649. *The Electrolytic Dissociation of Magnesium Sulphate and Lanthanum Ferricyanide in Mixed Solvents.*

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Conductivity measurements are reported for magnesium sulphate in water, dioxan–water mixtures, and glycine solutions, and for lanthanum ferricyanide in glycine solutions. Dissociation constants have been derived, and it is shown that a simple electrostatic explanation will account for the variation of dissociation constant with dielectric constant. A comparison is drawn between ion-pair sizes as calculated by Stokes's law and by Bjerrum's method.

NUMEROUS measurements have been made of the conductivities of salts in non-aqueous and in mixed solvents, and deviations from the limiting Onsager equation have in many cases been satisfactorily accounted for by the assumption of incomplete dissociation. Dissociation constants can be calculated, and in general it would appear that when ion-pairs are formed from large spherical ions, or from large and stably solvated ions, variation of dissociation constant with dielectric constant may be accounted for satisfactorily by Bjerrum's treatment (*Kgl. Danske Vidensk. Selskab.*, 1926, **7**, No. 9). Very few measurements appear to have been made in media of dielectric constant higher than that of water, however, and for this reason the present work has been carried out. It has recently been shown by Monk (*Trans. Faraday Soc.*, 1950, **46**, 645) that the conductivity of potassium chloride in aqueous glycine solutions is in agreement with the Onsager equation and it appeared to be of interest to examine the behaviour of electrolytes of higher valency type in such solutions. Magnesium sulphate was chosen as a suitable 2–2-valency type salt, not subject to hydrolysis, and conductivity measurements have been made on solutions in water, and in dioxan–water and glycine–water mixtures. Measurements have also been made on glycine–water solutions of lanthanum ferricyanide, a 3–3-valency type salt, for which the conductivities in water and in mixed solvents of lower dielectric constant than water have been reported in earlier papers (Davies and James, *Proc. Roy. Soc.*, 1948, *A*, **195**, 116; James, *J.*, 1950, 1094). An exploratory study of conductivities in urea–water solutions was made, but drift in solvent resistance, presumably due to hydrolysis, was too great for accurate measurements to be obtained.

EXPERIMENTAL.

Glycine was dissolved, filtered, and recrystallised thrice from conductivity water and finally dried to constant weight over potassium hydroxide *in vacuo*. Dioxan (" purissimus " grade) was purified by prolonged refluxing with sodium and fractional distillation (Kraus and Vingee, *J. Amer. Chem. Soc.*, 1934, **56**, 513). Magnesium sulphate (" AnalaR ") was recrystallised from water and dried over the partially dehydrated salt. Lanthanum ferricyanide, $LaFe(CN)_6,5H_2O$, was prepared and analysed as described by Davies and James (*loc. cit.*).

The conductivity equipment and experimental technique used have been described elsewhere (Davies, *J.*, 1937, 432; James, *loc. cit.*). Concentrations were determined by weight, and volume concentrations were calculated from the densities of the mixed solvents, it being assumed that the small amount of salt added did not appreciably alter the density. All measurements were made at 25° ±0·005°. Measurements of pH were made by the glass-electrode method, by using the " reproducible liquid junction " apparatus of Smith and Speakman (*Trans. Faraday Soc.*, 1948, **44**, 1031), standardisation being effected with suitable buffer solutions, as recommended by Hitchcock and Taylor (*J. Amer. Chem. Soc.*, 1937, **59**, 1812).

Dielectric constants for aqueous dioxan solutions were obtained from the data of Åkerlöf and Short (*ibid.*, 1936, **58**, 1241), densities from those of Hovorka (*ibid.*, p. 2264) and of Geddes (*ibid.*, 1933, **55**, 4832), and viscosities from those of Owen and Waters (*ibid.*, 1938, **60**, 2371) and of Geddes (*loc. cit.*). Densities for aqueous glycine solutions were obtained from Wyman's data (*ibid.*, 1934, **56**, 536); dielectric constants and viscosities were interpolated from the data listed by Monk (*loc. cit.*).

DISCUSSION.

Aqueous Magnesium Sulphate Solutions.—Although Owen and Gurry (*ibid.*, 1938, **60**, 3074) found that their conductivity data for aqueous zinc sulphate and copper sulphate solutions required appreciable correction for hydrolysis, magnesium hydroxide is relatively a much stronger base (cf. Davies, *J.*, 1951, 1256) and no hydrolysis is to be expected in magnesium sulphate solutions. Calculations based on Stock and Davies's value of $K = 2{\cdot}6 \times 10^{-3}$ for the second dissociation constant of magnesium hydroxide (*Trans. Faraday Soc.*, 1948, **44**, 856), the carbon dioxide content of the solutions (as determined from the specific conductivity of the solvent), and the pH's of the solutions (normally about 6·0) confirm this view.

