CCLXVIII.—*The Apparent Hydration of Ions. Part III. The Densities and Viscosities of Saturated Solutions of Ammonium Chloride in Hydrochloric Acid.*

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THE ammonium ion, having special structural features, offers scope for interesting comparisons with the ions of univalent metals. The work upon mixed salt and acid solutions already described in Parts I and II (J., 1928, 1917, 2381) has therefore been extended to the study of ammonium chloride in hydrochloric acid solution, the solubility in acid of various concentrations having been determined together with the densities and viscosities of the solutions, all at 25°. The experimental details were exactly as described in Part I.

The results are given in Table I. In col. 1 are the densities; col. 2 shows the viscosities (in c.g.s. units); cols. 3, 4, 5, and 6 respectively give the concentrations (mols./litre) of acid, salt, total solute (chloride), and water; col. 7, the sum of cols. 5 and 6, gives the total molarity; and col. 8 is the sum of cols. 4, 5, and 6 (see p. 2063).

TABLE I.

$d_{4°}^{25°}$.	$\eta \times 10^5$.	HCl.	NH_4Cl.	Total solute.	H_2O.	Total solution.	
1·0774	950·2	—	5·715	5·715	42·84	48·56	54·28
1·0787	975·3	0·433	5·285	5·718	43·31	49·03	54·32
1·0808	1008·7	1·031	4·732	5·763	43·85	49·61	54·34
1·0840	1051·3	1·710	4·133	5·843	44·43	50·27	54·40
1·0848	1063·4	1·857	4·000	5·857	44·59	50·45	54·45
1·0854	1072·6	2·073	3·814	5·887	44·73	50·62	54·43
1·0907	1138·6	3·103	3·017	6·120	45·31	51·43	54·45
1·0935	1170·7	3·560	2·706	6·266	45·46	51·73	54·44
1·0958	1187·6	3·880	2·498	6·378	45·55	51·93	54·43
1·1012	1235·0	4·575	2·092	6·667	45·66	52·33	54·42
1·1111	1317·5	5·683	1·563	7·246	45·54	52·79	54·35
1·1178	1370·5	6·322	1·336	7·658	45·29	52·95	54·29
1·1293	1459	7·345	1·058	8·403	44·68	53·08	54·14
1·1519	1655	9·116	0·810	9·926	43·09	53·02	53·83
1·1774	1936	11·05	0·75	11·80	40·77	52·57	53·32
1·2015	2250	12·92	0·87	13·79	37·95	51·74	52·61

Discussion of Results.

Densities and Solution Volumes.—The figures in col. 7 of Table I are lower than those recorded for the salts previously examined, and it is at once evident that ammonium chloride shows a high volume effect compared with, say, sodium chloride. The low densities of the solutions are largely due to this large volume occupied by the ammonium ion. The table shows a similarity to that for potassium chloride (Part I, *loc. cit.*) in that there is no initial drop in the total solute concentration upon the first addition of acid to the saturated solution of the pure salt. In the region of highest acid strength, the salt content passes through a minimum value and this, again, is like the behaviour of potassium chloride and unlike that of sodium chloride.

Ammonium chloride may be shown to have a solution volume of the same order as that of rubidium chloride. At 25° the saturated solution of the latter salt contains 6·025 mols. of salt and 42·86 mols. of water per litre. The water content is practically identical with that of the saturated ammonium chloride solution in pure water. Hence, if the water occupies the same space in both solutions (*i.e.*, if its solution volume is the same, which may only be approximately true), then 5·715 mols. of ammonium chloride occupy the same volume as 6·025 mols. of rubidium chloride. It is well known that the ammonium ion in a crystal of ammonium chloride approximates in size to the rubidium ion (Bragg, *Phil. Mag.*, 1926, **2**, 258; Goldschmidt, *Trans. Faraday Soc.*, 1929, **25**, 253; *ibid.*, Appendix, p. 282).

