Heat Capacity Changes of Alkyl-substituted Ammonium Chlorides in Aqueous Solutions

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The changes in the heat capacity for the dissolution in water, ΔC_p°, of *n*-alkylammonium chlorides (methyl to hexyl), di-*n*-alkylammonium chlorides (methyl to butyl), and tri-*n*-alkylammonium chlorides (methyl to propyl) at the room temperature were determined from measurements of the relation between the heats of solution of these salts in water and the temperature, and the results were compared with the ΔC_p° values for tetraalkylammonium salts in the literature. It was found that the effect of the coordination of the charge-bearing nitrogen atom by alkyl groups was definitely reflected in the ΔC_p° values. In the cases of $MeNH_3Cl$, $EtNH_3Cl$, Me_2NH_2Cl, and Me_3NHCl, the ΔC_p° values are negative, while in the cases of other higher homologues, the ΔC_p° values are positive; the increments in the ΔC_p° values per methylene group are discussed in terms of the hydrophobic hydration and the steric effect of alkyl chains.

Recently, studies of the behavior of electrolytes with attached nonpolar groups, particularly of tetraalkylammonium salts, R_4NX, have been extensively carried out by various experimental methods.[1-5] Measurements of the heat capacities of aqueous electrolytes solutions produce useful information about the influences of ions on the structure of solvent water.[6] The changes in the heat capacities for the dissolution in water of simple salts indicate negative values, whereas the changes in the heat capacities for the dissolution in water of nonpolar solutes indicate positive values. This characteristic relation has been applied to the study of R_4NX salts in water, and the behavior of R_4NX salts has been discussed in terms of the modification of the water structure around the nonpolar parts.[6-12] To elucidate the role of the alkyl groups on the coordination of the charge-bearing nitrogen atom, it seems of great interest to study the behavior of incompletely alkylated ammonium salts in water.

In this paper, we will report our experimental results on the changes in the heat capacity for the dissolution in water of *n*-alkylammonium chlorides RNH_3Cl (methyl to hexyl), di-*n*-alkylammonium chlorides R_2NH_2Cl (methyl to butyl), and tri-*n*-alkylammonium chlorides R_3NHCl (methyl to propyl); we will discuss the results in terms of the balance of two types of hydration-namely, electrostrictive hydration due to the ionic part and hydrophobic hydration due to the nonpolar part.

The change in the heat capacity for the dissolution at infinite dilution, ΔC_p°, may be obtained from the relation between the heat of solution at infinite dilution, ΔH_s°, and the temperature, T:[13]

$$d\Delta H_s^\circ/dT = \Delta C_p^\circ = \bar{C}_p^\circ - C_p \qquad (1)$$

where $\bar{C}_p^\circ$ is the partial molal heat capacity of the solute at infinite dilution, and C_p the heat capacity of the pure salt.

Experimental

NH_4Cl was a commercial sample of a G. R. grade. The other organic chemicals were obtained from Tokyo Kasei Kogyo Co. RNH_3Cl salts were the same samples as have been described elsewhere.[14] Pr_2NH_2Cl, Bu_2NH_2Cl, and Pr_3NHCl were prepared by the neutralization of the respective amines with gaseous hydrogen chloride in benzene. All the organic salts were recrystallized from suitable solvents: ethanol for Me_2NH_2Cl, Et_2NH_2Cl, Pr_2NH_2Cl, and Me_3NHCl; ethyl acetate for Pr_3NHCl; and ethanol–ethyl acetate mixtures for Bu_2NH_2Cl and Et_3NHCl. Water was redistilled from an alkaline permanganate solution.

The heats of solution were measured by means of a twin conduction microcalorimeter (Model CM-204D1 of Ōyodenki Kenkyujo) described in a previous paper.[15] The uncertainties of the heat-of-solution data obtained in this work were estimated to be within 0.03 kcal/mol at 10—25 °C and 0.05 kcal/mol at 30—45 °C. The concentration of the measured solution was 0.01 M, and the heat of dilution from a solution at 0.01 M to one at a large dilution is about $-0.03 \sim -0.04$ kcal/mol for NH_4Cl, $MeNH_3Cl$, Me_2NH_2Cl, and Me_3NHCl.[16] In view of this situation, the mean values of the heats of solution repeatedly measured at 0.01 M are presented in this paper. The ΔC_p° values are obtained by assuming that the change in the heat capacity at 0.01 M is equal to that at infinite dilution.[15]