TABLE I.

Conductivity of aqueous magnesium sulphate solutions.

Run	10^6K_{H_2O}	10^4c	$10^2c^{\frac{1}{2}}$	Λ	pK	Run	10^6K_{H_2O}	10^4c	$10^2c^{\frac{1}{2}}$	Λ	pK
1	0·251	1·6196	1·2726	127·31	2·216	2	0·264	1·7021	1·3046	127·11	2·225
		3·2672	1·8075	124·27	2·232			3·9871	1·9968	123·13	2·237
		5·3847	2·3204	121·34	2·222			6·1798	2·4859	120·33	2·226
		8·5946	2·9316	117·85	2·211			8·5401	2·9223	117·89	2·214
		12·011	3·4656	114·92	2·200			11·194	3·3456	115·50	2·207
		16·759	4·0937	111·61	2·184			14·393	3·7937	113·14	2·193
								17·692	4·2062	111·02	2·183

Results for aqueous magnesium sulphate solutions at 25° are given in Table I. Combination of the value $\Lambda_0(\text{Mg}^{\cdot\cdot}) = 53{\cdot}06$, given by Shedlovsky and Brown (*J. Amer. Chem. Soc.*, 1934, **56**, 1066), with Jenkins and Monk's value of $\Lambda_0(\text{SO}_4'') = 80{\cdot}00$ (*ibid.*, 1950, **72**, 2695) leads to the value $\Lambda_0 = 133{\cdot}06$ for the conductivity of magnesium sulphate at infinite dilution. The limiting Onsager equation for magnesium sulphate then becomes $\Lambda = 133{\cdot}06 - 242{\cdot}11I^{\frac{1}{2}}$, where I is the ionic strength. The results have been plotted in Fig. 3, and it can be seen that magnesium sulphate resembles other 2–2-valency type electrolytes in that the conductivities, even at high dilutions, show marked departure from the limiting Onsager slope. If these deviations are attributed to incomplete dissociation, then α, the degree of dissociation, may be calculated from the Onsager relation $\alpha = \Lambda/\{133{\cdot}06 - 342{\cdot}39(\alpha c)^{\frac{1}{2}}\}$, where c is the concentration in g.-equiv./l. Thermodynamic dissociation constants have been calculated for each point from the equation

$$\log K = -\text{p}K = \log\,[\alpha^2 c/2(1 - \alpha)] - 5{\cdot}760(\alpha c)^{\frac{1}{2}}$$

and are given in Table I. In this way the mean value pK = 2·21 ± 0·015 was obtained.

TABLE II.

	0·1 Molal glycine			0·25 Molal glycine			0·5 Molal glycine		
$c \times 10^4$	Λ	Corr.	$\Lambda_{\text{Corr.}}$	Λ	Corr.	$\Lambda_{\text{Corr.}}$	Λ	Corr.	$\Lambda_{\text{Corr.}}$
(A) *Conductivity of lanthanum ferricyanide in glycine–water mixtures.*									
2	130·60	0·34	130·94	128·61	0·73	129·34	125·03	0·87	125·90
3	123·59	0·27	123·86	122·69	0·50	123·19	120·41	0·70	121·11
4	118·05	0·23	118·28	117·98	0·41	118·39	116·72	0·61	117·33
5	113·63	0·20	113·83	114·10	0·35	114·45	113·65	0·44	114·09
6	110·00	0·18	110·18	110·87	0·31	111·18	110·85	0·39	111·24
7	106·84	0·17	107·01	108·06	0·28	108·34	108·52	0·36	108·88
8	104·14	0·16	104·30	105·52	0·25	105·77	106·46	0·33	106·79
9	101·80	0·15	101·95	—	—	—	104·48	0·30	104·78
10	99·64	0·14	99·78	—	—	—	102·67	0·28	102·95
(B) *Conductivity of magnesium sulphate in glycine–water mixtures.*									
2	123·86	0·20	124·06	120·20	0·26	120·46	115·35	0·52	115·87
3	122·10	0·17	122·27	118·82	0·21	119·03	114·22	0·44	114·66
4	120·65	0·14	120·79	117·66	0·19	117·85	113·25	0·38	113·63
5	119·35	0·13	119·48	116·65	0·17	116·82	112·40	0·34	112·74
6	118·23	0·12	118·35	115·71	0·15	115·86	111·62	0·31	111·93
7	117·21	0·11	117·32	114·86	0·14	115·00	110·92	0·29	111·21
8	116·30	0·10	116·40	114·07	0·14	114·21	110·25	0·27	110·52
9	115·44	0·10	115·54	113·33	0·13	113·46	109·63	0·26	109·89
10	114·64	0·09	114·73	112·61	0·12	112·73	109·04	0·24	109·28

