XXVIII.—*The Hydration of Strong Electrolytes, the Viscosity of their Aqueous Solutions, and the Dilution Law.*

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MANY attempts have been made to determine the hydration of strong electrolytes in aqueous solution. The results of different methods of investigation differ widely, some yielding relatively small hydration numbers, up to 20 molecules of water per molecule of a hydrated salt, whereas others give much larger values which are quoted in many text-books (*e.g.*, Nernst's " Theoretical Chemistry," 1923, p. 450; Freundlich, " Kapillarchemie," 1923, p. 81). In consequence of this uncertainty, it has not hitherto been possible to apply a hydrate theory to those properties of salt solutions which may be expected to depend on the hydration of the solute. An attempt has been made in this paper to apply, in a quantitative way, a new hydrate theory which is put forward as a result of the experimental work outlined in subsequent sections.

Determination of Hydration Numbers.

It has been shown by Frazer and Myrick (*J. Amer. Chem. Soc.*, 1916, **38**, 1907), Scatchard (*ibid.*, 1921, **43**, 2406), and Washburn (*Tech. Quart.*, 1908, **21**, 373), from the osmotic pressure, vapour pressure, and freezing-point depression respectively, that at moderate temperatures and at concentrations as high as molar, sucrose behaves as if it formed a hexahydrate in solution, and this fact forms a convenient starting point for testing other methods which are applicable both to electrolytes and to non-electrolytes. One such method was indicated by Philip (*Trans. Faraday Soc.*, 1907, **3**, 1),

who recalculated the experimental results of Knopp (*Z. physikal. Chem.*, 1904, **48**, 97), Steiner (*Wied. Ann.*, 1894, **52**, 275), and Muller (*Z. physikal. Chem.*, 1912, **81**, 483) on the solubility of gases in aqueous solutions of sucrose, potassium chloride, etc., and showed that the solubility of hydrogen, nitrogen, and oxygen in these solutions was considerably less than might be expected from their known water content. He suggested that this lowering of solubility might be accounted for by assuming that some of the water was attached to the solute as water of hydration and thereby removed from its rôle of solvent, and that the lowering of solubility afforded a direct measure of this " fixed " water. Philip and Bramley (J., 1915, **107**, 377, 1831) employed the distribution method to measure this effect, while H. E. Armstrong and his collaborators (*Proc. Roy. Soc.*, 1906, **78**, *A*, 272; 1907, **79**, *A*, 576, 579, 586; 1908, **81**, *A*, 102; 1912, **87**, *A*, 582; J., 1911, **99**, 349, 371), by investigating the velocity of reactions such as the inversion of sucrose and the hydrolysis of methyl acetate by dilute acids, alone and in presence of their salts, calculated the hydration of the salt by estimating the amount of water required to be added to the solution in order to restore the velocity coefficient to its original value. In view of the approximate agreement of the results obtained by these methods, it was thought desirable to make a further study of the problem by the distribution method, which is the most convenient.

The experimental conditions desirable on theoretical grounds were laid down by Philip and Bramley (*loc. cit.*), but these have been modified in that a system was sought in which the distributed solute (*a*) can be estimated quickly, preferably by simple titration, (*b*) is miscible in all proportions with both the aqueous and the non-aqueous phase, and (*c*) is distributed equally between the two solvent phases. Only one such system could be found, *viz.*, acetic acid distributed between water and amyl alcohol, which had been investigated by Herz and Fischer (*Ber.*, 1904, **37**, 4746; 1905, **38**, 1138). The distribution coefficient was found to vary somewhat with the source of the alcohol (usually about the figure 0·96) and to be independent of the concentration of the acetic acid when tested on the following systems : amyl alcohol and (*a*) water, (*b*) 2*N*-sodium chloride, (*c*) *N*-potassium nitrate, (*d*) 0·25 *N*-sucrose, and also of the time, showing that esterification in the alcohol phase did not take place. The objections to this system are (*a*) the two solvents are slightly miscible with each other, (*b*) some salts are not insoluble in amyl alcohol, (*c*) iodides are decomposed by the acetic acid and the liberated iodine dissolves in the alcohol, and (*d*) acetic acid cannot be estimated by titration in presence of

ammonium salts. Complete immiscibility is, however, not essential when the distribution coefficient is approximately unity, and other methods can be applied in the case of the soluble lithium, magnesium, and calcium salts and of ammonium salts.

If d_1 and d_2, and C_1 and C_2, are respectively the densities and distribution coefficients of water and a salt solution of normality n, the total weight of water per litre of solution is $1000d_2 - nE$ (E being the equivalent weight of the salt). The weight of free water is taken to be $1000d_1 . C_1/C_2$ ($d_1 = 0.99707$), and consequently the weight of water attached to n gram-equivalents of the salt is $1000d_2 - nE - 1000d_1C_1/C_2$ and the apparent equivalent hydration

$$H = 1000(d_2 - C_1d_1/C_2)/18n - E/18.$$

This calculation assumes the solvents to be completely immiscible, the quantity of acetic acid (actually 1 c.c. of acid per 200 c.c. of solvents) to be negligible, and the indicating substance (acetic acid) to be insoluble in the salt whose hydration is being determined.

In Table I are the results of the first experiments, with sucrose. The apparent molecular hydration, H, increases with dilution until

TABLE I.

n.	d.	C_1.	C_2.	H.	n.	d.	C_1.	C_2.	H.
2N	1·2532	0·9870	2·061	2·7	$N/4$	1·0300	0·9227	1·019	5·0
		0·9625	2·030	2·7			0·9625	1·042	5·2
N	1·1270	0·9780	1·376	4·2	$N/5$	1·0234	0·9663	1·029	5·1
		0·9625	1·360	4·3			0·9663	1·030	5·6
$N/2$	1·0623	0·9625	1·135	5·2	$N/7$	1·0153	0·9663	1·011	5·5
		0·9628	1·133	4·9			0·9659	1·012	6·1
$N/3$	1·0407	0·9663	1·072	4·8	$N/10$	1·0103	0·9628	0·9933	5·6
		0·9659	1·073	4·9			0·9628	0·9954	6·5

a value of 5 to 6 molecules of water is obtained. The method of estimating H is by difference, and the experimental error increases rapidly as the fraction of " fixed " water decreases, *i.e.*, as the dilution increases; in the case of sucrose a steady value is not indicated until a dilution is reached where the experimental error becomes appreciable, nevertheless the average value so obtained is in good agreement with that deduced from the osmotic properties of sucrose solutions.

Table II gives the results obtained for all the salts investigated, and Table IIA summarises those for the alkali metals.

In every case except the sulphates, a reasonably constant value of H was obtained, usually over the range $N - N/10$. The values in the column headed H(ex.) * are those which might be ascribed

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* Where the values of H over the range $N - N/4$ are reasonably constant, H (ex.) is taken as the average. Where H is large and the maximum value is not reached at normal concentration, *e.g.*, LiBr, LiBrO₃, less weight is attached to this determination.

TABLE II.

