Thermodynamic Quantities of Surface Formation of Aqueous Electrolyte Solutions IX. Aqueous Solutions of Ammonium Salts.

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The properties of aqueous ammonium salt solutions at the air/water surface are presented. By comparison of the properties of ammonium halides solutions with those of sodium halide, we note a close similarity, which indicates that the surface tension increments may be explained in relation to the hydration enthalpy of anions. We find that the behaviors of the salts with nitrate anion which are polyatomic are also explained by hydration enthalpy in the same way. On the other hand, salts with the ammonium cation which are polyatomic show deviation from a monotonous relationship between the surface tension increments and hydration enthalpies observed for alkali metal halides. These results can be explained by ion pair formation in the surface region.

INTRODUCTION

The usefulness of the thermodynamic properties of aqueous electrolytes at the surface region is mainly concerned with the increment of surface tension (γ) caused by the adsorption of salts [1 – 9]. The variation of γ with salt concentration is linear and very small, being characteristic of each salt. The experimental data are reported in the form of a slope of surface tension versus molality (*m*) curves of electrolyte solutions and used to distinguish the individual characteristics of electrolytes. The measurements have been repeated mainly for uni-univalent alkali metal halides because they lack something that is necessary to express a factor concerning the behavior of ions in the surface region. Ions of hydrophilic properties would be expected to show an idea of the magnitude of the repulsion from the hydrophobic surface. Indeed, the results for alkali metal halides with a common cation are surprisingly well represented by a single curve plotted against their heat of hydration. On the other hand, the specific dependence of the increments upon cations is totally different than that of anions when we compare values of surface tension and surface potentials for different pair of ions with a common anion [10]. Observations using such as sum-frequency generation technique and molecular dynamics simulations explain the microscopic difference in the distribution in the surface region between each of the anions and cations [11]. For the adsorption of sodium halide, anions are preferentially accumulated and associated with the water molecules [12], and the presence of anions in the surface region affect the hydrogen bonding of water molecules [13]. Thermodynamically, these specific properties of ions can be found in the behavior of dγ/d*m*. In general, the dγ/d*m* increases with increasing temperature for solutions containing a single electrolyte, while the values for sucrose solution is considered independent of the temperature [14]. This characteristic behavior is connected with the entropy change associated with the formation of the surface, Δs, by the relation

$$\frac{d}{dT}\left(\frac{d\gamma}{dm}\right)_{T,p} = \frac{d}{dm}\left(\frac{d\gamma}{dT}\right)_{p,m} = -\frac{d}{dm}\Delta s \ . \tag{1}$$

Since, for the pure salt solutions, left side of equation is always positive, the Δs decrease with increasing concentration. This is strong evidence that the variation of $d\gamma/dm$ with temperature is characteristic of electrolyte solutions which arise from ion pair interactions in the surface region, and is a useful thermodynamic quantity to specify the individuality of salt.

In continuing systematic study of the electrolytes in surface region, this report shows surface tension measurements for aqueous solution of ammonium halides, ammonium nitrate, and ammonium sulfate. The main purpose of these measurements is to provide information about the contribution of polyatomic cation. Since polyatomic anions of the type NO_3^- and SO_4^{2-} are already shown in previous works [15, 16], comparison of the ammonium salts with these data and with those for simple 1:1 electrolyte solutions will provide us with properties of ammonium ion in the surface region.

MATERIALS AND METHOD

Ammonium chloride, ammonium bromide, ammonium iodide, ammonium nitrate, and ammonium sulfate were of high grade, above 99.99% (Sigma-Aldrich), and were used without further purification. Water was first purified by Milipore system and then distilled from dilute alkaline permanganate solution before use. Surface tension was measured by the drop volume method which has been used through this series of measurements on the electrolyte solutions [16]. Measurements were made using glass dropping tips whose diameter was determined at 25 ^{o}C using the value of pure water 71.96 mN m^{-1}. The densities of aqueous solutions were measured using a vibrating tube

density meter (Anton Paar DMA 60-602). The precision of the evaluated surface tension data was better than 0.05 mN m^{-1}.

