particularly in view of the fact that the simple correction in the Debye–Hückel treatment is only meant to apply to dilute solutions and a similar correction for activity coefficient data is valid only up to concentrations of about 0.1 *M*. If the correlation is real, and if a more explicit relationship between these terms can be found, it may be possible to calculate the self-diffusion coefficients of large unhydrated ions from viscosity data and a knowledge of the mean distance of approach of the ions. Alternatively, a value for the $\mathring{a}$ parameter might be determined from diffusion and viscosity data.

A very simple picture of the self-diffusion process for "unhydrated" ions is suggested by this treatment. We visualize a charged body moving through a viscous medium and having restraints imposed upon its passage from two sources acting essentially independently of one another. The first restraint is due to the necessity for the solvent molecules to move out of the ion's path and so is approximately proportional to the macroscopic viscosity. The second is imposed by the necessity of the ion to acquire enough energy to be displaced from its atmosphere; this is quantitatively related to its total potential due to the ion atmosphere. Thus the larger the hydrated counter ions, the further from the central ion will be the average charge of the ion atmosphere, and the smaller will be the binding potential at the central ion. Thus, if the diffusion rate is so related to the potential imposed upon the ion, then, after viscosity has been corrected for, the I^- ion in LiI should diffuse faster than in KI and NaI and faster again than in RbI which is in complete accord with the experimental data.

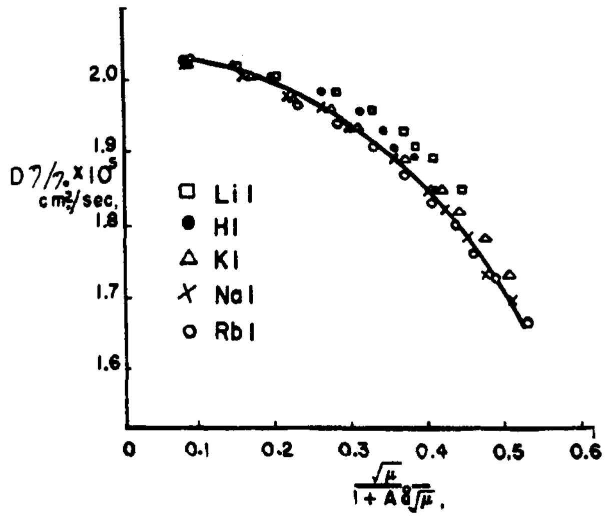

Fig. 3.—Diffusion–viscosity product *vs.* a function including the Debye–Hückel $\mathring{a}$ parameter for iodide ion diffusing in aqueous iodides.

Acknowledgments.—We express our thanks to Professor Lindsay Helmholz for his suggestions leading to the correlation of the self-diffusion coefficients with $\mathring{a}$ values, and to Mr. Arnold Friedman for his assistance and for permission to quote some of his results prior to publication. We also wish to thank Dr. J. H. Wang for permission to use his preliminary results on the self-diffusion of I^- in NaI, in Figs. 2 and 3.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

The Effect of Some Salts on the Solubility of Potassium Bromide in Acetic Acid at 30°

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The solubility of potassium bromide in acetic acid at 30° is 0.01837 molal. Its solubility in the presence of various uni-univalent added salts, in concentrations ranging from roughly 0.001 to 0.1 *m*, has been determined. Sodium acetate, sodium trichloroacetate, sodium formate, lithium acetate and lithium formate each produce a marked increase in solubility, which can be accounted for quantitatively by assuming that the salts exist almost completely undissociated in solution (probably as ion-pairs), and that exchange reactions of the type $KBr + MX \rightleftarrows MBr + KX$, proceeding until equilibrium is established, are responsible for the increased solubility. Potassium acetate, potassium formate and sodium bromide, each having one ion in common with potassium bromide, produce only a slight effect on the solubility, a very small increase. This appears to be attributable to an association reaction of the type $KBr + KX \rightleftarrows A$, occurring to a small extent.