Conc. (N.).	d_2.	C_1.	C_2.	H.
LiCl.				
1·516	1·0332	0·9526	1·2990	8·7
1·0	1·0214	0·9526	1·1714	9·3
0·5	1·0095	0·9526	1·0052	9·8
0·25	1·0034	0·9526	1·0006	9·75
0·1	0·9995	0·9526	0·9698	8·8
NaCl.				
2·0	1·0794	0·9780	1·3660	6·9
1·0	1·0380	0·9424	1·1150	7·0
0·5	1·0180	0·9526	1·0331	8·0
0·25	1·0078	0·9600	1·0006	8·1
0·1	1·0013	0·9628	0·9759	6·5
KCl.				
2·0	1·0872	0·9820	1·1940	3·3
1·0	1·0427	0·9600	1·0534	3·3
0·5	1·0206	0·9424	0·9868	3·5
0·25	1·0091	0·9600	0·9808	3·3
0·1	1·0019	0·9520	0·9605	3·3
LiBr.				
1·232	1·0735	0·9410	1·1533	6·9
0·616	1·0353	0·9410	1·0504	8·1
0·308	1·0162	0·9410	0·9922	7·9
0·1232	1·0047	0·9410	0·9600	7·5
NaBr.				
2·0	1·1503	0·9520	1·3024	6·0
1·0	1·0747	0·9520	1·1045	6·2
0·5	1·0360	0·9600	1·0343	6·4
0·25	1·0165	0·9526	0·9892	6·8
0·1	1·0045	0·9526	0·9663	6·3
KBr.				
2·0	1·1623	0·9520	1·1030	1·8
1·0	1·0802	0·9520	1·0240	1·9
0·5	1·0394	0·9520	0·9861	1·9
0·25	1·0181	0·9520	0·9687	1·9
0·1	1·0052	0·9520	0·9582	1·5
LiNO₃.				
0·900	1·0322	0·9410	1·0156	2·9
0·450	1·0147	0·9410	0·9820	3·5
0·225	1·0062	0·9410	0·9592	3·1
0·090	1·0006	0·9410	0·9478	2·8
NaNO₃.				
2·0	1·1040	0·9526	1·1032	2·0
1·0	1·0518	0·9600	1·0266	1·9
0·5	1·0247	0·9526	0·9815	1·6
0·25	1·0113	0·9600	0·9740	1·6
0·1	1·0028	0·9600	0·9625	1·6
KNO₃.				
1·0	1·0574	0·9600	0·9581	−2·4
0·5	1·0276	0·9600	0·9559	−2·6
0·25	1·0131	0·9520	0·9497	−2·6
0·125	1·0044	0·9520	0·9506	−3·0
NaClO₃.				
2·0	1·1335	0·9632	1·2150	3·6
1·0	1·0662	0·9632	1·0758	3·7
0·5	1·0319	0·9632	0·9736	3·7
0·25	1·0148	0·9632	0·9880	3·7
0·1	1·0044	0·9632	0·9716	2·9
KClO₃.				
0·25	1·0161	0·9526	0·9585	−1·2
0·1	1·0048	0·9526	0·9554	−0·9

Conc. (N.).	d_2.	C_1.	C_2.	H.
LiBrO₃.				
0·830	1·0809	0·9412	1·0962	7·5
0·415	1·0392	0·9412	1·0143	7·75
0·2075	1·0180	0·9412	0·9774	7·95
0·083	1·0058	0·9412	0·9527	6·4
NaBrO₃.				
1·0	1·1122	0·9632	1·1350	6·4
0·5	1·0550	0·9632	1·0437	6·6
0·25	1·0260	0·9632	1·0021	6·6
0·1	1·0089	0·9632	0·9770	6·0
KBrO₃.				
0·25	1·0290	0·9227	0·9405	2·0
LiIO₃.				
0·9927	1·1506	0·9227	1·1106	7·9
0·4963	1·0745	0·9412	1·0241	7·6
0·2482	1·0360	0·9227	0·9613	7·6
0·0993	1·0127	0·9227	0·9393	8·5
NaIO₃.				
0·25	1·0400	0·9412	0·9700	5·1
0·1	1·0141	0·9510	0·9616	4·5
KIO₃.				
0·25	1·0414	0·9227	0·9376	1·5
½Na₂SO₄.				
2·0	1·1150	0·9780	1·4160	7·9
1·0	1·0572	0·9780	1·1370	7·2
0·5	1·0283	0·9410	1·0020	6·3
0·25	1·0134	0·9410	0·9650	5·2
0·1	1·0043	0·9410	0·9443	2·0
½K₂SO₄.				
1·0	1·0638	0·9780	1·0570	3·0
0·5	1·0310	0·9410	0·9661	1·8
0·25	1·0137	0·9410	0·9491	0·8
MgCl₂.				
2·260	1·0790	0·9424	1·4567	16·0
1·130	1·0389	0·9424	1·1983	19·6
0·565	1·0183	0·9424	1·0632	21·0
0·2825	1·0077	0·9424	0·9998	19·4
0·113	1·0013	0·9424	0·9615	18·4
CaCl₂.				
2·186	1·0924	0·9510	1·4374	15·8
1·093	1·0458	0·9510	1·1804	18·6
0·546	1·0216	0·9400	1·0403	18·4
0·273	1·0095	0·9510	1·0050	18·9
0·109	1·0020	0·9510	0·9735	22·4
SrCl₂'				
2·0	1·1369	0·9510	1·4052	15·8
1·0	1·0679	0·9510	1·1690	18·6
0·5	1·0320	0·9510	1·0514	19·0
0·25	1·0150	0·9510	0·9980	18·8
0·1	1·0044	0·9510	0·9713	21·9
BaCl₂.				
2·0	1·1740	0·9632	1·3323	13·6
1·0	1·0869	0·9600	1·1387	15·8
0·5	1·0424	0·9780	1·0630	16·2
0·25	1·0198	0·9632	1·0036	16·3
0·1	1·0062	0·9632	0·9760	13·1
MgBr₂.				
1·7624	1·1302	0·9227	1·2845	15·9
0·8812	1·0641	0·9227	1·0960	18·2
0·4406	1·0308	0·9227	1·0090	19·8
0·2203	1·0140	0·9227	0·9623	19·0
0·0881	1·0040	0·9227	0·9402	21·6

TABLE II (continued).

Conc. (N.)	d_2	C_1	C_2	H.	Conc. (N.)	d_2	C_1	C_2	H.
	CaBr$_2$.					Ca(NO$_3$)$_2$.			
2·748	1·1706	0·9424	1·3282	12·8	2·18	1·1243	0·9400	1·1448	6·5
1·074	1·0848	0·9424	1·1323	15·3	1·09	1·0618	0·9400	1·0346	6·8
0·537	1·0412	0·9424	1·0365	16·8	0·545	1·0292	0·9400	0·9850	6·7
0·268	1·0193	0·9424	0·9857	16·2	0·2725	1·0130	0·9400	0·9619	6·7
0·1074	1·0063	0·9424	0·9603	17·9	0·109	1·0036	0·9400	0·9480	6·2
	SrBr$_2$.					Sr(NO$_3$)$_2$.			
2·0	1·2027	0·9400	1·2737	12·2	1·9736	1·1297	0·9510	1·1495	5·4
1·0	1·1008	0·9400	1·1011	14·0	0·9868	1·0775	0·9510	1·0373	6·7
0·5	1·0493	0·9424	1·0264	16·0	0·4939	1·0377	0·9510	0·9923	6·8
0·25	1·0231	0·9400	0·9795	15·7	0·2969	1·0176	0·9510	0·9715	7·0
0·1	1·0078	0·9400	0·9536	14·0	0·09868	1·0057	0·9510	0·9578	6·0
	BaBr$_2$.					Ba(NO$_3$)$_2$.			
2·0	1·2510	0·9424	1·2400	10·9	0·5	1·0494	0·9510	0·9825	4·2
1·0	1·1251	0·9424	1·0900	12·7	0·25	1·0233	0·9510	0·9660	4·0
0·5	1·0615	0·9424	1·0146	13·6	0·1	1·0076	0·9510	0·9565	3·5
0·25	1·0293	0·9424	0·9777	13·4		MgSO$_4$.			
0·1	1·0100	0·9424	0·9572	15·0	2·0	1·1104	0·9400	1·4855	20·0
	Mg(NO$_3$)$_2$.				1·0	1·0552	0·9400	1·1555	20·4
2·02	1·0993	0·9400	1·1448	7·2	0·5	1·0266	0·9400	1·0287	19·0
1·01	1·0489	0·9400	1·0394	8·0	0·25	1·0121	0·9400	0·9788	17·6
0·505	1·0231	0·9400	0·9889	8·3	0·1	1·0035	0·9400	0·9519	14·4
0·2525	1·0100	0·9400	0·9634	8·1					
0·101	1·0023	0·9400	0·9467	5·3					

to the salt from these experimental results alone, whilst under H are the most probable values for the apparent molecular hydration. Where the values in the two columns differ, the explanation is usually to be found in the solubility of the salt in the alcohol phase; the evidence upon which the final figure is based will appear in later sections. All previous work on hydration suggests that this

TABLE IIA.

