

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Solubility of Potassium Iodate and Zinc Iodate in Dioxane-Water Mixtures; Effect of Sorting of Solvent Molecules

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In the further study of the relationship between the solubility of electrolytes and the dielectric constant of the medium, measurements have been made of the solubilities of potassium iodate and zinc iodate in dioxane-water mixtures at 25° over the complete range of concentrations from 0 to 100% dioxane at intervals of 10% by weight; the measurements thus extend over a dielectric range from 2.10 to 78.55. The results have been used to test the empirical relation between the solubility of slightly soluble electrolytes and the dielectric constant of the solvent, previously reported by Ricci and Davis.¹ An attempt has also been made to estimate the mean ionic radius of these salts by using the Debye expression for the distribution of solvent molecules in a dielectric mixture around ions,² in conjunction with the fundamental Born equation relating electrolyte solubility, ionic radius and dielectric constant.³

Materials.—A c. p. grade of potassium iodate was used both for the solubility determinations and for the standardization of the silver nitrate solution used in the analyses.

The zinc iodate was prepared by mixing dilute solutions of sodium iodate and zinc nitrate in stoichiometric proportions. The solutions were poured slowly into a large beaker with constant mechanical stirring. The zinc iodate was obtained by evaporating some of the liquid, filtering, washing and drying at 100°. Volumetric analysis by the method described below gave a value of 99.3% Zn(IO₃)₂; the additional 0.7% probably represented water not readily driven off by heat without decomposition of the salt.

The dioxane was purified and its purity verified as described in similar investigations.⁴

Solubility Determinations and Analysis.—Mixtures of dioxane and water, prepared in the desired proportions by direct weighing, were stirred with excess of the salt, in 250-ml. glass-stoppered Pyrex bottles. To avoid the introduction of foreign matter into the solutions, vaseline was omitted entirely in stoppering the tubes containing solvents of high dioxane ratio. Sufficient time (two to seven days) was allowed for the attainment of equilibrium, which was verified by determining every solubility from both under- and super-saturation.

For the analysis of the saturated solutions, gravimetric methods were first tried, but discarded. Precipitation and weighing of the iodate as the silver or lead salt from solutions containing zinc ion, gave low results, possibly be-

cause of co-precipitation of zinc iodate. Iodometric titration also was discarded because of the difficulty involved in removing the interfering dioxane. Precipitation of barium iodate followed by iodometric titration of the washed precipitate also gave low results. The method finally used involved reduction of iodate to iodide by sodium bisulfite, the excess of reagent being removed by acidification and boiling with dilute sulfuric acid. Except in high dioxane solvents (> 77% for potassium iodate, > 40% for zinc iodate), in which the solubilities are very low, the resulting iodide solution was then analyzed volumetrically, at a pH of 9-10, by titration with standard silver nitrate, with eosin as indicator. An appropriate blank was calculated from a series of standardizations against pure potassium iodate similarly treated. For the very low solubilities the iodide was determined gravimetrically as silver iodide; the relative precision of some of these results is very low compared to the volumetric determinations.

Although the literature reports a di-hydrate of zinc iodate,⁵ the solid phase in the present experiments was apparently the anhydrous salt. The solid residue from several of the solubility determinations was analyzed after filtration and centrifuging, giving an average of 99.3% Zn(IO₃)₂, ranging between 99.0 and 99.5%. KIO₃ is known to form no hydrates, and no analysis was made of this salt as solid phase.

The results of the solubility determinations are given in Table I; each value is the average of at least one determination from each direction of approach to equilibrium. In the iodometric determinations the agreement between such values was about 2/1000 for potassium iodate and 6-7/1000 for zinc iodate. The gravimetric determinations were less precise. The necessary densities required for the calculation of molarities from weight percentages were

TABLE I
SOLUBILITY OF POTASSIUM IODATE AND ZINC IODATE IN
DIOXANE-WATER MIXTURES, AT 25°

Wt. % dioxane	Dielectric constant	KIO ₃		Zn(IO ₃) ₂	
		Wt. %	Moles/l.	Wt. %	Moles/l.
0	78.55	8.472	0.4238	0.6410	0.01548
10	69.71	5.300	.2598	.3746	.00910
20	60.81	3.172	.1531	.2301	.00562
30	51.91	1.815	.08770	.1158	.00285
40	43.00	0.8855	.04273	.0572	.00142
50	34.28	.4712	.02277	.0244	.000605
60	25.86	.1350	.00653	.0090	.00022
70	17.70	.0384	.00186	.0030	.000075
80	10.72	.0060	.00029	.0017	.000042
90	5.61	.0012	.000059	.0008	.000019
100	2.101	.0000	.00000	.0000	.00000