Several investigations of salt effects on the solubilities of other salts in acetic acid have been reported.[1] The results of some of these studies have been compared with values calculated from the Debye–Hückel theory, assuming complete ionic dissociation of the salts in solution. In general, moderately good agreement was obtained provided rather large values of the ion diameter *a* were used, and especially if the Gronwall, LaMer and Sandved[2] extension of the theory was employed. The work of Bjerrum[3] and of Fuoss and Kraus,[4] however, makes it appear probable that in acetic acid, as well as in other solvents of moderately low dielectric constant, dissolved salts exist largely as associated ion-pairs in equilibrium with relatively small concentrations of free ions. In the light of this view the application of the Debye–

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[1] (a) R. P. Seward and C. H. Hamblet, THIS JOURNAL, **54**, 554 (1932); (b) A. W. Scholl, A. W. Hutchison and G. C. Chandlee, *ibid.*, **55**, 3081 (1933); (c) A. W. Davidson and H. Geer, *ibid.*, **60**, 1211 (1938); (d) E. Griswold, A. Ash and L. McReynolds, *ibid.*, **67**, 372 (1945).

[2] T. H. Gronwall, V. K. LaMer and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

[3] N. Bjerrum, *Det. Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **7**, No. 9, 1 (1926).

[4] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476, 1019 (1933).

Hückel theory, together with the assumption of complete dissociation, to such systems would appear to be of doubtful validity, as has been pointed out.[5]

In the present investigation the solubility of potassium bromide at 30° in acetic acid solutions containing various added salts in concentrations ranging up to approximately 0.1 *m* has been determined. The added salts employed were sodium acetate, sodium formate, sodium trichloroacetate, lithium acetate, lithium formate, potassium acetate, potassium formate and sodium bromide. It will be pointed out that the results obtained may be interpreted in a rather satisfactory manner by assuming, first, that the dissolved salts exist predominately as undissociated ion-pairs, and, second, that metathesis between the heterionic ion-pairs may occur until equilibrium is reached. Some evidence for association of the ion-pairs into more complex units will also be discussed.

Experimental

Materials.—Anhydrous acetic acid was prepared by refluxing C.P. glacial acetic acid with a small excess of acetic anhydride, then distilling through a 1.5-meter fractionating column. The acid used melted at 16.6° or slightly higher. The salts used, with the exception of sodium trichloroacetate, were prepared from C.P. materials, recrystallized and suitably dried. Stock solutions of sodium trichloroacetate in acetic acid were prepared by dissolving equivalent quantities of sodium acetate and trichloroacetic acid in a known weight of solvent. In calculating the composition of the stock solution, allowance was made for the acetic acid formed by metathesis of the two compounds. Eastman Kodak Co. "white label" trichloroacetic acid was purified by recrystallizing it twice from benzene, then maintaining it at about 70° in a vacuum desiccator under suction until the benzene appeared to have been removed. The product melted at 59.8°. It was stored over phosphorus pentoxide, and all transfers involving it were carried out in a dry-box.

Method.—Stock solutions of a given added salt in acetic acid were made up, and a series of more dilute solutions were then prepared in 20-cm. test-tubes which had been previously drawn out. Excess potassium bromide was added, and the tubes were then sealed off. Care was taken throughout to prevent access of moisture. The sealed tubes were tumbled in a bath maintained at 30° for a period of ten days or longer, at the end of which time the solutions were filtered and the bromide content determined by the Volhard method. Preliminary analyses of synthetic mixtures approximating in composition those involved in this work established the suitability of the method.

Results[6]

The results of the solubility determinations are summarized briefly below, detailed values being given only for sodium acetate as added salt, in Table I. All concentrations are expressed in moles per thousand grams of acetic acid. The value of 0.01837 obtained for the solubility of potassium bromide in acetic acid alone is the mean of three independent solubility determinations for which the maximum deviation was one part per thousand. Analyses of the solid phase obtained from some of the mixtures having the highest concentration of added salt showed it to correspond to KBr.

TABLE I

SOLUBILITY OF POTASSIUM BROMIDE AT 30° IN ACETIC ACID CONTAINING SODIUM ACETATE

C Concn. $NaC_2H_3O_2$	*S* Concn. KBr	*K* eq. 5	*K* eq. 14
0	0.01837	....	....
0.000208	.01871	....	....
.00324	.01891	....	....
.000444	.01895	....	....
.001064	.01935	....	....
.001435	.01978	....	....
.001818	.01990	....	....
.002220	.02039	....	....
.002285	.02041	....	....
.003307	.02108	0.0123	0.0122
.005500	.02224	.0092	.0090
.007700	.02332	.0089	.0087
.009634	.02458	.0113	.0111
.01007	.02469	.0107	.0104
.01195	.02582	.0102	.0099
.01873	.02844	.0123	.0119
.01910	.02816	.0117	.0113
.01997	.02853	.0105	.0101
.02291	.02998	.0119	.0114
.02856	.03166	.0116	.0111
.03231	.03275	.0115	.0109
.04804	.03710	.0120	.0113
.05742	.03924	.0119	.0111
.05763	.03946	.0122	.0114
.07169	.04173	.0113	.0104
.07996	.04402	.0121	.0111
.09575	.04698	.0122	.0111
.09695	.04760	.0126	.0114
	Mean	0.0114	0.0108
	Av. dev.	.0008	.0006

