219. *The Electrostriction produced by Salts in Some Aliphatic Alcohols.*

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Part I. The Apparent Molar Volumes of Lithium Chloride in Some Aliphatic Alcohols.

It was observed by Butler and Lees (*Proc. Roy. Soc.*, *A*, 1931, **131**, 382) that the partial molar volume of lithium chloride is much smaller in ethyl alcohol than in water; *e.g.*, whereas at 18° the molar volume of solid lithium chloride is 20·5 c.c. and the partial molar volume in aqueous solution at $m = 1$ is 18·6 c.c., yet in ethyl alcohol at the same concentration the value is only 8·6 c.c. and diminishes rapidly as the concentration is decreased, becoming negative at small concentrations. It is evident that the electrostriction of the solvent produced by the salt is considerably greater in alcoholic than in aqueous solutions.

The study of this effect offers a very direct means of estimating the forces between ions and solvent molecules and possibly of distinguishing between the electrical and other factors in solvation. To get some idea of the variation of the apparent molar volume of a salt with the nature of the solvent, we determined the densities of solutions of lithium chloride in several aliphatic alcohols. Since it appeared that the electrostriction was greatest with the lower members of the series, measurements were then made by an improved method of a number of salts in methyl alcohol.

Experimental.

Materials.—Ethyl alcohol. Absolute alcohol which had been standing over freshly burnt lime for several weeks was refluxed for 8 hours and slowly fractionated. It was then distilled twice from anhydrous copper sulphate, and again refluxed and distilled from lime. The density was not changed during these operations; $d_{4^\circ}^{24\cdot9^\circ}$ 0·78544.

n-*Propyl alcohol.* The material contained some unsaturated compounds. Bromine was added until the yellow colour persisted. After standing over-night, the liquid was fractionated, dried over burnt lime for a week, and redistilled; $d_{4^\circ}^{24\cdot9^\circ}$ 0·79990.

n- *and* iso-*Butyl alcohol.* These were dried over burnt lime for several weeks, refluxed for a day, and fractionated; $d_{4^\circ}^{24\cdot9^\circ}$ 0·80625 and 0·79845 respectively.

Lithium chloride. This was purified by crystallisation from ethyl alcohol, and dried at 170° in a stream of dry hydrogen chloride, followed by hydrogen (Pearce and Hart, *J. Amer. Chem. Soc.*, 1922, **44**, 2411) (Found : Cl, 83·62. Calc. : Cl, 83·61%).

Determination of Density.—On account of the difficulty of purifying large quantities of some of the alcohols, a method requiring comparatively small quantities was employed. The pyknometer was a silica bulb, of about 33 c.c. capacity, having a capillary neck about 1 mm. in diameter, and fitted with a ground stopper. A mark was etched on the capillary, but to avoid the difficult operation of adjusting the meniscus exactly to the mark, the distance between meniscus and mark was measured by a reading microscope through a plate-glass window in the thermostat. The capillary neck was first calibrated by weighing when filled with water to various heights, and a calibration curve obtained, giving the volume of the bulb when filled to different points above the etched mark.

A fairly concentrated solution of the salt was prepared and its density determined. Part of the solution was then removed from the pyknometer by means of a protected pipette with a very fine capillary outlet which could pass through the neck of the pyknometer. This portion was weighed, diluted with water, and its salt content determined by addition of an excess of standard thiocyanate solution, followed by back titration with silver nitrate. This method of analysis appeared to be quite satisfactory in the presence of the alcohols. A quantity of the pure solvent was then introduced into the pyknometer through a fine thistle funnel, the pyknometer was shaken to ensure thorough mixing and placed in the thermostat. The position of the meniscus was then read, and after being dried and kept in the balance case, the pyknometer and its contents were weighed. These operations were then repeated a number of times so that the densities of a number of solutions were obtained in each series of dilutions.