Unlike the corresponding series of densities obtained in the case of the mixed solutions of sodium (or potassium) chloride in hydrochloric acid (Part I, *loc. cit.*), that for ammonium chloride shows a gradual increase with increasing acidity, there being no minimum. Owing to the high volume of the ammonium ion and to its low mass, the replacement of the salt by acid and water is marked throughout by a net mass gain of the solution. In spite of these differences in behaviour, it is found that the densities can be expressed by the formula

$$d_{4^\circ}^{25^\circ} = K + k_1a + k_2b$$

over the greater part of the series; *a* and *b* are respectively the concentrations of acid and of salt. By applying the method of Campbell ("Measurement and Calculation," Longmans, Green & Co., 1928) to the first twelve values in the table, the constants were evaluated as $K = 1{\cdot}0148$, $k_1 = 0{\cdot}01387$, and $k_2 = 0{\cdot}01097$. The same method of determining the constants when applied to the results for sodium and potassium chlorides leads to slight revision of the values previously published. The three equations then become

$$(\mathrm{NaCl})\quad d_{4^\circ}^{25^\circ} = 1{\cdot}0092 + 0{\cdot}01433a + 0{\cdot}03484b$$
$$(\mathrm{KCl})\quad d_{4^\circ}^{25^\circ} = 1{\cdot}0132 + 0{\cdot}01373a + 0{\cdot}03933b$$
$$(\mathrm{NH_4Cl})\quad d_{4^\circ}^{25^\circ} = 1{\cdot}0148 + 0{\cdot}01387a + 0{\cdot}01097b.$$

The equation for the first two series holds as far as the point of minimum density; that for the third series holds over the region of acid concentrations 0—6*N*. As has been pointed out elsewhere (Part II, *loc. cit.*), these formulæ are based upon assumptions of the constancy of solution volumes, and their chief value is for the calculation of these quantities over a given range of concentrations. The first 12 densities of Table I are here calculated by the above formula :

$d_{4^\circ}^{25^\circ}$(obs.) ...	1·0774	1·0787	1·0808	1·0840	1·0848	1·0854
,, (calc.) ...	1·0775	1·0788	1·0810	1·0839	1·0844	1·0854
$d_{4^\circ}^{25^\circ}$(obs.) ...	1·0907	1·0935	1·0958	1·1012	1·1111	1·1178
,, (calc.) ...	1·0909	1·0938	1·0959	1·1012	1·1108	1·1171

The solution volumes corresponding to the above equations are :

	Acid.	Salt.	Water.	Solid salt.
NaCl series	21·95	23·42	17·86	26·96
KCl ,, ...	22·54	34·77	17·79	37·44
NH_4Cl ,, ...	22·27	41·91	17·76	34·92

The apparent solution volume of ammonium chloride is considerably higher than the molecular volume of the solid, which is 34·92—34·96 at the ordinary temperature. It is interesting to observe, however, that the solid volume of rubidium chloride is 43·10, so that this salt has a solution volume of the same order as its solid volume (perhaps slightly less as indicated by comparison with ammonium chloride, which gives approximately the same solution volume). These facts are explained by reference to the crystal structures of the two salts, for, whilst rubidium chloride conforms to the sodium-chloride type, of co-ordination number 6, ammonium chloride at ordinary temperatures belongs to the cæsium-chloride group, of co-ordination number 8, having a more compact arrangement (Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 1547; Bartlett and Langmuir, *ibid.*, 1921, **43**, 84; Wyckoff, *Amer. J. Sci.*, 1922, **4**, 469).

The solution volume of the ammonium ion is 19·64, being the difference between the salt and acid values above if the hydrogen ion is assumed to have no volume effect. The behaviour of the ammonium ion may now be summarised. It has in the crystal lattice a radius slightly smaller than that of rubidium, but gives a rather larger solution volume than that ion. Both these ions are relatively large compared with the sodium and potassium ions, and will not be expected to show hydration to a measurable extent.

Viscosities.—The displacement of salt by acid in the solutions saturated with ammonium chloride causes an increase in viscosity throughout the series, the behaviour resembling that shown by potassium chloride. Comparison of the data for these two salts shows that, whilst the pure saturated solution of ammonium chloride (5·715*N*) has a lower viscosity than that of pure saturated potassium chloride (4·199*N*) solution, with increasing acidity the viscosities approach and become identical at approximately 2*N*-acid, after which the ammonium chloride–acid solutions have consistently higher values than those of the potassium chloride–acid series of corresponding acidity. A curve of the data for ammonium chloride runs almost parallel to that for hydrochloric acid alone (lying between Curves I and II of Fig. 2, Part I, *loc. cit.*) up to an acidity of about 8*N*, after which the viscosities increase more rapidly than for pure hydrochloric acid solutions of corresponding acidities. Taking into account the facts that the ammonium chloride solutions have throughout for equal acidities greater total solute concentrations than the potassium chloride solutions, and also that the latter salt is more rapidly precipitated as the acid concentration increases, the conclusion may be reached that any effects attributable to hydration are shown less by ammonium chloride than by potassium chloride. Thus the solutions containing potassium chloride below 2*N*-acidity owe their higher viscosities mainly to hydration of the potassium ions, although this may not be to a very high degree. Above this point, when the hydration and also the salt content have fallen off, the higher viscosities of the ammonium chloride solutions are mainly due to differences in total chlorine-ion concentration.