Effect of Other Heteroionic Salts. (a) Sodium Formate.—In the range of sodium formate concentration from 0.004240 to 0.09580, with solubilities increasing correspondingly from 0.02157 to 0.04577, the mean value of *K* calculated by equation 5 was 0.0102, with an average deviation of 0.006.

(b) Sodium Trichloroacetate.—Between about 0.013 and 0.061 *m* added salt the solubility varies from about 0.026 to 0.040, and $K = 118$, av. dev. 0.002.

(c) Lithium Acetate.—Between about 0.0048 and 0.093 the solubility increases from about 0.021 to 0.032, and $K = 0.00250$, av. dev. 0.00024.

(d) Lithium Formate.—With the concentration of added salt ranging from about 0.0044 to 0.030 the solubility changes from about 0.021 to 0.027, and $K = 0.00328$, av. dev. 0.00030.

Effect of Salts with a Common Ion. (a) Potassium Acetate.—Concentrations of added salt ranging from about 0.00010 to 0.098 *m* were employed. No significant decrease in solubility was observed, but rather a slight increase, the solubility being about 0.020 *m* in the most concentrated solution of potassium acetate.

(b) Potassium Formate.—The solubility increases slightly, reaching about 0.020 in 0.078 *m* solution of added salt.

(c) Sodium Bromide.—With the concentration of added salt extending only up to about 0.017 *m*,

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[5] A. A. Vernon, W. F. Luder and M. Giella, THIS JOURNAL, **63**, 862 (1941).

[6] The detailed tables of data supplementary to this article have been deposited as Document number 4063 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required; checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

no significant trend in solubility of potassium bromide was observed.

Discussion

The presence of heteroionic added salts causes a marked increase in the solubility of potassium bromide, as can be seen from the results described above. A preliminary comparison of these results with values calculated from the Debye–Hückel equation, assuming complete dissociation of all salts, indicated that in order to obtain approximate agreement at the lowest concentrations of added salt rather large values, of the order of 10 Å. or larger, for the ion diameter *a* were required. Moreover agreement at higher concentrations was not satisfactory. It is true that even at the lowest concentrations involved in this work the total salt concentration is roughly 0.02 *m*, which is, perhaps, too high for one to expect the Debye–Hückel equation to be applicable.

There is, however, a more cogent reason for questioning the applicability of the Debye–Hückel equation to the results of the present investigation. Fuoss and Kraus[4] have shown that conductance curves obtained for salts in solvents of moderately low dielectric constant can be very satisfactorily interpreted by assuming, in part, that an equilibrium obeying the law of mass action is established between the free ions in the solution and undissociated ion-pairs of the type postulated by Bjerrum.[5] Moreover, they have shown how it is possible to obtain numerical values of the ion-pair dissociation constants from conductance data. For a given salt this constant depends primarily upon the dielectric constant of the medium. For example, in a dioxane–water mixture having a dielectric constant of 5.84 at 25°, the ion-pair dissociation constant of tetraisoamylammonium nitrate was found to be 1.65×10^{-6}, although in water this salt is a strong electrolyte.

The dielectric constant of acetic acid at 30° is 6.20.[7] Conductance studies[8] with a number of the same salts employed in the present investigation give ion-pair dissociation constants of the order of 10^{-7}. Such small values of the constant strongly suggest that the explanation of the neutral salt effect described here cannot be given in terms of long range interionic effects, but must lie elsewhere.

Ion-pair Exchange.—One consideration that appears to have been rather generally overlooked in this connection is the possibility that reaction between heteroionic ion-pairs,[9] involving an exchange of ions between the pairs, can occur until equilibrium has been established. Thus, in addition to equilibria in the processes

$$\mathrm{KBr(s)} \rightleftarrows \mathrm{KBr\ (dissolved\ ion\text{-}pairs)} \rightleftarrows \mathrm{K^+ + Br^-} \qquad \text{(a)}$$

and

$$\mathrm{MX(ion\text{-}pairs)} \rightleftarrows \mathrm{M^+ + X^-} \qquad \text{(b)}$$

the reaction

$$\mathrm{KBr + MX} \rightleftarrows \mathrm{KX + MBr} \qquad \text{(c)}$$

should also be considered.

