245. *The Viscosity of Solutions of Strong Electrolytes.*

By V. D. LAURENCE and J. H. WOLFENDEN.

JONES and DOLE (*J. Amer. Chem. Soc.*, 1929, **51**, 2950) have proposed an empirical equation to represent the viscosities of solutions of strong electrolytes, *viz.*, $\eta = 1 + A\sqrt{c} + Bc$, where η = relative viscosity of the solution, c = concentration (in mols. per litre), and A and B are constants. They realised that the coefficient A is due to interionic forces, and later, Falkenhagen, Dole, and Vernon (papers summarised in *Phil. Mag.*, 1932, **14**, 537) deduced from the ion-atmosphere theory an equation evaluating A in terms of well-known physical constants. The validity of the two equations has been tested by Joy and Wolfenden (*Proc. Roy. Soc.*, 1931, **134**, *A*, 413), Jones and Talley (*J. Amer. Chem. Soc.*, 1933, **55**, 624, 4124), and Cox and Wolfenden (*Proc. Roy. Soc.*, 1934, **145**, *A*, 475), who have shown that for uni-univalent electrolytes in aqueous solution the agreement between the observed and theoretical values of A is very satisfactory.

Cox and Wolfenden (*loc. cit.*) showed that, within the experimental error of the existing data, the coefficient B was made up additively of two independent components characteristic of the anion and the cation respectively. The principal object of the work now described was to determine whether B is rigidly additive or only a first approximation. For this purpose the viscosities of solutions of several pairs of lithium and potassium salts with common anions were measured in order to ascertain whether the differences between the values of B for the pairs were constant and independent of the common anion.

EXPERIMENTAL.

Four Washburn–Williams viscometers (*J. Amer. Chem. Soc.*, 1913, **35**, 737) were used. Their times of flow for water at 25° ranged from 691 to 1614 secs. The " abstraction and addition " technique of Cox and Wolfenden was used; after the time of flow for water had been measured, a small volume was abstracted from the viscometer with a syringe pipette (Krogh and Keys, J., 1931, 2436), an exactly equal volume of a solution of known concentration was added, and the time of flow redetermined. The mean times of flow for water and the solutions were determined with an error not greater than 0·1 sec., as illustrated in the tables by the concordance of independent determinations on the same solution in different viscometers. In view of the high dilution of the solutions, kinetic-energy and surface-tension corrections were not applied.

Solutions of lithium iodate and of lithium and potassium acetates were prepared by neutralising the carbonate and hydroxides respectively with the appropriate acid. The other solutions were prepared from well-crystallised specimens of the salts.

Densities were taken from the International Critical Tables when sufficiently accurate data were available. In other cases they were determined by the Hartley and Barrett pyknometer (J., 1911, **99**, 1072); graphical interpolation from the following results was employed :

Salt.	Concn., N.	$d^{25°}_{25°}$ in air.	Salt.	Concn., N.	$d^{25°}_{25°}$ in air.
$LiIO_3$	0·1166	1·01836	LiOAc	0·1089	1·00293
	0·0233$_2$	1·00366		0·0217$_8$	1·00059

All the measurements were made at 25°.

Results.—The relative viscosities of the solutions were calculated from the expression

$$\eta = (t_s/t_w)(d_s - d_{air})/(d_w - d_{air})$$

where t_w and t_s = time of flow for water and solution respectively, and the d's represent the densities denoted by the subscript. The results are given in the table on p. 1145.

DISCUSSION.

The Jones–Dole equation may be written as $(\eta - 1)/\sqrt{c} = A + B\sqrt{c}$. If $(\eta - 1)/\sqrt{c}$ is plotted against $\sqrt{c}$, a straight line will be obtained, and its intercept on the $(\eta - 1)/\sqrt{c}$ axis will give the value of A, and its slope that of B.