The replacement by hydrogen ions of the metallic ions in the salt solutions considered, involves a general readjustment of the total number of particles present because of the small volume of the former ion. Thus the new solution may contain more water molecules although the increase in their number may be partly offset by an increase in the number of chlorine ions which are the largest species present. The effective number of particles in a given solution may be taken to be the sum of the metal ions, the chlorine ions, and the water molecules. Any allowance for hydration reduces the total number. The hydrogen ions will be non-effective as separate particles, being supposed to be combined as $H_3O^{\cdot}$ ions.

Sodium and lithium ions being small in themselves but hydrated to an effectively larger size, their replacement results in a fall in viscosity. The total number of effective particles probably increases, but any rise of viscosity due to this cause is masked. The variations in the total effective numbers of particles may be studied by referring to Tables I and II in Part I. Addition of columns 4, 5, and 6 (salt, total solute, and water concentrations) gives the total number of particles uncorrected for hydration. Allowing 2 units for the hydration in the case of sodium chloride, we see that the series of values for the effective number of particles shows a gradual increase from 49 to 54 (expressed as mols./litre), falling again in the regions of high acid concentration to 53. A similar test applied to the potassium chloride series gives descending values of 56·4—53 if no allowance is made for hydration allowance, and if one unit is allowed for this effect, the figures become 52—54·5, finally falling to 53. The changes of viscosity in these two series cannot, therefore, be directly governed by the numbers of particles, but must also be referred to the sizes and to any specific effects such as hydration.

On applying these ideas to the case of ammonium chloride, it is found that the number of effective particles (col. 8, Table I) shows a remarkable constancy over the greater part of the series, the values lying between 54·28 and 54·45, if no allowance is made for hydration. Any changes in viscosity may therefore be ascribed to factors not directly connected with the numbers of particles. The principal factors appear to be the alterations in the average size of particle present, and the consequent greater crowding, since the numbers remain the same.

The solutions may be regarded primarily as containing the following species : $NH_4^{\bullet}$, Cl', $H_3O^{\bullet}$, and H_2O. The order of sizes derived from measurements of radii in crystals is $NH_4^{\bullet}<H_2O<H_3O^{\bullet}<Cl'$. The values given by Goldschmidt (*loc. cit.*) for the ions ($NH_4^{\bullet}$ 1·43, Cl' 1·81, OH' 1·4—1·5) are taken together with the further evidence as to the sizes of the water molecule and the ion $H_3O^{\bullet}$ in relation to that of the ion OH', which may be obtained from the works of Rankine (*Trans. Faraday Soc.*, 1922, **17**, 719) upon the dimensions of gaseous hydride molecules, of Bragg and Bell (*Nature*, 1921, **107**, 107) upon hydrogen chloride, and of Bragg (*Proc. Physical Soc.*, 1922, **34**, 98) upon the structure of ice and the dimensions of the hydrogen and oxygen atoms in it. Thus the figures for ice give 2·76 for the sum of the diameters of the hydrogen and oxygen atoms, corresponding with the radius 1·38 for OH', which agrees with the lower limit above quoted. The increase for the formation of water based upon that found in the

case of hydrogen chloride will be of the order 0·26, giving 1·64, although actually this may be a high figure for the effective radius, since the two protons in the free molecule of water probably occupy the same orbit. Again, by taking the value 1·32 (Goldschmidt) for the ion O'' and comparing it with that of OH' (1·4—1·5), it may be argued that the radius of the water molecule will lie between somewhat higher limits, and will in fact be greater than that of the ammonium ion. Finally, the addition of the extra proton to give $H_3O^{\bullet}$ does not involve a large increase in radius, although it must have some effect in this direction, as in the case of the gaseous hydrides considered by Rankine.

