Ion Pair Formation in Acetic Acid

by

Mark M. Jones
B.S., Lehigh University, 1948
M.S., Lehigh University, 1949

Submitted to the Department
of Chemistry and the Faculty
of the Graduate School of the
University of Kansas in partial fulfillment of the requirements for the degree of
Doctor of Philosophy.

Advisory Committee:

Redacted Signature

Redacted Signature

Redacted Signature

August, 1952

Acknowledgement

I wish to express my appreciation for the encouragement and guidance offered me by Dr. Ernest Griswold during the course of this work. I also wish to thank him for the patience he has shown towards me in regards to discussion about this work and related topics. Other members of the staff who have been of direct assistance are Dr. Arthur Davidson and Dr. William Argersinger. The aid has certainly not been unappreciated. Finally I wish to thank those institutions which have provided financial support for the author during this work: The State of Kansas for the provision of an assistantship during the first two years and the E. I. duPont de Nemours Company for a fellowship during the final year.

Table of Contents

Introduction

The several studies of salt effects on solubility in acetic acid which have been reported (1)(2)(3)(4) show this effect to be very pronounced. In some instances the Debye-Hückel theory of interionic attraction, or the Gronwall, LaMer, and Sandved extension of it have been used in the interpretation of the data. With this interpretation it has been assumed, moreover, that the dissolved salts are completely dissociated into ions in this solvent. Such treatments lead to exceedingly small activity coefficients for the solute species.

However, over the past few decades a large number of investigations on solvents of low dielectric constant have indicated that solutions in such solvents may not be amenable to treatment by any theory which considers all electrolytic solutes to be completely ionized in solution. Most of the studies, especially of conductivities, have indicated that solutions of such salts as the alkali metal halides, for example, consist largely of ion-pairs in equilibrium with a relatively small number of free ions (5). In such cases the interionic effects would be unimportant in influencing the behavior of the solution, and some other explanation of the salt effect on solubility must be sought.

There is some evidence that the effects of one salt upon the solubility of another in acetic acid, which has the moderately low dielectric constant of 6.20 at 30° C., may be explained in terms of exchange among ion-pairs between the solute and the solvent salts (9). Such an exchange may be represented by the equation

$$MA_{(solid)} + R^+X^- \rightleftharpoons M^+X^- + R^+A^-$$

When such a reaction proceeds to equilibrium the solubility of the salt MA will be increased to an extent dependent upon the original concentration of RX and the equilibrium constant for the exchange.

Following the earlier work of Bjerrum (6), Fuoss and Kraus (7)(8) have shown how it is possible to obtain from conductance data values of equilibrium constants for the dissociation of individual ion-pairs as well as values of the limiting equivalent conductances of salts in such solutions. There is, however, little information of this type available on solutions in acetic acid.

The present investigation was undertaken to obtain additional information on salt solutions in acetic acid. While some information on solubility effects was obtained, the major portion of the work was devoted to a study of the conductivities of a series of salts in acetic acid and the information that could be obtained from such data. This information included the dissociation constants of the ion-pairs, the limiting equivalent conductances of the various salts studied, the probability of clusters of three or more ions and ionic radii and the size of ion-pairs.

Historical

The publication of the Debye-Hückel theory of interionic attraction in 1923 was followed by extensive tests of its validity for electrolyte solutions of various types. In general, the predicted dependence of the activity coefficient of an electrolytic solute upon valence type, ionic strength, and temperature was satisfactorily borne out by the experimental values in very dilute aqueous solutions. In more concentrated solutions the agreement was less satisfactory, and various modifications of the theory were proposed to account for the deviations.

In order to test more fully the predicted dependence of activity coefficients upon the dielectric constant of the medium, a number of investigations of non-aqueous solvents were carried out. Notable among these are the work of Noyes and Baxter in ethanol (10) and Webb in glacial acetic acid and liquid ammonia (11). These investigators used freezing point depression studies. A large number of other studies in non-aqueous solvents concern themselves with solubilities. Among these are the work of Kraus and Seward (4) in iso-propyl alcohol and methyl acetate, Williams (12) in methanol, Williams and Hansen (13) in ethanol-water mixture, Kraus and Seward in acetone (14), Robinson in acetone (1), Seward in ethylene dichloride (15), and Seward and Hamblett (2) and Scholl, Hutchison and Chandlee (3) in acetic acid. Although some of these workers found agreement with the Debye-Hückel theory, others, especially those working in solvents of low dielectric constant, found that there were serious discrepancies between experiment and the Debye-Hückel theory.