Results

The heats of solution obtained for three homologous series of RNH_3Cl, R_2NH_2Cl, and R_3NHCl are listed in Table 1. The ΔH_s° values at 25 °C reported by Krishnan and Friedman[17] for RNH_3Cl salts, Me_2NH_2Cl, Bu_2NH_2Cl, and Me_3NHCl are also included in Table 1. Except for Bu_2NH_2Cl, the heats of solution obtained in this work at 25 °C are in fairly good agreement with those reported by Krishnan and Friendman.[17] Taking account of the experimental uncertainties described above, the heats of solution can be regarded as approximately a linear function of the temperature over the range studied. The approximate linear relation between the heat of solution and the temperature in the range of room temperature has sometimes been reported.[10] The mean ΔC_p° values in the range of measurements are obtained from the average slope of the linear plots of the heats of solution against the temperature: the results are listed in Table 2. For comparison, the ΔC_p° values at room temperature reported for R_4NBr salts in the literature[7,10] are also included in Table 2. As will be explained below, the difference in ΔC_p° values due to the variation in halide ions for the same cation is very small. Therefore, the ΔC_p° values of R_4NBr salts may well be

TABLE 1. HEAT OF SOLUTION

R	RNH$_3$Cl 10 °C kcal/mol	25 °C kcal/mol	40 °C kcal/mol	45 °C kcal/mol
H	4.01	3.54	—	2.90
Me	1.80	1.42 1.42 a)	—	0.97
Et	2.15	2.05 2.08 a)	2.00	1.94
Pr	0.24	0.38 0.33 a)	0.56	0.60
Bu	−0.96	−0.64 −0.64 a)	−0.31	—
Pen	−0.76	−0.20 −0.23 a)	0.34	—
Hex	−0.50	0.31 0.28 a)	1.16	—

R	R$_2$NH$_2$Cl 10 °C kcal/mol	15 °C kcal/mol	25 °C kcal/mol	35 °C kcal/mol
Me	0.69	—	0.48 0.47 a)	0.34
Et	—	0.17	0.38	0.57
Pr	−2.55	—	−1.80	−1.28
Bu	−2.61	—	−1.43 −1.61 a)	−0.65

R	R$_3$NHCl 10 °C kcal/mol	25 °C kcal/mol	30 °C kcal/mol	35 °C kcal/mol
Me	1.01	0.85 0.83 a)	0.80	—
Et	0.68	1.04	—	1.29
Pr	−2.66	−1.51	—	−0.76

a) Ref. 17

TABLE 2. CHANGE IN HEART CAPACITY FOR DISSOLUTION (ΔC_p°) AND INCREASE IN ΔC_p° PER METHYLENE GROUP (ΔC_p°/–CH$_2$–)

R	ΔC_p° cal/K mol		ΔC_p°/–CH$_2$– cal/K mol	
	RNH$_3$Cl			
H	−32			
Me	−24		8	
Et	−6		18	
Pr	10		16	
Bu	22		12	
Pen	37		15	
Hex	55		18	
	R$_2$NH$_2$Cl			
Me	−14			
Et	20		17	
Pr	51		15.5	
Bu	78		13.5	
	R$_3$NHCl			
Me	−11			
Et	24		12	
Pr	76		17	
	R$_4$NBr			
Me	−11.3 a)	−10.1 b)		
Et	30 a)	33 b)	10.3 a)	10.8 b)
Pr	106 a)	112.5 b)	19 a)	20 b)
Bu	176 a)	179 b)	15 a)	17 b)

a) Ref. 10, b) Ref. 7.

used in place of R$_4$NCl salts for the purpose of considering the effect of alkyl chains on the behavior of alkyl-substituted ammonium salts in water.

Discussion

The $\Delta\bar{C}_p^\circ$ Value as the Ion-solvent Interaction Parameter. The $\bar{C}_p^\circ$ value is of thermodynamical importance for the study of electrolyte solutions.18) The $\bar{C}_p^\circ$ value can be obtained by the measurement of the heat capacities of solutions at dilute concentrations.18) There have been reports about the $\bar{C}_p^\circ$ values for methyl- and ethylammonium chlorides by Rüterjans, Schreiner, Sage, and Ackermann,19) for a series of *n*-alkylammonium bromide-by Leduc, Fortier, and Desnoyers.20) and for some di-*n*-alkylammonium chlorides by Cobani, Conti, Martinelli, and Matteoli.21) Alternatively, if the C_p value is known, the $\bar{C}_p^\circ$ value can be obtained by adding the C_p and ΔC_p° values by means of Eq. (1). Furthermore, it is assumed that the $\bar{C}_p^\circ$ value consists of two contributions; the first is the intrinsic heat capacity of the ions in the absence of ion-solvent interactions, while the second is the contribution arising from the influence which the ions exert on the solvent structure:11)

$$\bar{C}_p^\circ = \bar{C}_p^\circ(\text{int}) + \bar{C}_p^\circ(\text{solv}) \qquad (2)$$

Thus, in order to discuss the interaction of ion with solvent using the data of the $\bar{C}_p^\circ$ value, we must obtain the $\bar{C}_p^\circ$ (solv) value by substracting the appropriate value of the $\bar{C}_p^\circ$(int) value from the $\bar{C}_p^\circ$ value. For the $\bar{C}_p^\circ$(int) value, Visser and Somsen11,12) adopted the hypothetical liquid state of the salt. On the other hand, Leduc, Fortier, and Desnoyers20) assumed two limiting cases for the $\bar{C}_p^\circ$(int) value; one is as the liquid state, and the other is as the solid crystalline.