(1) J. E. Ricci and T. W. Davis, *THIS JOURNAL*, **62**, 407 (1940).(2) P. Debye, *Z. physik. Chem.*, Cohen Festband, 56 (1927).(3) M. Born, *Z. Physik*, **1**, 45 (1920).(4) T. W. Davis and J. E. Ricci with C. G. Sauter, *THIS JOURNAL*, **61**, 3274 (1939).(5) Mylius and Funk, *Ber.*, **30**, 1723 (1897).(6) All information concerning the dielectric constant of dioxane-water mixtures is taken from the measurements of G. Akarlot and O. A. Short, *THIS JOURNAL*, **58**, 1241 (1936).

determined by weighing appropriate filtered samples of the solutions delivered from calibrated pipets.

On the Rule of Constant Activity Coefficient.

—The results have first of all been used in testing further the empirical rule of constant activity coefficient for the calculation of solubilities.¹ It has been noted in many cases that the activity coefficient of a slightly soluble electrolyte in its pure saturated solution is practically constant, independent of the dielectric constant of the medium. Hogge and Garrett⁷ have recently reported such behavior for thallos chloride in alcohol–water mixtures up to 60% alcohol, and the same has also been observed for silver acetate in dioxane–water mixtures up to 50% dioxane.⁸ This rule of constant activity coefficient for an electrolyte at saturation, which is here being tested again, is still purely empirical. Although an analogy with the behavior of weakly solvated sols has been pointed out by W. Ostwald,⁹ a theoretical explanation of this rough constancy has not yet been found. Ostwald had noted, for weakly lyophilic sols such as arsenous sulfide, that the activity coefficient of electrolytes at concentrations causing coagulation is independent of the type of electrolyte and of the dielectric constant of the solvent.¹⁰

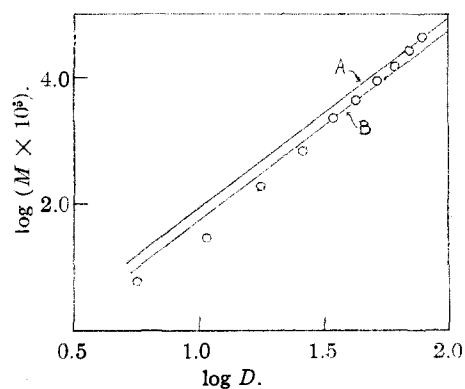


Fig. 1.—Solubility of potassium iodate in dioxane–water mixtures at 25°: A represents eq. 1, with 0% dioxane as reference; B, with 50% dioxane as reference.

As has already been shown,¹ the assumption of such constancy of the activity coefficient offers a simple way of predicting at least approximately the solubility, S_2 , in any medium of dielectric constant D_2 , from the solubility, S_1 , in a reference medium of dielectric constant D_1 , inasmuch as

by the application of the Debye–Hückel limiting law, it follows that

$$\log S_2 = \log S_1 + 3 (\log D_2 - \log D_1) \quad (1)$$

According to this equation the solubility in a series of media of varying dielectric will be given, on a plot of $\log M$ vs. $\log D$, by a straight line with a slope of +3 and passing through whichever point is taken as the reference solubility. Figure 1 represents the observed solubilities for potassium iodate in the dioxane–water mixtures as compared with the straight line expected according to equation (1): A, with the solubility in pure water as reference; B, with that in 50% dioxane as reference. On either basis, solubilities in the various media may be calculated and compared with the observed, the ratios of calculated to observed solubilities being summarized for both salts in Table II. The agreement is satisfactory at least as to the order of magnitude, and is about the same for both the valence types involved and despite a great difference in the actual solubilities of the two salts; the calculation furthermore is independent of any knowledge of ionic diameters necessary for the application of the theoretical equation of Born. The largest deviations in Table II are for zinc iodate in very high dioxane solvents, where, it must be pointed out, the experimental error is probably great. The best straight line drawn through the data for potassium iodate has a slope of about 3.5 as compared to 3 as required by the equation; the zinc iodate points likewise best fit a straight line with a slope of ~ 3.5 .