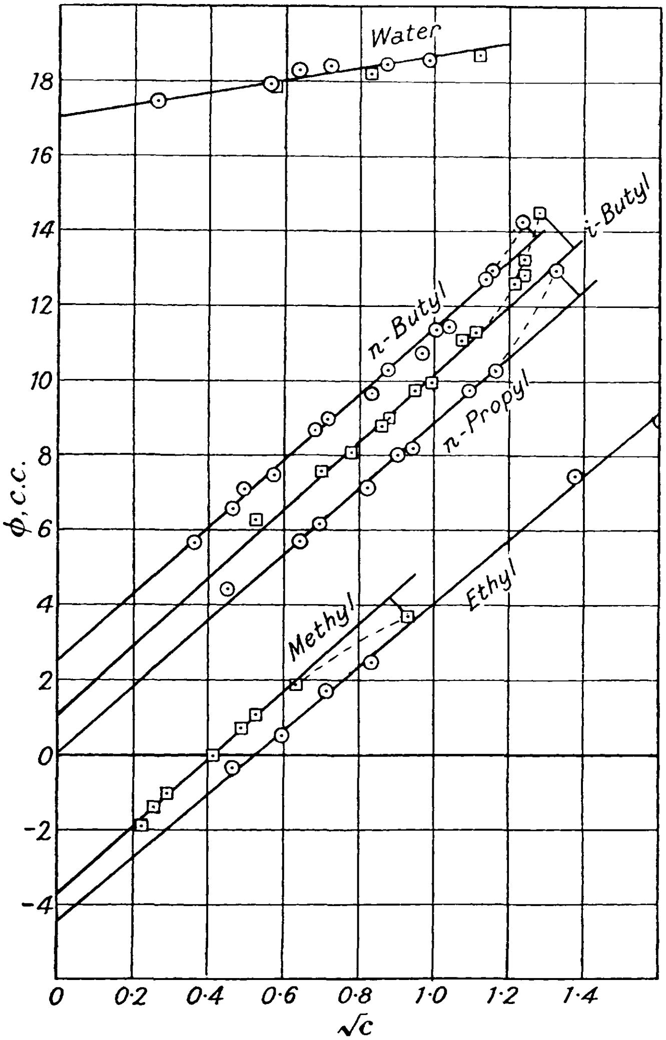
This procedure was not so satisfactory as we had expected. The chief source of error appeared to be the absorption of small quantities of water from the atmosphere during the filling operations. The accuracy obtained, *viz.*, ± 0·00002, is sufficient for the determination of the apparent volumes in fairly concentrated solutions, but insufficient for concentrations below $m = 0{\cdot}2$. The temperature of all the measurements, as determined by comparison with a thermometer calibrated by the N.P.L., was 24·90° ± 0·01°. Weighings were corrected to vacuum.

Results.

The measurements are given in Table I, where m is the concentration in g.-mols. of lithium chloride per 1000 g. of solvent, c the concentration in g.-mols. per l. of solution, d the density,

Fig. 1.

Apparent molar volumes of lithium chloride in various solvents, plotted against the square root of the molar concentration.



[*The squares on the curve for water are from the measurements of Baxter and Wallace* (J. Amer. Chem. Soc., 1916, **38**, 80). *The values for methyl alcohol are taken from Part II of this paper.*]

and ϕ the apparent molar volume of the salt. The volume of 1000 g. of solvent of density d_0 is $V_0 = 1000/d_0$, and that of a quantity of solution of density d containing Mm g. of lithium chloride in 1000 g. of solvent is $V = (1000 + Mm)/d$. The apparent molar volume of the salt is thus $\phi = (V - V_0)/m = [(1000 + Mm)/d - 1000/d_0]1/m$, M being the molecular weight. In Fig. 1 the values of ϕ are plotted against $\sqrt{c}$.

TABLE I.

Apparent Molar Volume of Lithium Chloride in Various Solvents.

A. Water, *d* = 0·99710.				B. Ethyl alcohol, *d* = 0·78546.			
m.	$\sqrt{c}$.	*d.*	ϕ.	*m.*	$\sqrt{c}$.	*d.*	ϕ.
0·0688	0·262	0·99879	17·44	0·2760	0·465	0·79466	−0·36
0·3163	0·560	1·00479	17·91	0·4494	0·594	0·80028	0·51
0·4068	0·635	1·00683	18·29	0·6548	0·716	0·80656	1·70
0·5269	0·721	1·00962	18·39	0·8868	0·834	0·81360	2·46
0·7693	0·870	1·01525	18·46	2·454	1·379	0·85497	7·43
0·9983	0·986	1·02035	18·58	3·375	1·608	0·87708	8·94
C. *n*-Propyl alcohol, *d* = 0·79992.							
0·2547	0·451	0·80783	4·40	1·144	0·953	0·83250	8·19
0·5196	0·644	0·81561	5·69	1·510	1·093	0·84126	9·73
0·5974	0·698	0·81778	6·14	1·720	1·165	0·84631	10·27
0·8492	0·822	0·82475	7·11	2·229	1·326	0·85575	12·96
1·027	0·903	0·82930	8·00				
D. *n*-Butyl alcohol, *d* = 0·80627.				E. *iso*Butyl alcohol, *d* = 0·79847.			
0·1611	0·360	0·81118	5·65	0·3470	0·526	0·80883	6·17
0·2660	0·463	0·81422	6·54	0·6157	0·700	0·81630	7·56
0·3009	0·492	0·81516	7·08	0·7650	0·780	0·82032	8·08
0·4084	0·573	0·81822	7·47	0·9345	0·861	0·82470	8·80
0·5803	0·683	0·82278	8·67	0·9755	0·880	0·82570	9·02
0·6394	0·716	0·82432	8·98	1·136	0·948	0·82959	9·75
0·8612	0·831	0·83016	9·64	1·248	0·994	0·83247	9·96
0·9590	0·876	0·83245	10·29	1·466	1·075	0·83727	11·09
1·176	0·969	0·83794	10·74	1·563	1·110	0·83952	11·32
1·262	1·003	0·83969	11·37	1·884	1·215	0·84618	12·63
1·350	1·039	0·84197	11·43	1·961	1·239	0·84729	13·24
1·630	1·137	0·84784	12·70	1·971	1·242	0·84807	12·84
1·687	1·156	0·84900	12·92	2·104	1·281	0·84908	14·50
1·931	1·234	0·85338	14·23	2·126	1·287	0·84955	14·49