The Debye-Hückel theory assumes that around a given ion there exists an "ion atmosphere" arising from a Boltzmann distribution of the other ions around it, in which on the average there is a slight preponderance of ions of opposite sign. The resulting charge density satisfies the Poisson relation, and the ion atmosphere makes a contribution to the electrical potential of the central ion which in turn is reflected in its chemical potential and in related thermodynamic properties. An interesting modification of this theory was proposed by Bjerrum (6) who considered the probability that a single ion of opposite charge might approach sufficiently close to a given ion to form an ion-pair with it. The resulting pair would constitute essentially a dipole, and might be considered neither to possess, nor to make any significant contribution to the ion atmosphere. The probability of formation of such an ion-pair would be favored by relatively high force fields around the ions such as would arise from high ionic charge, small ionic radius, or low dielectric constant of the surrounding medium. Also, of course, the probability of ion-pair formation would increase with increasing concentration. It is under these conditions that the Debye-Hückel theory has been least successful.

Bjerrum developed a method for calculating the relative numbers of paired and unpaired ions, and by combining this with a Debye-Hückel treatment of the free ions he was able to calculate the thermodynamic properties of such solutions. In general, the agreement with experiment was as good as that of the Debye-Hückel theory. In solvents of low dielectric constant Bjerrum's treatment was superior in that it fit the data with more reasonable values of the ionic radius parameter. The work of Bjerrum was considerably more tedious to apply, however, and it has never had the widespread use that the Debye-Hückel theory has enjoyed.

In 1933 Fuoss and Kraus (7)(8) used the ideas of Bjerrum in a treatment of electrolytic conduction. They were able to show that conductance minima, long known in solvents of low dielectric constant, could be readily explained in terms of equilibria among single-, double-, and triple-ions. In general such minima become noticeable at lower concentrations as the dielectric constant is lowered. They were also able to give the shape of the curve below such a minimum quantitatively. They examined solutes in dioxane-water mixture in which they were able to vary the dielectric constant over a wide range. In summary one may say that the use of Bjerrum's treatment, as amended by Fuoss and Kraus, provides a far more satisfactory picture of the behavior of many solvents of low dielectric constant than does the Debye-Hückel theory.

Although a number of papers on the properties of acetic acid solutions were published prior to 1925, they were generally more concerned with the presence of solvates than with the actual properties of the solutions. Interest in acetic acid as a solvent worthy of study in its own right stems mainly from the publications of Davidson and his co-workers. Starting in 1928, Davidson investigated solubilities of a large number of salts, acid and base relationships in acetic acid, transference numbers, and phase diagrams of various systems (16)(17)(18)(19)(20)(21)(22)(23)(24)(25). The solubility relations in acetic acid have also been studied by Griswold and his co-workers (26)(27)(28)(19).

Webb has evaluated some thermodynamic properties of lithium bromide, sodium bromide, and sodium acetate solutions in acetic acid from freezing point measurements. He succeeded in fitting his data on the activity coefficients of these solutes to an extended form of the Debye-Hückel expression. Other studies of activity coefficients include those of Hutchison and Chandlee(29) who used cells to study sulfuric acid solutions, those of Scholl, Hutchison and Chandlee (3) who used solubility studies on potassium perchlorate and barium chloride, and those of Seward and Hamblett (2) on the solubilities of potassium perchlorate and potassium nitrate. These authors used either the extended Debye-Hückel theory or the Gronwall, LaMer, and Sandved treatment in the discussion of their results. The data were fit satisfactorily in the first two instances, but Seward and Hamblett noticed discrepancies.

