CCLI.—*The Apparent Hydration of Ions. Part I. The Densities and Viscosities of Saturated Solutions of Sodium and Potassium Chlorides in Hydrochloric Acid.*

By JOHN WILLIAM INGHAM.

A REVIEW of the determined values of the hydration numbers of strong electrolytes in aqueous solutions shows that, whilst there is a certain unanimity with respect to the alkali chlorides and their ions, there is considerable doubt as to the relative position of the hydrogen ion.

Recent work by Sugden (J., 1926, 174), who studied the distribution of acetic acid between aqueous solutions of salts and amyl alcohol, and of Glasstone and his collaborators (J., 1925, **127**, 2660; 1926, 2935, 2939; 1927, 635), using the salting-out effect upon ethyl acetate and aniline, confirms much earlier work, to which these authors refer, in establishing the series $Li^{\cdot} > Na^{\cdot} > K^{\cdot}$, although the two methods give numerically different results for the hydration numbers :

	LiCl.	NaCl.	KCl.
Sugden	10·5	7·9	3·4
Glasstone	27	24	22

Sugden finds the chlorine ion to be non-hydrated, so his values for the salts are also those of the kations; on the other hand, Glasstone finds 10 for Cl', the corresponding kation values being $Li^{\cdot}$ 17, $Na^{\cdot}$ 14, $K^{\cdot}$ 12. These " hydration numbers " of Glasstone are for ions at infinite dilution, smaller values being found for higher concentrations. Sugden obtained reasonably constant values over a range of concentration N—$N/10$.

Neither of these methods is suitable for comparative determination with hydrochloric acid, the relative position of which has been found by other methods (for references, see General Discussion upon the Theory of Strong Electrolytes, *Trans. Faraday Soc.*, 1927, **23**). Remy (*ibid.*, p. 381) deduces from mobilities the values $H^{\cdot}$ 0·9, $K^{\cdot}$ 4·1, $Na^{\cdot}$ 7·4, $Li^{\cdot}$ 12·6 for the " water-sheaths " of these ions, Cl' having the value 3 dependent upon the assumption that large organic ions have no sheaths. Scatchard (*ibid.*, p. 454; *J. Amer. Chem. Soc.*, 1925, **47**, 2098; 1927, **49**, 217), from calculations of activities in water–alcohol solutions, concludes that lithium, sodium, potassium, and chlorine ions are not " chemically hydrated," but that the hydrogen ion may be present in the form $H_3O^{\cdot}$. This conception of the hydrogen ion has been used also by Fajans (*Trans. Faraday Soc.*, 1927, **23**, 357) in dealing with refractometric measurements upon hydrochloric acid solutions. It is necessary to distinguish between "chemical hydration" and the more general attraction between ions and solvent ("solvation"), such as is assumed to lead to the presence of aggregates of water molecules with ions as centres (compare Scatchard, *loc. cit.*).

Bjerrum (*Z. anorg. Chem.*, 1920, **109**, 275) calculated from heats of dilution that hydrochloric acid is associated with 8 molecules of water and that sodium and potassium chlorides are relatively non-solvated. It appears that some methods detect only chemical hydration and that others which indicate solvation as well have not yet been satisfactorily correlated.

The extension to concentrated solutions by Hückel (*Physikal. Z.*, 1925, **26**, 93) of the original theory of complete dissociation of strong electrolytes (Debye and Hückel, *ibid.*, 1923, **24**, 185), and the work of Harned (*J. Amer. Chem. Soc.*, 1926, **48**, 326) upon the activity of hydrochloric acid in concentrated solutions of lithium, sodium, and potassium chlorides, supporting the extended theory, have prepared the way for the examination of other properties of such solutions. The work now described is a contribution in this direction.

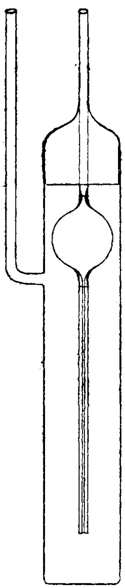
The solubilities of potassium and sodium chlorides in hydrochloric acid solutions of concentrations varying between the widest limits have been determined, together with the densities and viscosities of the solutions, all at 25°. Previous measurements of the solubilities of alkali chlorides in hydrochloric acid have been made at 0° by Engel (*Compt. rend.*, 1886, **102**, 113, 619) and at 30° by Masson (J., 1911, **99**, 1132). Others, including Armstrong and Eyre (*Proc. Roy. Soc.*, 1907, *A*, **79**, 564 *et seq.*) and Gibson and Denison (*Proc. Roy. Soc. Edin.*, 1911, **30**, 562), have studied in a more general way the precipitating action of the acid. A full review is given in the Reports of the British Association of 1910 and 1911 in the sections on Solubility. The viscosities do not appear to have been measured for such mixtures.