It has been shown that in aqueous solutions a relation of the type $\phi = \phi_0 + a\sqrt{c}$ holds for most salts over a considerable concentration range (Masson, *Phil. Mag.*, 1929, **8**, 218; Geffcken, *Z. physikal. Chem.*, 1931, **155**, 1; Scott, *J. Physical Chem.*, 1931, **35**, 2315). It can be seen that, except at the highest concentrations, a similar relation holds for the alcohols investigated, the slope a being approximately the same in each case and considerably larger than in aqueous solution. It being assumed that this linear relation continues to zero concentration, the following are the approximate values of ϕ_0.

TABLE II.

Apparent Molar Volume at Infinite Dilution of Lithium Chloride in Various Solvents.

Solvent.	H_2O.	$CH_3\cdot OH$.	$C_2H_5\cdot OH$.	*n*-$C_3H_7\cdot OH$.	*n*-$C_4H_9\cdot OH$.	*iso*-$C_4H_9\cdot OH$.
ϕ_0, c.c.	17·0	−3·8	−4·4	+0·1	+2·5	+1·1
r, Å.	2·09	2·28	2·30	2·37	—	—

PART II. THE APPARENT MOLAR VOLUMES OF SOME SALTS IN METHYL ALCOHOL.

IN order to obtain greater precision in the extrapolation of the apparent molar volumes to infinite dilution, it was desirable to obtain values in fairly dilute solutions, and it became evident that in order to reach the high accuracy necessary it was essential to avoid exposure of the alcoholic solutions to moist air. Measurements were made with five salts in methyl alcohol, using a different form of pyknometer and carrying out the essential operations with careful protection from moisture.

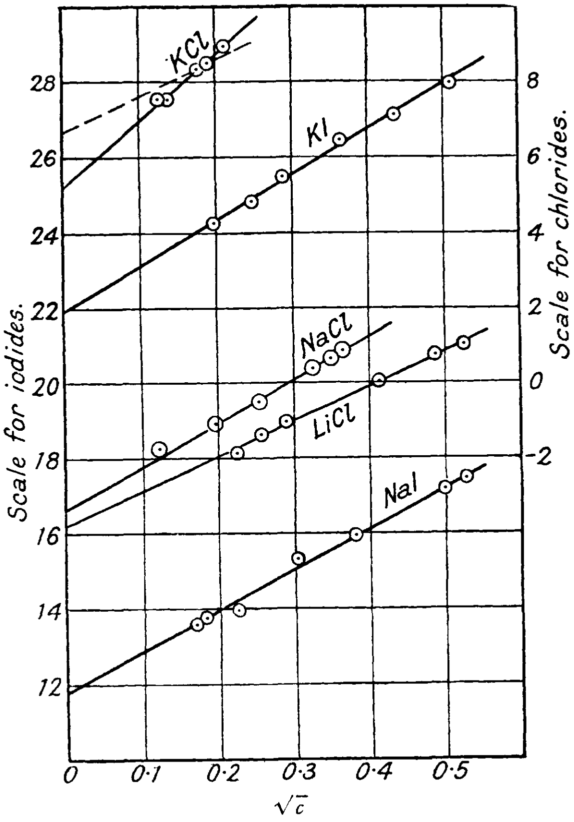
EXPERIMENTAL.

Apparatus.—The pyknometers (Parker and Parker, *J. Physical Chem.*, 1925, **29**, 130) were of Pyrex glass and of about 75-c.c. capacity. Pyrex flasks of 200-c.c. capacity, fitted with ground glass stoppers bearing tubes like a wash-bottle, were used for making up the solutions. The delivery tube of each of the flasks was ground to fit the tube of one of the pyknometers, so that solutions could be forced from the flask to the pyknometer without exposure to moist air.

To avoid contamination by atmospheric moisture, some of the operations were carried on in a dry atmosphere inside a galvanised iron box with a glass window in front. At the two sides it was provided with rubber gloves, allowing manipulations to be carried on inside without introducing moisture.

FIG. 2.

Apparent molar volumes (c.c.) of salts in methyl alcohol.



A water-bath maintained at 24·88° ± 0·01° was used for temperature regulation. The fluctuations of temperature during density determinations were seldom larger than 0·002°, as determined by a Beckmann thermometer, and usually less.