The increases in viscosity shown in Table I are due, therefore, to the replacement of the $NH_4^{\bullet}$ ions by the larger H_2O molecules, $H_3O^{\bullet}$ ions, and Cl' ions according to the way in which the numbers of these species change in a particular case. The ammonium ions are probably not hydrated. Had the potassium ions in the parallel series of solutions been non-hydrated, their smaller size in comparison with the ammonium ion would have resulted in the saturated solution of the pure salt having a viscosity lower than that of the saturated solution of pure ammonium chloride, and consequently the rate of increase with addition of acid would have been greater than for the latter salt, whereas actually it is less. The ammonium chloride series gives a standard of comparison.

More detailed quantitative examination of the data supports these arguments. First, there is the relationship already noted between the rates of increase of viscosity with increasing acidity for the ammonium chloride–hydrochloric acid series and for hydrochloric acid alone. Over a range of acid concentrations of 0—9*N*, the viscosity changes are practically the same for equal increments of acidity in the two series. The data for hydrochloric acid given by Green (J., 1908, **93**, 2033) have been used for comparison, values for acidities equal to those in Table I being obtained from a graph. Thus, for the first step, up to 0·433*N*-acid, the viscosities increase by 0·00025 in each case; for the next step, to 1·031*N*-acid, the differences are 0·00033 and 0·00032, and this close parallelism persists over the range stated. Since, in the one case the increase in acidity is accompanied by an equal increase in chlorine-ion concentration, whereas in the other case the sum of the diminution of the ammonium-ion and increase of chlorine-ion concentrations equals the increase in acidity, the conclusion is that the ammonium ion gives an effect upon the viscosity almost exactly equal and opposite to that of the chlorine ion. The relationship is not one of exact equality because the relative changes of viscosity in the two series are not the same, the viscosities of the pure acid solutions being throughout 5% lower, and also there are small differences in the numbers of effective particles in the pairs of solutions compared which will be in part responsible for the viscosity differences. From the roughly equal effects, it appears that the ammonium ion behaves as if it were as much smaller than a water molecule as the chlorine ion is larger, so that if the last be assigned its solution volume of about 22, the ammonium ion has an effective volume of about 14, water being taken as 18. The volume of the ammonium ion calculated in this way falls between that obtained for a partly hydrated potassium ion in a solution of low acidity and that for the same ion non-hydrated in solutions of high acidity. The result is therefore fully in accord with the viscosity data for these two salts.

The equality of effects of the removal of ammonium ions and addition of chlorine ions may also be demonstrated by means of the empirical formula used in Parts I and II, *viz.*, $\eta_2 - \eta_1 = \frac{1}{2}(\eta_1 + \eta_2) \times 2{\cdot}5\phi$. For pure hydrochloric acid solutions, ϕ is equal to the solution volume of the chlorine ion multiplied by the change of concentration in mols./c.c., *i.e.*, $\phi = 22{\cdot}43(c_2 - c_1)/1000$. Since the rate of change of viscosity is the same in the ammonium chloride–acid series the formula applies with the same term, but $(c_2 - c_1)$ now expresses the sum of the decrease of the ammonium-ion concentration and the increase of the chlorine-ion concentration. Hence a calculation will give the ammonium ion an apparent volume value equal to that of the chlorine ion. The following example (from the second and third lines in Table I) will make this clear, the solution volume of the chlorine ion being taken as 22·27, since this is the value from the density data of the series.

$$\left.\begin{matrix}\eta_2 = 0{\cdot}010087 \\ \eta_1 = 0{\cdot}009753\end{matrix}\right\} \begin{matrix}\eta_2 - \eta_1 = 0{\cdot}000334 \\ \eta_1 + \eta_2 = 0{\cdot}019840\end{matrix}$$

$$\text{Hence, total volume effect} = \frac{0{\cdot}000334 \times 2000}{0{\cdot}019840 \times 2{\cdot}5} = 13{\cdot}47 \text{ c.c./litre.}$$

Now, the change in chlorine-ion concentration is + 0·045 mol./litre, and its volume effect is 0·045 × 22·27 = 1·00 c.c.; therefore, the nett volume effect of the ammonium-ion change is 12·47 c.c., and, the actual change being – 0·55 mol./litre, it follows that the volume effect of the ammonium ion is 22·55.