Salt.	2N.	N.	N/2.	N/4.	N/10.	H (ex.).*	H.
LiCl	8·7	9·3	9·8	9·75	8·8	9·8	10·5
NaCl	6·9	7·6	8·0	8·1	6·5	8·0	7·9
KCl	3·3	3·3	3·5	3·3	3·3	3·4	3·4
LiBr	—	6·9	8·1	7·9	7·5	8·0	9·0
NaBr	6·0	6·2	6·4	6·8	6·3	6·6	6·4
KBr	1·8	1·9	1·9	1·9	1·5	1·9	1·9
LiNO$_3$	—	2·9	3·5	3·1	2·8	3·4	4·4
NaNO$_3$	2·0	1·9	1·6	1·6	1·6	1·8	1·8
KNO$_3$	—	−2·4	−2·6	−2·6	−3·0	−2·6	−2·7
LiClO$_3$	—	—	—	—	—	—	6·3
NaClO$_3$	3·6	3·7	3·7	3·7	2·9	3·7	3·7
KClO$_3$	—	—	—	−1·2	−0·9	−1·0	−0·8
LiBrO$_3$	—	7·5	7·75	7·95	6·4	7·8	9·2
NaBrO$_3$	—	6·4	6·6	6·6	6·0	6·6	6·6
KBrO$_3$	—	—	—	2·0	—	2·0	2·1
LiIO$_3$	—	7·9	7·6	7·6	8·5	7·7	7·7
NaIO$_3$	—	—	—	5·1	4·5	5·1	5·1
KIO$_3$	—	—	—	1·5	—	1·5	0·6
$\frac{1}{2}$Na$_2$SO$_4$	7·9	7·2	6·3	5·2	2·0	—	—
$\frac{1}{2}$K$_2$SO$_4$	—	3·0	1·8	0·8	—	—	—

quantity is not independent of the salt concentration, but the results now obtained (with the one exception) do not support this view, and, whilst it cannot be shown from them alone whether or not the constant value is retained as the dilution is still further increased, it will be convenient, for the time being, to regard these as fixed values. The sulphates are anomalous, the values of H actually decreasing on dilution. This may be due to the appearance and subsequent dissociation of intermediate ions of the type KSO_4, or to some idiosyncrasy of the sulphate ion; salts of the type $BaCl_2$ and $Sr(NO_3)_2$ behave in the normal way.

Potassium bromate and iodate are only sparingly soluble salts, consequently their hydration could not be determined with accuracy. Potassium nitrate and potassium chlorate both gave constant *negative* values for H. Analysis of the figures brings out the interesting fact that *the difference between the apparent molecular hydration of a sodium and a potassium salt is independent of the anion, hydration thus being an additive property* (Table III).

TABLE III.

	Cl.	Br.	NO_3.	ClO_3.	BrO_3.	IO_3.
Na	8·0	6·6	1·8	3·7	6·6	5·1
K	3·4	1·9	−2·6	−1·0	2·0	(1·5)
Diff.	4·6	4·7	4·4	4·7	4·6	(3·6)

The average value for the Na–K difference is 4·6 mols. H_2O. The determination of the corresponding Li–Na difference presented some difficulty, due to the solubility of lithium salts in amyl alcohol. Of those examined, the iodate alone was insoluble, so the difference (2·6 mols. H_2O) depends on only one determination; moreover, sodium iodate is a sparingly soluble salt and the most concentrated solution available was $N/4$, hence the value $H = 5·1$ for this salt is not known with the usual accuracy. Nevertheless, the difference value of 2·6 is probably not greatly in error; the hydration values for the other lithium salts tabulated in column H (Table II) are obtained by adding 2·6 to the hydration number of the corresponding sodium salts.

Table IV gives a summary of the values of H for the salts of the alkaline earths. The magnesium and calcium salts dissolved in the amyl alcohol and in each case the numbers in column H (ex.) are too small, but good values were obtained for the strontium and barium salts; the chlorides and bromides are heavily hydrated and hence the maximum value is in some cases not obtained until a dilution somewhat greater than normal is reached.

Table V indicates that hydration is additive in these salts also, and Table VI that the chloride–nitrate difference is common to both series.

TABLE IV.

Salt.	2N.	N.	N/2.	N/4.	N/10.	H (ex.).	H.
MgCl$_2$	16·0	19·6	21·0	19·4	18·4	20·0	24·8
CaCl$_2$	15·8	18·6	18·4	18·9	22·4	18·4	20·6
SrCl$_2$	15·8	18·6	19·0	18·8	21·9	18·8	18·8
BaCl$_2$	13·6	15·8	16·2	16·3	13·1	16·2	16·2
MgBr$_2$	15·9	18·2	19·8	19·0	21·6	19·2	21·8
CaBr$_2$	12·8	15·3	16·8	16·2	17·9	16·3	17·6
SrBr$_2$	12·2	14·0	16·0	15·7	14·0	15·9	15·8
BaBr$_2$	10·9	12·7	13·6	13·4	15·0	13·5	13·2
Mg(NO$_3$)$_2$	7·2	8·0	8·3	8·1	5·3	8·1	12·8
Ca(NO$_3$)$_2$	6·5	6·8	6·7	6·7	6·2	6·75	8·6
Sr(NO$_3$)$_2$	5·4	6·7	6·8	7·0	6·0	6·7	6·8
Ba(NO$_3$)$_2$	—	—	4·2	4·0	3·5	4·1	4·1
MgSO$_4$	20·0	20·4	19·0	17·6	14·4	—	—

TABLE V.

	Cl.	Br.	NO$_3$.
Sr	18·8	15·9	6·7
Ba	16·2	13·5	4·1
Diff.	2·4	2·4	2·6

TABLE VI.

	Na.	K.	½Sr.	½Ba.
Cl	8·0	3·4	9·4	8·1
NO$_3$	1·8	−2·6	3·35	2·05
Diff.	6·2	6·0	6·05	6·05

Negative Hydration.

The salts possessing negative hydration values are the chlorates and nitrates of potassium and presumably also of ammonium, rubidium, and cæsium. Since, so far as the additive nature of hydration is concerned, these salts are apparently normal, it is probable that this phenomenon is not an abnormality, but merely an extreme example of some property common to all strong electrolytes. In this particular case, the negative hydration is indicated by the fact that solutions of these salts exert a greater solvent power upon acetic acid than does pure water. An obvious explanation is that some measure of combination takes place between the salt and acetic acid, but several arguments may be raised against this. One of these (and others will appear later) is that the negative hydration, or, from the point of view of this explanation, the extent of combination between the two substances is independent of the concentration of both the potassium nitrate and the acetic acid over a wide range of concentration. The increased solvent power of potassium nitrate solutions is not confined to acetic acid alone; reference to the papers of Rothmund (*Z. physikal. Chem.*, 1900, **33**, 401), Biltz (*ibid.*, 1903, **43**, 41), Bray and Winninghoff (*J. Amer. Chem. Soc.*, 1911, **33**, 1663), and Glasstone and Saunders (J., 1923, **123**, 2134) shows that the property extends over a very wide range of compounds, including the particularly interesting case of lead nitrate (Glasstone and Saunders), which contains a common ion. Moreover, whereas the ordinary process

of hydration produces a concentrating effect upon other constituents of an aqueous solution, evidence is not lacking that these " negatively hydrated " salts actually produce a *diluting effect*, a property which has been noticed by Rennie, Higgin, and Cooke (J., 1908, **93**, 1162), Armstrong and Watson (*Proc. Roy. Soc.*, 1907, **79**, *A*, 586), Harned (*J. Amer. Chem. Soc.*, 1918, **40**, 1461), and Walton (*Z. physikal. Chem.*, 1904, **47**, 185).

Several explanations of these anomalies are to be found in the above papers, but in seeking a general interpretation which will cover these and other properties of solutions of strong electrolytes the possibility was considered that the anions and kations might react with the solvent in fundamentally different ways. All the published work on hydration of strong electrolytes agrees on two points : (1) if kations are arranged in the order of diminishing hydration, the cæsium ion occupies the lowest position, and (2) if the anions are so arranged, the chloride ion occupies the position of maximum hydration; this, together with the definite proof advanced by Washburn (*J. Amer. Chem. Soc.*, 1915, **37**, 694) that the least hydrated kation (cæsium) carries measurably more water than the (presumably) most heavily hydrated anion (chloride), suggests at once that anions are not hydrated, but possess properties which in certain cases are sufficiently developed to over-compensate the hydration effect of the kation.