Materials.—Five different preparations of methyl alcohol were used. Nos. 1 and 2 were purified as follows. Aldehydes and ketones were removed by the method of Bates, Mullaly, and Hartley (J., 1923, **123**, 403). The resulting solution was fractionated twice and treated twice with magnesium for dehydration (Lund and Bjerrum, *Ber.*, 1931, **64**, *B*, 210). The alcohol so obtained was protected from moisture, refluxed with anhydrous copper sulphate with a current of dry air passing through the fractionating column (Hartley and Raikes, J., 1925, **127**, 524), and finally distilled. It was preserved in glass-stoppered bottles of Jena glass kept in a dry atmosphere. Nos. 3, 4, and 5 were recovered from the solutions after the density determinations and dehydrated afresh.

The densities of the five preparations at 24·88° are given below, each value being the mean of two results agreeing within two units in the sixth decimal place. According to I.C.T. (Vol. III, p. 27), the density at 24·88° is 0·78671.

Prepn. No.	1	2	3	4	5
$d_{4^\circ}^{24\cdot88^\circ}$	0·786639	0·786645	0·786624	0·786632	0·786637

Lithium chloride was recrystallised twice from water and once from methyl alcohol. It was dried by heating at 170—200° in an atmosphere of hydrogen chloride and kept in a vacuum desiccator. Transfers from one vessel to another were made in a dry atmosphere. Sodium and potassium chlorides were recrystallised twice, fused, ground, and preserved in a desiccator. Sodium and potassium iodides were recrystallised twice, finely ground, and heated to constant weight at 160°.

The purity of the sodium and potassium salts was checked analytically by the method used in Part I for the lithium chloride solutions. The potassium chloride being assumed 100% pure and taken as the standard, the purity of the others was: sodium chloride, 100·00%; sodium iodide, 99·91%; potassium iodide, 99·92%. The slightly low results for the iodides are probably due to analytical error.

Procedure.—The pyknometers were standardised by conductivity water. The filling and adjustment of the level at 25° were carried out as described by Parker and Parker. A sealed counterbalance with a total volume within 1 c.c. of that of the pyknometer was used in weighing (Hartley and Barrett, J., 1911, **99**, 1072; Richards and Chadwell, *J. Amer. Chem. Soc.*, 1925, **47**, 2286; I.C.T., Vol. I, p. 79). Duplicate determinations of the volume gave results agreeing within 0·0004 c.c. in all cases.

The salts were weighed into one of the flasks described above, which was then introduced into the dry atmosphere where the bottles of methyl alcohol were kept, and 80—100 c.c. of the alcohol were forced from the bottle to the flask by pressure of dry air. The flask was then stoppered and the contents weighed, vacuum corrections being made.

The solution was transferred to the pyknometer by connecting the delivery tube of the flask to the inlet tube of the pyknometer by means of the ground joint and forcing the solution over by pressure of dry air. The pyknometer was placed in the bath, the level adjusted, and the scale reading taken, adequate time for temperature equilibrium being allowed. In some cases a little alcohol evaporated from the capillaries and condensed in the caps above the level of the thermostat water. This trouble was largely overcome by placing an electric-light bulb near the top of the pyknometer to heat it. Any methyl alcohol in the cap was removed by a current of air after the pyknometer was taken from the bath. The pyknometer was now washed with distilled water and wiped dry. It was allowed to hang in the balance case for two hours along with the counterbalance, and then weighed. A second weighing was made after another hour to test the constancy.

Corrections were made for the weight of air in the empty pyknometer, the buoyancy of air on the weights, and the air drawn into the pyknometer by contraction of the solution on cooling. The error in the densities is probably less than one part in 100,000.

Results.

The results are given in Table III, and the apparent molar volumes plotted against the square root of the concentration are shown in Fig. 2. The relationship $\phi = \phi_0 + a\sqrt{c}$ holds within the experimental error. The values of ϕ_0 obtained by extrapolating the most probable straight line to $\sqrt{c} = 0$ are given in Table IV, together with the values of Geffcken for water solutions.

TABLE III.

Densities and Apparent Molar Volumes of Salts in Methyl-alcoholic Solution.