Determination of Viscosities.

The method adopted was that due to Scarpa (*Gazzetta*, 1910, **40**, 271) with a viscometer (Fig. 1) similar to that used by Farrow (J., 1912, **101**, 347). The dimensions of the apparatus were : bulb 5 c.c., capillary length 10 cm., bore 0·4 mm.; the lower end of the capillary stood 2 cm. above the bottom of the outer cylindrical vessel, which was 3 cm. in diameter. The rest of the apparatus (negative pressure device and manometer) was like that of Farrow, except that a three-way stopcock was added in order to facilitate the operations.

The viscometer was standardised with conductivity water at 25° ± 0·02°, with a negative pressure of 300 mm. on the gauge, absolute alcohol being used as the gauge indicator liquid. The constant of the apparatus was thus determined, using the expression $k = \eta_w/[t_1t_2/(t_1 + t_2)]_w$, η_w, the coefficient of viscosity of water, being taken as 0·0891 (Thorpe and Rodger), and t_1 and t_2 being the times of flow upwards under the applied negative pressure and downwards by gravity. Rigorous precautions of cleanliness were taken throughout the whole of the experiments, and corrections were applied for variations in temperature of the gauge liquid which stood outside the thermostat. The constant of the viscometer was independent of the amount of water used in the outer vessel to within 0·1%, and was reproducible with this accuracy at intervals during the subsequent measurements with the solutions. It was also shown that a layer of well-washed garnets placed below the end of the capillary tube, even to a depth of 1 cm., had no influence on the constant; so that, in the case of solutions, any small layer of undissolved solid would have no effect in this way.

FIG. 1.



The apparatus was tested by determinations upon a sample of absolute alcohol ($d_{4°}^{25°}$ 0·78711) and comparisons were made with values found for the same liquid in (i) an ordinary Ostwald viscometer and (ii) an Ostwald constant-pressure viscometer, in the same thermostat. The results were :

η (Scarpa) 0·01107; η (Ostwald, i) 0·01108; η (Ostwald, ii) 0·01106.

With a higher negative pressure of 400 mm. the Scarpa method gave a lower value, *viz.*, 0·01098. It appeared that the Scarpa method, with a gauge pressure of 300 mm., would be accurate to 0·1% compared with the Ostwald ordinary method. (The adjustments required in the Ostwald constant-pressure method are tedious, and it seems likely that the Scarpa method could conveniently replace it when a method not requiring density measurements is required.)

Recently, King and Partington (*Trans. Faraday Soc.*, 1927, **23**, 528), using the Scarpa method with a different design of tube, found difficulty in obtaining satisfactory agreement with the Ostwald method carried out in the same tube. For some of their salt solutions values as much as 6% higher were calculated from the former; and for a sample of alcohol ($d_{4°}^{25°}$ 0·78507) they gave

η (Scarpa) 0·01065; η (Ostwald) 0·01071.

Whilst no explanation of these discrepancies can be offered, they should not be taken as reflecting on the accuracy of the present work, the results of which afford a testimony to the usefulness of the method.

For the determinations upon the salt and acid mixtures, the acid solution of approximately known strength, prepared from a stock of specially distilled acid, was heated in a flask on a water-bath at 50—60° with a moderate excess of the pure salt, and the saturated solution was subsequently brought to equilibrium by shaking in the thermostat at 25° ± 0·02°. A quantity of 35—40 c.c. of solution, together with a little of the salt, was then quickly poured into the viscometer vessel, which was stoppered and had a glass stirrer. The final equilibrium was thus attained in the viscometer, and before the introduction of the capillary tube, slightly warmed, any suspended salt crystals were allowed to settle. Even with the strongest and densest solutions a perfectly clear solution was readily obtainable. The times of flow, measured to 0·2 sec., were usually constant after the first run, and only infrequently was any trouble experienced due to crystals finding their way into the capillary. The viscosity was calculated from $\eta_s = k \times [t_1t_2/(t_1 + t_2)]_s$, the appropriate value of k for the observed gauge temperature being used.

