
**CONTRIBUTIONS TO THE CHEMISTRY OF HIGHLY CONCENTRATED
AQUEOUS ELECTROLYTE SOLUTIONS. XXIII.*****A DENSIMETRIC STUDY
OF THE NH_4^+ ION IN AQUEOUS SOLUTIONS**

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The densities of aqueous solutions of ammonium salts revealed — using the formerly developed model — that, in contrast to the H_3O^+ ion, the NH_4^+ ion in the solution is not hydrogen-bonded to the tetrahedral structure of liquid water but behaves as a spherical “water-unlike” particle that interacts with the neighbouring water molecules by the electrostatic orienting ion-dipole forces, similarly to the ions K^+ , Rb^+ and Cs^+ .

In our preceding papers¹⁻⁵ a model has been presented which can be used for the determination of the ion hydration in aqueous solutions from apparent ionic volumes. In the present paper these considerations are applied to the ammonium ion.

There are no definite data on the hydration of the NH_4^+ ion in the aqueous solutions. From the NMR spectra and from the Wien's effect in the aqueous solutions of ammonia it has been concluded⁶ that the molecule of ammonia (which can be regarded as a deprotonized form of the NH_4^+ cation) is, for the most time, not hydrated in the solution. From the total 90% of the period, in which no proton is shifted to the NH_3 molecule from the neighbouring water molecules, only about 15% correspond to the existence of the hydrogen bond $\text{H}_3\text{N} \rightarrow \text{HOH}$ while for full 75% of the period the molecule is present in its free state. (The remaining 10% of the period correspond to the state with a proton shifted to the NH_3 molecule, *i.e.* to the predissociation to $\text{NH}_4^+ + \text{OH}^-$).

The bond length of 2.78 Å has been found by the X-ray structural analysis in the crystalline hydrate $\text{NH}_3 \cdot \text{H}_2\text{O}$ for the bond $\text{N} \rightarrow \text{HO}$ whereas for the reverse bond $\text{NH} \leftarrow \text{O}$ a substantially higher value of 3.21–3.29 Å (ref.⁷) has been obtained. This indicates that the latter bond is much weaker in comparison with the former one. No data are available on the bonds between the NH_4^+ ion and water molecules in the solution but it is evident that the bond $\text{N} \rightarrow \text{HO}$ cannot be formed in this case as there is no free electron pair on nitrogen in the NH_4^+ ion. Therefore, only the weak reverse bonds $\text{NH} \leftarrow \text{OH}_2$ should be taken into consideration. In this case it can be theoretically expected that these bonds are stronger with NH_4^+ ions than with NH_3 molecules

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because the electron density on protons is lower in NH_4^+ than in NH_3 and the N—H bond should be more polarized for the former species (the partial positive charge on the proton is higher).

On the other hand, in NH_4^+ ions a relatively strong competition of electrostatic ion-dipole forces should be taken into account. This competition causes a radial orientation of H_2O dipoles in the central coulombic field of NH_4^+ cation, which, of course, is not in favour of the formation of hydrogen bonds. The available data are not sufficient for an *a priori* calculation of the relative importance of the two interactions: whether the free NH_4^+ ion, surrounded by a compact shell of radially oriented H_2O dipoles, will be the more stable one or whether it will be the NH_4^+ cation hydrogen-bonded into the tetrahedral bulk structure of liquid water, similarly as the hydroxonium ion at low concentrations^{3,8}. Moreover, there is no detailed information on the association or the bonds of the NH_4^+ cation with anions in the solution; it is not known whether there are associates of hydrated ions (ion pairs) or hydrogen bonds, etc.

In the preceding papers¹⁻⁴ a simplified model of the aqueous solutions of strong electrolytes has been outlined and experimentally confirmed. This model enables us to calculate the apparent ionic volumes in solutions from the corresponding crystallographic data. It is based on the assumption that ions (both mono- and polyatomic) behave in the solution as "water-unlike" particles surrounded by the electrostatically oriented hydration shells the structure of which differs from the tetrahedral structure of liquid water. This model can be used also for the evaluation of the apparent volume of the NH_4^+ ion under the assumption that it is a charged particle of an approximately spherical shape that interacts with the neighbouring water molecules by the electrostatic ion-dipole forces. The value of 1.43 Å, based on the crystallographic data (ref.⁷), has been accepted for its effective radius.