MeOH preptn.	G. per 1000 g. solvent.	*m.*	$\sqrt{c}$.	*d.*	ϕ.	MeOH preptn.	G. per 1000 g. solvent.	*m.*	$\sqrt{c}$.	*d.*	ϕ.
A. *Lithium chloride.*											
3	2·705	0·0638	0·224	0·788826	−1·87	2	12·796	0·3018	0·487	0·796572	0·73
3	3·538	0·0834	0·256	0·789478	−1·37	2	14·901	0·3515	0·526	0·798134	1·06
1	4·577	0·1079	0·291	0·790309	−1·03	2	21·693	0·5116	0·634	0·803105	1·87
1	9·254	0·2183	0·414	0·793916	+0·02	1	47·02	1·109	0·931	0·820974	3·69
B. *Sodium chloride.*											
2	1·088	0·0186	0·121	0·787519	−1·72	2	7·853	0·1344	0·325	0·792789	+0·41
2	2·889	0·0494	0·197	0·788951	−1·09	2	9·032	0·1545	0·349	0·793689	0·65
1	4·775	0·0817	0·254	0·790422	−0·51	1	10·182	0·1742	0·370	0·794557	0·83
C. *Potassium chloride.*											
1	1·449	0·01944	0·124	0·787688	7·55	1	3·422	0·0459	0·190	0·789088	8·52
3	1·804	0·02420	0·138	0·787930	7·56	3	4·175	0·0560	0·210	0·789596	8·98
3	2·911	0·03905	0·175	0·788712	8·37						
D. *Sodium iodide.*											
5	5·453	0·03637	0·169	0·790620	13·58	4	27·617	0·1842	0·380	0·806495	15·92
4	6·211	0·04143	0·181	0·791163	13·76	5	47·401	0·3162	0·498	0·820418	17·17
4	9·679	0·06455	0·225	0·793684	13·94	4	53·043	0·3538	0·526	0·824349	17·47
5	17·611	0·1175	0·304	0·799359	15·31						
E. *Potassium iodide.*											
3	8·172	0·04921	0·197	0·792311	24·26	4	28·282	0·17034	0·365	0·806025	26·42
4	12·996	0·07828	0·248	0·795639	24·82	3	40·179	0·2420	0·435	0·814025	27·12
4	17·630	0·10620	0·289	0·798800	25·48	4	55·044	0·3315	0·509	0·823917	27·99

TABLE IV.

Apparent Molar Volumes (c.c.) at Infinite Dilution, 25°.

Salt.	LiCl.	NaCl.	KCl.	NaI.	KI.
In $CH_3{\cdot}OH$	− 3·8	− 3·3	(5·2)	11·8	21·9
In H_2O (Geffcken)............	17·1	16·3	26·4	35·0	45·2

DISCUSSION.

If dissociation is complete, the values of the apparent molar volumes at infinite dilution should be additive for the ions, and are so in aqueous solution but show a considerable deviation in methyl alcohol; *e.g.*, the difference of ϕ_0 for potassium and sodium chlorides is 8·5 c.c., while the corresponding difference for the iodides is 10·1 c.c. This discrepancy might be due to experimental error leading to an incorrect extrapolation, particularly in the case of potassium chloride, for which only a limited range of concentrations was accessible, owing to its small solubility. The broken line (Fig. 2) shows that the value required for additivity, *viz.*, $\phi_0 = 6·7$, would not be incompatible with the observed values if the points at the lowest concentrations were in error by 0·5 c.c.* The lack of additivity might also be due to failure of the linear relationship used for the extrapolation in the case of one or more of the salts at high dilutions. This, in turn, might be the result of incomplete dissociation of the salts at the concentrations employed. Measurements at still smaller concentrations are very desirable, but scarcely feasible with a pyknometer method.

The following table gives the values of the slope *a* of the salts in methyl alcohol together with their values in water as given by Geffcken; the average slope in the former is about six times that in the latter.

Values of *a* in $\phi = \phi_0 + a\sqrt{c}$.

Salt.	LiCl.	NaCl.	KCl.	NaI.	KI.	Mean.
a ($CH_3·OH$)	9·2	11·4	(17·6)	12·0	10·8	10·9
a (H_2O)	1·4	2·2	2·4	1·4	1·6	1·8

Redlich and Rosenfeld (*Z. physikal. Chem.*, *A*, 1931, **155**, 65) have given a calculation of the limiting value of this slope from the Debye–Hückel equation for the free energy of a strong electrolyte at small concentrations. For a uni-univalent electrolyte the latter may be written $\bar{F}_2 - \bar{F}_2^0 = 2RT \log m - 2 \times 2·303RThc^{1/2}$, where $\bar{F}_2$ is the partial molar free energy at the concentration m(or c), $\bar{F}_2^0$ a constant, and h is the Debye–Hückel constant $1/2·303(\varepsilon^2/DkT)^{3/2}(2N/1000)$. Differentiating with respect to the pressure P, we have $[\partial(\bar{F}_2 - \bar{F}_2^0)/\partial P]_{T,m} = \bar{V}_2 - \bar{V}_2^0 = -2 \times 2·3RT[\partial(hc^{1/2})/\partial P]_{T,m}$ or, $\bar{V}_2 - \bar{V}_2^0 = qc^{1/2}$, where $q = 2·3RTh(3\partial D/D\,.\,\partial P - \beta)$ and $\bar{V}_2$, $\bar{V}_2^0$ are the partial molar volumes in the given solution and at infinite dilution respectively, D the dielectric constant of the solvent, and $\beta = -\partial V/V\,.\,\partial P$, its compressibility. Using apparent molar volumes instead of the partial molar volumes, we have $\phi = \phi_0 + 2qc^{1/2}/3$, or $a = 2q/3$.