TABLE II
TEST OF EQ. (1): RATIO OF CALCULATED TO OBSERVED SOLUBILITIES; A WITH PURE WATER, B WITH 50% DIOXANE, AS REFERENCE

Wt. % dioxane	KIO ₃		Zn(IO ₃) ₂	
	A	B	A	B
0	..	0.7	..	0.5
10	1.1	.7	1.2	.6
20	1.3	.8	1.3	.6
30	1.4	.9	1.6	.7
40	1.6	1.1	1.8	.8
50	1.5	..	2.1	..
60	2.3	1.6	2.5	1.2
70	2.6	1.4	2.4	1.1
80	3.6	2.3	0.9	0.4
90	2.6	1.7	.3	.1

This at least approximate linearity between $\log M$ and $\log D$ indicates at once that the usual Born equation, requiring a linear relation between $\log M$ and $1/D$, must fail. Furthermore, it is interesting to note that because of a substantially

(7) E. Hogge and A. B. Garrett, *THIS JOURNAL*, **63**, 1089 (1941).

(8) J. E. Ricci and A. R. Leo, *J. Phys. Chem.*, **45**, 1096 (1941).

(9) W. Ostwald, *Koll. Z.*, **94**, 169 (1941).

(10) W. Ostwald, *J. Phys. Chem.*, **42**, 981 (1938); cf. refs. 8 and 9 for other references.

linear relation between $\log D$ and mole fraction of water in the solvents, the solubilities as $\log M$ are also related roughly linearly to mole fraction of water. These relations are shown simultaneously in Fig. 2, where the linearity is seen quite clearly if the points in almost pure dioxane, in which the determinations are themselves somewhat doubtful, are disregarded. The slopes of these curves (~ 7) are again the same for the two salts.

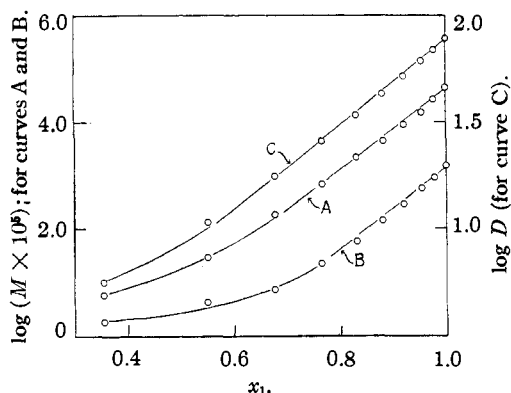


Fig. 2.—Relation between $\log M$, $\log D$, and x_1 , mole fraction of water in dioxane-water solvents: A, KIO_3 ; B, $\text{Zn}(\text{IO}_3)_2$.

The Born Equation.—In Fig. 3 the results are plotted in accordance with the usual Born equation

$$\log S_1/S_2 = \frac{0.4343 N e^2 z_+ z_-}{a R T} \left(\frac{1}{D_2} - \frac{1}{D_1} \right) \quad (2)$$

in which the change of solubility depends upon the ionic diameter, a ; the symbols N , e , z , R , T have their usual meaning. The theoretical limiting slopes have been calculated with 2.5 \AA . as a probable value of a for both salts, by analogy with similar electrolytes such as barium iodate⁴ and iodic acid,¹¹ giving slopes of 97 and 194 for potassium iodate and zinc iodate, respectively. It is again seen that except in very low dioxane solvents, the Born formula predicts solubilities in general far too low. Actually, the limiting slope for the potassium iodate data, as plotted on Fig. 3, corresponds to a value of only $\sim 1.9 \text{ \AA}$. for the diameter a .