RESULTS AND DISCUSSION

The surface tension of aqueous solutions of NH_4Cl, NH_4Br, NH_4I, NH_4NO_3, and $(NH_4)_2SO_4$ were measured in the temperature range of 15 to 35 ^{o}C at 2.5 ^{o}C intervals and concentration range of 0 to 1 mol kg^{-1}. The values of γ for the aqueous solution of NH_4I and $(NH_4)_2SO_4$ that show the smallest and largest dγ/dm values among these salts are plotted against concentration in Fig. 1 and 2 at each temperature. The solid curves represent the linear regression lines. The γ-versus-m relations of the other ammonium salts are also well represented by linear regression lines without exception, as well as those reported in this series of electrolyte solutions. Since the differences in slopes of these regression lines in a series of salts of the same valence type across the temperature range from 15 to 35 ^{o}C are too small to see on the figure, the coefficients of regression line,

$$\gamma = \gamma^0 + (d\gamma/dm)m, \qquad (2)$$

and the standard error of the estimate of γ on m are shown in Table 1.
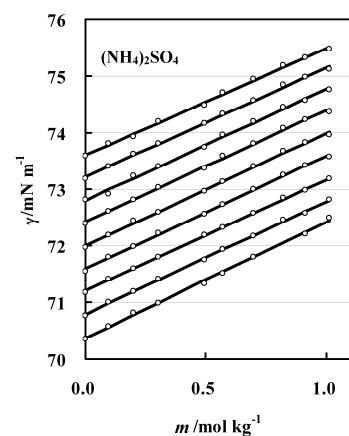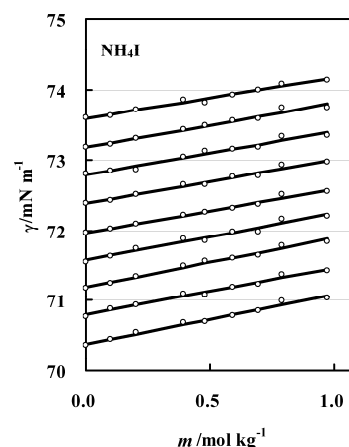
We note immediately a close similarity in the behavior of dγ/dm for ammonium halide and sodium halide solutions. The magnitude of dγ/dm due to adsorbed ions is appreciable and it decreases with the decreasing hydration force of the anions. Further, the results for solutions of ammonium nitrate are found in the order between NH_4Br and NH_4I as expected from previous work [15].

Since experimentally observed γ-versus-m curves over the concentration range 0 to 1 mol kg^{-1} show a good linear correlation with few exceptions, dγ/dm has been used as an empirical parameter to predict effectiveness of salts in promoting depletion depth. However, we have shown that the ratio of the surface excess density to the molality of salt solution, Γ^H/m, helps us more adequately for expressing the surface activity of salts than dγ/dm itself [16], because it is a kind of partition coefficient of the electrolytes between surface region and bulk solution. For a salt which dissociate v_+ cations and v_- anions, the Γ^H/m is given as

$$\frac{\Gamma^H}{m} = \frac{-1}{RT(v_+ + v_-)}\left(\frac{d\gamma}{dm}\right)_{T,p}\bigg/\left[1+\left(\frac{\partial \ln f_{\pm}}{\partial \ln m}\right)\right]_{T,p} , \qquad (3)$$

where $f_{\pm}$ is the mean activity coefficient of the salt. If we assume that the electroneutrality must be hold in the surface region, there are equalities,

$$\frac{\Gamma^H}{m} = \frac{\Gamma^H_+}{m_+} = \frac{\Gamma^H_-}{m_-} = \frac{\Gamma^H_+ + \Gamma^H_-}{m_+ + m_-} . \qquad (4)$$