(C) *Conductivity of more concentrated lanthanum ferricyanide solutions.*

0·1 Molal glycine				0·25 Molal glycine				0·5 Molal glycine			
$c \times 10^4$	Λ	Corr.	$\Lambda_{\text{Corr.}}$	$c \times 10^4$	Λ	Corr.	$\Lambda_{\text{Corr.}}$	$c \times 10^4$	Λ	Corr.	$\Lambda_{\text{Corr.}}$
22·197	84·05	0·09	84·14	21·024	87·44	0·20	87·64	25·088	87·49	0·23	87·72
33·744	76·30	0·07	76·37	30·606	80·60	0·16	80·76	35·177	81·83	0·19	82·02
36·023	75·22	0·07	75·29	37·449	77·19	0·15	77·34	41·889	78·96	0·18	79·14

(D) *Conductivity of magnesium sulphate in dioxan–water mixtures.*

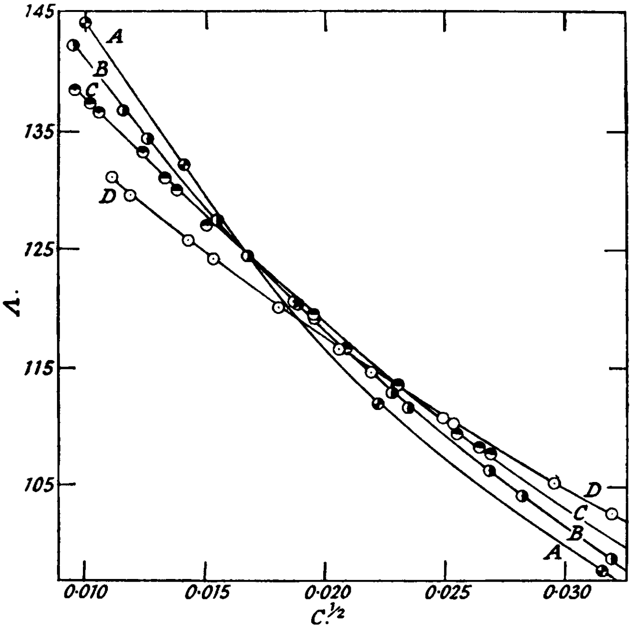
$c \times 10^4$	10% (w/w) dioxan, Λ	20% (w/w) dioxan, Λ	$c \times 10^4$	10% (w/w) dioxan, Λ	20% (w/w) dioxan, Λ	$c \times 10^4$	10% (w/w) dioxan, Λ	20% (w/w) dioxan, Λ
2	104·73	84·58	5	99·38	78·02	8	95·58	73·52
3	102·66	82·01	6	97·98	76·31	9	94·51	72·34
4	100·93	79·91	7	96·72	74·82	10	93·53	71·22

Owen and Gurry (*loc. cit.*) have stated that with aqueous zinc and copper sulphate solutions, values obtained for K were appreciably dependent upon the manner in which Λ was assumed to approach the limiting value. With the present results, calculation of α from Shedlovsky's equation (*J. Franklin Inst.*, 1938, **225**, 739), $\Lambda = \alpha\{\Lambda_0 - b(\Lambda/\Lambda_0)(\alpha c)^{\frac{1}{2}}\}$, gave a mean value of $pK = 2{\cdot}26_6 \pm 0{\cdot}007$. Where comparisons are made of dissociation constants obtained by consistent use of one extrapolation method, as in the present work, it seems unlikely that any marked error can be introduced by this slight dependency of K on the extrapolation method used.