When acetic acid is in equilibrium both with water and with amyl alcohol, its activity in each phase must be the same, and (if the solution is sufficiently dilute) proportional to its mole-fraction, which in the aqueous phase is assumed to depend on the " association factor " of water. If the mole-fraction (activity) of the acetic acid in the aqueous phase is increased by the removal of water as water of hydration, some of the acid will escape into the alcohol phase until equilibrium is re-established. Alternatively, if the association factor of water is decreased by any means whatsoever, the mole-fraction of the acetic acid will decrease and can only be restored by transference of the acid from the alcohol to the water phase. The suggestion is made, therefore, that whilst kations are invariably hydrated, probably as a result of the positive field (the intensity of which decreases as the ionic radius increases) round the ion and a stray field round the water molecule, anions are not hydrated but in all cases exert (in greater or less degree) a depolymerising action on the associated solvent, resulting in a shift of the equilibrium $(H_2O)_3 \rightleftarrows (H_2O)_2 + H_2O \rightleftarrows 3H_2O$ towards the right. The properties of solutions of strong electrolytes are thus to a large degree determined by the relative magnitudes of these two rival processes.

An action such as the above, which increases the effective mole-fraction of the water, will produce a species of water molecule which alone is found in the vapour phase; hence aqueous solutions of negatively hydrated salts should have abnormally high vapour pressures (compare Washburn, *J. Amer. Chem. Soc.*, 1910, **32**, 653, 1636; Washburn and MacInnes, *ibid.*, 1911, **33**, 1686; Bousfield, *Trans. Faraday Soc.*, 1919, **15**, 47; Glasstone and Saunders, *loc. cit.*; Sidgwick and Ewbank, J., 1924, **125**, 2273).

Hydration and the Equivalent Conductivity at Infinite Dilution.

Kohlrausch (*Proc. Roy. Soc.*, 1903, **71**, *A*, 348) suggested that "about every ion moves an atmosphere of the solvent the dimensions of which are determined by the characteristics of the ion,

FIG. 1.
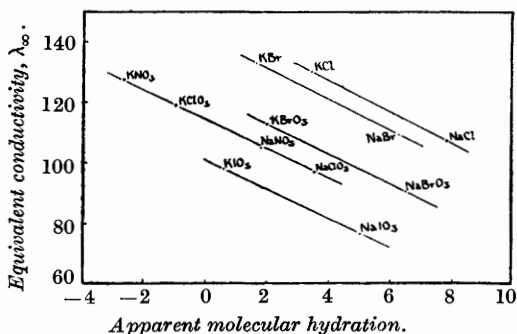
and the electrolytic resistance of an ion is a frictional resistance that increases with the dimension of the atmosphere"; consequently a quantitative relationship may be expected between λ_∞ and the hydration of the kations.* In order to correlate these properties, let it be assumed that H is independent of concentration up to infinite dilution. This assumption is not unreasonable in view of the facts presented in this paper, and further, it leads to conclusions which are supported by considerations based on the constancy of H over the experimental range $N - N/10$ only.

If the apparent molecular hydrations of the alkali chlorides are plotted against the equivalent conductivities at infinite dilution, the points lie on a smooth curve, which is slightly concave towards the origin. The shape of the curve is determined by the properties (λ_∞ and H) of the kations, and its position on the diagram by the equivalent conductivity of the anion. In a similar diagram drawn for the salts of a common kation, the points lie irregularly

---

* The hypothesis cannot be true universally if anions are not hydrated.

and can only be joined by a zig-zag line. This dissimilarity supports the hypothesis that anions and kations behave towards the solvent in different ways.

The curvature of the lines relating λ_∞ and H for the alkali metals (so far as their hydrations are known) is so slight that the purpose of the diagram is served equally well by plotting the values for the sodium and potassium salts only and joining the points by straight lines (Fig. 1). Two points of interest, which will be encountered again later, become evident : (a) the nitrates and chlorates fall on one line, and (b) the sequence of the curves for the bromates, chlorates, and iodates is unexpected.

Hydration of Strong Electrolytes and the Viscosity of their Aqueous Solutions.

Strong electrolytes may be divided into two classes according to their effect on the viscosity of water. The first (and smaller) class consists of the salts of the heavier alkali metals the aqueous solutions of which at the ordinary temperature have viscosities lower than that of the solvent. With increasing concentration, the viscosity falls at first to a minimum and then increases to a value which, in the case of very soluble salts, may exceed the viscosity of water. At higher temperatures the minimum becomes less marked and finally disappears, the solution then behaving as solutions of electrolytes of the second (and larger) class, the viscosities of which are always greater than that of water.

Many unsatisfactory and conflicting theories have been put forward to explain the negative viscosity ($\eta/\eta_0 - 1$ being negative) of some salt solutions, e.g., by Euler (Z. physikal. Chem., 1898, **25**, 536), Wagner (ibid., 1903, **46**, 871), Jones and Veazey (Amer. Chem. J., 1907, **37**, 405), and Taylor (Proc. Roy. Soc. Edin., 1907, **28**, 461).

Getman (J. Chim. Phys., 1907, **5**, 344; J. Amer. Chem. Soc., 1908, **30**, 721, 1077) ascribed negative viscosity at least partly to association of the solvent (potassium iodide in non-associated solvents having a positive viscosity), Bousfield (J., 1915, **107**, 1797) pointed out that " the viscosity of dilute aqueous solutions cannot be theoretically treated except in conjunction with the effect of the peculiar constitution of water," and Rabinowitsch (J. Amer. Chem. Soc., 1922, **44**, 954) showed, from theoretical considerations, that whilst hydration of ions can account for an increased viscosity, depolymerisation of the solvent alone supplies a rational explanation of the negative viscosity of some salt solutions.

When the kation is only slightly hydrated and the non-hydrated anion is small, or efficient in depolymerising the solvent, the effect

of the anion predominates, and the viscosity of the solution will be negative; but with increasing salt concentration, and therefore increasing depolymerisation, the average size of the water molecules becomes smaller, and hence the tendency of the kation to increase the viscosity will become more marked, eventually accounting for the minimum value and subsequent increase in the viscosity. Increase of temperature causes depolymerisation and consequently the disappearance of the minimum in the curve, the solvent functioning at higher temperatures as if it consisted only of simple molecules or complexes incapable of easy depolymerisation.

FIG. 2.

Apparent molecular hydration.
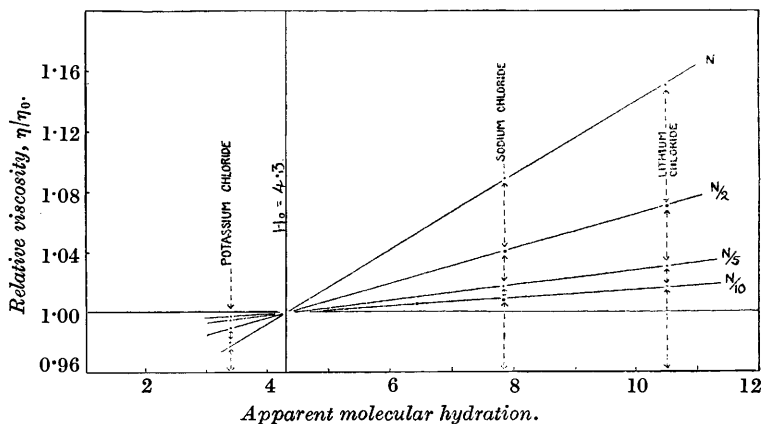
Fig. 2 shows the relation between the hydration of the alkali chlorides and the relative viscosity * of their solutions. If the latter is greater than unity, it is at all concentrations a linear function of the apparent molecular hydration of the salt; if less than unity, this relationship holds up to approximately semi-normal concentration. The straight lines in Fig. 2 all pass through a point where $\eta/\eta_0 = 1$ and $H = 4\cdot3$. If an alkali chloride had this hydration value of $4\cdot3$, all disturbing influences would exactly compensate one another and the viscosity of its solutions at all concentrations would be the same as that of pure water. The relative viscosities of solutions of the alkali chlorides are proportional to the differences between their apparent molecular hydrations and this " zero " value, which may be denoted by H_0. The point of origin $\eta/\eta_0 = 1$, $H = 4\cdot3$ is independent both of the concen-

* Except where otherwise stated, the accurate viscosity measurements of Grüneisen (*Wiss. Abhandl. Physikal.-Tech. Reichsanst.*, 1905, **4**, 239), and the collected data of Noyes and Falk (*J. Amer. Chem. Soc.*, 1912, **34**, 463) have been used.

tration and of the nature of the kation; it is determined by the anion, of which it is a specific property. The viscosities of these solutions depend, therefore, on (a) the value of H_0, which is fixed by the anion, (b) the hydration of the salt (determined largely by the kation), and (c) the concentration of the solution.

