LXXVII.—*The Apparent Hydration of Ions. Part IV. The Densities and Viscosities of Saturated Solutions of Silver Nitrate in Nitric Acid.*

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THE investigations in this series already described have dealt with solutions of alkali-metal and ammonium chlorides in hydrochloric acid (Parts I and II, J., 1928, 1917, 2381; Part III, J., 1929, 2059). The present paper deals with an extension of the work to solutions in nitric acid, the solute being silver nitrate, a choice which allows of accurate analytical control and is also convenient for comparison with the salt and acid pairs previously examined. The silver ion, having a radius of 1·13 Å.U. (Goldschmidt, *Trans. Faraday Soc.*, 1929, **25**, 253), which is between those of the sodium and potassium ions ($Na^{\cdot}$ 0·98, $K^{\cdot}$ 1·33), might be expected to show hydration effects of an intermediate nature. The nitrate ion, which resembles the chlorine ion in probably being not hydrated but differs from it in having a more complex and less symmetrical structure, might show specific effects due to these features. Differences might also be expected for these two ions on the basis of Sugden's theory (J., 1926, 174) that anions have not all the same activity as depolymerisers of the solvent.

The experimental work consisted of the determination of the densities and viscosities at 25° for a series of solutions of acid content covering the range 0—12N, and saturated with silver nitrate. A parallel series of determinations with acid alone was also made. The same apparatus was used as in the previous work, but a slight modification was made by placing the gauge for the Scarpa viscometer in the thermostat and substituting water for alcohol in it, thus making the control more certain. The results are in Tables I and II, concentrations being in mols./litre. The viscosities of the pure nitric acid solutions were determined both by the Scarpa and by the Ostwald U-tube method.

TABLE I.

$d^{25°}_{4°}$.	$10^5\eta$.	HNO_3.	$AgNO_3$.	Total solute.	H_2O.	Total solution.	Col. 8.
2·2969	2989	—	9·714	9·714	35·9	45·6	55·33
1·7376	1852	2·222	4·952	7·174	42·0	49·1	54·1
1·6343	1712	2·797	4·047	6·844	42·8	49·6	53·7
1·4669	1523	4·282	2·456	6·738	43·3	50·0	52·5
1·4236	1508	5·010	1·975	6·985	42·9	49·9	51·8
1·4014	1512	5·599	1·685	7·284	42·3	49·6	51·3
1·3742	1578	6·976	1·185	8·161	40·7	48·9	50·1
1·3690	1630	7·971	0·943	8·914	39·2	48·1	49·1
1·3695	1712	9·093	0·724	9·82	37·4	47·2	48·0
1·3741	1784	10·12	0·589	10·71	35·3	46·0	46·6
1·3856	1883	11·69	0·393	12·08	32·3	44·4	44·8

TABLE II.

	$10^5\eta$.				
$d^{25°}_{4°}$.	(Scarpa).	(Ostwald).	HNO_3.	H_2O.	Total solution.
0·99707	891	891	—	55·35	55·35
1·0297	917	914	0·987	53·7	54·7
1·0633	954	951	2·010	52·0	54·0
1·0892	989	991	2·810	50·6	53·4
1·1193	1049	1042	3·744	49·0	52·8
1·1542	1123	1120	4·863	47·1	51·9
1·1787	1195	1187	5·667	45·6	51·3
1·2245	1335	1327	7·257	42·6	49·9
1·2678	1497	1487	8·900	39·2	48·1
1·3397	1764	1758	11·92	32·7	44·6

Col. 8 of Table I gives the sum of Cols. 4, 5, and 6; on the assumption that the solutes are completely dissociated and that the hydrogen ions are present as $H_3O^{\cdot}$ ions (or, alternatively, that they have no effective size as free individuals), these figures give the relative numbers of particles having effective volume, the water molecules being treated as unpolymerised and no allowance being made for hydration of the silver ions. Col. 6 in Table II gives the corresponding figures for the pure acid solutions, the values in this case being identical with "Total solution."

Discussion of Results.