Density determinations were made by pipetting with a warmed pipette sufficient liquid to fill a 25 c.c. density bottle which was suspended in the thermostat. The bottle had a cap over the stopper and was calibrated with pure water. The contents of the bottle were suitably diluted, and the acid was estimated by titration and the total chloride by weighing as silver chloride.

Redeterminations of the viscosities were frequently made upon the liquid remaining after the first withdrawal, with or without fresh additions, and the value was found to be unaltered and independent of the amount of liquid in the outer vessel. The usual order of agreement was to 0·1%, and the variation never exceeded 0·3%.

All apparatus used in the analyses was carefully calibrated and duplicate determinations were made, the total chloride estimations agreeing at least to 0·05%. The salts were tested and proved to be very pure. Acid solutions of high concentration were obtained by generating pure dry hydrogen chloride from the stock acid by a method which was shown to give no contamination with sulphuric acid.

In Table I are the results for solutions containing potassium chloride. In col. 1 are the absolute densities, $d^{25°}_{4°} = 0{\cdot}99707\frac{w'}{w} - \left[\frac{0{\cdot}0012(w' - w)}{w}\right]$; in col. 2 is η, the coefficient of viscosity (in c.g.s.

units); cols. 3, 4, and 5 respectively give molar concentrations of acid, salt and total solute; col. 6 the molar concentration of water ($H_2O = 18{\cdot}016$); col. 7 is the sum of cols. 5 and 6.

Table II gives the data for solutions saturated with sodium chloride; and at the end are given the comparative values for pure water and for one solution of pure acid with no salt.

TABLE I.

$d_{4^\circ}^{25^\circ}$.	η.	HCl.	KCl.	Total solute.	H_2O.	Total solution.
1·1781	0·009710	—	4·199	4·199	48·00	52·20
1·1671	0·009918	0·464	3·748	4·212	48·32	52·53
1·1564	0·01020	0·990	3·288	4·278	48·56	52·84
1·1467	0·01044	1·492	2·887	4·379	48·67	53·05
1·1419	0·01063	1·833	2·604	4·436	48·90	53·34
1·1272	0·01109	2·743	1·951	4·694	48·95	53·64
1·1191	0·01155	3·570	1·449	5·020	48·90	53·92
1·1169	0·01178	4·008	1·227	5·235	48·81	54·04
1·1150	0·01216	4·665	0·963	5·608	48·50	54·11
1·1169	0·01279	5·672	0·607	6·279	48·01	54·29
1·1272	0·01380	7·144	0·309	7·453	46·27	53·72
1·1423	0·01519	8·433	0·267	8·700	45·22	53·92
1·1713	0·01788	10·68	0·215	10·89	42·52	53·41
1·1855	0·01943	11·74	0·20	11·94	41·22	53·16
1·1863	0·01952	11·81	0·22	12·03	41·04	53·06
1·2009	0·02121	12·96	0·24	13·19	39·46	52·65

TABLE II.

			NaCl.			
1·1981	0·01779	—	5·4325	5·4325	48·85	54·28
1·1867	0·01694	0·503	4·880	5·383	49·03	54·41
1·1781	0·01641	0·886	4·483	5·369	49·06	54·43
1·1511	0·01492	2·265	3·149	5·414	49·10	54·52
1·1352	0·01419	3·185	2·310	5·495	49·08	54·58
1·1319	0·01405	3·487	2·079	5·566	48·98	54·55
1·1282	0·01391	3·830	1·797	5·627	49·05	54·68
1·1200	0·01358	4·500	1·333	5·834	48·73	54·56
1·1160	0·01353	5·253	0·907	6·159	48·38	54·54
1·1158	0·01357	6·101	0·544	6·645	47·83	54·47
1·1213	0·01400	7·073	0·293	7·366	46·98	54·35
1·1302	0·01463	7·976	0·158	8·134	46·08	54·21
1·1458	0·01582	9·236	0·091	9·327	44·62	53·95
1·1970	0·02111	13·41	0·017	13·43	39·24	52·67
0·99707	0·00891	—	—	—	55·35	55·35
1·1203	0·01402	7·673	—	7·673	46·66	54·33

Discussion of Results.