Many empirical equations have been proposed connecting the viscosities and the concentrations of solutions of strong electrolytes. The simplest of these (Arrhenius, Z. physikal. Chem., 1887, **1**, 284),

$$\log \eta/\eta_0 = \theta c \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

where θ is a constant varying from salt to salt and c is the number of gram-molecules per litre, holds with considerable accuracy over a wide range of concentrations, provided the solutions are more viscous than water, whilst for solutions of negative viscosity its application is limited to dilutions greater than semi-normal. It is obvious from Fig. 2 that the constant θ may be expressed in terms of the apparent molecular hydration, H, and a more general constant, K :

$$\theta = K(H - H_0) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

whence

$$\log \eta/\eta_0 = Kc(H - H_0). \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

a general equation which has the same applicability as that of Arrhenius. In Table VII, K is evaluated for the alkali chlorides, the calculated values of η/η_0 being then obtained from the equation

$$\log \eta/\eta_0 = 0.01c(H - 4.3) \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

TABLE VII.

	LiCl.	$H = 10.5$.		NaCl.	$H = 7.9$.		KCl.	$H = 3.4$.	
c.	η/η_0.	K.	η/η_0 (calc.).	η/η_0.	K.	η/η_0 (calc.).	η/η_0.	K.	η/η_0 (calc.).
1.0N	1.150	0.0098	1.153	1.086	0.0101	1.085	0.9820	(0.0088)	0.9785
0.5N	1.072	0.0097	1.074	1.041	0.0099	1.042	0.9898	0.0097	0.9897
0.2N	1.031	0.0107	1.029	1.0167	0.0101	1.0164	0.9959	0.0097	0.9958
0.1N	1.016	0.0111	1.014	1.0086	0.0103	1.0082	0.9982	0.0097	0.9989
0.05N	1.008	0.0109	1.007	1.0046	0.0110	1.004	0.9991	0.0096	0.9998

Mean value of $K = 0.01$.

The figures in brackets in Tables VII and VIII refer to solutions for which $\eta/\eta_0 - 1$ is negative, and of such concentrations that equation (1) is no longer applicable.

The corresponding diagram for the alkali nitrates closely resembles that for the chlorides, except that the origin of the curves has shifted to the value $H_0 = 0$; however, the value of K (0.01) is the same (within the limits of experimental error), as will be seen from Table VIII.

<div align="center">TABLE VIII.</div>

	LiNO$_3$.	$H = 4.4$.		NaNO$_3$.	$H = 1.8$.		KNO$_3$.	$H = -2.7$.	
c.	η/η_0.	K.	η/η_0 (calc.).	η/η_0	K.	η/η_0 (calc.).	η/η_0.	K.	η/η_0 (calc.).
$1.0N$	1.1020	0.0094	1.1066	1.0540	0.0127	1.0423	0.9620	(0.0070)	0.9397
$0.5N$	1.0503	0.0095	1.0520	1.0219	0.0104	1.0209	0.9754	(0.0083)	0.9694
$0.2N$	1.0200	0.0096	1.0205	1.0082	0.0096	1.0084	0.9883	0.0095	0.9876
$0.1N$	1.0112	0.0107	1.0102	1.0044	0.0102	1.0039	0.9841	0.0094	0.9969

It is possible, therefore, that K may be a universal constant and the equation

$$\log \eta/\eta_0 = 0.01c(H - H_0) \quad . \quad . \quad . \quad . \quad (5)$$

a general one.

For the alkali iodates, which (with the exception of the lithium salt) are only sparingly soluble in water, the value of H_0 (Table IX) has been calculated from equation (5) instead of being obtained by the graphical method. The average value is $- 5.5$.

<div align="center">TABLE IX.</div>

	c.	η/η_0.	H_0.	η/η_0 (calc.).
LiIO$_3$	1.00N	1.3380	-4.9	1.3552
	0.20N	1.0620	-5.4	1.0627
	0.05N	1.0158	-5.7	1.0153
	0.025N	1.0086	-6.7	1.0076
NaIO$_3$	0.20N	1.0496	-5.4	1.0481
KIO$_3$	0.20N	1.0270	-5.2	1.0285

The negative sign probably indicates that the iodate ion is sufficiently large of itself to increase the viscosity of water, an effect which is, of course, independent of its depolymerising action.

The values of H_0 for the bromides (4.1) and chlorates (0.0) were similarly found. In the case of the bromates, owing to lack of data, new viscosity measurements were made ($H_0 = 1.6$).

<div align="center">TABLE X.</div>

|	LiBrO$_3$.	$H = 9.2$.			NaBrO$_3$.	$H = 6.6$.	
c.	η/η_0.	H_0.	η/η_0 (calc.).	c.	η/η_0.	H_0.	η/η_0 (calc.).
0.830N	1.154	1.7	1.156	1.0N	1.122	1.6	1.122
0.415N	1.076	1.6	1.075	0.5N	1.059	1.6	1.058
0.207N	1.036	1.8	1.037	0.25N	1.027	2.0	1.029
0.083N	1.014	1.5	1.015	0.1N	1.013	1.0	1.012

The values of H_0 thus found are 4.3 for Cl, 4.1 for Br, 1.6 for BrO$_3$, 0.0 for NO$_3$, 0.0 for ClO$_3$, and $- 5.5$ for IO$_3$. The chlorates and nitrates form one system here as in Fig. 1 and the sequence of the curves in Fig. 1 is that of these H_0 values. Fig. 3 shows the relation between the spacing of the curves in Fig. 1 as measured by the

value of λ_∞ at $H = 0$, and the values of H_0. This curve can be accurately described by the empirical equation

$$\lambda_\infty = 100 + 13\cdot5 \times 1\cdot327^{H_0} \qquad . \quad . \quad . \quad . \quad (6)$$

It indicates a lower limit for the position of the curves in Fig. 1, only slightly below that of the iodate curve. Moreover, the smooth curve in Fig. 3 is of some importance, for whereas the values of H_0 are obtained from the viscosities of solutions over a concentration range similar to that available for the determination of hydration by the distribution method, the sequence and spacing of the curves in Fig. 1 depend on the application of these hydration values at infinite dilution. Fig. 3 therefore supplies some justification for extending the use of these hydration numbers to infinitely dilute solutions, since no serious error is thereby introduced. It must be mentioned, however, that " the viscosity concentration curve for all salts has a change of curvature at the dilute end in

FIG. 3.
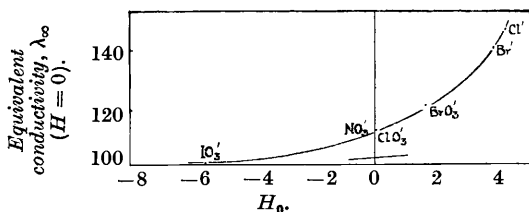
the sense that the first particles of salt added have a greater effect in increasing, or a less effect in diminishing the viscosity of water than subsequent additions. The change in curvature is scarcely noticeable unless the curve is plotted on a large scale " (Applebey, J., 1910, **97**, 2000; see also Grüneisen, *loc. cit.*).

Salts of the type $BaCl_2$ can be treated in exactly the same way as those of the type KCl. By substituting the viscosity and apparent molecular hydration of barium chloride in equation (5), the value $H_0 = 7\cdot4$ is obtained. On the assumption that H_0 is determined solely by the anion the value for a bivalent chloride might be expected to be $8\cdot6$. The agreement, therefore, is not unsatisfactory, and supports the assumption that K in equation (5) is a universal constant.*

* It appears not unlikely that the size of a (unhydrated) kation is less than that of an average water molecule; consequently some small part of the water of hydration may be needed to adjust this difference, whilst the remainder tends to increase the viscosity of salt solutions. Hence H_0 for a bivalent chloride might be expected to be slightly less than twice the value for a univalent chloride, since, although the number of anions per molecule is doubled, that of the kations remains the same.