The apparent volume of the second model of the NH_4^+ ion, where the central nitrogen atom is bound by four hydrogen bonds $\text{NH} \leftarrow \text{O}$ to water molecules, can be estimated under the assumption that the volume of the aggregate $\text{N}(\text{H}-\text{OH}_2)^+$ is equal to the effective volume of the NH_3 molecules in liquid ammonia at the same temperature (which is equal to 27.9 ml mol⁻¹ at the density of 0.61 g ml⁻¹) plus the effective volume of four H_2O molecules in liquid water (72.2 ml mol⁻¹) plus the effective volume of one bound hydrogen atom² (0.5 ml mol⁻¹). This must be diminished by the contraction of hydrogen bonds in the field of the central charge, estimated from the data of Conway, Bockris and Linton for the hydroxonium ion⁸ ($\approx 4 \times 1.0$ ml . mol⁻¹). At infinite dilution the correction for electroconstriction, as calculated from the Born model by the method mentioned in one of our previous papers³ (≈ 1.0 ml mol⁻¹) where this approach has been verified on the hydrogen ion, must still be subtracted.

The values of the apparent molar volume in the interval between the two limits, the values for which have been thus obtained (*i.e.* for the "anhydrous" state of the solution, $c = c^0$, and for the infinitely diluted solution, $c = 0$), can be determined by an interpolation using the Mason square-root rule the validity of which has been proved for the entire interval in our previous papers on other ions and for both the first^{1,2} and the second³ type of hydration. The conclusions on the nature of the NH_4^+ ion in the solution can be drawn from the comparison of the experimental values of the apparent volumes of ammonium salts in solutions with the curves calculated by the above-described method for the two assumed models of hydration of NH_4^+ .

RESULTS AND DISCUSSION

As there are abundant data on the densities of aqueous solutions of ammonium salts available in the literature, no direct measurements of the dependence of their apparent molar volumes on c using samples added to the base-electrolyte solution were necessary as it was the case in our preceding studies⁹. The molar volumes of small

additions of each of the studied ammonium salts into the solution of the same salt (these values are close to their partial molar volumes) have been evaluated from the tabulated data for the density of their solutions^{10,11} at 25°C by the method described in our preceding paper⁹. Because the Masson rule has been used, these values have been plotted against the square root of the solutions's molarity c so that the calculated curves appear as straight lines. The concentrations c^0 (corresponding to the "anhydrous" state of the solution) that are necessary for drawing these straight lines have been adopted from our previous papers^{2,9} or, respectively, they were calculated from the equation

$$c^0 = 1000/V^0, \quad (1)$$

where V^0 (ml mol^{-1}) is the apparent molar volume of the salt in the "anhydrous" state of the solution calculated from the model of the corresponding form of the ammonium cation. The limit volumes V_i^0 and V_i^∞ for $c = c^0$ and $c = 0$, respectively, that are necessary for the calculation of the theoretical curves, are listed in Table I for all the participating ions.

The comparison of the experimental data with the curves calculated for the two assumed models (Fig. 1 and 2) shows that up to the highest concentrations the ammonium ion corresponds by its apparent volume in aqueous solutions to a free spherical particle surrounded by an electrostatically oriented hydration shell which continually diminishes with the increasing concentration. This is the same structure that has been found² for the ions of heavy alkaline metals (K^+ , Rb^+ and Cs^+) from their apparent

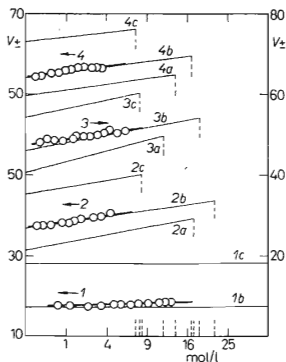


FIG. 1

Apparent Volumes V_{\pm} (ml mol^{-1}) of Ammonium Salts and Ammonia Added in Small Amounts to the Solution of the Same Electrolyte

1 NH_3 , 2 NH_4Cl , 3 NH_4NO_3 , 4 NH_4J .

The points are calculated from the tabulated densities of solutions. The calculated straight lines: a monohydrate of NH_4^+ , b free NH_4^+ , c the NH_4^+ ion hydrogen-bonded to the structure of liquid water.

molar volumes. This also explains the numerous similarities between the behaviour of solutions of ammonium salts and of salts of the above-mentioned metals.

Subtracting the apparent volume of the anion from the experimental values of the apparent molar volumes of salts extrapolated to $c = 0$, the volume of the ammonium cation $V^\infty(\text{NH}_4^+) = 14.0 \pm 0.5 \text{ ml mol}^{-1}$ (at 25°C) has been obtained, which is by about $4\text{--}5 \text{ ml mol}^{-1}$ more than the hard-sphere volume of the "naked" ammonium cation calculated with $r_1 = 1.43 \text{ \AA}$ and $V_H = 0.5 \text{ ml mol}^{-1}$. (The positive difference arises from the structural discontinuity in the array of water molecules on the periphery of the electrostatically oriented hydration shell). In comparison with the volume in the "anhydrous" state of the solution, there is a contraction of -3.2 to -4.2 ml mol^{-1} due to the electrocontraction of water in the field of the ion. From the nomogram calculated in one of the preceding papers¹ for the given type of hydration it follows that in the infinitely diluted solution the number of water molecules oriented electrostatically in the field of the NH_4^+ cation amounts to 3 or 4. This number decreases to zero as the concentration increases.

