The Volumetric Behavior of Several Ammonium Chlorides in Aqueous 18-Crown-6 Solutions

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Synopsis. The complexation of 18-crown-6 with primary ammonium chlorides [$H(CH_2)_nNH_3Cl$, n=0, 1, 2, and 4] caused an increase in volume, which was attributable to the dehydration of the ammonium moieties. On the other hand, the apparent molal volumes of $(CH_3)_{4-n}NH_nCl$ (n=0—2) were not affected appreciably by the presence of the crown ether, and their complex stability seemed to be insignificant.

A positive change in volume was found for the formation of aqueous complexes between crown ethers and metallic cations, and this increase was attributed to the partial dehydration of the guest ions.[1,2] The volumetric behavior of several ammonium chlorides was investigated in aqueous 18-crown-6 solutions in order to obtain information about the change in the dissolution state of these solutes during complexation.

Experimental

The following chemicals were obtained from the indicated suppliers: NH_4Cl (99%), CH_3NH_3Cl (99%), $(CH_3)_2NH_2Cl$ (99%), $(CH_3)_3NHCl$ (98%), $(CH_3)_4NCl$ (99%) (Nakarai Chemicals); $C_2H_5NH_3Cl$ (99%), n-$C_4H_9NH_3Cl$ (99%) (Tokyo Chemical Industry Co.); 18-crown-6 (99%) (Aldrich Chemical Co. and Nippon Soda Co.). The NH_4Cl, the CH_3NH_3Cl, and the other salts were recrystallized twice from ethanol–water, ethanol–methanol, and ethanol–acetone mixtures respectively and dried under a vacuum at 50—55 °C for 24 h. The 18-crown-6 was dissolved in acetonitrile, and the resultant adduct was precipitated from the solution by cooling in an ice–acetone bath.[3] The weakly bound acetonitrile was removed under a vacuum at 30—35 °C for 24 h. The purified product had a melting point of 39.2—40.5 °C, in satisfactory agreement with the literature values of 39—40 °C[4] and 39.5—40.5 °C.[5] The water was distilled and deionized before use.

The solution densities were measured at 25.00±0.002 °C on an Anton Paar densimeter, Model 60/601, with an accuracy of $\pm 2\times10^{-6}$ g cm^{-3}. Each set of measurements was made on condition that X_w (see below) was maintained constant. The apparent molal volumes (ϕ_v) were calculated from the following equation:

$$\phi_v = (d_0-d)/mdd_0X_w + M/d,$$

where M is the molecular weight of an ammonium salt; m, its molality; X_w, the weight fraction of water in a binary solution consisting of water and crown ether; d_0, the density of this binary solution or that of pure water when $X_w=1$, and d, the density of a ternary solution prepared by the addition of the ammonium salt to the binary solution, the weight fraction of water of which is X_w.

Results and Discussion

The ϕ_v values of alkylammonium chlorides in water were fitted into the Redlich-Meyer equation:

$$\phi_v = \bar{V}^\circ + S_v\sqrt{c} + b_vc,$$

where $\bar{V}^\circ$ is the limiting partial molal volumes of the salts; c, the molar concentration; S_v, the Debye-Hückel limiting slope, and b_v, an empirical constant. The values of $\bar{V}^\circ$/cm^3 mol^{-1} and b_v/cm^3 dm^3 mol^{-2} thus obtained were 53.87 and -0.4_0, 72.43 and -1.0_8, 90.62 and -0.9_3, 107.51 and -1.6_6, 71.24 and -0.9_1, and 103.39 and -1.8_7 for CH_3NH_3Cl, $(CH_3)_2NH_2Cl$, $(CH_3)_3NHCl$, $(CH_3)_4NCl$, $C_2H_5NH_3Cl$, and n-$C_4H_9NH_3Cl$ respectively. These values were in excellent agreement with other reported values.[6,7] The ϕ_v values of NH_4Cl in water were taken from the data in the literature.[8] The ϕ_v of 18-crown-6 in water (ϕ_{CR}) was given by:

$$\phi_{CR}/\text{cm}^3\,\text{mol}^{-1} = 223.26 - 2.9_4\, m_{CR}/\text{mol kg}^{-1},$$

where m_{CR} is the molality of 18-crown-6.

As is shown in Fig. 1, the presence of the crown ether causes a large increase in ϕ_v. Similar results were obtained for the ϕ_v of methylammonium, ethylammonium, and butylammonium chlorides. In contrast, the ϕ_v of NH_4Cl was hardly affected by the presence of triethylene glycol dimethyl ether, in which system the complex formation need not be considered. These findings lead to the conclusion that the complexation between the cations and the crown ether causes a volume increase, the origin of which will be discussed below.

