonelectrolytes. A comparative tabulation of the various theories of salting-in and -out with their features are given by Conway(3). The scaled particle theory(4,5) among others has been successfully applied to the calculation of solubilities of nonpolar gases such as H_2 , O_2 , N_2 , hydrocarbons, and noble gases in aqueous salt solutions(6-8). On the other hand, as far as we have surveyed the literature, it seems that no attempt has been made to calculate theoretically the Setchenow coefficients of polar nonelectrolytes in aqueous salt solutions.

As was reported in previous papers(9-12), we measured the activity coefficients of ammonia in various 1 - 1 electrolyte solutions of different concentrations at 25°C. In the present work, therefore, the Setchenow coefficients of ammonia in 1 - 1 salt solutions were calculated according to the scaled particle theory, and compared with the experimental values in order to examine the applicability of this theory to polar nonelectrolyte systems.

2 PROCEDURES FOR THEORETICAL ESTIMATION OF SETCHENOW COEFFICIENTS OF AMMONIA

Shoor and Gubbins(6) derived from the scaled particle theory the following expression for k_s in molar units.

$$k_s = [d(\bar{g}_1^h/2.3kT)/d(c)]_{c \rightarrow 0} + [d(\bar{g}_1^s/2.3kT)/d(c)]_{c \rightarrow 0} = k_\alpha + k_\beta \quad (2)$$

where k is the Boltzmann constant, T is the temperature in degrees Kelvin, c is the concentration of the salt in molar units, and $\bar{g}_1^h$ is the Gibbs energy when a cavity large enough to accommodate the nonelectrolyte molecule is formed in the solution, and $\bar{g}_1^s$ is the Gibbs energy required to place the nonelectrolyte molecule in this cavity in the face of interactions with the water molecules and the ions of the electrolyte. k_α and k_β represent the contributions to the salting coefficient of each of the two terms on the left of Eq.2. The present problem is to derive the expressions for k_α and k_β in terms of parameters characteristic of the nonelectrolyte, the solvent, and the ions of the 1 - 1 salt. In what follows we use subscript 1 to represent the parameters for

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the nonelectrolyte (ammonia), 2 those for the solvent (water), 3 those for the cation, and 4 those for the anion.

Expression for k_α This expression may be the same as that derived previously by Shoor and Gubbins (6), regardless of whether the nonelectrolyte is polar or nonpolar. According to them, the final expression for k_α is given by Eq. 3.

$$k_\alpha = \{d(\bar{g}_1^h/2.3kT)/d(c)\}_{c \rightarrow 0} = 2.15 \times 10^{20}(\sigma_3^3 + \sigma_4^3) - 2.47 \times 10^{-4} \times \phi_0 + \\ \sigma_1[6.45 \times 10^{20}(\sigma_3^2 + \sigma_4^2) + 1.34 \times 10^{28}(\sigma_3^3 + \sigma_4^3) - 4.23 \times 10^4 \phi_0] + \\ \sigma_1^2[6.45 \times 10^{20}(\sigma_3 + \sigma_4) + 4.01 \times 10^{28}(\sigma_3^2 + \sigma_4^2) + 1.32 \times 10^{36}(\sigma_3^3 + \\ \sigma_4^3) - 4.17 \times 10^{12} \phi_0] \quad (3)$$

where σ 's are the diameters of the species in cm units and ϕ_0 the apparent molal volume of the salt at infinite dilution in $\text{cm}^3\text{mol}^{-1}$ units.

Expression for k_β The k_β term for the polar nonelectrolyte should be different from that for the nonpolar one derived previously (6) according to the Lennard-Jones potential taking account of the ion-induced dipole interaction.