The investigations on the conductivities of acetic acid solution are practically limited to the work of Weidner, Hutchison and Chandlee (30) (31), and of Kolthoff and Willman (32)(33). These authors investigated a large number of salts but gave neither a quantitative nor a complete qualitative explanation of their results. Their data are presented but nothing further. The salts investigated by Weidner, Hutchison and Chandlee were H_2SO_4, $LiCl$, KCl, $LiNO_3$, KNO_3, $(CH_3)_4NCl$, $(CH_3)_3(nC_4H_9)NBr$, $NaCl$, NH_4Cl, $NaNO_3$, $CsNO_3$, $(CH_3)_4NBr$ and NaOAc; by Kolthoff and Willman were $HClO_4$, H_2SO_4, HCl, HBr, HNO_3, $LiCl$, KOAc, NaOAc, and pyridine.

A survey of the literature on the subject thus reveals on the one hand that the thermodynamic data for solutions of electrolytes in acetic acid ~~is~~ are comparatively meager, and where attempts have been made to give a theoretical interpretation ~~to~~ of the data, these have involved application of the Debye-Hückel theory with the assumption of complete ionization of the solutes. On the other hand, good evidence exists, based especially on conductance data, that, at least in other non-aqueous solvents of dielectric constants even somewhat higher than acetic acid, dissolved electrolytes are by no means completely dissociated into ions but, instead, they appear to be largely associated. To be sure, there is at present little conclusive evidence one way or the other bearing on this point in relation to acetic acid solution. Nevertheless it seems important to consider this possibility in connection with solubility effects and other related phenomena in acetic acid.

Theoretical

Shortly after the Debye-Hückel theory appeared, Bjerrum published the results of his theoretical investigation of the effects of ionic association (6). Bjerrum calculated the probability of finding an ion in the immediate neighborhood of a second ion as a function of their distance of separation. He assumed that the intermolecular forces were purely coulombic and further, that two ions of opposite sign closer together than a certain critical radius formed a single particle as far as colligative properties were concerned. This particle was an ion-pair M^+X^-. As a result of its possessing no net charge, it did not contribute to the conductance of the solution. These ion-pairs were assumed to exist in equilibrium with single ions and this equilibrium could be represented by an equilibrium constant expression:

$$M^+X^- \rightleftharpoons M^+ + X^-$$

$$K = \frac{[M^+][X^-]}{[M^+X^-]} \tag{I}$$

In his original article Bjerrum calculated activity coefficients and ionic radii for several strong electrolytes and compared them with the values obtained from the Debye-Hückel theory. In most cases the comparison was quite favorable to Bjerrum's theory. Since it is Bjerrum's theory which will be used to discuss this problem, a short outline of it is not out of place.

To begin with, Bjerrum considers the probability of finding an ion of the i-th kind within a spherical shell of thickness dr at a distance r away from a given central ion to be expressed by

$$H(r)\,dr = \frac{Nc_i}{1000}\,4\pi r^2 dr \cdot e^{\frac{\varphi}{kT}} \qquad \text{(II)}$$

C_i is the molarity of the i-th species of ion

N is Avogadro's number

φ is the work of separation of the ion from the central ion

From Coulomb's Law Bjerrum writes

$$\varphi = \frac{z_i z_k \varepsilon^2}{D r} \tag{III}$$

D is the dielectric constant

ε is the electronic charge

z_i is the charge on the i-th ion

This probability function $H(r)$ has a minimum value at

$$r_{min.} = \frac{z_i z_k \varepsilon^2}{2DkT} \tag{IV}$$

Bjerrum then assumes that an ion of opposite charge lying closer to the central ion than r_{min} is to be considered as paired with it. Bjerrum next integrates the probability equation from the distance of closest approach a to r_{min} and considers this result to be the degree of association.

$$\alpha = \frac{4\pi N c_i}{1000} \int_a^{r_{min.}} r^2 e^{\frac{z_i z_k \varepsilon^2}{D r k T}} dr \tag{V}$$

where α represents the degree of association into ion-pairs.

To evaluate this integral in the case of a single uni-univalent electrolyte it is transformed to

$$\alpha = \frac{4\pi Nc}{1000}\left(\frac{\varepsilon^2}{DkT}\right)^3 Q(b) \qquad \text{(VI)}$$

where

$$Q(b) \equiv \int_2^b e^y y^{-4}\,dy \; ; \; y = \frac{\varepsilon^2}{DrkT} \; ; \; b = \frac{\varepsilon^2}{DakT} \qquad \text{(VII)}$$

$Q(b)$ has been calculated for various values of b ranging from 2 to 80 and the results are given in the tables of Bjerrum (1) or of Fuoss and Kraus (2).