Correction for Solvent Segregation around Ions.—Since the simple Born equation as just used assumes media of uniform dielectric constant, it should be possible to explain part of the discrepancy between observed and calculated solubilities in these cases by taking into account the non-uniformity of the dielectric constant in the

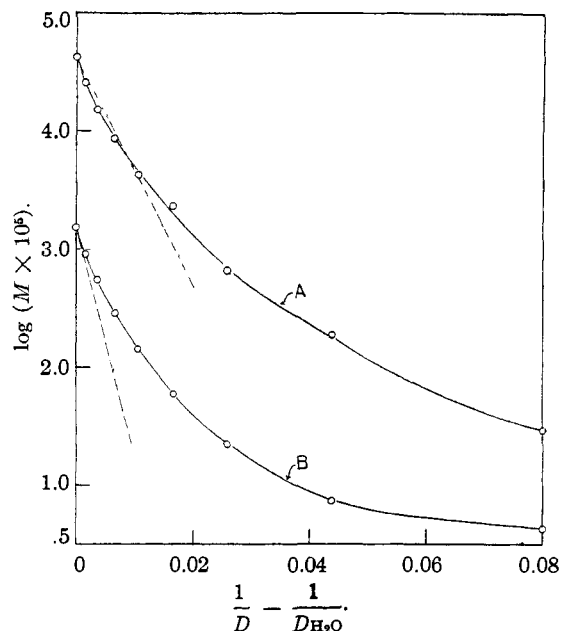


Fig. 3.—Observed solubilities compared with predictions of eq. 2: A, KIO_3 ; B, $\text{Zn}(\text{IO}_3)_2$.

vicinity of charged ions in media consisting of two solvents. We have, therefore, attempted to apply Debye's original treatment² for the calculation of this sorting or selective concentration of the more polar solvent by ions in mixed solvents, in order to see to what extent this factor might account for the deviation from the simple Born equation, and in order to derive, if possible, by means of this treatment, following the suggestion of Dunning and Shutt,¹² a value for the mean ionic radius of the electrolytes involved, since Debye's equation requires the sorting of the solvent molecules to be a function of the radial distance from the center of the ion.

According to Debye, this distribution of the two components of a mixed solvent (component 1 having the higher dielectric constant) is given as a function of the ionic charge, the distance from the ion and certain properties of the binary mixture, by the following equation, which we shall call the Debye equation

$$r^4 \left(\frac{\bar{v}_2}{\bar{v}_1} \ln \frac{x_1}{x_1^0} - \ln \frac{x_2}{x_2^0} \right) = \frac{e^2 z_i^2}{8\pi R T D^2} \left(\frac{\bar{v}_2}{\bar{v}_1} \frac{dD}{dc_1} - \frac{\delta D}{\delta c_2} \right) \quad (3)$$

The subscripts refer to the two components of the mixed solvent; the quantities x_1 , x_2 , \bar{v}_1 , \bar{v}_2 and D are values of mole fraction, partial molal volumes and dielectric constant, at the distance r from the center of the ion of valence z_i ; x_1^0 and x_2^0 are the

(11) S. Naidich and J. E. Ricci, *THIS JOURNAL*, **61**, 3268 (1939).

(12) W. J. Dunning and W. J. Shutt, *Trans. Faraday Soc.*, **34**, 1192 (1938).

over-all mole fractions, or x at $r = \infty$; c_1 and c_2 , moles of each component per cc. of the mixture.

Since the distribution of dielectric will not be the same in two different mixtures of two solvents, it will be necessary to calculate this distribution and from it to calculate the corresponding value of the free energy change between a solvent of uniform dielectric (H_2O as reference, for example) and a mixed solvent of varying dielectric (or with D as $f(r)$), and if necessary, for each separate ion, inasmuch as this distribution varies with the valence of the ion.

A simplified form of this equation is suggested by Scatchard,¹³ for cases in which $d(1/D)/dc_2 = a$ constant, K , when it follows that

$$r^4 \left(\frac{\bar{v}_2}{\bar{v}_1} \ln \frac{x_1}{x_2} - \ln \frac{x_2}{x_1} \right) = \frac{e^2 z_+ z_- K}{8\pi RT} \quad (4)$$

As seen in Fig. 4, this constancy holds only very roughly and for low concentrations of dioxane, in the present system.