Density and Volume Relations.—The changes which take place when acid replaces salt in the solutions can be expressed in terms of the molecular and ionic solution volumes of the constituents. In view of the order of ionic sizes as deduced from crystal lattice measurements by Wasastjerna (*Soc. Sci. Fenn. Comm. Phys. Math.*, 1923, **38**, 1), the various species to be considered would fall in series $H^{\cdot} < Na^{\cdot} < K^{\cdot} < H_2O < HCl < NaCl < KCl$, and the hydrogen ion may be assumed to have negligible volume, or, if combined in the form $H_3O^{\bullet}$, it may provisionally be put equal to O'' or to H_2O.

The first addition of acid to the saturated sodium chloride solution results in a slight decrease in the total chloride (Table II, col. 5), accompanied by a small increase in water concentration and in the total number of molecules per litre (cols. 6 and 7). Rather more than an equivalent of salt is precipitated and hence there is more room for water to enter.

With further additions of acid the total solute concentration rises and, as the main factor influencing the volume effects is the chlorine ion (or radical), the amount of water which can remain begins to fall. The increase in chlorine-ion concentration more than balances the effect due to the decrease in sodium-ion concentration.

The volume effects are accompanied by mass changes reflected in the densities and this value falls at first, reaches a minimum, and then rises when the mass influence of the increasing chlorine-ion concentration preponderates.

The case for the potassium chloride mixtures is slightly different, and there is no lowering of the total solute content on the first addition of acid to the saturated solution of the pure salt. The removal of the larger potassium ions (compared with sodium ions), more nearly equal in size to water molecules, allows more room for chlorine accompanying hydrogen. The total solute concentration and the total number of molecules per litre both increase, and this continues until most of the potassium has been removed. Then, first the water concentration, and subsequently the total number of molecules, diminish as with the sodium chloride solutions. The mass effects again show in the densities, but the minimum occurs at a lower salt concentration. It can be seen that potassium chloride is not completely precipitated, and at the end of the series in solutions of high acid concentration it is still appreciably soluble, there being actually a slight increase in solubility.

The solubility effects thus appear to be dependent to a large degree upon the volumes in these series of mixed solutions of high concentration.

The above considerations can be extended in a quantitative way. Masson (*loc. cit.*) used an expression of the form $d = K + k_1a + k_2b$ to connect the densities with the molar concentrations of acid (a) and salt (b), K, k_1, and k_2 being constants. The constants k_1 and k_2 represent terms such as $(M - \alpha d_w)/1000$, where M is the molecular weight of the acid or salt, α the molar solution volume, and

d_w the density of the solvent in solution. The equation may be rewritten :

$$1000(d_{4^\circ}^{25^\circ} - d_w) = a(M_a - \alpha d_w) + b(M_b - \beta d_w).$$

This gives the difference in mass of one litre of solution and the same volume of water of the same apparent density as that in the solution. Thence also :

$$d_{4^\circ}^{25^\circ} = d_w + (a/1000)(M_a - \alpha d_w) + (b/1000)(M_b - \beta d_w).$$

Masson's conclusion, that the molecular solution volumes of water, salt, and acid remain constant over considerable ranges, is borne out.

Instead of the above formula, there may be substituted for it a similar expression in which the ionic solution volumes are used instead of the molecular values of the acid and salt. This reads

$$d_{4^\circ}^{25^\circ} = K + 0{\cdot}001a + k_2'b + k_3c.$$

K is the same as before, and since the ionic volume of the hydrogen ion is very small and its mass is approximately unity, k_1' has become 0·001, a, b, and c being the concentrations of hydrogen (ion), sodium (ion), and chlorine (ion) respectively. The data have been tested and constants deduced for this formula. The constants were first determined for the sodium chloride series, and it was then found that only k_2' had to be changed in order to obtain agreement with the data for potassium chloride. Having determined k_2' for each salt, the constants for the simpler formula of Masson could be obtained by direct summation, since for this equation

$$k_1 = 0{\cdot}001 + k_3 \text{ for the acid } (\mathrm{H}^{\cdot} + \mathrm{Cl}'),$$
$$k_2 = k_2' + k_3 \text{ for the salt } (\mathrm{Na}^{\cdot} + \mathrm{Cl}').$$

The two formulæ give, of course, practically identical results when tested on the same data, and hold good for each series as far as the point of minimum density. Tables III and IV give the results of these calculations, the appropriate values of the constants being included.

TABLE III. (NaCl.)