For the first equilibrium in (a) the following equation can be written

$$[\mathrm{KBr}]\gamma_{\mathrm{KBr}} = \text{const.} \equiv S_0 \qquad (1)$$

It is clear that reaction c must have the effect of increasing the solubility of the potassium bromide. For this reaction one may write the equilibrium equation

$$\frac{[\mathrm{KX}][\mathrm{MBr}]}{[\mathrm{KBr}][\mathrm{MX}]} \times \frac{\gamma_{\mathrm{KX}}\gamma_{\mathrm{MBr}}}{\gamma_{\mathrm{KBr}}\gamma_{\mathrm{MX}}} = K' \qquad (2)$$

If, now, it is assumed (1) that the activity coefficients of the ion-pairs are equal and remain constant throughout, and (2) that the concentrations of the free ions are negligible in comparison with those of the ion-pairs, then the entire increase in solubility of potassium bromide, ΔS, in the presence of an added salt of initial concentration *C*, may be attributed to reaction (c). That is

$$[\mathrm{KX}] = [\mathrm{MBr}] = \Delta S \qquad (3)$$

and

$$[\mathrm{MX}] = C - \Delta S \qquad (4)$$

Combining equations 1 and 2 and substituting from (3) and (4), with the assumptions made above, the following relation is obtained

$$\frac{[\mathrm{KX}][\mathrm{MBr}]}{[\mathrm{MX}]} = \frac{(\Delta S)^2}{C - \Delta S} = K \qquad (5)$$

It is thus possible to test the explanation proposed above in a very simple manner. The third column in Table I gives the values of *K* calculated from equation 5. For very small concentrations of added salt, where ΔS is also small, the denominator of the left-hand member is very sensitive to small deviations, and the results are of little significance. It will be noted, however, that for concentrations of added salt ranging roughly from 0.004 to 0.1 *m* the values of *K* calculated from equation 5 do indeed appear to remain very nearly constant. The applicability of equation 5 is, perhaps, more strikingly emphasized by Fig. 1, in which the solid curve I represents the dependence of the solubility of potassium bromide upon the concentration of added salt as calculated from equation 5 using $K = 0.0114$. The circles correspond to experimental points for sodium acetate as added salt. To avoid confusion in the diagram, many of the points at the lower concentrations have been omitted. Curve II in Fig. 1 shows a similar comparison for lithium acetate as added salt. For the theoretical curve, $K = 0.00250$. Similar agreement is obtained for the other heteroionic added salts using suitable values of *K*. The fact that the observed increases in solubility over so wide a range in concentration can be closely represented by the one-parameter equation 5 lends considerable support to the hypothesis that in the systems investigated here, ion-pair exchange reactions of the type represented by equation c are of major importance in accounting for the neutral salt effect.

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(7) C. P. Smyth and H. E. Rogers, This Journal, **52**, 1824 (1930).

(8) Unpublished work from this Laboratory.

(9) Although the term "ion-pair" is used throughout this discussion, it is not actually necessary for the present purpose to make any assumption concerning the specific nature of the undissociated salts in solution.

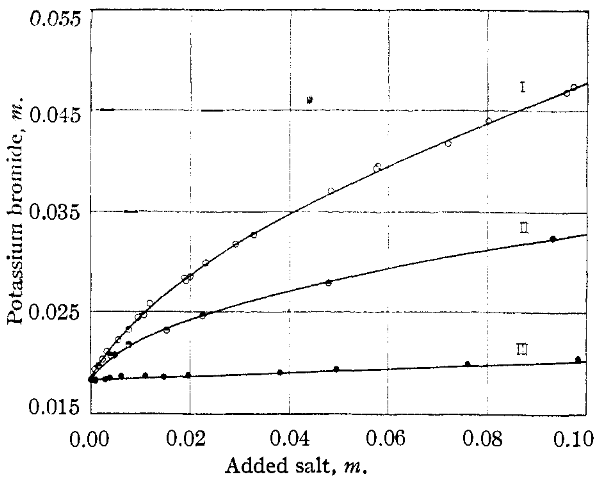

Fig. 1.—Comparison of experimental and calculated dependence of the solubility of potassium bromide upon concentration of added salts in acetic acid at 30°: solid lines, calculated: I, equation 5, $K = 0.0114$; II, equation 5, $K = 0.00250$; III, equation 9, $K_A = 0.020$; circles, experimental points: ○, added salt sodium acetate; ◒, added salt lithium acetate; ●, added salt potassium acetate.