If we regard $\bar{C}_p^\circ$(int) as the capacity of the solid crystalline, ΔC_p° in Eq. (1) corresponds to $\bar{C}_p^\circ$(solv) in Eq. (2). In other words, the ΔC_p° value is a measure of ion-solvent interactions if the standard state of the salt is taken as the solid state.

A variety of simple salts show negative $\bar{C}_p^\circ$ values in water, which may be interpreted in terms of electrostrictive hydration.22) For example, the $\bar{C}_p^\circ$ values for NaCl, NaBr, and NaI are −22.1, −23.3, and −23.4 cal/K mol at 25 °C respectively.23) If we use 11.9, 12.5, and 13.0 cal/K mol for the corresponding C_p values at 25 °C in the literature,24) the ΔC_p° values become −34.0, −35.8, and −36.4 cal/K mol respectively. Likewise we can conclude that the ΔC_p° values for other alkali halides do not vary greatly with the different halide ions, such as Cl$^-$, Br$^-$, and I$^-$ ions. On the other hand, the ΔC_p° values for organic solutes with nonpolar groups, such as alkyl alcohol,25) alkane carboxylic acids,26) and alkylamines,26) are all positive, which may be interpreted in terms of the promotion of the water structure around the nonpolar groups in water (hydrophobic hydration).

RNH_3Cl Salts. NH_4Cl is a typical simple salt, the $\Delta C_p°$ value being as low as -32 cal/K mol, as may be seen in Table 2. In a previous study of viscosity *B* coefficients,[14] we proposed that the $-NH_3^+$ ionic part is an electrostrictive structure-breaker. Table 2 indicates the negative $\Delta C_p°$ values for $MeNH_3Cl$ and $EtNH_3Cl$. Leduc, Fortier, and Desnoyers[20] showed that the $\bar{C}_p°$—$\bar{C}_p°$(int) values for $MeNH_3Br$ and $EtNH_3Br$ are negative, whether the $\bar{C}_p°$(int) value is taken as a liquid or a solid state. Therefore, it may be concluded that the electrostrictive hydration due to the charge-bearing nitrogen atom may interfere with the interaction of hydrophobic methyl or ethyl groups with water in RNH_3Cl salts. In the cases of $PrNH_3Cl$ and higher homologues, the $\Delta C_p°$ values become positive, and they increase with an increase in the chain length. They are classifiable as hydrophobic structure-making solutes. The average increment in the $\Delta C_p°$ values per methylene group from $MeNH_3Cl$ to higher homologues is about 16 cal/K mol; this value corresponds approximately to the value in the series of nonelectrolytes such as alcohol.[25]

Previous studies of the viscosity *B* coefficient[14] and the surface activity[27] seem to indicate that $EtNH_3Cl$ may be classified as a weak hydrophobic structure-making solute. Although it is difficult to draw any definite conclusions, the ambiguity in the behavior of this salt in water is probably attributable to the fact that $EtNH_3Cl$ is a borderline solute.

R_2NH_2Cl Salts. As may be seen in Table 2, the $\Delta C_p°$ value for Me_2NH_2Cl is negative, but the value is less negative than that of $MeNH_3Cl$, showing the cooperative hydrophobic effect of the two methyl groups. In the cases of Et_2NH_2Cl, Pr_2NH_2Cl, and Bu_2NH_2Cl, the $\Delta C_p°$ values become positive, and they are hydrophobic structure-makers. The increments in the $\Delta C_p°$ values per methylene group from Me_2NH_2Cl to Bu_2NH_2Cl are about 15 cal/K mol, suggesting that the two alkyl chains can interact independently with water in R_2NH_2Cl series.

R_3NHCl and R_4NBr Salts. The $\Delta C_p°$ values for Me_3NHCl and Me_4NBr are about -11 cal/K mol, only slightly less negative than that of Me_2NH_2Cl. Although the $\Delta C_p°$ values for ethyl salts and higher homologues are positive in R_3NHCl and R_4NBr salts, the increments in the $\Delta C_p°$ values per methylene group from methyl salt to ethyl salt are 10—12 cal/K mol; the values are smaller than the average value of 16 cal/K mol in a series of straight-chain solutes. These facts suggest that methyl and ethyl groups cannot freely interact with water due to the steric configuration in both series. However, judging from the increments in the $\Delta C_p°$ values per methylene group from Et_3NHCl to Pr_3NHCl salts and from Et_4NBr to Bu_4NBr salts, the methylene groups of the C-3 position and the longer parts of the alkyl chains attached to the charge-bearing nitrogen atom are free from the steric effect on the interaction with water in both series.

In conclusion, all the methyl salts of the four types of alkyl-substituted ammonium salts in water are predominantly governed by electrostrictive hydration. $EtNH_3Cl$ is probably a borderline solute. The other salts studied are hydrophobic structure-makers, but the effect of alkyl groups on the hydrophobic hydration is slightly weakenened as a result of the steric configuration in R_3NHCl and R_4NX series.

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