For this purpose, the ϕ_v of the complex ($\phi_{complex}$) should be estimated. In ternary solutions of water, ammonium or alkylammonium chloride (MCl), and crown ether (CR), the following equilibrium exists:

$$M^+ + Cl^- + CR \rightleftharpoons [M\cdot CR]^+ + Cl^-.^{9)}$$

The apparent molal volumes determined therefore contain a contribution from the complexed species. The $\phi_{complex}$ was estimated on the basis of the additivity of the apparent molal volumes:

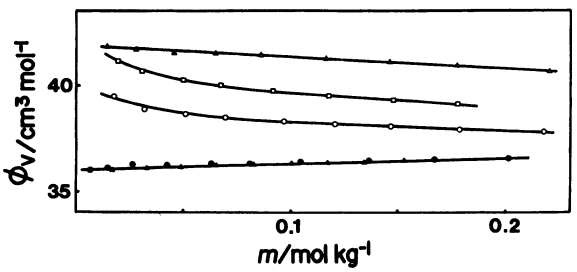

Fig. 1. Apparent molal volumes of NH_4Cl against its molality at 25 °C.
▲: In water, ○, □, and △: in 0.04996, 0.09085, and 0.2112 mol kg^{-1} aqueous 18-crown-6 solutions, respectively, ●: in 0.04915 mol kg^{-1} aqueous triethylene glycol dimethyl ether solution.

Table 1. Volume increase for the formation of 18-crown-6 complexes

Guest molecule	NH_4Cl	CH_3NH_3Cl	$CH_3CH_2NH_3Cl$	$CH_3(CH_2)_3NH_3Cl$	$CH_3(CH_2)_5NH_3Cl$[a]
ΔV/cm^3 mol^{-1}	6.9	2.4	2.5	2.9	3.1

a) Ref. 16.

$$(m_{MCl}+m_{CR})\Phi_v = m_{MCl}(1-\alpha)\phi_{MCl} + (m_{CR}-\alpha m_{MCl})\phi_{CR} + \alpha m_{MCl}\phi_{complex},$$

in which Φ_v is the mean apparent molal volumes of ternary solutions, m_{MCl} and m_{CR} are the total concentrations (including the complexed species) of MCl and CR in the ternary solutions respectively, ϕ_{MCl} and ϕ_{CR} are the apparent molal volumes of the solute species in water at the ionic strength of m_{MCl}, and α is the fraction of MCl in the complexed state. The values of α were calculated from the reported values of stability constants.[10] The $\phi_{complex}$ was evaluated on the additional assumption that the ϕ_{CR} does not depend on the ionic strength in solutions. Since the $\phi_{complex}$ thus obtained had a slight dependence on the ionic strength and the concentration of the crown ether, the partial molal volume at an infinite dilution ($\bar{V}^\circ_{complex}$) was determined by the extrapolation of $\phi_{complex}$ to $\sqrt{m_{MCl}}=0$ and $m_{CR}=0$. Table 1 tabulates the changes in volume for the complex formation, $\Delta V=\bar{V}^\circ_{complex}-(\bar{V}^\circ_{MCl}+\bar{V}^\circ_{CR})$.

The conventional heavy-atom technique has revealed the crystal structure of the 18-crown-6–NH_4Br complex, in which the ammonium cation is too large to fit into the cavity of the crown ether and the nitrogen atom makes three hydrogen bondings through its hydrogen atoms with the three oxygen atoms of the crown ether. Presumably a similar structure holds for the complex in solutions; this also seems to be the case for the primary alkylammonium ion complexes under investigation, as has been generally accepted on the basis of the examination of the CPK molecular models of possible complexes.[12,13] It is highly possible that the dense structure of water molecules electrostricted around the ammonium moieties is released during complexation because of the hydrogen bonding between the host and guest molecules. This process should, therefore, be accompanied by an increase in volume. A volume change caused by the dehydration of ions can be evaluated from their intrinsic and partial molal volumes.[14] For an ammonium ion was obtained an increase of 7.5 cm^3 mol^{-1}, which is comparable to the ΔV value in Table 1. This indicates that the main contribution to ΔV is the removal of water molecules from around the ammonium ion on complexation, although it is still possible for the complexed ion to contact water in the direction perpendicular to the plane of the crown-ether ring. The effect of the crown ether itself on ΔV is, though still obscure, probably small.

The substitution of a CH_3 group for H on NH_4^+ leads to a marked decrease in ΔV values. The hydrophobic residue, because of its bulkiness, occupies a volume where, in the case of the formation of the 18-crown-6 complex with NH_4^+, some water molecules to be dehydrated are located, thus leading to a decrease in ΔV. An alternative or an additional reason is that the water to be released from near the CH_3 group is not so dense as the electrostricted molecules. A similar situation is to be expected for the complex formation of the other *n*-alkylammonium ions, so nearly the same values of ΔV were obtained.

In contrast to the volumetric behavior of primary ammonium salts, only a slight decrease was found for the ϕ_v values of dimethylammonium, trimethylammonium, and tetramethylammonium ions in the presence of the crown ether. This finding suggests the insignificant stability of complexes with these cations,[15] for which the reduction in the number of hydrogen bondings available for the host-guest interaction may be responsible.

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15) **Note added in proof.** The stability of the complex with the dimethylammonium ion was examined by a modified potentiometric method of the literature procedure.[10] An appropriate amount of 18-crown-6 was added to a solution of $(CH_3)_2NH_2Cl$ which had been titrated to half the equivalence point with LiOH. The change in the pH of the solution caused by the addition of the crown ether gave no significant values for the stability constant.
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