Having obtained H_0 for these salts, it is possible to calculate, from the equation

$$\log \eta/\eta_0 = 0.01c(H - 7.4) \quad . \quad . \quad . \quad (7)$$

the values of H for magnesium chloride ($H = 24.8$) and calcium chloride ($H = 20.6$). Where the final value of H differs from the experimental value H (ex.), (*i.e.*, for soluble salts), it is obtained (*a*) in Table IIA, from the additive property of hydration and (*b*) in Table IV, from this semi-empirical hydration–viscosity equation.

Hydration of Strong Electrolytes and the Dilution Law.

According to the theory here developed, the apparent molecular hydration, H, which represents the resultant of two opposing factors, *viz.*, hydration of kations (decrease of the effective mole-fraction or activity of water) and depolymerisation by anions (increase of the effective mole-fraction or activity of water), may be applied to determine the effective mole-fraction of water and thus the corrected van 't Hoff factor, i.

Washburn (*Tech. Quart.*, 1908, **21**, 373) has shown that the effective mole-fraction, n', of the solute may be calculated from the freezing-point depression, Δt°, by means of the equation

$$n' = 0.00969 (\Delta t - 0.00425\Delta t^2) \quad . \quad . \quad . \quad (8)$$

This equation may be used for freezing-point depressions as large as $7°$, and the mole-fraction is given with an accuracy equivalent to an experimental error of $0.001°$ in measuring Δt. Equation (8) may be equated to (*a*) $ni/(ni + N)$ and (*b*) $ni_c/(ni_c + N - Hn)$, where n and N are the numbers of gram-molecules of solute and solvent, and i and i_c the uncorrected and corrected van 't Hoff factor, respectively.

van 't Hoff's factor is defined on the basis of the classical theory by the equation (for a uni-univalent salt) $i = 1 + \alpha$, where α is the " degree of dissociation." Alternatively, $(1 - \alpha)$ may be regarded simply as the " osmotic deficiency," *i.e.*, the fraction by which the osmotic properties deviate from those required for an ideal solution of a completely dissociated salt. It was necessary, therefore, to review the recorded freezing-point depressions, more especially those referring to concentrated solutions where the hydration correction is considerable. Probably the most trust-worthy measurements are those of Washburn and MacInnes (*loc. cit.*), who selected lithium chloride, potassium chloride, and cæsium nitrate as being representative of the whole range of hydrated salts, lithium chloride being presumably the most and cæsium nitrate the least heavily hydrated of the uni-univalent strong

electrolytes. In addition, the results of Noyes and Falk (*J. Amer. Chem. Soc.*, 1910, **32**, 1011), Jones and Pearce (*Amer. Chem. J.*, 1907, **38**, 683), Ponsot (*Ann. Chim. Phys.*, 1897, **10**, 79), de Coppet (*J. Physical Chem.*, 1904, **8**, 531; *Z. physikal. Chem.*, 1897, **22**, 239), Biltz (*Z. physikal. Chem.*, 1902, **40**, 185), Jahn (*ibid.*, 1904, **50**, 129; 1907, **59**, 31), Adams (*J. Amer. Chem. Soc.*, 1915, **37**,

FIG. 4.

Concentration (cube root scale).
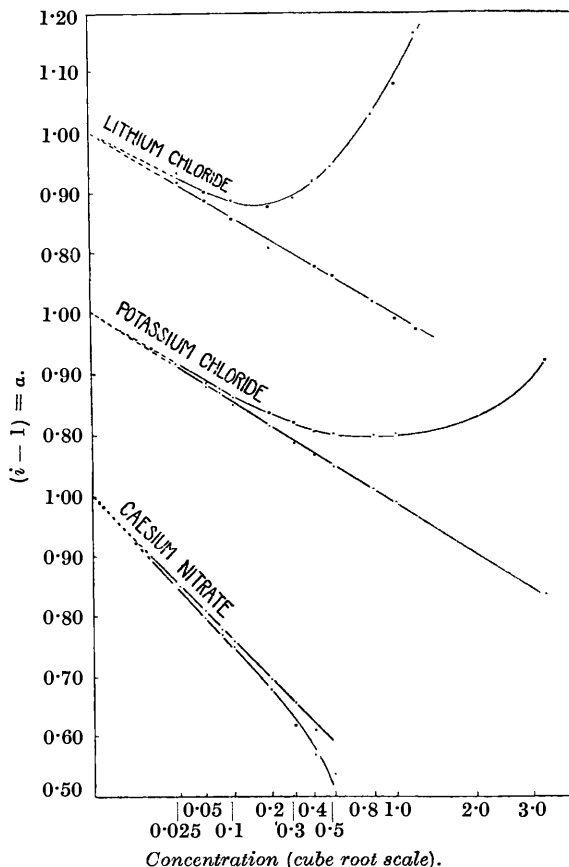
481), Harkins and Hall (*ibid.*, 1916, **38**, 2658), Rodebush (*ibid.*, 1918, **40**, 1204), and Rivett (*Z. physikal. Chem.*, 1912, **80**, 546) have been used for the calculations, of which a selection is given in Table XI. In applying the hydration correction it was assumed that the hydration is (*a*) independent of the concentration and (*b*) has the same value at the freezing point as at 25°, the temperature at which the hydration determinations were made.

Table XI refers to lithium chloride, potassium chloride, and cæsium nitrate. In these three cases the corrected van 't Hoff factor, i_c, obeyed the dilution law

$$2 - i_c = K\sqrt[3]{n} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

or

$$(1 - \alpha_c) = K\sqrt[3]{n} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

with great accuracy, that is, the corrected " osmotic deficiency " $(1 - \alpha_c)$ is proportional to the cube root of the concentration or inversely proportional to the linear distance between the ions. The calculations were extended for potassium chloride to the cryohydric concentration, i.e., 3·3 gram-molecules of salt per 1000 grams of solvent,* at which concentration the hydration correction † amounts to 20·2% of the total solvent present, an amount approximately the same as for molar lithium chloride solution. The figures for cæsium nitrate apply also to the cryohydric point of a 0·5 molar solution. The hydration of cæsium nitrate was obtained from Washburn's transport measurements (J. Amer. Chem. Soc., 1915, 37, 694) and the known value for potassium nitrate. Fig. 4 shows in a striking way the effect of the corrections, the straight lines representing the corrected and the curves the uncorrected values of α, plotted against the cube root of the concentration.

These results, obtained for three salts of the uni-univalent type, covering a wide hydration range appear to establish the cube root law as being the " dilution law " for strong electrolytes. The experimental difficulties in working with solutions more dilute than the above are very great. Moreover, a small error in Δt corresponds with a large error in $(1 - \alpha)$ and consequently in K, whilst the use of a constant value for H may not be justified in those dilute regions where the small change in curvature in the viscosity–concentration curve has been detected. It is, therefore, a difficult matter to test the applicability of the cube root law (applied to corrected values of α) to very dilute solutions. The curves in Fig. 4 differ, however, from the somewhat similar curves obtained by plotting the equivalent conductivity against the cube root of the concentration in this important respect, that whereas the extension of the latter to zero concentration involves an extrapolation to an unknown destination, λ_∞, the gap in these new curves may be bridged by a *linear interpolation*, since $(1 - \alpha)$ must be zero at zero concentration. Hence it appears probable that the cube root law may still be valid in this region; altern-

* This involves the use of Washburn's equation to a f. p. depression of 11°, but the small error thus introduced is probably not greater than the uncertainty with which the cryohydric temperature is known.

† Stated in the tables under the heading " %."

TABLE XI.