(i) $d_{4^\circ}^{25^\circ} = 1{\cdot}01275 + 0{\cdot}001a + 0{\cdot}0214b + 0{\cdot}01275c.$

(ii) $d_{4^\circ}^{25^\circ} = 1{\cdot}01275 + 0{\cdot}01375a + 0{\cdot}03415b.$

a.	$d_{4^\circ}^{25^\circ}$ (obs.).	$d_{4^\circ}^{25^\circ}$ (calc.).	a.	$d_{4^\circ}^{25^\circ}$ (obs.).	$d_{4^\circ}^{25^\circ}$ (calc.).
0	1·1981	1·1982	3·830	1·1282	1·1268
0·503	1·1867	1·1866	4·500	1·1200	1·1201
0·886	1·1781	1·1780	5·253	1·1160	1·1160
2·265	1·1511	1·1514	6·101	1·1158	1·1152
3·185	1·1352	1·1354	7·073	1·1213	1·1200
3·487	1·1319	1·1317	7·976	1·1302	1·1277

TABLE IV. (KCl.)

(i) $d_{4^\circ}^{25^\circ} = 1{\cdot}01275 + 0{\cdot}001a + 0{\cdot}0267b + 0{\cdot}01275c$.
(ii) $d_{4^\circ}^{25^\circ} = 1{\cdot}01275 + 0{\cdot}01375a + 0{\cdot}03945b$.

a.	$d_{4^\circ}^{25^\circ}$ (obs.).	$d_{4^\circ}^{25^\circ}$ (calc.).	a.	$d_{4^\circ}^{25^\circ}$ (obs.).	$d_{4^\circ}^{25^\circ}$ (calc).
0	1·1779	1·1783	3·570	1·1191	1·1190
0·464	1·1671	1·1670	4·008	1·1169	1·1163
0·990	1·1564	1·1561	4·665	1·1150	1·1149
1·492	1·1467	1·1471	5·672	1·1169	1·1147
1·832	1·1419	1·1408	7·144	1·1272	1·1232
2·743	1·1272	1·1274			

It appears that if the ionic solution volumes of the constituents remain constant in the mixtures for which the calculations hold good, then the molecular volume of the water also is constant and the apparent density of the water is $d_w = 1{\cdot}01275$. From this value, the ionic and molecular solution volumes can be obtained, these being presented in the following table, together with values calculated from the ionic lattice radii of Wasastjerna (*loc. cit.*) on the assumption that the ionic volumes bear the same relation to the solution volumes as does the volume of the bivalent oxygen atom O″ (ion) to the water molecule H_2O, taken as 18. The molecular volumes of the acid and salts are taken as the sums of the ionic volumes, the hydrogen ion being assumed to have negligible volume.

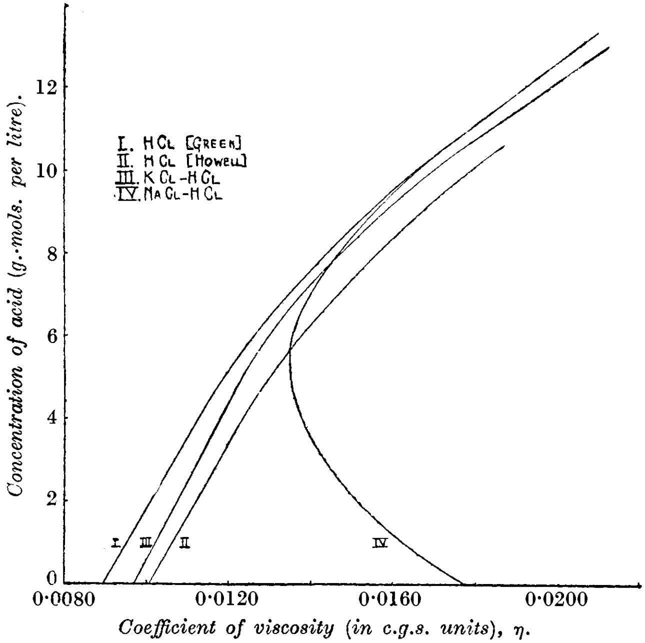
	Na˙.	K˙.	Cl′.	H_2O.	HCl.	NaCl.	KCl.
From data	1·58	12·25	22·43	17·795	22·43	24·00	34·66
From lattice radii ...	8·06	17·60	39·83	18·000	39·83	47·89	57·43

The further removed in size the ion is from the water molecule, the smaller is its apparent solution volume compared with that calculated from lattice radii (compare Hartley and Raikes, *Trans. Faraday Soc.*, 1927, **23**, 393). The values for the acid and salts are roughly half those so derived.