From our value of α we can readily obtain the equilibrium constant for ion-pair formation in a solution containing a single uniunivalent electrolyte.

$$K = \frac{a_{M^+}\, a_{X^-}}{a_{M^+X^-}} \tag{VIII}$$

$$K = \frac{(1-\alpha)c(1-\alpha)c}{\alpha c}\,\frac{f_\pm^2}{f_u} = \frac{(1-\alpha)^2 c}{\alpha}\,\frac{f_\pm^2}{f_u} \tag{IX}$$

$$K = \frac{\left[1 - \frac{4\pi Nc}{1000}\left(\frac{\varepsilon^2}{DkT}\right)^3 Q(b)\right]^2 c\, f_\pm^2}{\frac{4\pi Nc}{1000}\left(\frac{\varepsilon^2}{DkT}\right)^3 Q(b)\; f_u} \tag{X}$$

where $f_\pm$ is the mean activity coefficient of the free ions of the electrolyte, and f_u is the activity coefficient of the ion-pairs, assumed to be unity.

In dilute solutions this simplifies to

$$K^{-1} = \frac{4\pi Na}{1000}\left(\frac{\varepsilon}{DkT}\right)^3 Q(b) \tag{XI}$$

It may be seen from equations (VI) and (XI) that Bjerrum's expressions give $\alpha = \frac{c}{K}$, which from (X) leads to the absurd result that $f_{\pm} = \frac{1}{1-\alpha}$. Moreover, it is not strictly correct to set

$$\alpha = \int_{a}^{r_{min}} H(r)\, dr$$

since

$$\int_{a}^{\infty} H(r)\, dr \neq 1$$

Fuoss and Kraus (7)(8) have modified Bjerrum's probability function in a reasonable manner which eliminates these objections. Their procedure yields equation (XI) for the ion-pair dissociation constant, but modifies equation (VI) such that it is approached only in the limit of infinite dilution.

It is seen that K will be determined by b. This parameter must be obtained by other measurements discussed below.

Since the constants of interest are the dissociation constants of weak electrolytes (in acetic acid) we may obtain these from conductance data by using the method of Fuoss and Kraus (3). This method is essentially a modernization of the Ostwald Dilution Law and the work of Kraus and Bray. For a weak electrolyte Ostwald wrote the dissociation constant expression as

$$K = \frac{\Lambda^2 c}{\Lambda^0(\Lambda^0 - \Lambda)} \qquad \text{(XII)}$$

Kraus and Bray rewrote this in the form

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^0} + \frac{c\Lambda}{K(\Lambda^0)^2} \qquad \text{(XIII)}$$

Fuoss and Kraus modified these equations to take into account the Onsager equation for conductance

$$\Lambda = \Lambda^0 - (A + B\Lambda^0)\sqrt{c} \qquad \text{(XIV)}$$

and the Debye-Huckel limiting equation for activity coefficients

$$\log f_\pm = - S_f \sqrt{\alpha c} \tag{XV}$$

In dilute solutions of an electrolyte with a degree of dissociation of α the Onsager equation becomes

$$\Lambda = \alpha\left(\Lambda^0 - S_\Lambda \sqrt{\alpha c}\right) \tag{XVI}$$

where S_Λ is the Onsager slope.

From this

$$\alpha = \frac{\Lambda}{\Lambda^0\left(1 - \frac{S_\Lambda \sqrt{\alpha c}}{\Lambda^0}\right)} \tag{XVII}$$

If one substitutes this value of α back into the denominator of this equation, the term in parentheses may be replaced by a continued fraction

$$F(Z) = 1 - Z\left\{1 - Z\left[1 - Z(\text{etc.})^{-\frac{1}{2}}\right]^{-\frac{1}{2}}\right\}^{-\frac{1}{2}} \tag{XVIII}$$

where

$$Z = S_\Lambda \sqrt{\Lambda c}\,\left(\Lambda^0\right)^{-3/2} \tag{XIX}$$

From this

$$\alpha = \frac{\Lambda}{\Lambda^0 F(z)} \tag{XX}$$

Fuoss has tabulated values of $F(z)$ for various values of the argument z .