Lithium chloride.

c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.
0·00707	1·0013$_8$	0·016$_4$
0·00707	1·0014$_5$	0·017$_2$
0·02821	1·0048$_6$	0·028$_9$
0·02884	1·0055$_2$	0·032$_5$
0·05641	1·0090$_9$	0·038$_3$
0·05641	1·0092$_8$	0·039$_1$
0·05767	1·0098$_7$	0·041$_1$
0·05767	1·0099$_6$	0·041$_5$
0·08462	1·0133$_6$	0·045$_9$
0·08651	1·0138$_5$	0·047$_1$
0·08651	1·0138$_1$	0·047$_0$
0·08651	1·0140$_8$	0·047$_9$
0·11110	1·0172$_1$	·0051$_6$
0·11358	1·0185$_0$	0·054$_9$
0·13758	1·0213$_9$	0·057$_7$
0·16773	1·0259$_0$	0·063$_2$
0·16773	1·0259$_3$	0·063$_3$
0·21855	1·0336$_6$	0·072$_0$

Lithium bromide.

0·00843$_0$	1·0016$_4$	0·017$_9$
0·01686	1·0028$_3$	0·021$_8$
0·02529	1·0038$_6$	0·024$_3$
0·03372	1·0050$_3$	0·027$_4$
0·04147	1·0060$_0$	0·029$_5$
0·04921	1·0070$_8$	0·031$_9$
0·05695	1·0079$_0$	0·033$_2$
0·07181	1·0098$_4$	0·036$_7$

Lithium iodide.

c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.
0·00986$_3$	1·0012$_0$	0·012$_1$
0·00986$_3$	1·0012$_1$	0·012$_2$
0·00986$_3$	1·0013$_0$	0·013$_1$
0·01973	1·0022$_0$	0·015$_7$
0·01973	1·0022$_7$	0·016$_2$
0·02959	1·0030$_4$	0·017$_7$
0·02959	1·0031$_7$	0·018$_4$
0·02959	1·0032$_8$	0·019$_1$
0·03885	1·0038$_9$	0·0197
0·03885	1·0039$_7$	0·0202
0·04811	1·0050$_3$	0·022$_9$
0·05737	1·0055$_9$	0·023$_3$
0·07475	1·0072$_2$	0·026$_4$

Potassium iodide.

0·00275	0·9999$_4$	−0·001$_1$
0·00544	0·9998$_0$	−0·002$_8$
0·01102	0·9995$_7$	−0·004$_1$
0·02203	0·9988$_1$	−0·008$_1$
0·02203	0·9987$_5$	−0·008$_4$
0·02965	0·9981$_5$	−0·010$_7$
0·02965	0·9981$_5$	−0·010$_7$
0·02965	0·9978$_7$	−0·012$_4$
0·04006	0·9971$_6$	−0·014$_2$
0·05047	0·9962$_5$	−0·016$_7$
0·05929	0·9957$_4$	−0·017$_5$
0·05929	0·9956$_5$	−0·017$_9$
0·07890	0·9941$_4$	−0·020$_8$
0·08773	0·9935$_0$	−0·021$_9$
0·09696	0·9929$_6$	−0·022$_6$

Lithium iodate.

c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.
0·00297	1·0014$_2$	0·026$_0$
0·00588	1·0024$_5$	0·031$_9$
0·00595	1·0023$_4$	0·030$_4$
0·01190	1·0043$_4$	0·039$_8$
0·01190	1·0044$_8$	0·041$_1$
0·01785	1·0063$_3$	0·047$_4$
0·02380	1·0082$_5$	0·053$_5$
0·02380	1·0084$_0$	0·054$_4$
0·02380	1·0089$_5$	0·055$_1$
0·02938	1·0101$_2$	0·059$_0$
0·03569	1·0120$_6$	0·063$_8$
0·03569	1·0122$_4$	0·064$_8$
0·04068	1·0140$_4$	0·069$_6$
0·04662	1·0152$_3$	0·070$_5$
0·04662	1·0158$_2$	0·0733
0·05757	1·0186$_2$	0·077$_6$
0·05803	1·0191$_1$	0·0793
0·06920	1·0227$_9$	0·086$_6$
0·06920	1·0227$_9$	0·086$_6$
0·07969	1·0259$_5$	0·091$_9$
0·09018	1·0294$_7$	0·0981

Potassium iodate.

c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.
0·00505	1·0011$_2$	0·015$_8$
0·01010	1·0020$_0$	0·019$_9$
0·01516	1·0027$_8$	0·022$_6$
0·01516	1·0028$_3$	0·023$_0$
0·01990	1·0036$_4$	0·025$_8$
0·02938	1·0050$_3$	0·029$_3$
0·04458	1·0072$_0$	0·034$_1$
0·04458	1·0072$_6$	0·034$_4$

Potassium acetate.