Densities and Solution Volumes.—The data in Col. 8, Table I, and Col. 6, Table II, show a close parallelism and, when plotted against acid normalities, give graphs which are superimposable except in the region 0—5*N*, where the solutions containing silver nitrate have slightly higher numbers of "effective particles" (the maximum divergence being 0·3 unit/litre). The saturated solution of silver nitrate in pure water, having 55·33 for this number, may be compared with pure water itself, for which the value is 55·35. If the solution volume of the water were the same in the two cases, then that of the silver nitrate would be exactly twice as much. Caution must, however, be observed in making such deductions, and due regard must be given to the possibility of an alteration in the values for the water molecule itself. For instance, a change of the condition of the solvent, such as depolymerisation, might lead to an adjustment of the volume effectively shown. Similarly, the packing of ions amongst the water molecules and the interactions of "hydration" will undoubtedly lead to modifications of the volume which the solvent molecule apparently occupies. These various effects may all be regarded as readjustments of the amount of "free space" in the liquids. This free space is normally included in the apparent solution volumes of the constituents of a solution, whether solute or solvent. Usually, in dealing with aqueous solutions, a constant value is assumed for the water, based upon the density of the pure solvent, and any variations are arbitrarily expressed as those of the solute: an example is that of lithium chloride (Green, J., 1908, **93**, 2023), discussed by the author in Part II (*loc. cit.*). On the other hand, the type of expression suggested by Masson (J., 1911, **99**, 1132), and used in the present series of investigations, makes provision for changes in the apparent solution volume of the solvent in the solution as compared with the pure liquid. The solution volumes deduced by these methods all include a proportion of "free space" except for the two smallest ions $\text{Li}^{\cdot}$ and $\text{Na}^{\cdot}$, in which cases the apparent solution volumes were found to be less than the gram-ionic volumes calculable from lattice radii. These are the ions which definitely show hydration effects. The case of the ammonium ion was especially interesting, for it gave an unexpectedly high solution volume of 19·64 c.c. (Part III), compared with the value 7·43 c.c. deduced from the ionic radius. At the same time, this ion was shown to have a negative effect on the viscosity. It is suggested that the appropriation of this large amount of free space, accompanied by a repulsion of the solvent molecules, causes the ammonium ion to show a lower viscous effect than its apparent solution volume would otherwise indicate. The ammonium ion, in fact, behaves as a "loose spot" (compare Part II).

The application of Masson's formula, $d_{4^\circ}^{25^\circ} = K + k_1 a + k_2 b$, to the data of Table I may now be considered. The series of densities resembles that for the NaCl–HCl and KCl–HCl mixtures (Part I), there being a minimum value; since, however, the data for silver nitrate cover a much wider range of salt concentrations, it is not surprising that the formula has a more restricted application. Constants were determined by (i) the method of least squares and (ii) Campbell's method (see Part III, *loc. cit.*), the corresponding equations being

(i) $d_{4^\circ}^{25^\circ} = 1{\cdot}0350 + 0{\cdot}02647a + 0{\cdot}1299b$;

(ii) $d_{4^\circ}^{25^\circ} = 1{\cdot}0306 + 0{\cdot}02702a + 0{\cdot}1305b$.

The second of these is preferred, and the densities calculated by means of it compare well with those observed except for the end values of the series; *e.g.*,

$d_{4^\circ}^{25^\circ}$ (obs.)	2·2969	1·7376	1·6343	1·4669	1·4236
,, (calc.)	2·2986	1·7368	1·6343	1·4669	1·4236
$d_{4^\circ}^{25^\circ}$ (obs.)	1·4014	1·3742	1·3690	1·3695	1·3741
,, (calc.)	1·4017	1·3737	1·3690	1·3706	1·3808

The solution volumes corresponding to the constants of the equations differ only slightly according to the equation used, thus:

	$AgNO_3$.	HNO_3.	H_2O.
(i)	38·66	35·32	17·41
(ii)	38·14	34·92	17·48

The values may be compared with those derived from other sources. Jabłczynski, in a paper on the dimensions of ions in aqueous solutions (*Rocz. Chem.*, 1923, **3**, 362), has discussed the data for many salts, including nitrates and chlorides. He gives the solid volume of silver nitrate as 39·04, and calculates the upper and lower limiting solution volumes to be w_1 39·34 and w_0 25·91, respectively, these being deduced from data by means of empirical formulæ, and the solution volumes being calculated from density data by means of the ordinary equation $w = \frac{1}{N}\left(1000 - \frac{1000d - MN}{d_0}\right)$, where d_0 is the density of pure water. The lower limiting values w_0 were, for the chlorides of sodium potassium, cæsium, and rubidium, shown to agree with the molecular volumes calculated from the lattice radii of the ions as given by Bragg (*Phil. Mag.*, 1920, **40**, 169), but the revised data for the radii nullify this agreement, which in any case did not extend to other salts. The agreement found between the upper limiting values w_1 and the solid volumes in the case of many salts, including silver nitrate, is apparently significant, although too much importance must not be attached to it, since the result is obtained by neglecting the effect of changes of the packing arrangements upon the volume occupied by the water. All that can be safely concluded is that, in solutions of high concentration, the solution volume of the salt approaches that of the solid in many cases, and if the ionic radii remain the same, the "free space" associated with the ions in solution is of the same order as that for the solid state. The mean value deduced for silver nitrate in the mixed salt and acid solutions, *viz.*, 38·40, is thus seen to be satisfactory. The fact that the value remains constant over the greater part of the series may be attributed to the relatively small variation in total solute strength, so that the apparent volume of the nitrate ion, which accounts for the major portion of the total volume of the salt, remains constant. This would not be the case in a simple series of solutions of silver nitrate alone, varying over the same range of salt concentration, *viz.*, 0—10*N* (app.), as in the mixtures. The same argument applies to the acid itself, so the acid volume deduced for the mixed solutions will not be expected to apply to any considerable part of Table II. Actually, it does apply for the concentration region 6—9*N*, for which solutions the densities can be fairly accurately calculated by the formula $d_{4^\circ}^{25^\circ} = 1{\cdot}0306 + 0{\cdot}02702a$, but outside these limits there is rapid divergence.

The difference (3·28) between the means of the above values of the volumes, *viz.*, $\phi'_{AgNO_3} = 38{\cdot}40$, $\phi'_{HNO_3} = 35{\cdot}12$, is taken as the volume of the silver ion, and ϕ'_{HNO_3} will be provisionally assumed to be the value of $\phi'_{NO_3'}$ also.* The value for the silver ion falls between those obtained for Na˙ (1·58) and K˙ (12·25) in Part I. Furthermore, if these values are used to derive values for the nitrate ion from the limiting values of sodium and potassium nitrates given by Jabłczyński, *viz.*, $w_1(NaNO_3) = 37{\cdot}87$, $w_1(KNO_3) = 47{\cdot}61$, the values for this ion are 36·29 and 35·36, respectively, the latter being in very close agreement with the value deduced above. In this connexion, it may be noted that lithium nitrate (w_1 30·24) is not in agreement. This again is probably due to the method of obtaining the solution volumes without regard to changes of the water volume. In the case of lithium chloride (Part II, *loc. cit.*), it was shown that for a 5·407*N*-solution, the solution volume (22·43) obtained by using a density for water of 1·01275 was considerably higher than either the solid volume (20·94) or the solution volume (20·24 at 5*N*) calculated by Green (*loc. cit.*). A difference in the assumed density of the solvent water of about 1% therefore makes a considerable difference to the calculated salt volumes, and this is most marked for lithium salts, so the above apparent discrepancy of lithium nitrate is probably capable of a similar explanation.