$$F(z) = \frac{4}{3}\cos^2\frac{1}{3}\cos^{-1}\left(-\frac{3\sqrt{3}\,z}{2}\right) \tag{XXI}$$

We may substitute from (XX) into the expression for the thermodynamic ionization constant

$$K = \frac{c\,\alpha^2 f_\pm^2}{1-\alpha} \tag{XXII}$$

and, rewriting, obtain the expression

$$\frac{F(z)}{\Lambda} = \frac{1}{\Lambda^0} + \frac{C\Lambda f_\pm^2}{F(z)\,K(\Lambda^0)^2} \tag{XXIII}$$

$f_\pm$ may be calculated from the Debye-Hückel relation

$$\log f_\pm = -S_f\sqrt{\alpha c} \tag{XV}$$

A plot of $F(z)/\Lambda$ against $\frac{c\Lambda f_{\pm}^{2}}{F(z)}$ should then yield a straight line of slope $1/K(\Lambda^{0})^{2}$ and intercept $1/\Lambda^{0}$. Actually this procedure is repeated until the same value of Λ^{0} used to obtain $F(z)$ and α is actually obtained as an intercept. This is the method by which the individual K's were obtained for the salts studied.

The theory of Bjerrum, Fuoss, and Kraus underlying equation (XX) has not gone without criticism. Gronwall, LaMer, and Sandved (34) and Gross and Halpern (35)(36), in particular, have leveled sharp criticisms against certain aspects of the theory. These appear to have been met adequately, however (37)(38)(39).

The probability functions obtained by these investigators involved only a Coulomb potential. In consequence the function cuts off sharply with a relatively high peak value of $\frac{4\pi N}{1000} a^{2} \exp\left\{\frac{\varepsilon^{2}}{DkTa}\right\}$ at the distance of closest approach a. With increasing r the function goes through a minimum at $r = \frac{\varepsilon^{2}}{2DkT}$, then rises. Bjerrum's function rises without limit, but the modified function of Fuoss and Kraus goes through a maximum and then falls to zero.

The introduction of a repulsion term in the potential, of a form similar to that for ions in crystals, would affect the form of the probability curve mainly in the region of closest approach. Thus if the mutual potential energy of a central ion i and an ion j is given by

$$W = -\frac{z_i z_j \epsilon^2}{Dr} + Be^{-r/\rho} \tag{XXIV}$$

then Bjerrum's form of the probability function becomes

$$P(r) = \frac{4\pi C_j}{1000} r^2 \exp\left\{\frac{z_i z_j \epsilon^2}{Dr kT} - \frac{Be^{-r/\rho}}{kT}\right\}$$

Using $B = 200 \times 10^{-10}$ ergs molecule^{-1} and $\rho = 0.345$ Å (40)(41) the values of $\frac{1000\, P(r)}{4\pi C_j}$ given in Table I are calculated for various values of r. The values of B and ρ used here are those used by Born for the alkali metal halides. Since these were derived from data on the crystalline compounds they should not be expected to represent the exact repulsion potential for the ions in solution, but rather the type of curve which is expected.

Table I

$r \times 10^8$ cms	$\frac{P(r)}{1000 N c_i}$
1	0 (i.e. $\sim 10^{-20}$)
2	3.16×10^{-2}
3	3.51×10^{-3}
4	5.76×10^{-6}
5	1.25×10^{-7}
6	9.0×10^{-8}
7	1.47×10^{-9}
8	3.84×10^{-10}
9	1.62×10^{-10}
10	8.0×10^{-11}

The condition for the extremum value of $P(r)$ is

$$\frac{\partial P(r)}{\partial r} = 0$$

In this case the condition gives

$$r_{ext.} = \frac{Z_+Z_-\epsilon^2}{2DkT} - \frac{Br^2e^{-r/\rho}}{2kT\rho}$$

There are two extremum values of interest. There is an $r_{min.}$ corresponding to Bjerrum's $r_{min.}$ but very slightly smaller than his. There is also an r value corresponding to a maximum in the $P(r)$ curve in the region of closest approach. An approximate calculation shows this distance to be in the neighborhood of 2 Å.