Methods for the direct extrapolation of conductivity data for weak electrolytes have been put forward by Davies (*J.*, 1933, 645) and by Shedlovsky (*loc. cit.*). The Davies extrapolation gives $\Lambda_0 = 132{\cdot}9$; the Shedlovsky extrapolation is rather more nearly linear and leads to $\Lambda_0 = 132{\cdot}8$. Both are in good agreement with the "independent" value $\Lambda_0 = 133{\cdot}06$.

FIG. 1.

The conductivity of lanthanum ferricyanide in water and in glycine–water mixtures.



A. *Water (from data of Davies and James,* loc. cit.).
B. 0·1M-*Glycine solution.*
C. 0·25M-*Glycine solution.*
D. 0·5M-*Glycine solution.*

Mixed Solvents.—The results are given in Table II, interpolated values being given for the more dilute solutions, to save space.

A careful study of the solvent correction to be applied to conductivity data for unhydrolysed salts in glycine solutions has been made by Monk (*loc. cit.*), who concludes that a simple subtraction of the initial glycine solution conductivity represents the true solvent correction. Since the mobilities of solute ions are slightly lowered by the presence of solvent ions, a correction, $\Delta\Lambda$ is required for this interionic attraction effect (Davies, *Trans. Faraday Soc.*, 1929, **25**, 129), and has been calculated from $\Delta\Lambda = b\{(I + I_G)^{\frac{1}{2}} - I^{\frac{1}{2}}\}$, where b is the Onsager slope and I_G is the ionic strength of the glycine solution. Values for I_G were obtained from the pH's of the glycine solutions and the known ionisation constants of glycine, as described by Monk (*loc. cit.*), and the true ionic strength of the solute ions, I, was calculated by a method of successive approximations. Equivalent conductivities at infinite dilution and values for α, the degree of dissociation, were obtained by Davies's extrapolation method (*loc. cit.*), uncorrected conductivity values being used; approximate values for I could then be found. Conductivity corrections, $\Delta\Lambda$, were then calculated from the above equation, and the corrected conductivity values used to derive more accurate values for Δ_0, α, and I. Approximations were continued in this way until steady values for Λ_0, α, I, and $\Delta\Lambda$ were obtained. These corrections are given in Table II, and also the corrected conductivity values finally obtained.

The pH changes caused by addition of magnesium sulphate or lanthanum ferricyanide to glycine solutions were never greater than 0·05 pH unit, about the order to be expected as a result of the alteration in ionic strength.

FIG. 2.

The conductivity of magnesium sulphate in water, and in glycine–water mixtures.

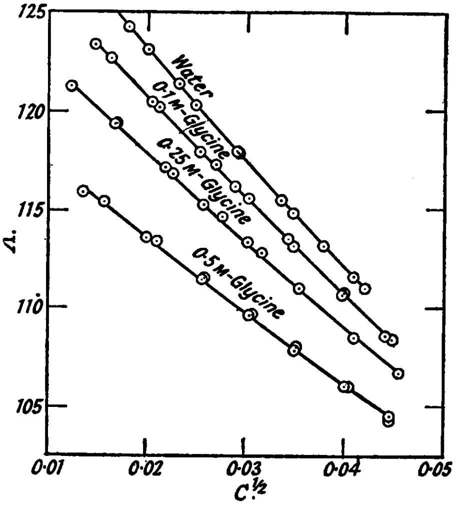
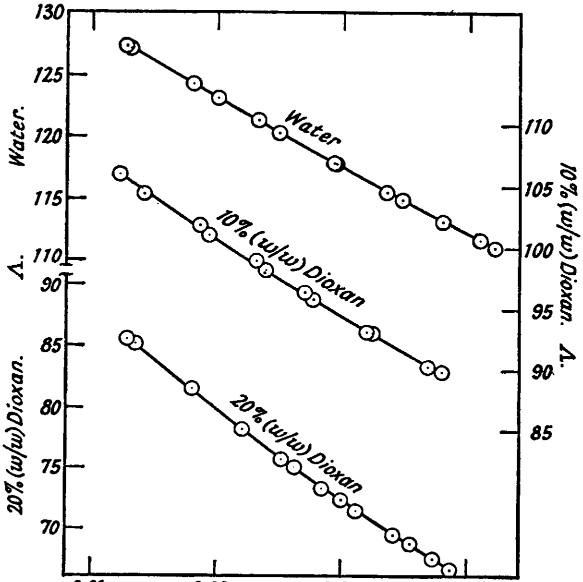


FIG. 3.

The conductivity of magnesium sulphate in water and in dioxan–water mixtures.