Redlich and Rosenfeld calculated for water $q = 2·7 \pm 0·8$ (16°). A similar calculation for methyl alcohol, with $h = 2·1$, $D = D_0(1 + 1·0 \times 10^{-4}P)$ (I.C.T., Vol. VI, p. 78), $\beta = 1·2 \times 10^{-4}$, gives $q = 21$, and $a = 14$. Taking into account the uncertainty of $\partial D/\partial P$, the agreement with the observed values is reasonable (cf. above table).

According to Redlich and Rosenfeld's equation, all uni-univalent salts should have the same limiting slope. The differences which have been observed in the actual slopes at fairly high concentrations are somewhat greater than can be accounted for by experimental error, with the possible exception of potassium chloride. Disagreement with the theory at moderately high concentrations is not surprising in view of the fact that the theory is based on the Debye–Hückel limiting law. No adequate reason why the square root relation should hold over such a considerable concentration range has yet been suggested.†

PART III. CALCULATION OF THE ELECTROSTRICTION BY IONS IN SOME ALCOHOLS.

A THEORY of the volume change produced by electrostriction in the vicinity of an ion has been given by Webb (*J. Amer. Chem. Soc.*, 1926, **48**, 2589). If $-\Delta V_r/V$ is the fractional

* In such a dilute solution an error of 0·6 mg. in a total weight of 58 g. would account for an error of this magnitude.

† The Debye–Hückel equation for concentrated solutions may be written as $\bar{F}_2 - \bar{F}_2^0 = 2RT \log m - 2 \times 2·303RThc^{1/2}/(1 + Ac^{1/2}) + Bc$, where the denominator of the second term on the right gives to a first approximation the correction for finite ionic radius, and the term Bc in a broad sense includes effects due to solvation. If the last term is independent of the pressure, the partial molar volumes will be calculable from the pressure variation of the second term alone. The term in the denominator may be capable of accounting for the small differences of slope of the various salts.

change of volume at a distance r from the centre of the ion, where the pressure is p_r, the total contraction of the solvent round an ion is given by

$$C = \int_{r_0}^{\infty} -(\Delta V_r/V) \,.\, 4\pi r^2 \,.\, dr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where r_0 is the radius of the ion, *i.e.*, the region into which no solvent molecules can enter. The fractional volume change can either be obtained directly from the observed relative volume of the solvent at the pressure p_r, or by the equation

$$-\Delta V_r/V = -\int_0^{p_r} \partial V/V\partial p \,.\, dp = -\int_0^{p_r} \beta \,.\, dp,$$

where β, the compressibility, is a function of the pressure. It is therefore necessary to know the pressure as a function of r.

Let δ be the dielectric displacement, E the electric field strength, K the internal field strength, and P the polarisation per unit volume at a point at a distance r from the centre of an ion of charge e. These quantities are connected by the equations, $\delta = e/r^2$; $\delta = E + 4\pi P$; $K = E + 4\pi P/3$. Writing $4\pi P/3 = \Lambda$, we have $\delta = K + 2\Lambda = e/r^2$, and therefore the expression $4\pi r^2 \,.\, dr$ can be replaced by

$$2\pi e^{3/2}(1 + 2\Lambda')/(K + 2\Lambda)^{5/2} \,.\, dK,$$

where $\Lambda' = d\Lambda/dK$.

Then (1) becomes

$$C = 2\pi e^{3/2} \int_0^{K_0} \left(\frac{-\Delta V}{V}\right) \frac{1 + 2\Lambda'}{(K + 2\Lambda)^{5/2}} \,.\, dK \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where K_0 is the value of K at the surface of the ion.

The pressure p at a point in the solvent where the internal field strength is K_m is

$$p = n\alpha K_m{}^2/2 + nKT \log(\sinh x/x) - 3\Lambda^2/8\pi. \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where $x = \mu K_m/kT$, n is the number of solvent molecules per c.c., α the optical polarisability of the solvent molecules, and μ their dipole moment, k the Boltzmann constant per molecule, and Λ_m is given by

$$\Lambda_m = 4\pi/3[n\alpha K_m + n\mu L(x)],$$

and $L(x)$ is Langevin's function ($\coth x - 1/x$).

The proper choice of μ for the solvents presents some difficulty, for a comparison of the dielectric constants of the liquids with the moments of the permanent dipoles as determined in the vapour state indicates that a considerable amount of dipole association has taken place (cf. Smyth, " Dielectric Constant and Molecular Structure," p. 169). A weak electric field would probably have little effect on the associated units, and the proper value of μ in these circumstances would appear to be the effective moment per molecule in the liquid state. The intense fields of force near the ions are probably much greater than the forces causing the association of dipoles, and each solvent molecule may be expected to react independently with the field. In this case the proper value of μ appears to be that of the permanent moment of the isolated molecule. On the other hand, it is found that the value of p, according to (3), for large values of K depends only slightly on the value of μ, the terms containing α being more important. We have therefore used the effective dipole moment of the liquid, calculated from the dielectric constant ε by the formula

$$(\varepsilon - 1)M/(\varepsilon + 2)d = P_E + 4\pi N\mu^2/9kT$$

where P_E, the electronic part of the molecular polarisation, has been taken as equal to the molecular refractivity for the D line (R_D). Similarly $\alpha = 3R_D/4N$.