Since $d\ln f_{\pm}/d\ln m$ approaches zero as m approaches zero, the numerical values of Γ^H/m at infinite dilution will be evaluated provided that dγ/dm is practically independent of concentration. In order to show the close correlation between Γ^H/m and hydration forces, the
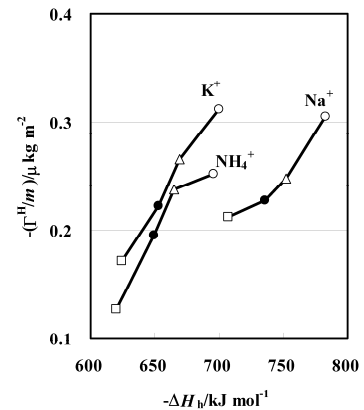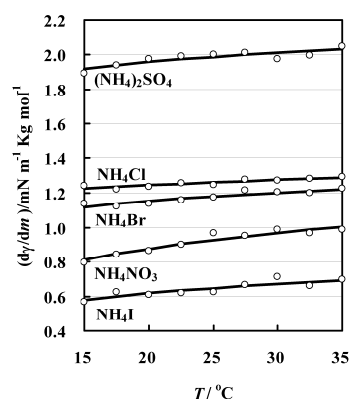
Γ^{H}/m values of ammonium salts at infinite dilution are plotted in Fig. 3 against enthalpy change of hydration ΔH_h given in the textbook by Marcus [17], together with those for sodium and potassium salts. Solid lines are used to represent a series of salts with a common cation such as from right to left sodium, ammonium, and potassium salts; and markers are used to distinguish anions. It can be seen from the figure that the observed slopes of three solid lines are comparable each other, and that the plots show simple regularity. The order for the anions is chloride, bromide, nitrate, and iodide. Moreover, we clearly see that the Γ^{H}/m of the salts of the polyatomic anion nitrates lie on the same line as that of halides. This observation confirms that the hydration force is predominantly relevant to the contribution of univalent anions.

It is generally recognized that anions are accumulated in the upper layer of the surface region and cations are adsorbed next to the anion layer [11, 12, 18]. This behavior of ions implies that the ion – water or ion – air interaction in the surface region will afford a specific explanation, depending on the positive or negative charge of them. For the cations, in fact, the results shown in Fig. 3 are the demonstrations that Γ^{H}/m show no simple correspondence with hydration force. The hydration of alkali metal chloride which decreases in the order LiCl > NaCl > KCl > CsCl will not account for the order of the magnitude of Γ^{H}/m, although the reverse is true for NaI and KI. For alkali metal nitrate, we have shown that change in the cation species does not affect on the magnitude of dγ/dm [15]. When the magnitudes for ammonium salts are compared with those for alkali metals salts of common anion, it is obvious that the negative departures from the lines connecting potassium and sodium salts show the individuality

of the ammonium salts. It is to be noted that this deviation does not observed for salts with polyatomic nitrate anion.

The variations observed in the values of dγ/dm with temperature given in Table 1 are plotted in Fig 4. It increases with increase in temperature and concave downward. Although the magnitude of the dγ/dm has been used in relation to the hydration force, the plots with a positive slope do not indicate the enhancement of the hydration at higher temperatures. It indicates that the adsorption of salts at the surface accompany a decrease in the entropy change of the surface formation. The slope of the plots is steep at low temperature and gradually decreases as the temperature increases. Equation (1) suggests that magnitude of the decrease in the entropy change decreases with increasing temperature. We have shown that the slope of the dγ/dm versus temperature for sodium halides decreases in the order NaI > NaBr $\approx$ NaCl > NaF which is in the reverse order to the hydration [10]. For ammonium chloride, the plot lies closer to those for bromide but it exhibits smaller slope than bromide and iodide as expected from the hydration of these salts.

We have shown that the slopes of the plots of dγ/dm against temperature are very sensitive to contamination of ions. For ammonium salts, hydrolysis reaction leads to a shift of a proton from ammonium ion to water molecule and a decrease in hydroxyl anions from solution. Using the ionization constants of ammonia in aqueous solution, 1.77×10^{-5} [19], and assuming that molality can be used instead of activity, it is possible to calculate the concentration of each species in solution. The pH of aqueous