The solution volumes of the silver and nitrate ions, *viz.*, 3·28 and 35·12 respectively, may be compared with ionic volumes deduced from lattice radii. For the former ion, the values given by Goldschmidt (*loc. cit.*), 1·13, and by Pauling, 1·26 (quoted by Goldschmidt), lead to gram-ionic volumes of 3·665 and 5·079 respectively. The value 3·28 now found for the solution volume is thus, as with lithium and sodium ions, less than that calculated from the lattice radius. The nitrate ion has a structure with the centres of the four atoms in one plane, the oxygen atom centres being at the corners of an equilateral triangle, and that of the nitrogen atom being at the mid-point (Bragg, *Phil. Mag.*, 1926, **2**, 258). The

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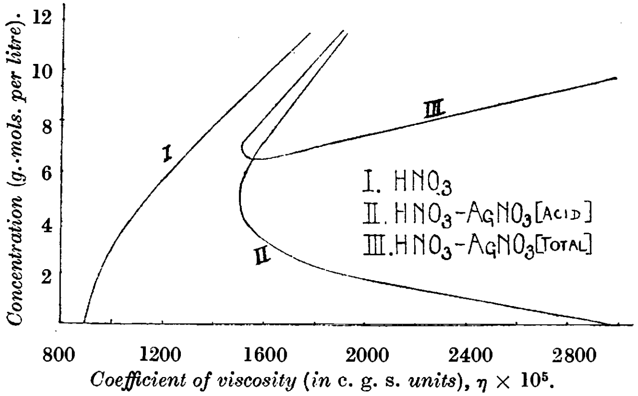
* ϕ is used for the volume of ions added to 1 c.c. of solution; ϕ' is used for the gram-ionic volume of an ion.

inter-atomic distances of the oxygen atoms are given as 2·25 Å.U. and their radii as 1·35 Å.U. These dimensions imply a very close packing of the oxygen atoms round the central nitrogen atom, with considerable deformation of the former. These results have been confirmed and amplified in a comprehensive survey of the type of compound ABX_3 by Zachariasen (*Norske Videnskaps-Akad.*, 1928, **1**, *mat.-nat. Klasse*, 4). Thus, in lithium nitrate the distance from an oxygen centre to the nitrogen centre is 1·25 Å.U., which is practically the same as in the Bragg structure. It appears to be well established that both the nitrate ion and the carbonate ion, which has almost identical dimensions, preserve well-defined identities. The exact volume occupied by such an ion is not easy to determine, but as an upper limit that of the triangular prism containing it may be taken. This is calculated to be 34·4 for the gram-ion. Actually, this will be somewhat high, and if the lower limit be chosen as the volume of three oxygen atoms ($r = 1·32$), giving 17·5, it seems probable that the true volume will lie between these two limits. The solution volume determined is actually quite close to the upper limit thus obtained, and it will be shown that the volume influence of this ion upon viscosity is of the same order.

FIG. 1.



Viscosities.—The graphs of the data shown in Fig. 1 may be compared with those in Fig. 2, Part II, for hydrochloric acid solutions alone or containing sodium chloride. Aqueous hydrochloric acid solutions have higher viscosities than those of nitric acid of equal normality. Nitric acid appears to have a simpler behaviour, the curve being linear above 5*N*. Starting from pure water and comparing the two acids, it is found that the viscosity differences at corresponding normalities (i) at first increase from 42 ($\times 10^{-5}$) units at $N = 1$ to 73 at $N = 3$; (ii) they then diminish until the value 43 is again reached at $N = 8$, after which (iii) there is a rapid increase to 146 at $N = 12$. These effects might be interpreted as being due to (i) a more rapid depolymerisation of the water by nitrate than by chlorine ions in the earlier stages of 1—3N; (ii) the influence of the larger size of the former ion tending to a greater viscosity effect and hence a making up of some of the ground lost during the initial period; (iii) the entry of some specific effect in the solutions of high concentration of hydrochloric acid which is not paralleled in those of nitric acid or else is offset by a difference in the numbers of particles of all kinds, which numbers are considerably less in the case of nitric acid. The effective numbers of particles as defined by Col. 6, Table II, for nitric acid, and falling from 55·35 to 44·60, show much greater variation than for hydrochloric acid, for which (from Green's data) the range is 55·35—53·24 for the corresponding range 0—12N. Another possible factor causing such differences of behaviour would be incomplete ionisation of the nitric acid in solutions of high concentration, since, as will be shown later, the increase of viscosity caused by adding a given ion is partly dependent upon the strength of the field into which it is placed. There is, however, no evidence that nitric acid is less dissociated than hydrochloric acid and, in fact, the behaviour in dilute solutions suggests the complete dissociation of both acids (MacInnes and Cowperthwaite, *Trans. Faraday Soc.*, 1927, **23**, 400).