According to Shoor and Gubbins (6), $\bar{g}_1^s$ in a single salt solution is approximated by Eq. 4.

$$\bar{g}_1^s = \sum_{j=2}^4 \rho_j \int_{\sigma_{1j}}^{\infty} u_{1j}(r) 4\pi r^2 dr \quad (4)$$

where ρ_j is the number density (particles/ cm^3) of a solution species, σ_{1j} is assumed to be equal to $(\sigma_1 + \sigma_j)/2$, and $u_{1j}(r)$ is the pair potential between the nonelectrolyte and species j at a distance of r . For the 1-1 electrolyte (7)

$$\rho_3 = \rho_4 = Nc/1000 \quad (5)$$

where N is Avogadro's number. The number density of water is given by Eq. 6 (7).

$$\rho_2 = (Nd_2/M_2)[1 - c\phi/1000] \quad (6)$$

in which d_2 is the density of pure water, M_2 the molecular weight of water, and ϕ the apparent molal volume of the salt. The pair potential $u_{1j}(r)$ for the interaction between the polar nonelectrolyte (ammonia) and species j was assumed to be expressed in terms of the Stockmayer potential (13) as is written by Eqs. 7a and 7b, $u_{12}(r)$ being derived after averaging the interaction between the permanent dipole of the polar solute and that of the water molecule over all orientations.

$$u_{12}(r) = 4\epsilon_{12}[(\sigma_{12}/r)^{12} - (\sigma_{12}/r)^6] - (2/3kT)\mu_1^2\mu_2^2r^{-6} \quad (7a)$$

$$u_{1j}(r) = 4\epsilon_{1j}[(\sigma_{1j}/r)^{12} - (\sigma_{1j}/r)^6] \quad (\text{for } j = 3 \text{ and } 4) \quad (7b)$$

where ϵ_{1j} ($j = 2 - 4$) is the mixture potential parameter, which is related to the pure component parameters ϵ_1 and ϵ_j by the approximate mixing rule (13),

$$\epsilon_{1j} = (\epsilon_1\epsilon_j)^{1/2} \quad (8)$$

and μ_1 and μ_2 are the dipole moments of the nonelectrolyte and water molecule, respectively. Substituting the above expressions for ρ_2 , ρ_3 , ρ_4 , $u_{12}(r)$, and $u_{1j}(r)$ into Eq. 4 and performing the integrations give

$$\bar{g}_1^s/2.3kT = -(32\pi Nc/9000 \times 2.3kT)[\epsilon_{13}\sigma_{13}^3/k + \epsilon_{14}\sigma_{14}^3/k] - (32\pi Nd_2/9 \times 2.3 \times \\ kTM_2)[1 - c\phi/1000] \times \epsilon_{12}\sigma_{12}^3/k - (8\pi Nd_2/9 \times 2.3k^2T^2M_2)[1 - \\ c\phi/1000]\mu_1^2\mu_2^2/\sigma_{12}^3 \quad (9)$$

If the derivative of Eq.9 is taken with respect to c and numbers for the various constants ($M_2 = 18.02$; $d_2 = 0.997$ g/cm³; $N = 6.02 \times 10^{23}$ /mol; $k = 1.38 \times 10^{-16}$ erg/K (erg = 10^{-7} J); $T = 298$ K) are inserted, the final expression for k_β is obtained.

$$\begin{aligned}
 k_\beta &= [d(\bar{g}_1^s/2.3kT/d(c))_{c \rightarrow 0}] = -9.80 \times 10^{18} [\epsilon_{13} \sigma_{13}^3/k + \epsilon_{14} \sigma_{14}^3/k] + 5.43 \times \\
 &\quad 10^{17} \phi_0 \epsilon_{12} \sigma_{12}^3/k + 2.39 \times 10^{46} \phi_0 \mu_1^2 \mu_2^2 / \sigma_{12}^3 \\
 &= -1.23 \times 10^8 [(\epsilon_1/k)^{1/2} (\epsilon_3/k)^{1/2} (\sigma_1 + \sigma_3)^3 + (\epsilon_1/k)^{1/2} (\epsilon_4/k)^{1/2} (\sigma_1 + \sigma_4)^3] + \\
 &\quad 6.79 \times 10^{16} \phi_0 (\epsilon_1/k)^{1/2} (\epsilon_2/k)^{1/2} (\sigma_1 + \sigma_2)^3 + 1.91 \times 10^{47} \phi_0 \mu_1^2 \mu_2^2 / \\
 &\quad (\sigma_1 + \sigma_2)^3 \quad (10)
 \end{aligned}$$

