CCCXV.—*The Apparent Hydration of Ions. Part II. The Densities and Viscosities of some Mixed Aqueous Solutions of Lithium Chloride and Hydrochloric Acid.*

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THE methods described in Part I (this vol., p. 1917) for the investigation of the hydration of potassium and sodium chlorides in concentrated aqueous solutions containing hydrochloric acid have now been applied to certain mixed solutions of lithium chloride and hydrochloric acid. The densities and viscosities at 25° have been determined for a series of solutions containing different proportions of the acid and the salt with approximately the same total solute concentration as a saturated solution of sodium chloride, such a concentration being chosen so that a direct comparison might be made of the behaviour of the two salts under similar conditions.

The experimental work was carried out in the same way as for Part I, but, since the solutions were not saturated, they were made by mixing stock solutions of known concentration. The opportunity was taken of further testing the Scarpa method for measuring the viscosities by carrying out determinations in an Ostwald tube upon the same solutions. The same viscometers were used as for Part I. The results confirmed the previous conclusions as to the accuracy of the Scarpa method. In Table I, col. 1 shows the densities calculated from the formula

$$d_{4^\circ}^{25^\circ} = 0{\cdot}99707 W'/W - 0{\cdot}0012(W' - W)/W\,;$$

cols. 2 and 3 the coefficients of viscosity in c.g.s. units; cols. 4, 5, and 6 the concentrations (mols./litre) of acid, salt, and water, respectively; and col. 7 the hydration numbers, x. The total solute concentrations varied between 5·459 and 5·402, that previously found for saturated sodium chloride solution at 25° being 5·4325.

TABLE I.

$d_{4^\circ}^{25^\circ}$.	η (Scarpa).	η (Ostwald).	HCl.	LiCl.	H_2O.	x.
1·1176	0·01951	0·01944	0	5·407	49·20	2·49
1·1147	0·01849	0·01839	0·546	4·913	49·20	2·36
1·1116	0·01748	0·01746	1·091	4·364	49·20	1·81
1·1087	0·01667	0·01664	1·635	3·799	49·29	2·12
1·1050	0·01581	0·01579	2·176	3·248	49·29	1·91
1·1019	0·01509	0·01508	2·702	2·708	49·34	1·89
1·0985	0·01440	0·01435	3·246	2·160	49·32	1·72
1·0957	0·01384	0·01384	3·789	1·635	49·30	1·82
1·0920	0·01320	0·01318	4·330	1·072	49·34	1·80
1·0893	0·01267	0·01263	4·890	0·540	49·29	

Except in the case of the first two solutions, the agreement between the viscosities obtained by the different methods was good. The viscosity of the stock lithium chloride solution (5·407*M*) as found by the Scarpa method was in better agreement with Green's data for that salt (J., 1908, **93**, 2023) than was the value given by the Ostwald method. Any errors in density determinations are reflected in the latter method and do not affect the Scarpa values.

Discussion of Results.

Densities and Solution Volumes.—It is found that, although the densities can be calculated by means of the formula $d_{4^\circ}^{25^\circ} = K + k_1a + k_2b$ previously applied to the potassium chloride (or sodium chloride)–hydrochloric acid solutions, yet some adjustment of the constants is required. The solution volume of either the acid or the water is different, and if the value of K is retained at 1·01275, the expression

$$d_{4^\circ}^{25^\circ} = 1{\cdot}01275 + 0{\cdot}01355a + 0{\cdot}0193b \quad . \quad . \quad . \quad \text{(i)}$$

gives fair agreement for the calculated densities (see below). The corresponding solution volumes of the acid and the salt are 22·62 and 22·80, and the lithium ions show only a small apparent volume in solution. The apparent density of the water in the solutions is then the same as in those containing sodium chloride or potassiun chloride. This result, in the light of Masson's work (J., 1911, **99**, 1132), can only be regarded as conclusive if no other constants satisfy the expression. Examination of the data shows that the solution volumes of the lithium chloride and the acid are nearly equal. Assuming equality, and taking the value HCl = 22·43 as found in Part I, the values of the constants for the density expression may be deduced from this value together with that obtained for the water from the equation $w\gamma + a\alpha + b\beta = 1000$, where α, β, and γ are the molar solution volumes of acid, salt, and water, and a, b, and w the molar concentrations per 1000 c.c. (Masson, *loc. cit.*). The mean value of γ is 17·82 ($\alpha = \beta = 22{\cdot}43$), and hence $K = d_{\text{w}} = 1{\cdot}0110$; k_1 and k_2 are then calculated from $k_1 = (M_{\text{a}} - \alpha d_{\text{w}})/1000$ and $k_2 = (M_{\text{b}} - \beta d_{\text{w}})/1000$, M_{a} being the molecular weight of the acid, and M_{b} that of the salt, and it is found that $k_1 = 0{\cdot}0138$ and $k_2 = 0{\cdot}0197$. The equation