The most noteworthy feature in the graphs for the silver nitrate–nitric acid solutions is the obvious similarity to those for sodium chloride in hydrochloric acid, both sets showing the approach to a minimum viscosity as salt is replaced by acid. It should be noted that the minimum does not occur at the point of minimum total solute concentration.

The linear relation for nitric acid of concentrations exceeding 5N is expressed by

$$\eta = 0{\cdot}006822 + 0{\cdot}0009077C$$

for the Scarpa series (if the mean of the Scarpa and Ostwald series is taken, the first constant becomes 0·006787). If this equation is compared with one of the form deduced by Einstein (*Ann. Physik*, 1906, **19**, 289), *viz.*, $\eta = \eta_0 [1 + \text{constant} \times \phi]$, and if it be assumed that the nitrate ions contribute the main effect in altering the viscosities in proportion to their volume, so that $\phi = C\phi'/1000$, ϕ' is given by $[0{\cdot}0009077 \times 1000]/[0{\cdot}006787 \times (\text{constant})]$. If the value 4·5 be taken for the constant in the Einstein equation (compare Hatschek, *Trans. Faraday Soc.*, 1913, **9**, 80), $\phi_{NO_3'}$ becomes 29·7 c.c. and n_0 would be 0·006787. It might be argued that the latter quantity represents the fundamental viscosity of depolymerised water at 25°, and hence it might be used to calculate the degree of polymerisation in ordinary water by comparing it with the viscosity of ordinary water and employing the equation $\eta = \eta_0 (1 + 2{\cdot}55\,\phi)$, which with the constant 2·55 might be considered applicable to the case of the uncharged water polymerides. This calculation, with $\eta_w = 0{\cdot}00891$, gives ϕ as 0·1225 c.c., or 122·5 c.c. per litre, corresponding with a polymerisation of 12·3%. The significance of the value of η_0 as thus suggested is open to question, for at present there is no evidence of its applicability to solutions other than those here considered. Further, the equation $\eta = \eta_0 (1 + 4{\cdot}5\,\phi)$ is not satisfactory either for the data for the mixed solutions of silver nitrate and nitric acid or for correlating hydrochloric acid and the mixed chloride solutions. It may be compared with the equation of Smoluchowski (*Kolloid-Z.*, 1916, **18**, 194) put in the form $\eta = \eta_0\{1 + 2{\cdot}5\phi\,(1 + x)\}$, where the term $(1 + x)$ takes account of the effect of the charge on the particles and presumably varies with the total number of these. If it is accepted that the volume 29·7 c.c. represents the effective value for the nitrate ion, then the factor $(1 + x)$ for nitric acid solutions of $5N$ upwards remains constant and equal to 4·5/2·5. This again assumes the fundamental significance of η_0. It is probable, therefore, that the linear relationship for nitric acid is due to a balance of a number of effects, and is not to be interpreted fully on these simple lines.