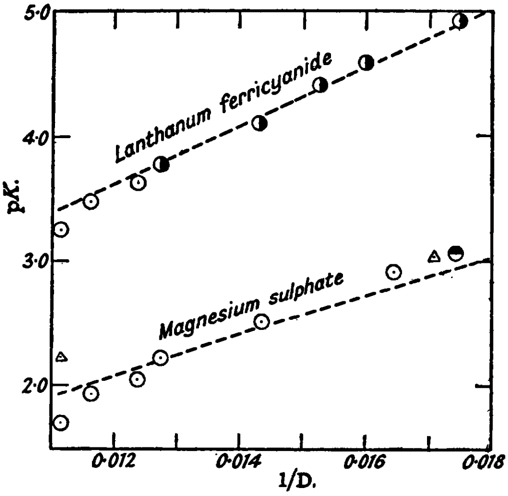
Results for lanthanum ferricyanide in glycine–water mixtures are shown in Fig. 1, together with the results in water given by Davies and James (*loc. cit.*). The curves show an interesting transposition in order with increasing salt concentration, probably as a result of the opposing influences of the viscosity and dielectric constant of the medium. At very low concentrations (<0·0004N.) the effect of viscosity predominates, and conductivities, in consequence, decrease with increasing glycine concentration (*i.e.*, with increase in viscosity). At higher concentrations ($>0{\cdot}0006$N.) the effect of the increase in dissociation, caused by increase in dielectric constant, becomes predominant and conductivities increase with increase in glycine concentration.

Results for magnesium sulphate in water, glycine–water, and dioxan–water mixtures are given in Figs. 2 and 3. The extent of ion association in salt solutions is, in general, proportional to the valency product of the ions concerned and is much smaller with the 2–2-valent magnesium sulphate than with the 3–3-valent lanthanum ferricyanide. In consequence, the curves for magnesium sulphate in glycine solutions do not intersect over the concentration range studied, the decrease in ionic mobilities caused by increasing solvent viscosity outweighing the effect of the increase in dissociation caused by dielectric constant increase. In dioxan–water mixtures, the effect of both viscosity and dielectric constant change is to cause the conductivity to decrease with increase in the dioxan concentration.

We have treated the above data by ascribing deviations from the limiting Onsager equation to ion association and applying the treatment given by Davies for incompletely dissociated electrolytes (*loc. cit.*). For each series of measurements, values of Λ_0 and α have been calculated, corrections, $\Delta\Lambda$, for the interionic attraction effect of the solvent ions on the solute conductivity being derived simultaneously, as described on p. 2927. Thermodynamic dissociation constants have been calculated for each point from the equations

FIG. 4.

Variation of dissociation constant with dielectric constant in mixed solvents.



⊙ *Present work.*
◑ *Davies and James* (loc. cit.), *James* (loc. cit.).
● *James* (*unpublished work*).
△ *Mason and Shutt* (loc. cit.), *from dielectric-constant data.*

The broken curves have been calculated from the Bjerrum equation, on the assumption of a = 7·20 Å *for lanthanum ferricyanide, and* a = 5·06 Å *for magnesium sulphate, in water.*

$$\log K = \log\,[\alpha^2c/3(1-\alpha)] + \log f_\pm{}^2 \text{ for lanthanum ferricyanide}$$

and

$$\log K = \log\,[\alpha^2c/2(1-\alpha)] + \log f_\pm{}^2 \text{ for magnesium sulphate}$$

where c is the concentration in g.-equivs./litre. Values for $f_\pm$, the mean ionic activity coefficient, were calculated from the limiting Debye–Hückel equation. The mean dissociation constant values obtained are expressed as pK's in Table III, together with related data for the mixed solvents, and in Fig. 4, pK's have been plotted against reciprocal dielectric constants, D^{-1}. Data for lanthanum ferricyanide in dioxan–water mixtures (James, *J.*, 1950, 1094) have also been plotted, for comparison.

Mason and Shutt (*Proc. Roy. Soc.*, 1940, A, **175**, 234) have determined the dielectric constants of dilute solutions of magnesium sulphate in dioxan–water and urea–water solutions at 20°, and have calculated ion-pair dissociation constants from these measurements. Their results in dioxan–water are in good agreement with ours, where comparison is possible (see Fig. 4),

TABLE III.