The constancy of the apparent density of the water in the solutions over the ranges indicated is connected with the constancy of the molar concentration of water over these regions, and when the acid concentration rises further, the calculated densities become increasingly lower than the observed values. If the molar or ionic volumes of acid and salt still remain constant, an increase in the apparent density of the water must be assumed.

Thus, to account for the density of the solution for which $a = 7{\cdot}976$ and $b = 0{\cdot}158$ in Table II, the value of K would have to be about 1·0150, and k_1 and k_2 0·0137 and 0·0341, respectively, giving $d_{4^\circ}^{25^\circ}$ (calc.) 1·1296. It would be possible to express the densities of all the solutions of higher acid strength in a similar way. The changes in the apparent density of water can also be followed in solutions of pure hydrochloric acid, and for this purpose the data of Green (J., 1908, **93**, 2023) and Ellis (*J. Amer. Chem. Soc.*, 1916, **38**, 750) have been examined. Calculations based on $d_{4^\circ}^{25^\circ} = 1{\cdot}01275 + 0{\cdot}01375a$ give fair agreement for those regions of acid concentration comparable with the total solute concentrations in the acid–salt mixtures for which the same formula holds, thus indicating that the molecular volumes of water and acid are the same, or nearly so, as in the mixed solutions. There is, however, undoubtedly, a continuous change in the water value as the acid concentration rises from zero.

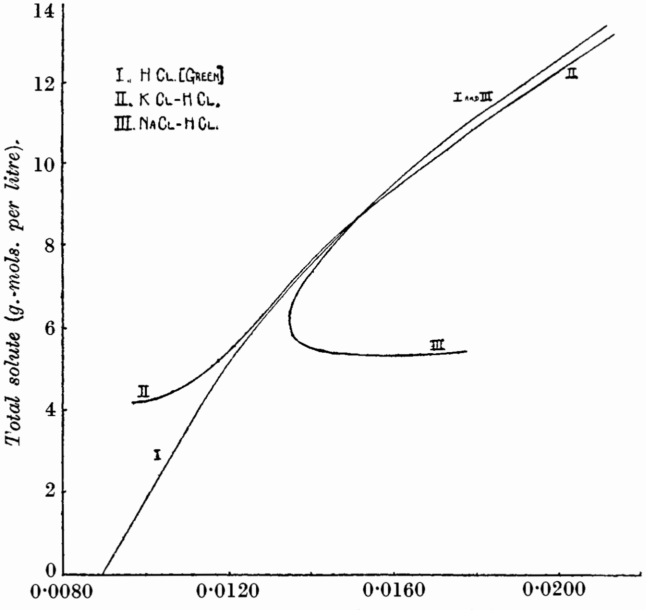
FIG. 2.



Viscosities.—From Tables I and II, it is seen that for the solutions containing potassium chloride the viscosities increase throughout with increasing acid concentration, and that the case for the solutions containing sodium chloride is essentially different, there being a pronounced minimum. In Fig. 2 are plotted the coefficients of viscosity as abscissæ against acid concentration as ordinates. For comparison the curves for the data of Green (*loc. cit.*) at 24·9° and of Howell (J., 1927, 168) at 20° for aqueous solutions of hydrochloric acid alone are also drawn. The positions of the curves in the regions of high acid concentration afford excellent evidence of the accuracy of the method used. The outstanding features of the curves in the regions of medium and low acid concentration are :

first, the parabolic form for the sodium chloride mixtures, and, secondly, the quite different form, similar to that for pure acid solutions, for the potassium chloride mixtures. As shown by Table V, the data for the sodium chloride solutions can be fairly accurately represented by the expression $6700(\eta - \eta_m) = (C - C_m)^2$, where η_m is the minimum viscosity, and C_m the acid concentration of the corresponding solution, η and C being the values for other solutions between $C = 0$ and $C = 10$. Above the latter concentration scarcely any salt is present and the curve is almost linear.

FIG. 3.



The interpretation of this relationship is not yet clear and in the meantime another method of approach has been considered.

TABLE V.

$6700 (\eta - \eta_m) = (C - C_m)^2$; $\eta_m = 0{\cdot}01353$; $C_m = 5{\cdot}300$.