$$d_{4^\circ}^{25^\circ} = 1{\cdot}0110 + 0{\cdot}0138a + 0{\cdot}0197b \quad . \quad . \quad . \quad \text{(ii)}$$

gives at least as good agreement as is obtained with the other values for the constants, as is shown by the following comparison.

$d_{4^\circ}^{25^\circ}$ (obs.)	1·1176	1·1147	1·1116	1·1087	1·1050
(calc., i)	1·1171	1·1150	1·1116	1·1082	1·1049
(calc., ii)	1·1175	1·1153	1·1118	1·1084	1·1050
$d_{4^\circ}^{25^\circ}$ (obs.)	1·1019	1·0985	1·0957	1·0920	1·0893
(calc., i)	1·1016	1·0984	1·0957	1·0921	1·0894
(calc., ii)	1·1016	1·0984	1·0955	1·0919	1·0891

It seems that this type of calculation is in the nature of a compromise, involving an assumption of constant solution volumes for the series of solutions, which is probably not strictly justifiable. The variations in the solution volumes, as calculated from the different constants, are, however, not very great, and are unimportant for the subsequent discussion of viscosities. The solution volumes may now conveniently be reviewed in tabular form and compared with values calculated from ionic radii. Calculations have been made in two ways: (1) The expression $\frac{4}{3}\pi r^3 N$ is used to obtain the ionic volume for the g.-ion, r being the radius as given by Wasastjerna (*Soc. Sci. Fenn. Comm. Phys. Math.*, 1923, **38**, 1) and N the Avogadro number. (2) It is assumed that the ionic volumes bear the same relationship to the solution volumes as does the bivalent oxygen atom (or ion) O″ to the water molecule, taken as 18; the molar volumes are then obtained by summing the ionic volumes. Conversely, the experimental solution volumes of the salts and the acid may be divided into the respective ionic solution volumes, the hydrogen ion in the case of the acid having no appreciable volume.

Ionic volumes.

	Li$^{\cdot}$.	Na$^{\cdot}$.	K$^{\cdot}$.	Cl′.	O″ (H_2O).
r, in Å.U.	0·72	1·01	1·30	1·72	1·32
r^3, ,, ...	0·373	1·030	2·197	5·088	2·300
$\frac{4}{3}\pi r^3 N$, in c.c.	0·946	2·616	5·578	12·92	5·84
$r^3 \times 18/2{\cdot}300$	2·921	8·063	17·60	39·83	18·00
ϕ (found) (i)	0·18	—	—	22·62	—
(ii)	0·0	—	—	22·43	17·82
(iii)	—	1·58	12·25	22·43	17·795
(iv)	0·33	—	—	22·58	17·795

The solution volumes found (ϕ) are those obtained according to the values adopted for the constants in the density calculations; thus (i) and (ii) are based on the values used in equations (i) and (ii) respectively, (iii) is based on the values used in Part I, and (iv) on the values $K = 1{\cdot}01275$, $k_1 = 0{\cdot}0136$, $k_2 = 0{\cdot}0192$.

Molar volumes.

	HCl.	LiCl.	NaCl.	KCl.	H_2O.
ϕ (found) (ii)	22·43	22·43	—	—	17·82
(iii)	22·43	—	24·00	34·66	17·795
(iv)	22·58	22·91	—	—	17·795
$\frac{4}{3}\pi(r_1^3 + r_2^3)N$ ...	12·921	13·87	15·54	18·50	5·84 (O″)
ϕ for solids	—	20·54	26·96	37·44	—

The values for the solids are derived from density data due to Baxter (*Amer. Chem. J.*, 1904, **31**, 558). Green (*loc. cit.*) obtained values for the solution volume of lithium chloride ranging from 17·53 to 20·94 according to the concentrations, the values in concentrated solution being in close agreement with Baxter's figure for the solid. Since Green's calculations involve the use of the density of pure water, no change in this value being allowed for in the concentrated solutions, it need not necessarily be concluded that the actual solution volume is the same as the solid volume. On the other hand, it is difficult to see why the solution volume obtained by the author (22·43) is higher than that of the solid—in the case of sodium and potassium chlorides the solution volumes are less than the solid volumes. The table shows also that the volumes deduced from the lattice radii are considerably less than the apparent solution volumes.