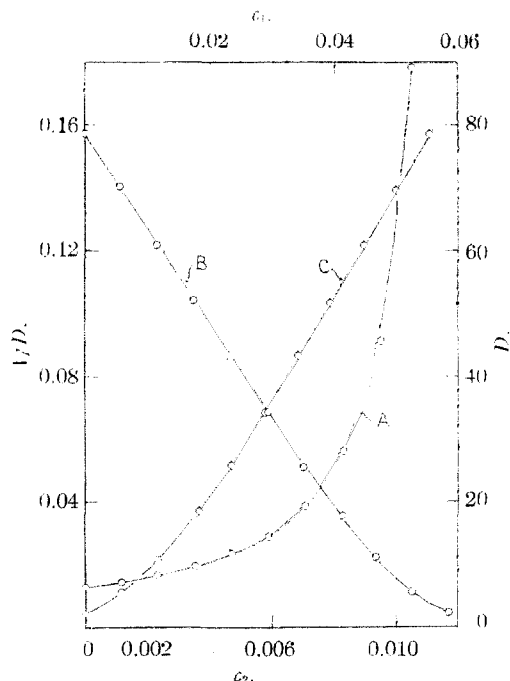


Fig. 4.—Variation of D and of $1/D$ with respect to moles of component per cc., in dioxane-water system: A, $1/D$ with c_2 , moles of dioxane per cc.; B, D with c_2 ; C, D with c_1 , moles of water per cc.

It is, therefore, necessary to use the original Debye equation, for which, fortunately, it is found that the derivatives dD/dc_1 , and dD/dc_2 are quite constant, up to 60% dioxane, as seen in Fig.

(13) G. Scatchard, *J. Chem. Phys.*, **9**, 34 (1941).

4; they have the values + 1656 and -7550, respectively, for mixtures from 0 to 60% dioxane.

The data for the physical properties of the system water-dioxane required for Fig. 4 and for the use of eq. (3) were taken from the literature.¹⁴ The distribution (r for various values of x_1 and x_2 and hence D as a function of r) was calculated for a univalent ion ($z_i = 1$), in three chosen mixtures of dioxane and water, namely, the 20, 50 and 80% dioxane mixtures (see Table III).

The curve for the distribution around a univalent ion in 50% dioxane is shown in Fig. 5 (curve A), together, for comparison, with the curves, B, for the value of $(1/Dr^2)$ around such an ion in pure water, *i. e.*, a uniform medium with a constant value of $D = 78.55$, and C, for that in a uniform medium with $D = 34.28$, the over-all limiting value of the dielectric constant in the 50% mixture.

TABLE III

SOLVENT SEGREGATION IN WATER-DIOXANE MIXTURES AROUND UNIVALENT IONS, CALCULATED THROUGH EQ. (3)

% Dioxane	$r, \text{\AA}$	$10^4/Dr^2$	$r, \text{\AA}$	$10^4/Dr^2$	$r, \text{\AA}$	$10^4/Dr^2$
0.00001	1.79	39.7	1.70	43.8	1.63	49.6
0.0001	1.94	34.0	1.81	38.8	1.68	45.1
0.001	2.17	27.1	1.97	32.9	1.79	40.1
0.005	2.50	21.0	2.16	28.0		
0.01	2.76	17.6	2.29	25.6	1.98	34.3
0.02	3.27	13.3				
0.03	3.93	9.69				
0.04	5.19	5.79				
0.0425	6.05	4.38				
0.0450	9.77	1.71				
0.04667	∞	0				
(= x_2^0 , 20% D)						
0.05			3.02	18.2	2.38	29.1
0.10			4.08	12.7	2.78	26.1
0.15			6.44	6.43		
0.16			7.86	4.52		
0.165			9.49	3.17		
0.169			14.60	1.36		
0.1699			∞	0		
(= x_2^0 , 50% D)						
0.2					3.94	21.4
0.3					5.54	16.6
0.4					8.81	9.79
0.42					10.40	7.61
0.44					14.23	4.41
0.45					∞	0
(= x_2^0 , 80% D)						

Considering separate ions (z_+ and z_-) and separate media (D_1 and D_2), the Born equation may be written as follows

(14) Dielectric constant from ref. 6; densities and partial molal volumes from H. Hovorka, R. A. Schaefer and D. Dreisbach, *THIS JOURNAL*, **53**, 2264 (1926); **53**, 2753 (1927).

$$\ln \left(\frac{S_1}{S_2} \right) = \frac{Ne^2}{(\nu_+ + \nu_-)2RT} \left(\int_{r_i}^{\infty} \frac{\nu_+ z_+^2 dr}{D_2 r^2} + \int_{r_i}^{\infty} \frac{\nu_- z_-^2 dr}{D_2 r^2} - \int_{r_i}^{\infty} \frac{\nu_+ z_+^2 dr}{D_1 r^2} - \int_{r_i}^{\infty} \frac{\nu_- z_-^2 dr}{D_1 r^2} \right) \quad (5)$$

Here ν_+ and ν_- are the number of positive and negative ions formed from the molecule of the electrolyte and r_i is the effective ionic radius of each ion in each medium.