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ammonium chloride solution is measured to be 5.1 for 0.1 mol kg^{-1} solution and 4.6 for 1 mol kg^{-1} solution. The concentration of NH_4^+ is the same with the weighed concentration of the salts to the fourth significant figure. There is a possibility of obtaining a disturbed dγ/dm versus temperature curves by hydrolysis products. However, there is no proof that this really happened, since the positive slope of dγ/dm versus temperature plot is observed. Comparison of dγ/dm values with the average values of the reported data which occur in the literature for ammonium salts shows higher values of order of 5 to 16% than our results [20]. Table 1 shows 0.64 at 25 ^{o}C for NH$_4$I solution which shows largest discrepancy of 16%, while literature value is given as 0.74 at 18°C. If we assume that literature value increases with temperature at the same rate as our results, it will show about 0.84. The possibility of contamination remains, but we believe that the surface tension measurements in general are subject to systematic error caused by experimental conditions.
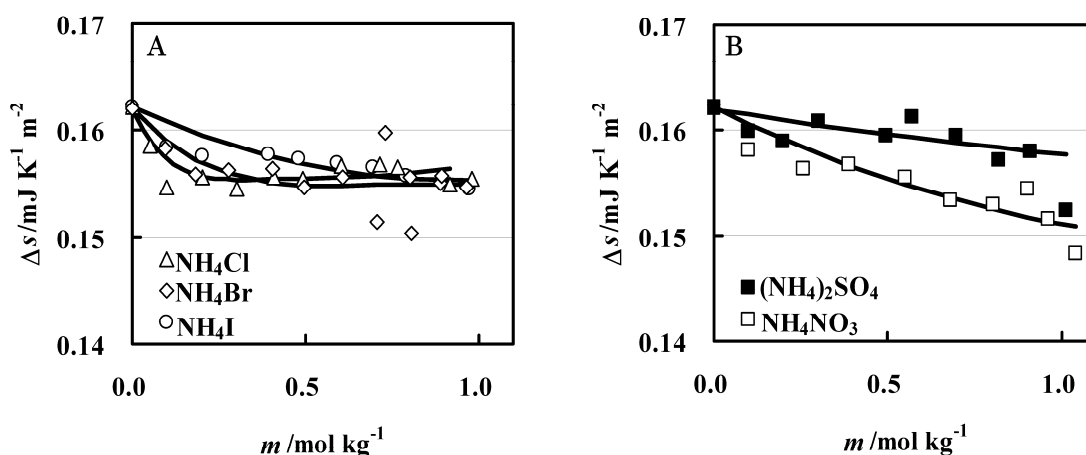

Figure 5A shows the graphs of the entropy change associated with the formation of the surface, Δs, of the ammonium halides. The Δs of pure water/air surface shows positive value of 0.162 mJ K^{-1} m^{-2} and it decreases gradually to about 0.15 mJ K^{-1} m^{-2} with the

increase in the salt concentration. The positive value of pure water/air sruface can be attributed to the mixing and expansion of the air and water at the surface. However, the decreases in Δs are ascribed to a formation of the ionic double layer at the surface rather than the increased interactions between ions and water. For sodium halide solutions, this lowering in Δs is greater the smaller the hydration of anions; the Δs of NaI solution decreases to about 0.15 mJ K^{-1} m^{-2} while that of NaF solution is very limited [10]. For ammonium halide solution, the distinction among three salts is not found clearly but show lowering in Δs of the same magnitude. Since, however, the roughly estimated magnitude of the slope of the curve shown in Fig.3 for NH_4Cl. NH_4Br, and NH_4I are 0.0029, 0.0049, and 0.0054 mN m^{-1} $mole^{-1}$ kg K^{-1} at 25 ^{o}C, respectively, we can note that the tendency observed for sodium halides is also observed for ammonium halides. Figure 5B illustrates the slight though measurable lowering of the value for 1:2 valence type $(NH_4)_2SO_4$ and the definite lowering caused by 1:1 type NH_4NO_3, and confirms this tendency.

It is possible to represent graphically the Γ^H/m versus ΔH_h for a series of salts with a common cation on smooth curves as shown in Fig. 3, but it is hard to extrapolate the empirical curves to a point for a salt of different valence type. It is therefore practicable to explain the observed specificity of ammonium sulfate by comparing its Γ^H/m with those of the salts of the same

valence type. In Fig 6, the Γ^H/m of them at infinite dilution are plotted against the enthalpy change of hydration. There is no doubt that the plots for alkali-metal sulfate
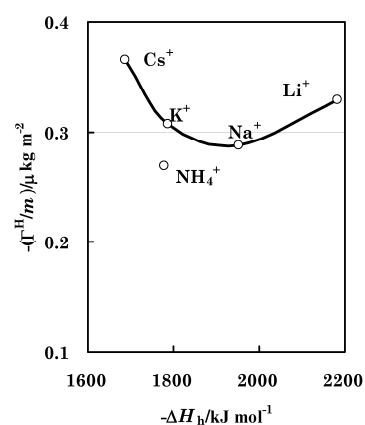
will be connected by a smooth curve which is concave upward; although we have no satisfactory explanation of the shape of the curve. The same plot yields the curve with negative slope for alkali metal chlorides and almost horizontal line for alkali metal nitrate, respectively. These observations indicate that magnitude of the Γ^H/m and $d\gamma/dm$ would be parameters characteristic of the individual salt instead of the combination of the properties of ions. It is therefore assumed that the deviation of the parameters of ammonium sulfate from the smooth curve can be attributed to interactions between cation and anion in the surface region instead of the hydration force.