Viscosities.—The empirical method of calculating the degree of hydration of ions, as used in Part I, has been applied to the results for lithium chloride and leads to values which are comparable with those obtained for potassium and sodium. As expected, lithium chloride is more highly hydrated and the generally accepted series relationship $Li^{\cdot} > Na^{\cdot} > K^{\cdot}$ is indicated. The fall in viscosity which occurs when hydrochloric acid replaces lithium chloride is accounted for by assuming that the lithium ions are hydrated, whilst the hydrogen and chlorine ions are not solvated to any marked extent. Changes of viscosity due to changes of chlorine-ion concentration are expressed by the equation $\eta_1 - \eta_2 = \frac{1}{2}(\eta_1 + \eta_2) \times 2{\cdot}5\phi$, where ϕ is the volume of ions added to or removed from 1 c.c. of solution, and is given by $\phi = (C_2 - C_1) \times 22{\cdot}43/1000$. The volume 22·43 is that of the chlorine ion in solution. If the hydrogen ions have no specific effect, as appears to be the case for solutions of pure acid, then on comparing a solution of hydrochloric acid with one of lithium chloride of equal chlorine-ion concentration, complete dissociation being assumed, any difference in viscosity may be attributed to the solvated lithium ions. It is further assumed that their effect is proportional to their volume, as with the chlorine ions, and the volume of hydrated lithium ions is calculated from the above equation. The ϕ value so obtained is divided by the concentration of lithium chloride in solution, and this gives the effective volume of 1 g.-ion of lithium ions, from which the volume of water accompanying the 1 g.-ion is deduced. From the following data, *viz.*, $C = 5{\cdot}407$, $\eta(\mathrm{LiCl}) = 0{\cdot}01951$, $\eta(\mathrm{HCl}) = 0{\cdot}01220$ (from Green's data), $\phi = 0{\cdot}1829$ c.c. (or 182·9 c.c. per litre), one obtains in this way 33·82 c.c. per g.-ion of lithium, corresponding to a hydration with practically the same amount of water, since the lithium ion has an almost negligible solution volume; thus x, the hydration number, is 1·88. This value is decidedly higher than that obtained for sodium ions ($x = 1{\cdot}44$) in the same way and at practically the same concentration.

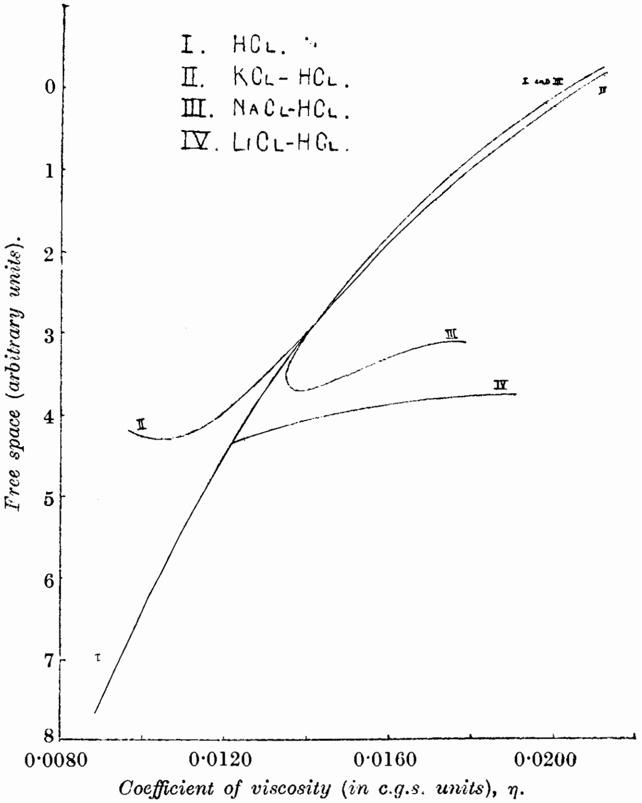
A more trustworthy result is probably obtained by calculating the hydration numbers for each successive pair of solutions in the series of salt and acid mixtures. The values so obtained are given in the last column of Table I. Any changes of chlorine-ion concentration are allowed for in making the calculations.