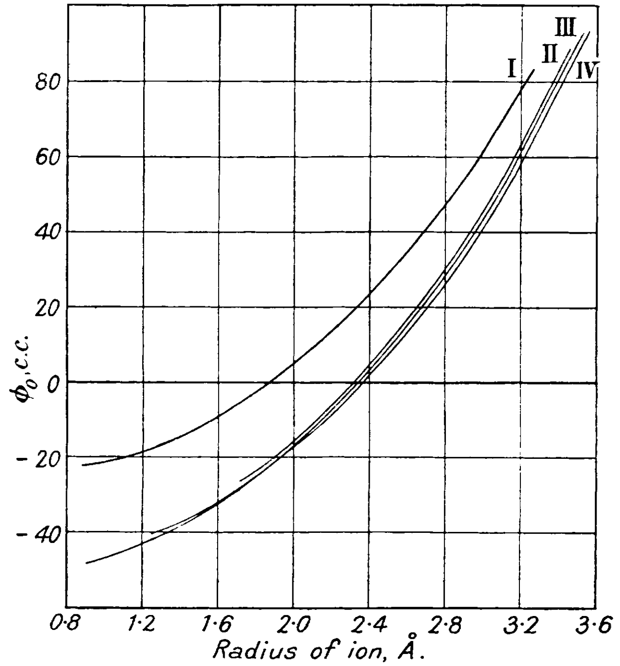
It is not clear what value of μ was used by Webb in his calculations for water, and the formula used by him for determining the compressibilities is inadequate at high pressures. We have therefore repeated the calculation using the value of μ obtained as above and have made similar calculations for methyl, ethyl, and *n*-propyl alcohols. The values of the constants employed are given below.

	$\mu \times 10^{18}$ (effective).	$a \times 10^{24}$.	$n \times 10^{-22}$.
H_2O	0·814	1·46	3·35
$CH_3{\cdot}OH$	1·17	3·24	1·51
$C_2H_5{\cdot}OH$	1·37	5·04	1·04
n-$C_3H_7{\cdot}OH$	1·47	6·91	0·812

The volume changes at high pressures at 25° were obtained by interpolation from the data of Bridgman (I.C.T., Vol. III, p. 41), and extrapolated to pressures beyond his range by the straight-line plot of V against log p, which is probably reliable up to 10^5 atmospheres. At low pressures the following compressibilities were used, H_2O, $\beta = 49 \times 10^{-6}$; $CH_3{\cdot}OH$, 120×10^{-6}; $C_2H_5{\cdot}OH$, 110×10^{-6}; $C_3H_7{\cdot}OH$, 98×10^{-6}. Intermediate values were obtained by drawing a smooth curve of ΔV against p, to fit the measured compressibility at low pressures and Bridgman's data at 500 and 1000 atmospheres.

FIG. 3.

Calculated apparent molar volumes (c.c.) at infinite dilution of ions in various solvents at 25°.



I, H_2O; II, CH_3OH; III, C_2H_5OH; IV, *n*-C_3H_7OH.

Table V gives for each of the four solvents (1) the internal field strength K_m, (2) the value of r at which it applies, (3) the pressure p_r at this distance in megadynes/cm.², (4) the fractional contraction $-\Delta V_r/V$, (5) the total contraction C by electrostriction for 1 g.-mol. of ions of radius r, (6) the calculated apparent volume at infinite dilution, $\phi_0 = 4\pi r^3/3 - C$, for 1 g.-mol. of ions. The last data are plotted against r in Fig. 3.

It is now necessary to see how far the calculated volumes are in accordance with the experimentally observed values. Qualitatively, it is obvious that the theory gives a considerably greater electrostriction for a given radius in the alcohols than in water, and the difference is of the right order of magnitude. A closer comparison can be made by finding the mean ionic radii for the various salts which are required to give agreement with the observed molar volumes. This was done by reading off the ionic radii corresponding to half the observed apparent molar volumes from the curves of Fig. 3. The radii so obtained, which are given in Table VI for water and methyl alcohol, are *mean* values for the salt, and no attempt was made to assign radii to the separate ions.

For agreement with the theory it is thus necessary to assume that the ions have radii 6—10% larger in methyl alcohol than in water. Since some importance factors, such as the variation of the electronic polarisability owing to electric saturation in very intense fields, have been neglected, and the value of the proper effective moment is uncertain, the agreement is quite reasonable.

On the other hand, the calculations give a slightly increasing electrostriction for a constant radius as we pass from methyl to propyl alcohol. Similar calculations on *iso*butyl alcohol, in so far as data were available, indicated values which were scarcely distinguishable from those of *n*-propyl alcohol. Although the observed apparent molar volume of lithium

TABLE V.