Since a satisfactory interpretation of the data for the mixed solutions could not be obtained on the above lines, recourse was had to the empirical equation, $\eta_2 - \eta_1 = \frac{1}{2}(\eta_2 + \eta_1)2{\cdot}5\,\phi$, employed in previous parts of this series. According to this formula a change of viscosity occasioned by the addition of a quantity of ions of nett volume ϕ is proportional to that volume and to the mean viscosity of the solutions concerned. It appears that introduction of the mean viscosity in this way is equivalent to making allowance for the effect of the charges on the ions, but in a different way from that of Smoluchowski. Thus the effect of an addition ϕ is greater in solutions of high total-ion strength than in those of lower concentration. By applying this to the solutions of nitric acid alone, in the first case, and using successive pairs of values from Table II, the ϕ' values of the nitrate ion are calculated. Thus, from the fourth and fifth experiments (Scarpa values)

$\eta_1 = 0{\cdot}00989$; $\eta_2 = 0{\cdot}01049$; $\eta_2 - \eta_1 = 0{\cdot}00060$; $\eta_2 + \eta_1 = 0{\cdot}02038$; $C_2 - C_1 = 0{\cdot}934$;

$$\phi' = \frac{\Delta\eta \times 1000 \times 2}{2{\cdot}5 \times (\eta_2 + \eta_1)\Delta C} = \frac{0{\cdot}00060 \times 2000}{2{\cdot}5 \times 0{\cdot}02038 \times 0{\cdot}934} = 25{\cdot}23.$$

and the values for the complete series are as follows :

C	0		0·987		2·010		2·810		3·744		4·863		5·667
ϕ'		11·7		15·5		18·0		25·2		24·4		30·9	

C	5·667		7·257		8·900		11·92
ϕ'		27·8		27·9		27·3	

The mean value for $C > 5N$ is $\phi' = 27·6$, which may be compared with that derived directly from the linear relationship discussed above, *viz.*, 29·7 : these values fall between the limits already adduced for the volume of this ion and they approximate to the solution volume found. These facts, in conjunction with the fair constancy of the values in the above table for solutions of concentrations above $3N$, are taken to indicate an absence of hydration effects for the nitrate ion. The initial rise in the series is attributed to the depolymerising action of this ion, whereby the apparent ϕ' value is reduced. The tendency for the values to fall, over the range 5—$12N$, may be connected with the falling off in the total number of particles present. An alternative explanation might be that incomplete ionisation in the very concentrated solutions causes an apparent reduction of the effective volume—an actual reduction due to changes in the packing arrangements of the ions and water molecules and equivalent to a loss of free space is not excluded. In this connexion, the difference between nitric and hydrochloric acids is noteworthy. It was shown that with the latter (Part I) the ϕ' value of the chlorine ion (22·43) which could be used to account for the viscosities of solutions of 3—$6N$ on the above lines was quite inadequate for the values at higher concentrations, and the apparent ϕ' values would rapidly increase with increasing acidity, this being due apparently to some specific effect such as the formation of a complex molecule (? H_3OCl) which has no parallel in the nitric acid solutions.

The value 28 being accepted for the effective volume of the nitrate ion in solutions containing that ion in concentrations from 7 to $10N$, the data of Table I may be used to calculate the apparent ϕ' values for the silver ions in the mixed solutions of total concentrations between these limits. Thus, for the first pair of solutions there is a fall in viscosity accompanying a fall in concentration of 2·540 in the nitrate ion and of 4·762 in the silver ion, and the calculation is made as follows :

$$\eta_1 = 0·02989 ; \quad \Delta\eta = 0·01137 ;$$
$$\eta_2 = 0·01852 ; \quad (\eta_1 + \eta_2) = 0·04841 ;$$

$$1000\ \phi = \frac{0·01137 \times 2000}{0·04841 \times 2·5} = 187·9 \text{ c.c. per litre.}$$