If $D_2 = f(r)$ from r_i to r_0 and is practically equal to the over-all D_2 at $r = r_0$, and if D_1 is independent of r , as is assumed to be the case with water as the reference medium, we then have, for a 1:1 electrolyte, in which the distribution of D in a mixture is the same for both ions

$$\ln(S_1/S_2) = \frac{Ne^2}{2RT} \left(\int_{r_i}^{r_0} \frac{dr}{D_2 r^2} + \int_{r_0}^{\infty} \frac{dr}{D_2 r^2} - \int_{r_i}^{\infty} \frac{dr}{D_1 r^2} \right) \quad (6)$$

and for a 2:1 or 1:2 electrolyte

$$\ln(S_1/S_2) = \frac{Ne^2}{2RT} \left[\frac{4}{3} \left(\int_{r_{i(\pm 2)}}^{r_0} \frac{dr}{D_2 r^2} + \int_{r_{0(\pm 2)}}^{\infty} \frac{dr}{D_2 r^2} - \int_{r_{i(\pm 2)}}^{\infty} \frac{dr}{D_1 r^2} \right) + \frac{2}{3} \left(\int_{r_{i(\pm 1)}}^{r_0} \frac{dr}{D_2 r^2} + \int_{r_{0(\pm 1)}}^{\infty} \frac{dr}{D_2 r^2} - \int_{r_{i(\pm 1)}}^{\infty} \frac{dr}{D_1 r^2} \right) \right] \quad (7)$$

In equations (6) and (7), the integrals $\int_{r_i}^{r_0} \frac{dr}{D_2 r^2}$ are to be evaluated graphically in each case from the area below the curve of $1/D_2 r^2$ against r , as plotted in Fig. 5. The limits, r_i and r_0 , are taken in each case as those values of r where $1/D_2 r^2$ approaches the limit of the corresponding value for H_2O , at the same r , (r_i), and where $1/D_2 r^2$ approaches the limit of the corresponding value for 20% or 50% dioxane (r_0). The values of these integrals together with the limits used in their graphical evaluation, are shown in Table IV.

TABLE IV
VALUES REQUIRED IN EQS. (6) AND (7)

Mixture, %	z_i	r_i	r_0	$10^4 \int_{r_i}^{r_0} \frac{dr}{D_2 r^2}$
20	1	2	9	55.7
	2	3	7.5	27.9
50	1	2	8	70.3
	2	2.5	10	52.2
80	1	1.75	14	167.2
	2	2.5	20	119.0

The calculations for the case of $z_i = 2$ are simplified by noting that for fixed values of x_1 and x_2 , and hence of D , in a given solvent mixture, the corresponding radial distances, $r_{(2)}$ and $r_{(1)}$, from the centers of divalent and univalent ions, respectively, are related as follows

$$r_{(2)} = 2r_{(1)}; \text{ whence} \quad (8a)$$

$$1/Dr_{(2)}^2 = (1/2) 1/Dr_{(1)}^2; \text{ and} \quad (8b)$$

$$\int \frac{dr}{Dr_{(2)}^2} = \frac{1}{2} \int \frac{dr}{Dr_{(1)}^2} \quad (8c)$$

in which the integration is performed up to the same value of x_2 or of D .

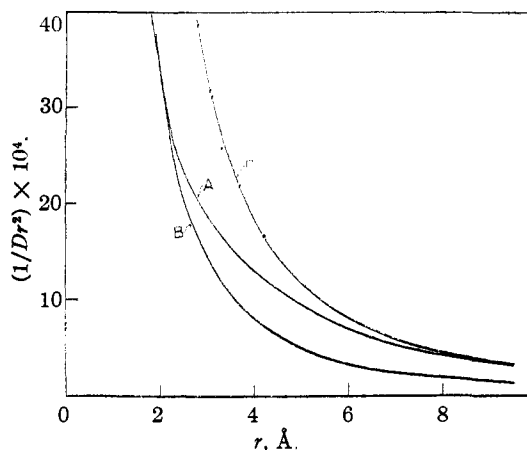


Fig. 5.—Solvent distribution in 50% dioxane-water, around univalent ions: Curve A, calculated from Table III; B, for uniform $D = 78.55$, as in pure water; C, for uniform $D = 34.28$, as in 50% dioxane-water.