LiCl. $H = 10.5$. $K = 0.31$.

n.	Δt.	a.	a (corr.).	K.	a (calc.).	%.
0·025	0·090°	0·939	0·9295	0·241	0·910	0·48
0·050	0·177	0·9075	0·889	0·300	0·8865	0·94
0·075	0·265	0·905	0·880	0·285	0·873	1·44
0·1	0·351	0·8925	0·857	0·308	0·857	1·91
0·2	0·694	0·875	0·804	0·335	0·820	3·82
0·3	1·049	0·893	0·781	0·327	0·794	5·73
0·4	1·416	0·924	0·778	0·301	0·773	7·65
0·5	1·791	0·947	0·763	0·303	0·756	9·55
0·8	2·966	1·031	0·721	0·302	0·714	15·3
1·0	3·792	1·083	0·690	0·310	0·690	19·1

KCl. $H = 3.4$. $K = 0.32$.

n.	Δt.	a.	a (corr.).	K.	a (calc.).	%.
0·025	0·089	0·917	0·914	0·294	0·907	0·15
0·050	0·175	0·886	0·880	0·326	0·883	0·31
0·075	0·262	0·878	0·870	0·309	0·869	0·46
0·1	0·345	0·8605	0·849	0·325	0·852	0·62
0·2	0·680	0·837	0·814	0·318	0·814	1·24
0·3	1·009	0·820	0·787	0·318	0·787	1·86
0·4	1·335	0·805	0·765	0·317	0·766	2·48
0·5	1·658	0·802	0·746	0·325	0·747	3·10
0·8	2·635	0·798	0·710	0·313	0·705	4·92
1·0	3·287	0·801	0·691	0·309	0·680	6·20
1·989	6·46	0·791	0·583	0·331	0·600	11·8 †
3·30 *	11·10	0·922	0·535	0·312	0·527	20·2 ‡

CsNO₃. $H = 3.3$. $K = 0.52$.

n.	Δt.	a.	a (corr.).	K.	a (calc.).	%.
0·025	0·086	0·833	0·851	0·510	0·848	−0·15
0·05	0·168	0·807	0·812	0·510	0·809	−0·30
0·075	0·247	0·774	0·783	0·514	0·781	−0·45
0·1	0·352	0·753	0·763	0·511	0·759	−0·60
0·2	0·622	0·680	0·700	0·513	0·696	−1·2
0·3	0·897	0·618	0·647	0·527	0·652	−1·8
0·4	1·160	0·571	0·608	0·532	0·617	−2·4
0·5 *	1·419	0·539	0·585	0·531	0·588	−3·0

Washburn's values, except where marked † (Kistiakowski) and ‡ (de Coppet).

* Cryohydric concentration.

atively, if any departure from the law is involved, not one but two changes in curvature would be necessary in order that the osmotic deficiency should not have a finite value at infinite dilution.

The freezing-point measurements of Adams (*loc. cit.*) and Hovorka and Rodebush (*J. Amer. Chem. Soc.*, 1925, **47**, 1614) apply to dilute solutions, and are of a high order of accuracy, the former having been used to establish the freezing-point laws of Lewis and Linhart and of Brønsted. In Table XII their values of α_c are compared with the calculated values : $s = $ g.-mol. of salt in 1000 g. of water.

The figures for potassium chloride agree (within the limits of experimental error) with one another and with the calculated values, but those for the nitrates show considerable divergences

TABLE XII.

s.	0·001	0·002	0·005	0·01	0·02	0·05	0·1
$(1-a) = 0.32\sqrt[4]{n}$.	0·968	0·960	0·945	0·931	0·914	0·883	0·852
KCl. Adams.	—	0·969	0·961	0·942	0·920	0·883	0·851
,, H. & R.	0·962	—	0·956	0·933	—	—	—
,, W.	—	—	—	—	—	0·880	0·849
KNO₃. Adams.	—	0·967	0·958	0·938	0·910	0·853	0·797
CsNO₃. H. & R.	0·966	—	0·950	0·934	—	—	—
,, W.	—	—	—	—	—	0·812	0·763
$(1-a) = 0.52\sqrt[3]{n}$.	0·948	0·934	0·911	0·888	0·859	0·808	0·759

TABLE XIII.

NaCl. $H = 7.85$. $K = 0.32$.

n.	Δt.	a.	a (corr.).	K.	a (calc.).	%.
0·005	0·01815°	0·953	0·952	0·281	0·945	0·07
0·01	0·036	0·938	0·936	0·297	0·931	0·14
0·02	0·0714	0·921	0·916	0·310	0·912	0·28
0·05	0·176	0·894	0·881	0·323	0·881	0·71
0·10	0·348	0·876	0·850	0·323	0·850	1·42
0·1168	0·406	0·875	0·8435	0·320	0·8435	1·66
0·235	0·808	0·859	0·797	0·329	0·802	3·32*
0·434	1·449	0·856	0·7445	0·340	0·760	6·0*
0·6148	2·068	0·831	0·6715	0·374	0·728	8·4†
0·9291	3·145	0·853	0·609	0·400	0·688	13·1†

NH₄Cl. $H = 3.3$. $K = 0.32$.

n.	Δt.	a.	a (corr.).	K.	a (calc.).	%.
0·005	0·01818	0·947	0·946	0·316	0·941	0·04
0·01	0·036	0·928	0·927	0·339	0·931	0·06
0·02	0·071	0·908	0·906	0·346	0·912	0·12
0·05	0·1744	0·880	0·874	0·342	0·881	0·30
0·1	0·344	0·856	0·845	0·334	0·850	0·60
0·2	0·6784	0·832	0·811	0·323	0·813	1·2
0·2619	0·889	0·835	0·801	0·313	0·795	1·55*
0·3	1·0086	0·819	0·783	0·324	0·786	1·8
0·7974	2·658	0·820	0·734	0·287	0·703	4·75*
1·0523	3·51	0·830	0·715	0·283	0·675	6·3*
2·32	7·72	0·863	0·611	0·294	0·576	13·9‡
3·727	12·52	0·934	0·506	0·319	0·504	22·1‡

RbCl. $H = 2.9$. $K = 0.32$.

n.	Δt.	a.	a (corr.).	K.	a (calc.).	%.
0·1095	0·379	0·867	0·856	0·301	0·845	0·58*
0·2404	0·812	0·826	0·800	0·322	0·799	1·27*
0·4061	1·347	0·7985	0·7605	0·323	0·762	2·12*
0·5866	1·927	0·788	0·732	0·320	0·730	3·06*
0·7608	2·483	0·792	0·721	0·306	0·705	4·0*

CsCl. $H = 2.7$. $K = 0.32$.

n.	Δt.	a.	a (corr.).	K.	a (calc.).	%.
0·02	0·0717	0·931	0·929	0·262	0·912	0·1
0·05	0·1757	0·893	0·889	0·301	0·881	0·25
0·1	0·3454	0·863	0·854	0·315	0·850	0·50
0·2	0·677	0·8285	0·810	0·325	0·811	1·0
0·3	1·002	0·808	0·780	0·327	0·784	1·5
0·4	1·322	0·792	0·755	0·332	0·762	2·0
0·5	1·637	0·778	0·734	0·340	0·744	2·5
0·693	2·24	0·761	0·6995	0·340	0·714	3·5*

Noyes and Falk's values, except those marked * (Biltz), † (Ponsot), and ‡ (Rodebush).

(compare KNO_3 Adams with $CsNO_3$ Washburn) and in the most dilute solutions agree better with the calculated value for chlorides ($K = 0\cdot32$) than for nitrates ($K = 0\cdot52$).

Table XIII refers to the four remaining univalent chlorides. With the exception of sodium chloride, they all obey the law in a satisfactory way, having a common value of $K = 0\cdot32$. Sodium chloride deviates somewhat, the value of K increasing with concentration for solutions above $0\cdot25N$. This is unexpected, since the viscosity is normal, and lithium chloride with its greater hydration number obeys the law, as does sodium bromide (Table XIV).

Table XIV gives a representative selection of the other salts investigated, $viz.$, sodium bromide, magnesium chloride, barium chloride, and strontium nitrate, and it will be seen that in each

TABLE XIV.

NaBr. $H = 6\cdot4$. $K = 0\cdot29$.

$n.$	$\Delta t.$	$a.$	a (corr.)	$K.$	a (calc.)	%.
0·02	0·0722°	0·944	0·944	0·203	0·923	0·23†
0·05	0·1775	0·910	0·903	0·263	0·895	0·56†
0·1	0·3507	0·891	0·867	0·286	0·868	1·1†
0·2	0·6926	0·871	0·829	0·292	0·833	2·2†
0·3	1·031	0·860	0·798	0·301	0·809	3·4†
0·4872	1·691	0·886	0·783	0·276	0·772	5·4‡
0·6434	2·232	0·890	0·755	0·284	0·750	7·2‡
0·9731	3·413	0·923	0·707	0·296	0·713	10·9‡
1·1632	4·112	0·946	0·694	0·291	0·695	13·0‡
1·3544	4·820	0·965	0·670	0·291	0·671	15·1‡

$MgCl_2$. $H = 24\cdot8$. $K = 0\cdot49$.