C.	η (obs.) $\times 10^5$.	η (calc.). $\times 10^5$.	C.	η (obs.) $\times 10^5$.	η (calc.) $\times 10^5$.
0	1779	1772	4·500	1358	1363
0·503	1694	1696	5·253	1353	1353
0·886	1641	1644	6·101	1357	1363
2·265	1492	1490	7·073	1400	1400
3·185	1419	1420	7·976	1463	1460
3·487	1405	1403	9·236	1582	1584
3·830	1391	1385	13·41	2111	2336

In Fig. 3, the viscosities are plotted against *total solute*, the curve for Green's data again being included. It is now seen that the curve for potassium chloride mixtures lies to the left of that for the pure acid (except at very high concentrations), whilst that for sodium chloride mixtures lies to the right, and solutions of equal chlorine (ion) concentration have in the one case lower and in the other case higher viscosities than for the pure acid solutions. The curves merge at concentrations of about $8{\cdot}7N$ and above this point those for pure acid and for sodium chloride mixtures are indistinguishable, the concentration of salt being very low; the curve for potassium chloride mixtures in this region diverges from the others, having crossed the pure acid curve at the above point.

Dealing first with the case for the sodium chloride mixtures, for which the volume relations are simpler (since the total number of molecules, water concentration, and chlorine-ion concentration do not vary so much as in the potassium chloride solutions during the replacement of the major portion of the salt by the acid), there has to be explained a large relative fall in viscosity caused by the substitution almost equivalent by equivalent of hydrogen for sodium. The changes are roughly proportional to the fractions of salt precipitated, almost as far as the point of minimum viscosity. The conclusion that the sodium ions are present in the form of particles of relatively large effective size and that they are solvated to a higher degree than the hydrogen ions seems very reasonable.

To obtain an idea of the magnitude of the solvated sodium ions ($Na^{\cdot},xH_2O$), which would quantitatively account for the effects found, the following procedure may be considered.

The formula $\eta_2 = \eta_1(1 + 2{\cdot}5\phi)$ can be applied to calculate the changes of viscosity for hydrochloric acid solutions of from $3{\cdot}5$ to $6N$, η_1 and η_2 being the viscosities for two different concentrations c_1 and c_2; ϕ is a term $0{\cdot}02243(c_2 - c_1)$, and is therefore the volume of chlorine ions added to 1 c.c. of solution and replacing a volume of water. The volume $22{\cdot}43$ for Cl' is that already deduced from the density data of these solutions and the mixed solutions. The formula, which is a modification of that of Einstein (*Ann. Physik*, 1906, **19**, 289), gives good agreement when tested on Green's data. Better agreement is, however, obtained by using the formula $\eta_2 - \eta_1 = \frac{1}{2}(\eta_1 + \eta_2) \times 2{\cdot}5\phi$, which expresses the variations about the mean viscosity value in terms of the volumes of ions added or removed, any specific effect of the hydrogen ions being for the present neglected. The formula may now be used to calculate approximately the volume of the sodium ions in a saturated solution of sodium chloride, by comparing this solution with a solution of hydrochloric acid of equal chlorine (ion) concentration, it being assumed that the hydrated sodium ions have, like the chlorine ions, an effect proportional to their volume. The resulting calculation made from the figures

$$c = 5{\cdot}43;\ \eta(\mathrm{NaCl}) = 0{\cdot}01779;\ \eta(\mathrm{HCl}) = 0{\cdot}01226, \text{ from graph}$$

gives for the 5·43 g.-ions of sodium in the litre a volume of 147·2 c.c. Hence the volume of ($Na^{\bullet},xH_2O$) is 27·1 c.c. If the value 1·58 found for the $Na^{\bullet}$ ion alone be subtracted, the volume 25·54 c.c. is obtained for the water accompanying 1 g.-ion of sodium, and the hydration number is 1·44, using $d_w = 1{\cdot}01275$.

In a somewhat similar way the series of sodium chloride–hydrochloric acid solutions may be used to obtain the volumes of the $Na^{\bullet},xH_2O$ ions and the hydration numbers, the hydrogen ions being again supposed to have no volume effect. In Table VI are the results of calculations made from values taken from the graphs of the original data, changes of concentration of sodium chloride of 0·5*N* being taken as convenient.

TABLE VI.