Ion-pair Association.—In those mixtures in which the added salt has an ion in common with the solute salt, an exchange reaction of type c would have no significance insofar as increasing the solubility of the solute salt is concerned. Moreover, if both salts are negligibly dissociated into free ions there should be no appreciable decrease in solubility arising from the familar common-ion effect. Thus, if no additional effects are involved, salts with a common ion should have no significant effect whatever upon the solubility of the solute salt. The results given above show that the solubility of potassium bromide is indeed not much affected by the presence of potassium acetate, potassium formate or sodium bromide. Such effect as is shown is actually a small increase in solubility. This effect suggests that association of the ion-pairs into more complex aggregates may be occurring to a small extent. Assume, for example, that a reaction represented by

$$\mathrm{KBr} + \mathrm{KX} \rightleftarrows \mathrm{A} \qquad \text{(d)}$$

takes place, in which A stands for an association product of the two ion-pairs. The corresponding equilibrium relation may be written

$$\frac{[\mathrm{A}]}{[\mathrm{KX}]}\,\frac{\gamma_{\mathrm{A}}}{\gamma_{\mathrm{MX}}} = K_{\mathrm{A}}'[\mathrm{KBr}]\gamma_{\mathrm{KBr}} \equiv K_{\mathrm{A}} \qquad (6)$$

Assuming as before the equality and constancy of the activity coefficients, and neglecting the very small concentrations of free ions, then

$$[\mathrm{A}] = \Delta S \qquad (7)$$

$$[\mathrm{KX}] = C - \Delta S \qquad (8)$$

and

$$\Delta S/(C - \Delta S) = K_{\mathrm{A}} \qquad (9)$$

From equation 9 values of ΔS have been calculated for various values of C using $K_A = 0.020$, and the corresponding solubilities are represented by the solid curve III in Fig. 1. The circles represent experimental solubilities, obtained with potassium acetate as the added salt. It is seen that the agreement is reasonably good.

Returning now to the effects of heteroionic salts, it is, of course, not unreasonable to suppose that some association of ion-pairs might occur here also, in addition to the exchange reaction previously discussed. Thus, besides reaction c, the reaction represented by

$$\mathrm{KBr} + \mathrm{MX} \rightleftarrows \mathrm{A} \qquad \text{(e)}$$

may be considered for which, since the solution is saturated with potassium bromide

$$[\mathrm{A}]\gamma_{\mathrm{A}}/[\mathrm{MX}]\gamma_{\mathrm{MX}} = K_{\mathrm{A}} \qquad (10)$$

Making the same assumptions as before, the increase in solubility of potassium bromide is now given by

$$\Delta S = [\mathrm{A}] + [\mathrm{KX}] = [\mathrm{A}] + [\mathrm{MBr}] \qquad (11)$$

Also

$$C - \Delta S = [\mathrm{MX}] \qquad (12)$$

and from (10) and (11)

$$[\mathrm{KX}] = [\mathrm{MBr}] = \Delta S - K_{\mathrm{A}}(C - \Delta S) \qquad (13)$$

Substitution of (12) and (13) into (2) gives finally

$$\frac{(\Delta S)^2}{C - \Delta S} - 2K_{\mathrm{A}}\Delta S - K_{\mathrm{A}}^2(C - \Delta S) = K \qquad (14)$$

Values of K have been calculated from the sodium acetate data by means of equation 14 with $K_A = 0.02$. The results are given in the fourth column of Table I. They do exhibit a slightly better degree of constancy, perhaps, than those calculated by equation 5. A similar slight improvement is obtained for the other sodium salts, but it has not seemed worthwhile to tabulate the results here.

Although the solubility effects described in this paper can be rather simply explained in terms of exchange and association reactions between ion-pairs in acetic acid solution, it seems likely that in solvents of distinctly larger dielectric constant it would be necessary to take into account the increased ionic dissociation of the salts. On the other hand, in solvents of quite low dielectric constant the formation of associated units of varying degrees of complexity would become of major importance.

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