0·0562	0·282	0·852	0·818	0·475	0·812	2·60‡
0·1180	0·580	0·827	0·757	0·495	0·760	5·3‡
0·1665	0·822	0·834	0·735	0·482	0·730	7·45‡
0·25072	1·235	0·835	0·682	0·504	0·691	11·5
0·5046	2·6768	0·999	0·622	0·475	0·610	22·5
0·76106	4·433	1·09	0·552	0·491	0·553	34·0
0·9608	6·062	1·34	0·503	0·504	0·517	43·0

$BaCl_2$. $H = 16\cdot2$. $K = 0\cdot55$.

0·05005	0·2477	0·833	0·817	0·497	0·797	1·46
0·07514	0·3613	0·796	0·762	0·564	0·768	2·2
0·1003	0·4792	0·789	0·751	0·536	0·745	2·8
0·16312	0·757	0·754	0·695	0·558	0·699	4·75§
0·1727	0·804	0·758	0·694	0·550	0·694	5·05§
0·4043	1·902	0·779	0·628	0·502	0·593	11·8
1·205*	7·85	1·33	0·443	0·524	0·415	35·5‖

$Sr(NO_3)_2$. $H = 6\cdot8$. $K = 0\cdot58$.

0·1004	0·4587	0·733	0·718	0·607	0·730	1·2
0·2528	1·0817	0·655	0·620	0·601	0·634	3·1
0·5116	2·0849	0·609	0·541	0·574	0·537	6·15
0·7771	3·0453	0·574	0·472	0·570	0·467	9·4
1·0506	3·9983	0·544	0·411	0·579	0·411	12·7
1·530 *	5·75	0·543	0·352	0·562	0·332	18·4‖

Jones's values, except those marked † (Noyes and Falk), ‡ (Rivett), § (Ponsot), and ‖ (de Coppet).

* Cryohydric concentration.

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case the cube root law is obeyed and applies equally well to bi-univalent salts of the type $BaCl_2$, $Sr(NO_3)_2$, etc.

In addition to the above salts, calculations have been made for a number of others with the following results : sodium nitrate ($K = 0.38$), potassium nitrate ($K = 0.50$), and rubidium nitrate ($K = 0.51$) obey the cube root law, with the possible deviation of potassium nitrate in dilute solution (see Table XII and comments). The small value of K for sodium nitrate should be noted. Potassium bromide gave less satisfactory results, K decreasing from 0.31 for dilute solutions to 0.24 at the eutectic (3.836-weight normal). This salt behaves as if the hydration value of 1.9 is too small; the experimental result, however, is beyond suspicion. An increase of H by one unit (which is not justified on any other grounds) would give a constant value of K at all concentrations.

Calcium chloride ($K = 0.47$), strontium chloride ($K = 0.48$), cobalt chloride ($K = 0.45$), and copper chloride ($K = 0.52$) are all satisfactory. With barium nitrate ($K = 0.80$), the constant tends to rise slightly, and with lead nitrate ($K = 0.93$) to fall slightly, both in dilute solution; but this is thought to be due to possible small errors in the freezing-point measurements. Copper bromide gives a small but constant value ($K = 0.31$), whilst barium bromide resembles the potassium salt, the values of K decreasing from 0.44 to 0.36.

Thus far, the results for twenty-two salts have either been given in detail or commented upon, and considerable evidence has been adduced in favour of the cube root law. In only three of the above cases do deviations occur, viz., sodium chloride and potassium and barium bromides, but five other salts were found not to obey the law. These are the nitrates of lithium, magnesium, calcium, copper, and cobalt, for which K decreases continuously with increasing concentration : e.g., magnesium nitrate $n = 0.05$, $K = 0.46$; $n = 1.0423$, $K = 0.13$; calcium nitrate $n = 0.05$, $K = 0.58$; $n = 1.05$, $K = 0.42$; lithium nitrate $n = 0.04$, $K = 0.52$; $n = 1.016$, $K = 0.24$. These salts all contain heavily hydrated kations, and anions which are very active in dissociating the solvent. Although the hydration numbers of these salts are relatively small, since they represent the *difference* between two competing processes, they do not afford a measure of the great disturbance suffered in these cases by the solution.

The apparent molecular hydration of magnesium nitrate is 12.8 H_2O; in a molar solution of this salt, not less than half the solvent is attached to the magnesium ions and the activity of the remainder is increased by 50% by the nitrate ions. It is doubtful, therefore, whether the use of a *constant* hydration correction is

permissible, even if Washburn's equation is applicable to cases where the solvent equilibrium is so violently disturbed. Where the absolute hydration correction is small (potassium chloride) the cube root law is followed with great exactness, even for dilute solutions, and it appears probable that an ideal strong electrolyte (anion inert, kation not hydrated) would obey the law over the whole concentration range.

The Hydration Theory and the Conductivity Ratio.

According to the theory of complete dissociation, the conductivity ratio λ_v/λ_∞ must be regarded solely as a ratio of mobilities, the mobility of the ions decreasing as the concentration increases, and this decrease is probably to a large degree due to the decreasing distance between the charged ions. If no other influence intervened, it is to be expected that the conductivity ratio would depend only on the type of salt and be independent of the ion carrying the charge. We know, however, that the so-called "dissociating power" of a solvent depends on the magnitude of its dielectric constant, whilst the latter is related to the molecular association of the solvent. The hydration theory suggested in this paper postulates a continuous decrease in the association of the solvent, and consequently a decrease in the dielectric constant, with increasing salt concentration, whilst the efficiency of the depolymerisation process varies with different anions. The conductivity ratio, therefore, should not only decrease as the concentration of salt increases, but it should do so at rates which depend on the sequence of the hydration numbers (see p. 186). For the potassium salts at semi-normal concentration at 18°, the order of the conductivity ratios is that required by the hypothesis, viz., KCl, 0·779; KBr, 0·766; KClO$_3$, 0·703; KNO$_3$, 0·688.

EXPERIMENTAL.

The amyl alcohol was washed with dilute sulphuric acid and with water, dried over potassium carbonate, and distilled, the fraction boiling at 128—132° being collected. The distribution coefficients were determined by shaking together 100 c.c. of the alcohol, 100 c.c. of the solution to be examined, and 1 c.c. of purified acetic acid at 25° until equilibrium was established. After the two phases had separated completely, the alcoholic layer was drawn off rapidly and the acid content determined by titration with $N/20$-barium hydroxide and phenolphthalein. Owing to the different nature of the two solvents it was found advisable to wash out the pipette with either 20 c.c. of water or 20 c.c. of purified ethyl alcohol, according as the aqueous or non-aqueous

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phase was being examined. In the latter case, the ethyl alcohol brought the amyl alcohol into complete solution and so facilitated the titration. It was necessary to carry out blank experiments on each batch of amyl alcohol, owing to slight variations of the coefficient with different samples (presumably due to differences in the proportion of the isomerides present). The average value of the coefficient alcohol to water was 0·96.

The viscosity measurements were carried out in an Ostwald viscosimeter at 20°, and whilst no outstanding accuracy is claimed for these results, all ordinary precautions were observed.

Summary.

The hydration of sucrose and some strong electrolytes has been determined from the distribution of acetic acid between their aqueous solutions and amyl alcohol. The results indicate that the hydration is (over the concentration range examined) independent of dilution and is an additive property which may have either a positive or a negative value.

A modified hydration theory is suggested according to which only kations are hydrated whilst anions depolymerise the solvent molecules. The first process tends to decrease and the second to increase the activity of the water. Hydration is therefore a composite effect, the salts having negative hydration numbers being those in which the influence of the anion predominates. Solutions of such salts have abnormally high vapour pressures.

The hydration theory has been correlated with viscosity phenomena and a semi-empirical equation established by means of which hydration values can be calculated from viscosity data.

A hydration correction has been applied to calculations of the " degree of dissociation " of strong electrolytes from freezing-point measurements, and evidence is adduced in favour of a cube root dilution law $(1 - \alpha) = K\sqrt[3]{n}$. Many salts have been shown to obey the law with great exactness, and those which do not do so are extreme cases in which the application of the correction is least certain.

Corroborative evidence for the new theory has been obtained from a consideration of the conductivity ratios of a number of strong electrolytes.