The Setchenow coefficient k_s can be calculated by adding k_α (eq.3) and k_β (Eq.10). Parameters necessary to calculate k_s are the apparent molal volume of the salt at infinite dilution (ϕ_0), the diameters for $\text{NH}_3(\sigma_1)$, $\text{H}_2\text{O}(\sigma_2)$, the cation(σ_3), and the anion(σ_4), the dipole moments of $\text{NH}_3(\mu_1)$ and $\text{H}_2\text{O}(\mu_2)$, and the energy parameters for ammonia(ϵ_1/k), $\text{H}_2\text{O}(\epsilon_2/k)$, the cation(ϵ_3/k), and the anion(ϵ_4/k). The apparent molal volumes were calculated from those for ions given by Friedman and Krishnan(14). The diameters for alkali and halide ions given by Waddington(15) were accepted, since it was found(16) that the observed k_s values for nonpolar nonelectrolytes in alkali halide solutions gave the best agreement with those calculated from the scaled particle theory by simply doubling Waddington's crystallographic radii. As the diameter for NO_3^- ion was accepted $\sigma_4 = 3.92 \times 10^{-8}$ cm, which was estimated in such a way that the k_s values for nonpolar solutes in alkali nitrate solutions calculated from the scaled particle theory fitted to the experimental values(16). The crystal diameter for ClO_4^- ion = 4.81×10^{-8} cm was taken from Gmelins Handbuch(17). The parameters for $\text{NH}_3(\sigma_1, \mu_1, \epsilon_1/k)$ and $\text{H}_2\text{O}(\sigma_2, \mu_2, \epsilon_2/k)$ for the Stockmayer potential were from Hirschfelder et al.(13). The parameter values described above are listed in Table 1. The energy parameters for the cations and anions,

Table 1. Parameter values for calculating Setchenow coefficients of ammonia

species	$\sigma \times 10^8/\text{cm}$	$\mu \times 10^{18}/\text{cgs esu}^*(1)$	$\alpha \times 10^{24}/\text{cm}^3$	$\phi_0/\text{cm}^3 \text{mol}^{-1} *2)$	$\epsilon/k/\text{K}$
NH_3	2.60	1.47			320
H_2O	2.65	1.83			380
Li^+	1.48			-6.3	5645
Na^+	2.02			-6.6	556
K^+	2.64			3.6	300
Cl^-	3.64		3.02	23.2	218
Br^-	3.96		4.17	30.1	302
I^-	4.48		6.28	41.6	326
NO_3^-	3.92		3.60	34.4	243
ClO_4^-	4.81		4.16	49.5	110

*1) cgs esu = 3.33×10^{-12} Cm; *2) partial molal volumes for ions, from which a ϕ_0 value for a given electrolyte can be calculated by the algebraic summation of the ϕ_0 values for the component ions.

which are not available, were estimated as follows. As was pointed out in a previous paper(9), the interaction of ammonia with anions would be weak compared with that with cations. Thus, the energy parameters for the anions were assumed to be estimated from the Mavroyannis-Stephen theory(18). According to the theory, the expression for ϵ_4/k for the anion is given by Eq.11.

$$\epsilon_4/k = 2.28 \times 10^{-8} \alpha_4^{3/2} z_4^{1/2} / \sigma_4^6 \quad (11)$$

where α_4 is the polarizability of the anion, and z_4 the total number of electrons in the anion. Ion polarizabilities were taken from Conway(19) for the halide ions, Landolt-Börnstein(20) for NO_3^- ion, and Gmelins Handbuch(17) for ClO_4^- ion. The values of ϵ_3/k for the cations (Li^+ , Na^+ , and K^+), which are expected to make strong interactions with ammonia, were then evaluated so as to fit the k_s values in LiCl , NaCl , and KCl solutions predicted from the scaled particle theory to the observed values. The ϵ_3/k and ϵ_4/k values thus calculated are given in Table 1.