If the NH_4^+ ion were bound into the tetrahedral structure of water by hydrogen bonds similarly as the H_3O^+ ion, its volume should be substantially higher (Fig. 1 and 2). Also the coordination of an anion in the inner coordination sphere of the ammonium ion leading to the formation of nonhydrated molecules $[\text{NH}_4\text{X}]^0$ would result — according to the model used — in significantly higher apparent molar volumes in the solution⁹. On the other hand, the spherical packing of the co-

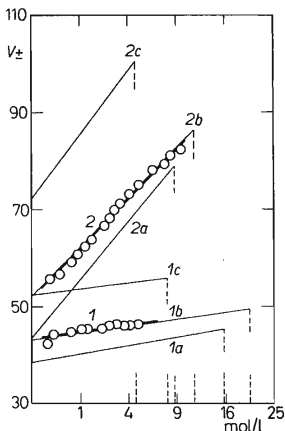


FIG. 2
Apparent Molar Volumes of Ammonium Salts in Aqueous Solutions
 V_{\pm} (ml mol^{-1}): 1 NH_4Br , 2 $(\text{NH}_4)_2\text{SO}_4$.
For all the other data see Fig. 1.

ordinated water molecules around the central ion in an aquo complex would correspond to a substantially lower volume, by about 4 to 5 ml mol⁻¹ per each bound water molecule (Table I and ref.⁹). According to these results, the NH₄⁺ ion in the aqueous solution forms neither true aquo complexes as metal cations do nor is it bound by hydrogen bonds to the adjacent water as the H₃O⁺ ion nor coordinating anions of strong mineral acids in the inner coordination sphere. Association constants given in literature¹² relate therefore to the formation of ion pairs in which the ions retain their hydration sheaths as in a free state. In all these respects this behaviour is the same as that that was obtained for the cations K⁺, Rb⁺ and Cs⁺, respectively, from their molar volumes.

Finally, the described procedure has been verified on the aqueous solutions of ammonia for which data, obtained by an independent method⁶, are available. According to the model used, molecules of NH₃, if hydrogen-bonded to the unperturbed structure of the surrounding water, would have in an aqueous solution the molar volume of liquid ammonia at the same temperature, *i.e.* 27.9 ml mol⁻¹; on the other hand, for free molecules distributed at random between the molecules of water, the structure of which has been thus perturbed, the apparent molar volume is 17.2 ml mol⁻¹. This value has been derived from the above-mentioned model using the same constants as for the NH₄⁺ ion ($r_i = 1.43 \text{ \AA}$, $V_H = 0.5 \text{ ml mol}^{-1}$) and it is concentration-independent because for the electroneutral molecules the electrocontraction of the neighbouring water is supposed to be negligible.

TABLE I

Apparent Molar Volumes in the "Anhydrous" State of the Solution, V^0 , and in the Infinitely Diluted Solution at 25°C, V^∞ , ml mol⁻¹

Species ^a	V^0		V^∞	
	<i>b</i>	<i>c</i>	<i>b</i>	<i>c</i>
[NH ₄] ⁺	17.7	17.7	14.1	14.1
[N(H—OH ₂) ₄] ⁺	96.5	24.3	95.5	23.3
[NH ₄ ·H ₂ O] ⁺	31.8	13.7	27.5	9.4
[NH ₄ ·Cl] ⁰	45.0	45.0	45.0	45.0
[NO ₃ ·H ₂ O] ⁻	54.3	36.2	49.1	31.0
Cl ⁻	26.0	26.0	22.0	22.0
Br ⁻	31.8	31.8	29.0	29.0
I ⁻	41.7	41.7	40.5	40.5
SO ₄ ²⁻	52.0	52.0	26.2	25.2

^a The values for anions are experimental data evaluated from the published densities of solutions¹⁰, all other values were calculated from the models described in this paper and elsewhere¹⁻⁴.

^b Calculated volumes of species. ^c Net volume increment of the species after subtraction of the volume of water consumed on its formation.

Experimental data, calculated from the tabulated densities of aqueous solutions of NH_3 , lie very close to the straight line of the free molecules and they are shifted but slightly towards the straight line of ammonia bound by hydrogen bonds (Fig. 1). This agrees quite well with the results obtained from Wien's effect⁶ which indicate that only about one fifth of the nondissociated ammonia is hydrogen-bonded to water molecules and the remaining four fifths are free. This fact — together with the results on the H^+ ion (the points for which lie, however, on the straight line calculated for the structure with H-bonds) — witnesses for the applicability of the described simplified models and thus also corroborates the above-mentioned conclusions on the nature of the NH_4^+ ion in the solution.

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