The above methods of calculating the degrees of hydration can only be regarded as trustworthy if it is shown that viscosity changes can be related to changes in the mean sizes of the molecules composing a liquid mixture. The original equation of Einstein $\eta = \eta_0(1 + 2{\cdot}5\phi)$ is not concerned with the actual size of the suspended particles, but deals with their total volume. Smoluchowski's extension of this equation (*Kolloid-Z.*, 1916, **18**, 194), introducing a correction for the charge upon the suspended particle, involves the radius; but in the present state of the knowledge of the applicability of this formula, it seems hardly possible to extend its use to the salt and acid solutions here considered. The problem may be approached from another point of view. Dunn (*Trans. Faraday Soc.*, 1926, **22**, 401) has developed a kinetic theory of viscosity of liquids, which, whilst it is primarily concerned with the effect of change of temperature, is of interest in that it deals with the attractive forces between the molecules and the factors governing the slipping between the planes. One of these factors is the possession by some of the molecules of a certain critical energy in virtue of which they are subject to negligible cohesion, and hence represent "loose spots" in the adjacent planes. It seems that the number of such molecules in a given liquid will depend partly upon the amount of free space. The question of the relation between free space and viscosity has been investigated by McLeod (*ibid.*, 1923,

19, 6), who suggested that for normal liquids viscosity should be inversely proportional to free space. It is of interest, therefore, to see how this bears upon the problem of the salt and acid solutions. It is essential to show that the variations of free space alone cannot account for the viscosity effects.

The molar volumes obtained by calculation from the lattice radii are taken as the limiting volumes of the various species, and for a given solution the free space is calculated from the molar concentrations of salt, acid, and water (*i.e.*, 1000 — space occupied). Even if the resulting values are not numerically equal to the actual free space, they should be comparable amongst themselves. They are plotted against the viscosities in Fig. 1, the curve for hydrochloric acid being derived from Green's data (*loc. cit.*). The curves are very similar to those obtained by plotting total solute concentration against viscosity (see Fig. 3, Part I).

FIG. 1.



If the free space alone governed the viscosity, the changes would be in the direction of lower viscosity for greater free space. As acid displaces salt in the sodium chloride–acid solutions, the free space increases at first and the viscosity falls. The rate of fall is, however, much more rapid than for corresponding free-space change in pure acid solutions. At a later stage in the mixed solutions, free space decreases with increase of total solute concentration, and the curve finally becomes identical with that for pure acid.

The curve for the potassium chloride–acid mixtures shows that the free space at first increases whilst viscosity rises, and this is in accord with the idea that the latter effect is partly due to the substitution of larger water molecules for smaller potassium ions. The subsequent increase of viscosity may be more largely due to the decrease in free space.

Lithium chloride solutions have much higher viscosities than potassium chloride solutions of equal free space. The total solute concentrations are, however, also higher in this case.

When lithium chloride is compared with sodium chloride, it is seen that whilst the viscosities are comparable for solutions of approximately the same total concentration and the same relative amounts of salt and acid, yet those containing lithium chloride have more free space. The effect of the greater free space has been more than counterbalanced by the presence of the more highly hydrated lithium ions.

Summary and Conclusions.

1. Densities and viscosities have been determined at 25° for a series of concentrated mixed aqueous solutions of lithium chloride and hydrochloric acid. The methods of Scarpa and Ostwald for measuring viscosities have been again compared and found to agree.

2. Formulæ of the type $d = K + k_1a + k_2b$ can be used to calculate the densities with fair accuracy. The assumption of the strict constancy of the molar solution volumes is not, however, justifiable. The packing of the ions amongst the water molecules may be supposed to involve a reduction of the free space depending upon the numbers and sizes of the various ions. The apparent volume of the water in solution may therefore vary from one solution to another.

3. The replacement of lithium chloride by hydrochloric acid results in a fall in viscosity which is interpreted as being due to the higher hydration of the lithium ions than of the hydrogen ions. Hydration numbers are calculated which indicate (i) a greater degree of hydration for lithium than sodium under similar conditions, (ii) a fall in the degree of hydration as the proportion of acid in the solution increases.

4. The influence of "free space" upon the viscosities in mixed solutions of lithium, sodium, or potassium chloride and hydrochloric acid is discussed.

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