0·00932	1·0025$_2$	0·026$_5$
0·00932	1·0025$_4$	0·026$_3$
0·01864	1·0049$_8$	0·036$_5$
0·01864	1·0051$_4$	0·037$_7$
0·02796	1·0070$_7$	0·042$_3$
0·02796	1·0075$_1$	0·044$_9$
0·03728	1·0098$_0$	0·050$_8$
0·04546	1·0115$_9$	0·054$_4$
0·06296	1·0157$_8$	0·062$_9$

Lithium acetate.

0·01110	1·0051$_1$	0·048$_5$
0·01110	1·0051$_2$	0·048$_5$
0·02198	1·0096$_2$	0·064$_9$
0·03331	1·0146$_8$	0·080$_5$
0·04441	1·0186$_6$	0·088$_6$
0·06457	1·0275$_9$	0·108$_8$
0·09393	1·0393$_8$	0·128$_5$

The graphs of this function derived from our results show that the equation is obeyed in all cases over the concentration range covered by the measurements. The values of A and B, calculated by the method of least squares, are given in the following table, together with the theoretical values of A calculated from Falkenhagen's expression.

Electrolyte.	$A_{\text{obs.}} \times 10^4$.	$A_{\text{calc.}} \times 10^4$	$B \times 10^3$.	Electrolyte.	$A_{\text{obs.}} \times 10^4$.	$A_{\text{calc.}} \times 10^4$.	$B \times 10^3$.
LiCl	64 ± 10	67	139 ± 5	$LiIO_3$	79 ± 10	82$_5$	299 ± 5
LiBr	79 ± 10	66	106 ± 5	KIO_3	66 ± 10	68	132 ± 5
LiI	42 ± 10	67	81 ± 5	LiOAc	66 ± 10	93	397 ± 5
KI	41 ± 10	49$_5$	88 ± 5	KOAc	38 ± 10	30	238 ± 5

The observed and theoretical values of A agree within the probable experimental error, except for lithium iodide, bromide, and acetate, where the divergence is not more than the maximum possible error. In the case of the last salt the gradient of the plot of $(\eta - 1)/\sqrt{c}$ is rather steep, and a larger error is to be expected.

The limits within which B is an additive quantity are shown in the following table of differences between B values for lithium and potassium chlorides, bromides, iodides, iodates, and acetates. The values of B for potassium chloride and bromide, taken from the work of Jones and Talley (*loc. cit.*), have been included in this scheme. The probable error is ± 0·008 throughout.

Common anion	Cl′	Br′	I′	IO_3'	OAc′
$B_{Li^\cdot} - B_{K^\cdot}$	0·153$_3$	0·155$_4$	0·170$_0$	0·167$_5$	0·159$_6$

It will be seen that the spread of the values of $B_{Li^\cdot} - B_{K^\cdot}$ for the five anions concerned is 0·017, which is about twice the probable error of any single value. Although it is just possible that $B_{Li^\cdot} - B_{K^\cdot}$ is truly constant, we are of the opinion that the additivity of B is only a first approximation. On the other hand, viscosities of uni-univalent electrolytes calculated from a series of B values for individual ions will not differ from the observed viscosities by more than 0·1% up to 0·1N. The additivity of B is therefore a very satisfactory first approximation.

The Attribution of B *Values to Individual Ions.*—As an expedient necessary to the provisional attribution of B values to individual ions, Cox and Wolfenden drew a parallel between the viscosity of a colloid, as expressed by the Einstein equation (*Ann. Physik*, 1906, **19**, 289; 1911, **34**, 591), and the viscosity of an electrolyte made up of large ions. On this assumption, the contribution of large ions to the viscosity of an electrolyte is proportional to the ionic volume, and therefore to the cube of the " Stokes radius " derived from the ionic mobility. The assumptions underlying the derivation of Stokes's law and the Einstein viscosity equation are sufficiently similar to suggest that the admittedly crude parallelism between colloid and electrolyte is most plausible in the case of ions obeying Stokes's law. For this reason, Cox and Wolfenden selected lithium iodate as the electrolyte whose B value was to be sub-divided in the inverse ratio of the cube of the ionic mobilities, because its ions are large and because they obey Stokes's law in the sense that the temperature coefficient of their mobilities is very nearly equal to that of the fluidity of water.