The values of $\log S_1/S_2$ then calculated through equations (6) and (7) are shown in Table V. These values refer to 25°, with water as the first medium, ($D_1 = 78.55$ and assumed uniform throughout).

TABLE V RESULTS CALCULATED BY EQS. (6) AND (7)		
Mixture, %	Electrolyte type	Log (S_1/S_2)
20	1/1	0.125
	1/2	.203
50	1/1	.521
	1/2	.839
80	1/1	1.95
	1/2	3.15

Before testing these calculated ratios on the observed solubilities, it must be pointed out that the Born equation refers theoretically to solubilities in zero ionic strength, μ ; comparisons of actual solubilities simply neglect inter-ionic effects. The solubilities have therefore all been corrected to $\mu = 0$, by means of the usual Debye-Hückel expression

$$\log S_{\mu=0} = \log S - \frac{(352.6/D^{1/2})\mu^{1/2}}{1 + (2.914 a/D^{1/2})\mu^{1/2}} \quad (9)$$

and using the values of a cited above in connection with equation (2). The results of these corrections and of the application of the ratios of Table V, are shown in Table VI. The solubilities of the salts silver acetate, silver sulfate and barium

iodate, in dioxane-water mixtures, are taken from ref. 4. The third column in this table, "Obs." $S_{\mu=0}$, lists the actual solubilities as corrected to $\mu = 0$ through eq. (9). Column 4 lists the corresponding solubilities, also at $\mu = 0$, calculated in each case from the limiting aqueous solubility through the ratios of Table V. Column 5 shows that with the exception of the 1:2 electrolytes in very high dioxane solvents, the solubilities thus calculated are distinctly too high, whereas (column 6) solubilities calculated through the uncorrected Born equation (equation 2) are in better agreement with observation in the 20% mixture, but distinctly low in higher dioxane ratios, as may be seen of course from Fig. 3.

TABLE VI
TEST OF THE CALCULATED RATIOS OF TABLE V

Salt	Solvent, % di- oxane	"Obs." $S_{\mu=0}$ moles/l.	Calcd. $S_{\mu=0}$	Ratio Calcd./ "Obs."	Ratio, Born - Calcd./ "Obs."
KIO ₃	0	0.2590			
	20	.0937	0.194	2.1	1.2
	50	.0136	.0780	5.7	0.48
	80	.00020	.0029	14.5	.042
Ag ₂ C ₂ H ₃ O ₂	0	.0531			
	20	.0282	.0398	1.4	1.1
	50	.00623	.0160	2.6	.76
	80	.00036	.00060	1.7	.0011
Ag ₂ SO ₄	0	.0157			
	20	.00516	.00984	1.9	.54
	50	.000433	.00228	5.2	.017
	80	.000016	.000011	0.7	.0136
Zn(IO ₃) ₂	0	.01010			
	20	.00378	.00634	1.7	.51
	50	.000436	.00147	3.4	.014
	80	.000025	.0571	0.3	.0131
Ba(IO ₃) ₂ ·H ₂ O	0	.03729			
	20	.03230	.000457	2.0	.60
	50	.04258	.000106	4.1	.018
	80	.0560	.0652	0.1	.0137

The value of $\log (S_1/S_2)$ according to the simple Born equation, without taking into consideration the dielectric distribution resulting from solvent segregation, is proportional to the area in Fig. 5 between curves B and C, while according to the modified equation (6 and 7) $\log S_1/S_2$ is measured by the smaller area between the water-curve B and the curve A for the actual mixture. The correction is therefore seen to be in the right direction, increasing the calculated solubilities in low dielectric mixtures. But it was expected that this correction would account for only part of the discrepancy noted in the last column of Table VI and Fig. 3, inasmuch as it seems that still another factor would tend to increase the solubility over that calculated on the ionic basis, namely, the association of ions in low dielectric solvents. The present calculations, however, show a distinct

and rather large over-correction. The apparent agreement obtained in the case of the 1:2 electrolytes in very high (80%) dioxane solvents, resulting from the lower and hence "better" calculated solubilities for these cases, must evidently be attributed to the strong influence here of ion association, because of which the observed total or analytical solubilities should always be greater than the ionic concentrations calculated theoretically.