Calculation of electrostriction and apparent molar volumes of ions.

(1) K_m	10^5	2×10^5	4×10^5	6×10^5	10^6	2×10^6	4×10^6
			Water.				
(2) r, Å.	4·26	3·24	2·50	2·13	1·71	1·25	0·90
(3) Press., $p_r \times 10^{-3}$	0·26	1·69	7·13	14·7	35·2	115	391
(4) $-\Delta V_r/V$	0·0116	0·0636	0·196	0·301	0·456	0·729	1·151
(5) C, c.c.	1·97	5·0	10·4	14·1	18·3	22·8	25·6
(6) ϕ_0, c.c.	194	81·4	29·3	10·4	− 5·6	−17·8	−22·5
			Methyl alcohol.				
(2) r, Å.	4·47	3·44	2·61	2·20	1·75	1·27	0·91
(3) Press., $p_r \times 10^{-3}$	0·357	2·20	6·40	12·9	30·6	91·6	364
(4) $-\Delta V_r/V$	0·034	0·140	0·268	0·377	0·565	0·905	1·60
(5) C, c.c.	7·6	15·8	27·6	33·2	39·1	44·8	49·4
(6) ϕ_0, c.c.	219	87·5	17·5	−6·2	−25·5	−39·6	−47·5
			Ethyl alcohol.				
(2) r, Å.	4·57	3·50	2·64	2·21	1·75	1·27	0·90
(3) Press., $p_r \times 10^{-3}$	0·386	1·72	5·98	12·2	29·5	102	369
(4) $-\Delta V_r/V$	0·036	0·116	0·256	0·371	0·561	0·941	1·605
(5) C, c.c.	8·9	17·9	28·6	34·4	40·7	46·6	50·7
(6) ϕ_0, c.c.	233	90·9	18·1	−7·0	−27·1	−41·4	−48·8
			n-*Propyl alcohol.*				
(2) r, Å.	4·66	3·54	2·65	2·21	1·75	1·25	0·89
(3) Press., $p_r \times 10^{-3}$	0·394	1·66	5·79	11·7	28·9	102	377
(4) $-\Delta V_r/V$	0·033	0·102	0·215	0·302	0·433	0·677	1·00
(5) C, c.c.	12·4	20·9	30·9	35·4	40·5	45·8	49·0
(6) ϕ_0, c.c.	245	91·8	16·3	−8·0	−26·9	−40·8	−47·2

TABLE VI.

Mean atomic radii of ions in salts from apparent molar volumes.

Salt.	LiCl.	NaCl.	KCl.	NaI.	KI.
Mean radius, Å., H_2O	2·09	2·08	2·19	2·28	2·38
Mean radius, Å., $CH_3{\cdot}OH$	2·28	2·29	2·37	2·43	2·51

chloride is less in ethyl than in methyl alcohol, as is in accordance with the calculations, the values in the higher alcohols are appreciably greater. The mean radii of the ions which are required to make the calculated agree with the observed values are given in the last line of Table II. Their variation is not unreasonably large and may represent a real increase in the radius of the cavities containing the ions as we pass up the series. It is possible, however, that the behaviour of lithium chloride is somewhat anomalous, for its apparent molar volume is slightly less in methyl alcohol and slightly greater in water than that of sodium chloride. A fuller discussion of the volumes of salts in these solvents must therefore await further experimental material.

In the course of the calculations it was found that in some circumstances, *viz.*, with large values of μ and small values of K, Λ as calculated by Webb's expression may become greater than K and consequently negative values of p are obtained. This does not arise with the effective moments employed above, but if the actual moments of the molecules are used, a negative pressure is obtained with the lower members of the series for small values of K, and the theory would require in these circumstances an expansion of the solvent instead of electrostriction for very large ions. This effect, which apparently has not been previously noticed, may be of importance in connexion with the large apparent volumes in aqueous solution of some of the heavier ions.

SUMMARY.

1. The apparent molar volumes of lithium, sodium, and potassium chlorides and sodium and potassium iodides in methyl alcohol and of lithium chloride in four of the lower aliphatic alcohols have been determined.

2. All the salts obey the equation $\phi = \phi_0 + a\sqrt{c}$ over the concentration range examined, except when approaching saturation in some of the higher alcohols. The differences of a for the various salts in methyl alcohol are greater than the experimental error, but the average value of a, which is six times the value in water, is in approximate agreement with the limiting value for uni-univalent salts in this solvent calculated by the equation of Redlich and Rosenfeld.

3. The electrostriction by the ions is considerably greater in the alcoholic than in aqueous solutions. The extrapolated values of the apparent molar volumes at infinite dilution in water and methyl alcohol are in reasonable agreement with values calculated by Webb's theory of electrostriction. In the propyl and *n*- and *iso*-butyl alcohols a small variation of the mean ionic radius of lithium chloride is sufficient to make the calculated values of ϕ_0 agree with those observed.

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