3 RESULTS AND DISCUSSION

The predicted k_s values with the relative contributions of the two terms k_α and k_β to k_s are compared with the observed ones in Table 2.

Table 2. Comparison between observed and calculated Setchenow coefficients k_s for ammonia with k_α and k_β values

salt	obsd k_s	est		
		k_s	k_α	k_β
LiCl	-0.038 ^{*1)}	-0.038 ^{*6)}	0.095	-0.133
NaCl	0.041 ^{*5)}	0.041 ^{*6)}	0.114	-0.073
KCl	0.060 ^{*3)}	0.060 ^{*6)}	0.101	-0.041
LiBr	-0.033 ^{*2)}	-0.040	0.097	-0.137
NaBr	0.017 ^{*3)}	0.039	0.117	-0.078
KBr	0.035 ^{*3)}	0.058	0.105	-0.047
LiI	-0.062 ^{*2)}	-0.019	0.111	-0.131
NaI	-0.007 ^{*3)}	0.060	0.131	-0.072
KI	0.017 ^{*3)}	0.079	0.120	-0.041
LiNO_3	-0.023 ^{*4)}	-0.034	0.076	-0.110
NaNO_3	0.038 ^{*4)}	0.045	0.095	-0.050
KNO_3	0.060 ^{*4)}	0.064	0.083	-0.019
LiClO_4	-0.065 ^{*4)}	0.068	0.125	-0.058
NaClO_4	0.003 ^{*4)}	0.147	0.144	0.002

*1) Unpublished result; *2) from Ref.1; *3) from Ref.2;
*4) from Ref.9; *5) from Ref.12; *6) fitted to the observed k_s values in order to estimate the energy parameters for the cations.

It is apparent that k_α is positive, while k_β is negative, irrespective of the types of the salts. An exception is the NaClO_4 system. The fact that k_α increases with increasing ionic size denotes that it becomes more difficult to

form a cavity and thus the Gibbs energy for cavity formation becomes more positive. The k_g values become more negative with decreasing cationic size in salt systems with a common anion, which indicates that the attractive forces between NH_3 and cations become stronger.

The predicted k_g values in the bromide and nitrate salt solutions are in reasonable agreement with the observed ones, if it is taken into account that since the experimental k_g values at $c \rightarrow 0$ have been determined with the data at relatively high salt concentrations, they may have rather high uncertainties. Although the discrepancies between the predicted and observed k_g values in the iodide salt solutions are rather large, at least the sign of k_g values is consistent with that of the observed ones except the NaI system. The perchlorate salt systems yield the poorest agreement between the predicted and observed k_g values. From these findings it may be said that the agreement becomes poorer with increasing ionic size. Masterton and Lee(7) pointed out that the k_g values calculated from the scaled particle theory are very sensitive to ionic size and the effect is particularly serious with large ions, and that with smaller ions crystal radii can be used for satisfactory values of σ_3 and σ_4 . If their indication is taken into account, it may be said that part of the large deviations in the perchlorate solutions is due to the employment of the crystal radius for σ_4 . On the other hand, the good agreement in the nitrate solutions may be partly ascribed to the fact that the σ_4 value for the nitrate ion used in the calculations has been determined so as to fit the predicted k_g values to the observed ones for nonpolar solutes in the alkali nitrate media(16). Thus, it may be necessary to determine σ_4 values for large anions by a method similar to that employed for the nitrate ion in order to get good agreement with experiment. Unfortunately, k_g values for nonpolar solutes in perchlorate salt solutions do not seem to have been reported.

In conclusion, in view of various assumptions introduced in the theoretical evaluation and uncertainties of observed k_g values, the estimated and observed Setchenow coefficients of ammonia are in fairly good agreement in the alkali bromide and nitrate solutions, which suggests the applicability of the present procedures as have been made on the basis of the scaled particle theory to the prediction of k_g values for polar nonelectrolytes in aqueous solutions of salts with small ionic sizes.

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