Conclusions

The surface tension measurements show that cations especially ammonium ions have strong propensity for the magnitude of $d\gamma/dm$ in contrast to anions which satisfy the expectation that the surface tension increments should be related to the extent of hydration. The variation of the entropy change associated with the surface formation shows a formation of the ionic double layer similarly as observed for simple alkali metal halides. These results indicate that interactions between anions and cations in the surface region are responsible for a considerable part of the surface tension increments.

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FIGURE READINGS

Figure 1. Surface tension of ammonium iodide solutions as a function of concentration. Temperatures of solutions are, from bottom to top, 35.0, 32.5, 30.0, 27.5, 25.0, 22.5, 20.0, 17.5, and 15.0 $^{\circ}$C, respectively.

Figure 2. Surface tension of ammonium sulfate solutions as a function of concentration. Temperatures of solutions are, from bottom to top, 35.0, 32.5, 30.0, 27.5, 25.0, 22.5, 20.0, 17.5, and 15.0 $^{\circ}$C, respectively.

Figure 3. Variation of the surface activity of uni-univalent salts with enthalpy change of hydration at 25 $^{\circ}$C. Solid lines connect a series of salts with a common cation such as from right to left, sodium, ammonium, and potassium salts. Markers are used to distinguish chlorides (open circles), bromides (triangles), nitrates (closed circles), and iodides (squares), respectively. The value of KI solution is the experimental data from ref. [20].

Figure 4. Dependence of dγ/dm upon temperature.

Figure 5. Plots of entropy change associated with the formation of the surface Δs. A: ammonium halides. B: ammonium sulfate and nitrate.

Figure 6. Comparison of the surface activity of alkali metal sulfates and the ammonium sulfate. The alkali metal sulfates are connected by a solid line.

TABLE 1

Coefficients of the regression line, $\gamma = \gamma^0 + (d\gamma/dm)m,$ and standard error of estimate

of γ on m (SE)

T	γ^0	$d\gamma/dm$	SE	T	γ^0	$d\gamma/dm$	SE
	NH$_4$Cl				NH$_4$Br		
15.0	73.56	1.24	0.018	15.0	73.58	1.14	0.041
17.5	73.18	1.22	0.015	20.0	73.20	1.12	0.028
20.0	72.78	1.23	0.022	22.5	72.80	1.14	0.027
22.5	72.39	1.26	0.017	22.5	72.39	1.16	0.047
25.0	71.98	1.25	0.020	25.0	71.99	1.18	0.038
27.5	71.60	1.28	0.021	27.5	71.59	1.22	0.043
30.0	71.20	1.27	0.022	30.0	71.20	1.20	0.036
32.5	70.80	1.28	0.020	32.5	70.83	1.20	0.055
35.0	70.41	1.29	0.023	35.0	70.41	1.23	0.047
	NH$_4$I				NH$_4$NO$_3$		
15.0	73.59	0.57	0.032	15.0	73.59	0.80	0.029
17.5	73.18	0.63	0.037	17.5	73.18	0.84	0.038
20.0	72.80	0.61	0.043	20.0	72.79	0.86	0.027
22.5	72.38	0.62	0.030	22.5	72.38	0.90	0.027
25.0	71.96	0.63	0.027	25.0	71.95	0.97	0.027
27.5	71.58	0.67	0.043	27.5	71.56	0.95	0.014
30.0	71.19	0.71	0.029	30.0	71.16	0.99	0.019
32.5	70.80	0.66	0.032	32.5	70.79	0.97	0.019

35.0	70.38	0.70	0.030		35.0	70.38	0.99	0.013

	(NH$_4$)$_2$SO$_4$		
15.0	73.60	1.89	0.035
17.5	73.22	1.94	0.030
20.0	72.80	1.97	0.042
22.5	72.42	1.99	0.033
25.0	71.00	2.00	0.032
27.5	71.59	2.01	0.028
30.0	71.20	1.98	0.016
32.5	70.79	2.00	0.023
35.0	70.37	2.05	0.038