Solvent	D	$10^3\eta$	Magnesium sulphate Λ_0	$\Lambda_0\eta$	pK	Lanthanum ferricyanide Λ_0	$\Lambda_0\eta$	pK
0·5 Molal glycine ...	89·78	9·49	119·9	1·138	1·699	144·7	1·373	3·252
0·25 „ ...	86·08	9·21	125·4	1·155	1·938	154·6	1·424	3·473
0·1 „ ...	80·80	9·05	129·2	1·169	2·054	161·9	1·465	3·621
Water	78·54	8·949	133·06	1·191	2·211	168·9	1·511	3·740
10% (w/w) Dioxan...	69·75	10·9	111·9	1·220	2·512	—	—	—
20% (w/w) Dioxan...	60·79	12·9	9·39	1·213	2·906	—	—	—

but their pK values in urea–water solutions appear to be considerably higher than our values in glycine–water solutions.

Assuming that forces between oppositely charged ions obey the simple Coulomb law, Bjerrum (*loc. cit.*) has shown that the equilibrium constant for an ion-pair should be given by

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{|z_1z_2|\varepsilon^2}{DkT}\right)^3 . Q(b)$$

where $Q(b)$ is defined by the integral $Q(b) = \int_2^b e^y y^{-4} . dy$, in which $y = |z_1z_2|\varepsilon^2/rDkT$, $b = |z_1z_2|\varepsilon^2/aDkT$, and a is the distance of closest approach of the ions. Values of $Q(b)$ have been tabulated by Bjerrum (*loc. cit.*) for the range $2 \leqslant b \leqslant 15$ and by Fuoss and Kraus (*J. Amer. Chem. Soc.*, 1933, **55**, 1019) for $15 \leqslant b \leqslant 80$. In water, at 25°, we have for magnesium sulphate, pK = 2·21, and for lanthanum ferricyanide, pK = 3·740 (Davies and James, *loc. cit.*). On substitution of these values into the above equation, the " Bjerrum distances," a, are found to be 5·06 Å and 7·20 Å, respectively. These values being assumed to remain unchanged, the variation of K with D predicted by the Bjerrum equation has been calculated, and is shown by the dashed curves in Fig. 4. Agreement with experimental results is good and there can be little doubt that, over the dielectric-constant range studied, the extent of hydration remains substantially unchanged, and that the observed increase in extent of dissociation with increase in dielectric constant can satisfactorily be accounted for on a simple Coulomb's law basis.

TABLE IV.

Lanthanum ferricyanide

Solvent	Radii of ion-pairs (Å) Bjerrum equation	Stokes law
0·5 Molal glycine	8·32	7·39
0·25 „	7·42	7·12
0·1 „	7·52	6·92
Water	7·20	6·67
* 9·67% (w/w) Dioxan	7·17	6·80
* 14·84 „	7·08	6·58
* 18·08 „	7·08	6·51
* 24·07 „	7·19	6·67

Magnesium sulphate

Solvent	Radii of ion-pairs (Å) Bjerrum equation	Stokes law
0·5 Molal glycine	7·24	6·01
0·25 „	5·79	5·92
0·1 „	5·85	5·85
Water	5·06	5·75
10% (w/w) Dioxan	4·84	5·60
20% „	4·53	5·64

* From James's data (*J.*, 1950, 1094).

It is generally assumed that Stokes's law is applicable to the movement of large spherical ions, and that such an ion, of radius r and valency z, acted upon by an electric force $Xz\varepsilon$, would be maintained at a velocity $v = Xz\varepsilon/6\pi\eta r$ in a homogeneous medium of viscosity η. In terms of the limiting ionic mobility, Λ_{i0}, at 25°, this equation becomes $r = 8{\cdot}197 \times 10^{-9}z/\Lambda_{i0}\eta$ (Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, p. 184). With a solvated ion it seems probable that the ion and its attached solvent molecules move as a single entity under an applied electric field and that Stokes's law gives a direct measure of primary ionic solvation (Bockris, *Quart. Reviews*, 1949, III, 173). In Table IV, values for the mean diameters, a, of ion-pairs have been obtained by addition of cationic and anionic radii derived from the above equation, it being assumed that the transport numbers of the ions do not change with change in the solvent. Values for a calculated from the Bjerrum equation are given for comparison; agreement between the two methods is very reasonable. An appreciable increase in a occurs in glycine–water solutions, possibly because of solvation by glycine. In dioxan–water mixtures it is probable that water dipoles alone solvate the ions and that dioxan molecules, with their large size and relatively small dipole moment, do not enter the ionic solvation sheaths in the mixed solvents studied.

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