The total ϕ of 187·9 c.c. per litre is reduced by that of the nitrate ions, *viz.*, 2·540 × 28 = 71·1 c.c., and the difference (187·9 − 71·1 = 116·8 c.c.) divided by the fall in the silver-ion concentration (4·762) gives the effective volume of the silver gram-ion, *i.e.*, $\phi'_{Ag} =$ 24·53 c.c. This may be taken to represent the mean effective volume of the hydrated silver ion for the particular range considered, and the apparent hydration may be calculated after subtracting the volume of the silver ion, 3·28, derived from the densities. Each successive pair of solutions in Table I might thus be treated, but in that part of the table embracing the minimum point of viscosity, $\Delta\eta$ becomes inconveniently small, hence in this region wider steps have been used. Further, for certain pairs, *e.g.*, the sixth and seventh solutions, η increases whilst $C_{NO_3'}$ increases and $C_{Ag\cdot}$ diminishes, so the ϕ value calculated is the nett effect $\phi_{NO_3'} - \phi_{Ag\cdot}$, and the subsequent calculation of $\phi_{Ag\cdot}$ must be modified accordingly. The series of values relating to the different parts of the table may now be considered, the ordinal numbers referring to the successive pairs of solutions. The values in brackets are indirectly derived, being weighted values deduced from others first obtained from wider steps of the table; *h* is the hydration factor or apparent hydration.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
$\phi'_{Ag\cdot}$	24·5	24·5	27·5	[25	20	19	22]	26·2	26·6
h	1·21	1·21	1·38	1·24	0·95	0·90			

This series of values may be compared with that obtained for sodium ions in sodium chloride–hydrochloric acid solutions (Table VI; Part I), which commences at 32·0 for the pure saturated solution and falls to 23·5 at the point of minimum viscosity. After this point is reached, in both cases the values begin to rise, but, as the concentrations of the salts are then becoming low, the values may be subject to considerable error partly owing to the smallness of the effects actually attributable to these ions, and partly because other specific effects coming into play in solutions of higher acidities are automatically included in the values for the metal ions. Only the first portion of the series of figures for silver nitrate is therefore useful for the discussion of the hydration. The calculated hydration factors are lower than those obtained for sodium ions at corresponding parts of the series. The initial tendency to rise may be due to the very considerable fall in total solute strength of the solutions in the early parts of the series. This effect is very slight or non-existent in the case of sodium ions. The method of treatment given places the silver ion between the ions of sodium and potassium as regards hydration, in agreement with the idea that the order should be that of the ionic radii, the smaller the radius the greater being the tendency for hydration.

Summary and Conclusions.

Determinations have been made at 25° of the solubility of silver nitrate in aqueous nitric acid of concentrations up to $12N$. The densities and the viscosities of the solutions have been measured together with those of a comparable series for the acid alone.

The formula $d = K + k_1a + k_2b$ applies to the densities of the mixed solutions of total solute concentration below $9N$, a and b being the concentrations of acid and salt respectively. The constants K and k_1 also apply to the pure acid solutions of concentrations 6—$9N$. The corresponding solution volumes are discussed and compared with those derived by other investigators. The silver ion behaves like lithium and sodium ions in having an apparent volume less than that calculated from its radius in the crystal lattice.

The viscosity data are interpreted by means of the empirical formula $\eta_2 - \eta_1 = \frac{1}{2}(\eta_2 + \eta_1)2{\cdot}5\,\phi$. A change of viscosity caused by the addition to a solution of ions of volume ϕ is proportional to this volume but also depends upon the mean viscosity of the solutions considered. It is suggested that this latter factor takes account of the electrical effects, and hence the equation allows of the volume effect being separately estimated. The formula, which has previously been applied only to chlorides and their ions, is now found to give a satisfactory account of the data for nitric acid and for its mixed solutions with silver nitrate. The volume effect of the nitrate ion remains substantially constant except in 0—$5N$-solutions of the acid alone, where apparent variations due to the depolymerising action of the ion are indicated. This depolymerisation of the water is more easily effected by the nitrate ion than by the chlorine ion. The volume of the nitrate ion determined from the viscosities approximates to the solution volume calculated from the densities and is also in agreement with values deduced from the data for the size of this ion in crystals; hence it is concluded that this ion is not hydrated. Nitric acid shows a less complex behaviour in solutions of high concentration than does hydrochloric acid, and this suggests the absence of complex ions in the former case.

The silver ions in the mixed solutions show effects attributable to hydration, which is less than that previously found for sodium but greater than for potassium, and this is in accordance with the expected results deduced from the sizes of the ions. Hydration factors for silver ions varying from 1·4—0·90 are found, whereas those for sodium ions were 1·7—1·2.

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