The tetraethylammonium and picrate ions conform to Stokes's law in this sense even more closely, however, so it seemed desirable to attempt an attribution of individual B values using the corresponding salt as the starting point. For this purpose the viscosity of solutions of tetraethylammonium picrate, lithium picrate, and tetraethylammonium bromide were measured at 25°. The results are shown in the following tables, together with the values of A and B derived from them.

Densities.

Salt.	Concn., M.	$d_{25°}^{25°}$ in air.
Lithium picrate	0·03218	1·00354
	0·02439	1·00269
Tetraethylammonium bromide	0·01671	1·00067
	0·00827	1·00035
,, ,, picrate	0·01830	1·00179*
	0·00918	1·00089*

* These apparent specific gravities are those determined by Cox and Wolfenden at 18°. At such low concentrations, they are nearly independent of temperature.

Viscosities.

Lithium picrate.

c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.	c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.	c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.	c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.
0·00419	1·0023$_8$	0·036$_8$	0·01258	1·0066$_3$	0·059$_1$	0·01577	1·0087$_4$	0·067$_5$	0·02833	1·0140$_3$	0·083$_4$
0·00419	1·0024$_9$	0·038$_5$	0·01258	1·0068$_9$	0·061$_4$	0·02063	1·0105$_7$	0·073$_6$	0·03218	1·0164$_3$	0·091$_6$
0·00839	1·0046$_6$	0·050$_9$	0·01577	1·0085$_6$	0·066$_1$	0·02439	1·0125$_7$	0·080$_5$	0·03572	1·0176$_7$	0·093$_1$
0·00839	1·0047$_2$	0·051$_5$									

Tetraethylammonium picrate.†

c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.	c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.	c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.	c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.
0·00397	1·0034$_4$	0·054$_5$	0·00970	1·0082$_6$	0·083$_9$	0·02007	1·0161$_8$	0·114$_3$	0·02007	1·0168$_0$	0·118$_6$

Tetraethylammonium bromide.

c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.	c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.	c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.	c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.
0·00418	1·0019$_5$	0·030$_2$	0·01253	1·0051$_9$	0·046$_4$	0·01671	1·0069$_0$	0·053$_4$	0·02054	1·0083$_9$	0·058$_6$
0·00418	1·0019$_9$	0·030$_8$	0·01253	1·0052$_6$	0·047$_0$	0·01671	1·0069$_3$	0·053$_6$	0·02821	1·0110$_3$	0·065$_7$
0·00829	1·0035$_5$	0·039$_1$	0·01671	1·0066$_6$	0·051$_5$	0·02037	1·0082$_3$	0·057$_7$	0·03542	1·0137$_3$	0·072$_9$
0·00835	1·0036$_2$	0·039$_6$									

† The solubility of this salt in water is so low that the " abstraction and addition " technique cannot be used; B has been accurately evaluated for this salt at 18° by Cox and Wolfenden, and since the variation of B with temperature would be expected to be very small for this salt, the above approximate measurements were undertaken to confirm their results.

The method of least squares applied to the above results leads to the following values for the constants of the Jones–Dole equation (the values for lithium bromide being repeated from p. 1145):

Salt.	$A_{\text{obs.}} \times 10^4$.	$A_{\text{calc.}} \times 10^4$.	$B \times 10^3$.
Lithium picrate	91 ± 20	108	451 ± 5
Tetraethylammonium bromide	82 ± 20	69	343 ± 5
Tetraethylammonium picrate	106 ± 40	119	743 ± 20
Lithium bromide	79 ± 10	66	106 ± 5