This general over-correction means that the area between curves A and B of Fig. 5 is too small. One purpose of these calculations was to estimate if possible the effective value of r_i required to change this area in order to reproduce the observed value of $\log S_1/S_2$ between 0 and 20% dioxane, and, furthermore, by repeating the process for the ratio between 0 and 50% dioxane, to test the constancy of such a radius in media of varying dielectric. Such an application of the Debye equation, no. 3, was in fact made by Dunning and Shutt¹² to the solubility of silver chloride in water and in 1 *M* aqueous urea. Although they were able to derive thereby a value for the mean ionic radius of silver chloride in good agreement with crystallographic data, the applicability of the equation to the case of a mixture consisting of two solvents in which the second component (urea) has the higher dielectric constant, has been questioned by Scatchard.¹³ In the present case, however, it is obviously impossible to find a value of r_i satisfying the observed ratio of solubilities. At $r = 2-2.5$ Å. (the limit from which the integration is made), the curve for the mixture (curve A, Fig. 5) is already indistinguishable from that for pure water, both for the 20 and for the 50% solvents, so that the area between the curves cannot be extended by assuming smaller values of r_i ; any larger value for r_i of course increases the over-correction by decreasing this area. We thus meet with two unexpected results: (1) the application of the Debye equation for the distribution of molecules of a mixed solvent around charged particles leads to calculated effects distinctly greater than the observed excess of solubility above the simple Born equation; (2) it is apparently impossible to estimate the "ionic radius" by this method, inasmuch as the actual ion appears to be so intensively selectively solvated by the more polar solvent, that it may be said that the concept of effective ionic radius here loses its meaning.

The first of these results is somewhat surprising inasmuch as it had been believed that the correction would account for only part of the actual discrepancy. The most probable defect in the Debye treatment is the neglect of the discrete structure of the mixed solvent.^{13,15} The corpuscular or discontinuous nature of the mixture probably demands a statistical treatment taking into account the actual size, shape and polar properties of the solvent molecules. The other factor explicitly neglected by Debye is the electrostriction or dielectric saturation of the solvent molecules attached to ions. The magnitude of this effect is difficult to estimate¹³ but may be appreciable.¹⁶ It would seem, however, that such an effect, like the Debye segregation effect itself, would contribute further to the similarity in the dielectric properties of the medium immediately surrounding the ions, in a series of mixtures of two solvents. It would consequently lead, probably, as does the present calculation of the Debye effect, to the prediction of still smaller changes in solubility between one mixture and another, and thus increase rather than cancel the over-correction.

Concerning the second result, it is of interest to note a similarity between the results of the Born equation when corrected for the non-uniformity of mixed solvents and the empirical relation of Ricci and Davis.¹ In both cases the solubility in other media may be predicted from the solubility in water or in some reference medium without previous knowledge of the always uncertain quantity, ionic diameter. It is obvious that variation of r_i between 1 and 2.5 Å. will hardly change the

value of the integrals involved in the examples discussed. While this does not suggest a theoretical reason for the useful empirical equation, it does suggest that there is very possibly a fundamental reason why the effect of the ionic diameter may disappear when the solubilities are compared in different media of mixed solvents.

Summary

1. The solubilities of potassium iodate and zinc iodate have been determined at 25° in mixtures of water and dioxane, up to 100% dioxane.

2. The results are used to test further the empirical rule of the constancy of the activity coefficient of electrolytes at saturation. The agreement between observed and calculated solubilities is satisfactory, at least as to the order of magnitude for both salts.

3. The results are also used to test the applicability of the Born equation when modified for the segregation of solvent molecules by ions in mixed solvents, in an attempt to account at least in part for the generally large negative error in the calculated solubilities in low dielectric media. When this distribution of dielectric is calculated according to the original Debye treatment, the solubilities now predicted for mixtures of low dielectric constant are higher than the observed, indicating an over-correction from the application of the distribution equation.

4. A similarity between the results of the corrected Born equation and the empirical relation of Ricci and Davis is pointed out, in that in both cases the solubilities calculated seem to be independent of the value attributed to the "ionic radius."

(15) O. Halpern and P. Gross, *J. Chem. Phys.*, **2**, 184 (1934).

(16) H. S. Frank, *THIS JOURNAL*, **63**, 1789 (1941).