η.	NaCl.	HCl.	Total solute.	Vol. of $Na^{\bullet},xH_2O$.	x.
0·01779	5·43	—	5·43	32·02	1·71
0·01713	5·00	0·37	5·37	32·44	1·73
0·01644	4·50	0·86	5·36	31·78	1·70
0·01580	4·00	1·36	5·36	29·26	1·56
0·01525	3·50	1·90	5·40	26·48	1·40
0·01477	3·00	2·42	5·42	29·14	1·55
0·01433	2·50	3·03	5·53	26·32	1·39
0·01396	2·00	3·65	5·65	23·52	1·23
0·01367	1·50	4·30	5·80	32·44	1·73
0·01350	1·00	5·30	6·30		

In these calculations, due allowance has been made for changes of chlorine-ion concentration. It is seen that the degree of hydration (x) of the sodium ions required in order to account for the observed viscosities is quite low, being about 2 for the saturated solution of the pure salt. As acid is added the value falls, and this may be due to the formation of $H_3O^{\bullet}$ ions; but there is at present no direct evidence on this point, although there is evidence that the hydrogen ions are not more highly hydrated. The chlorine ions are probably not appreciably hydrated in these solutions.

The potassium chloride mixtures may now be examined and the hydration numbers derived. In this case we have to deal with the replacement of smaller particles (the potassium ions) by the larger water molecules, the viscosities rising with increasing acid concentration at a greater rate than would be accounted for by the increase in chlorine-ion concentration alone. By comparison of the saturated potassium chloride solution with the pure acid solution of equal concentration, the calculation for the volume of ions substituted gives, from $c = 4{\cdot}2$, $\eta(KCl) = 0{\cdot}00971$, and $\eta(HCl) = 0{\cdot}01143$, a value 15·5 c.c. for the potassium ion. Since, however, the exchange in this case is not that of H_2O for Cl', but of $K^{\cdot}$ for H_2O, this value really measures the size of a potassium ion compared with a water molecule, as though a water molecule had a volume equal to that of a chlorine ion, and the number requires reducing in the proportion 17·795 : 22·43. If this is done, the final value of 12·29 is obtained, which is almost exactly that previously deduced for the potassium ions from the density data. Hence these ions are not appreciably hydrated.

The series of potassium chloride–acid solutions gives, when examined in this way, as with the sodium chloride series, allowance being made for changes of chlorine-ion concentration, a series of volumes for the potassium ions falling from 15·68 to 12·20, whilst the potassium chloride concentration falls from 4·2 to 0·96, thus supporting the conclusion that the potassium ions do not show hydration to any marked extent. The calculations also further support the view that the chlorine ions are not hydrated, and that there is no hydration of the hydrogen ions beyond the stage $H_3O^{\cdot}$.

It is not suggested that these explanations give a complete account of the phenomena studied. In the regions of higher acid concentration, the viscosities rise much more rapidly than can be accounted for on the basis of the ionic and molar volumes deduced for the lower concentrations, and there are indications of the formation of other types of complex ions.

Summary and Conclusions.

The solubilities have been determined at 25° of potassium and sodium chlorides in aqueous solutions of hydrochloric acid of concentrations varying between 0 and 13·5*N*.

The densities and the viscosities of the same solutions have been measured, the method of Scarpa for the determination of relative viscosity being shown to be trustworthy with the apparatus used.

Complete dissociation of the acid and of the salts being assumed, a formula is developed connecting the densities of the solutions, on the one hand, with the ionic concentrations, ionic solution volumes, and the apparent density of the water in the solutions, on the other; this formula is used for the calculation of the solution volumes of all the constituents. For solutions of acid concentrations between 0 and 6*N*, with either salt, it is unnecessary to assume any variations in the solution volumes and the same values for the chlorine ion and the water molecule apply in both series. These values also give a satisfactory account of the densities of pure hydrochloric acid solutions of comparable total chloride strength.

Solutions of equal chlorine-ion concentration up to about $9N$ have either lower or higher viscosities than solutions of hydrochloric acid alone according as they are saturated with potassium or with sodium chloride. The solution volumes deduced from the densities are used to give an account of the viscosities of those solutions of hydrochloric acid alone and of potassium chloride–hydrochloric acid to which they refer. No hydration of the chlorine ions is indicated. The potassium ions are hydrated only to a slight extent, if at all. The hydrogen ions may be present in the form $H_3O^{\bullet}$ but are probably not more highly hydrated. The viscosities of the solutions containing sodium chloride cannot be accounted for on a similar basis without introducing a hydration factor of about 2. This value falls as the solutions become more strongly acid.

The author desires to express his thanks to Professor Boon for providing the facilities which have enabled the work to be carried out.

HERIOT-WATT COLLEGE, EDINBURGH. [*Received, May 5th,* 1928.]