A comparison of the B values for the four electrolytes derived from the four ions makes it obvious that here the principle of additivity breaks down to an extent far beyond the experimental error; *e.g.*, $(B_{\mathrm{NEt_4Pic.}} + B_{\mathrm{LiBr}})$ should be equal to $(B_{\mathrm{NEt_4Br}} + B_{\mathrm{LiPic.}})$, whereas the respective values are 0·850 and 0·794. Inasmuch as B_{LiBr} falls in line with the common value of $(B_{\mathrm{Li}^{\cdot}} - B_{\mathrm{K}^{\cdot}})$ differences, it seems almost certain that the anomaly is to be attributed to one or more of the electrolytes containing organic ions. It is perhaps significant that the conductivity data for lithium and tetraethylammonium picrates show deviations from the Onsager equation of 30% and 20% respectively. In these cases, there must be some specific interaction between the ions, such as ion-pair formation, and therefore the breakdown of the principle of the additivity of *B* for these electrolytes is not unexpected. Pending further investigations, the provisional attribution of individual *B* values made by Cox and Wolfenden on the basis of lithium iodate must be adopted.

The Effect of Charge on B.—Since the increment in viscosity produced by a colloid particle is increased by a charge on the particle (Smoluchowski, *Kolloid-Z.*, 1916, **18**, 190), it was thought interesting to compare the *B* coefficient of an ion with that of an uncharged particle of almost identical size. The viscosity of dilute solutions of acetic acid was therefore measured and B_{HOAc} compared with $B_{\mathrm{OAc}'}$.

Acetic acid.

c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.	c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.	c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.	c.	η.	$\frac{\eta - 1}{\sqrt{c}}$.
0·01082	1·0012$_0$	0·011$_5$	0·04181	1·0049$_2$	0·024$_1$	0·09734	1·0113$_5$	0·036$_4$	0·29202	1·0336$_7$	0·0623
0·01082	1·0013$_1$	0·012$_6$	0·05220	1·0060$_6$	0·026$_5$	0·12166	1·0139$_5$	0·040$_0$	0·38339	1·0445$_4$	0·0719
0·02143	1·0026$_3$	0·018$_0$	0·06241	1·0071$_0$	0·028$_4$	0·19468	1·0227$_2$	0·051$_5$	0·47479	1·0555$_7$	0·0803
0·03121	1·0036$_4$	0·020$_6$	0·09234	1·0104$_6$	0·034$_4$	0·29202	1·0335$_6$	0·062$_1$	0·56617	1·0657$_3$	0·0874

By the method of least squares these results give $A = 0{\cdot}0006 \pm 0{\cdot}001$, the theoretical value being zero for an un-ionised solute, and $B = 0{\cdot}117 \pm 0{\cdot}005$. The value of *B* for the acetate ion, from Cox and Wolfenden's values for $B_{\mathrm{Li}^{\cdot}}$ and $B_{\mathrm{K}^{\cdot}}$, is 0·252 or 0·246, according to whether the *B* value of lithium acetate or potassium acetate is used. In accordance with expectation, *B* for the charged anion is substantially larger than *B* for the acetic acid molecule.

SUMMARY.

(*a*) The relative viscosity of aqueous solutions of lithium chloride, bromide, iodide, iodate, acetate, and picrate, potassium iodide, iodate, and acetate, acetic acid, tetraethylammonium bromide and picrate has been measured at 25°.

(*b*) The *A* and *B* coefficients of the Jones–Dole equation have been calculated. The *A* values are in good agreement with the Falkenhagen–Dole–Vernon equation. The *B* values for the inorganic salts show that the additivity of *B* coefficients for individual ions is probably no more than a satisfactory first approximation. The principle of the additivity of *B* breaks down unmistakably for the salts containing the tetraethylammonium and the picrate ion, perhaps owing to ion-pair formation.

(*c*) Comparison of the values of *B* for the acetate ion and the acetic acid molecule shows that the effect of an electric charge is to increase the value of *B* considerably.

The authors are indebted to Imperial Chemical Industries and to the Chemical Society for grants which defrayed the cost of part of the apparatus used.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL COLLEGE & TRINITY COLLEGE, OXFORD.

[*Received, July 9th,* 1934.]