The mean value for the first ten experiments of the series is 22·65, the individual values varying between the limits 24·6 and 20·3. The constancy of the value is satisfactory in view of its derivation from relatively small viscosity differences. This constancy of effect of the ammonium ion is good evidence of the absence of hydration, variations of which would otherwise have led to considerable variations in the volume effects in the sense of a regular fall in the series, whereas the actual values vary irregularly round the mean.

It is seen that the volume of the ammonium ion deduced from the viscosities, *i.e.*, 14, as compared with 22 for the chlorine ion and 18 for water, is not in agreement with the value obtained from the densities, *i.e.*, 19·64, this being greater than the corresponding value of water. The explanation of this discrepancy may be that the water molecule, not having complete spherical symmetry, has a proportionately larger effect upon viscosity than the completely symmetrical ions, whilst, as regards packing and its effect upon density, it retains its smaller volume effect. This would then mean that the series of values (Cl' 22, H_2O 18, $NH_4^{\cdot}$ 14) derived from the viscosities is merely an index of relative influence as regards this property alone, and the fact that the chlorine-ion value (22·43) appears in the empirical formula for the viscosities would lose its direct physical significance of identity with the solution volume. Finally, the validity of the hydration values of the sodium and lithium ions given in Parts I and II would be open to question, since the whole series of values for the volumes of ions now determined from the viscosities, which runs approximately

$K^{\cdot}$ 12 (not hydrated), $NH_4^{\cdot}$ 14, $K^{\cdot}$ 16 (partly hydrated), H_2O 18, Cl' 22, $Na^{\cdot}$ 32—23 (varying hydrations), $Li^{\cdot}$ 45—35,

would be affected similarly. This, however, remains a matter for further investigation.

In conclusion, we may consider the application to the present work of McLeod's theory (*Trans. Faraday Soc.*, 1923, **19**, 6) of the connexion between free space and viscosity. The calculations of the free space have been made as in Part II, the radius 1·43 being used for the ammonium ion, the corresponding molecular volume for ammonium chloride being 20·35. The curve representing free space plotted against viscosity may be compared with those in Fig. 1, Part II. It lies above that for potassium chloride, commencing at a point 33·6, $\eta = 0{\cdot}0095$, and falling with increasing free space to a point 34·5, $\eta = 0{\cdot}01073$, after which it rises with diminishing free space, finally crossing the curve for pure hydrochloric acid solutions, as does the potassium chloride–hydrochloric acid curve, but at a higher point. Probably if an allowance were made for the small extra volume effect of $H_3O^{\cdot}$ compared with water, the initial droops on both these curves would disappear and the free space values would diminish throughout, but not at a sufficient rate to account for the observed viscosity changes in comparison with solutions of hydrochloric acid alone. The fact that the curve for ammonium chloride lies above that for potassium chloride, especially as regards solutions of low acidities, brings out clearly the dependence of the viscosities upon other factors, the smaller numbers of particles and the absence of hydration for the former salt being the chief distinguishing features.

Summary and Conclusions.

The solubility of ammonium chloride in aqueous solutions of hydrochloric acid of concentration up to 13N has been determined at 25°. The densities and viscosities of the saturated solutions have also been measured.

The results are compared with those previously obtained by the author for sodium and potassium chlorides and lithium chloride. The same type of formula, $d = K + k_1a + k_2b$, is found to apply for the relation between densities and the concentrations a and b of acid and salt. The solution volume of the acid is substantially the same as in the solutions containing the other salts. The apparent density of the water is highest, and hence its solution volume lowest, in the solutions containing ammonium chloride. This salt gives a solution volume comparable with that of rubidium chloride, the ammonium ion having a relatively high volume compared with sodium and potassium, in accordance with the evidence from the measurements of radii in crystals.

The principal factors governing the viscosities are the numbers of particles present and their sizes relative to that of the water molecule, which is the predominant species. The general treatment of the viscosity data is in agreement with these ideas if the relative sizes of the particles are based upon measurements of the radii of ions and atoms in crystals.

The removal of an ammonium ion results in an increase in viscosity which is almost exactly equal to that caused by the addition of a chlorine ion. The effects of both of these ions remain constant over a large part of the series of solutions examined. This constancy is taken as an indication of the absence of hydration for these ions. The ammonium ion has an effect upon viscosity relatively less than that of either the water molecule or the ion $H_3O^{\bullet}$. Its effective size as regards viscosity is somewhat larger than that of a non-hydrated potassium ion, but smaller than that of the partially hydrated potassium ions in a saturated potassium chloride solution.

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