The above analysis follows Bjerrum's and does not differ from it at any but the smallest r values. A similar treatment following Fuoss leads to an integral equation of considerably greater complexity. The general shape of the probability curve could be hazarded as following that of Fuoss for all $r > 2$ Å, and behaving much like the above function for small r ($r < 2$ Å).

Recently the concept of ion-pairs has been used to explain certain solubility effects noted in some acetic acid solutions (9). The increase in solubility of a given salt in acetic acid on the addition of a second salt not containing an ion in common with the first is attributed to the formation of mixed ion-pairs.

If it is assumed that electrolytes dissolved in acetic acid exist largely as ion-pairs in equilibrium with very small concentrations of free ions, then when two salts, KBr and MX, for example, are mixed together in such a solvent, it is to be expected that a reaction of the following type would take place

$$(\overset{+}{K}\overset{-}{Br}) + (\overset{+}{M}\overset{-}{X}) \rightleftharpoons (\overset{+}{K}X^{-}) + (M^{+}Br^{-})$$

The equilibrium expression for this reaction may be written as

$$K' = \frac{[K^{+}X^{-}][M^{+}Br^{-}]\,\gamma_{K^{+}X^{-}}\,\gamma_{M^{+}Br^{-}}}{[K^{+}Br^{-}][M^{+}X^{-}]\,\gamma_{K^{+}Br^{-}}\,\gamma_{M^{+}X^{-}}} \qquad \text{(XXV)}$$

Since the activity of the dissolved KBr must remain constant (it is in equilibrium with solid KBr) we may write

$$\gamma_{K^{+}Br^{-}}[K^{+}Br^{-}] = S_{0}\gamma_{0} \qquad \text{(XXVI)}$$

S_0 is the solubility of solid KBr in the absence of any added salt, and γ_0 is the corresponding activity coefficient.

Assuming that the concentration of the free ions can be neglected in comparison with those of the ion-pairs, then it can easily be seen that

$$[K^+X^-] = [M^+Br^-] = \Delta S \qquad \text{(XXVII)}$$

and

$$[M^+X^-] = C - \Delta S \qquad \text{(XXVIII)}$$

where ΔS is the increase in solubility of potassium bromide and C is the concentration of added salt. If, moreover, we assume the activity coefficients of the ion-pairs to be equal to one another and essentially constant

$$\gamma_{K^+Br^-} = \gamma_{M^+X^-} = \gamma_{M^+Br^-} = \gamma_{K^+X^-} = \gamma_0 \qquad \text{(XXIX)}$$

then

$$K' = \frac{\Delta S^2}{S_0(C - \Delta S)} \qquad \text{(XXX)}$$

or, since S_0 is a constant,

$$K = K' S_0 = \frac{(\Delta S)^2}{C - \Delta S} \tag{XXXI}$$

This particular equation has been found to apply satisfactorily to data on the solubility of potassium bromide in acetic acid solutions of some half-dozen different uniunivalent salts (9) over a concentration range of about 0.004 molal to 0.1 molal. As will be pointed out in the next paragraph, conductance measurements should make it possible to obtain a completely independent value of the constant in equation (XXVI).

The method by which this was attempted is as follows. Griswold's original expression for K'

$$K' = \frac{[K^+X^-][M^+Br^-]\,\gamma_{K^+X^-}\,\gamma_{M^+Br^-}}{[K^+Br^-][M^+X^-]\,\gamma_{K^+Br^-}\,\gamma_{M^+X^-}} \tag{XXXII}$$

can be written in another form. For each salt we may write an ion-pair dissociation reaction

$$K^+X^- \rightleftharpoons K^+ + X^-$$

$$M^+Br^- \rightleftharpoons M^+ + Br^-$$

$$K^+Br^- \rightleftharpoons K^+ + Br^-$$

$$M^+X^- \rightleftharpoons M^+ + X^-$$

and for each of these reactions an equilibrium constant expression

$$K_{K^+X^-} = \frac{[K^+][X^-]\,\gamma_\pm^2}{[K^+X^-]\,\gamma_{K^+X^-}} \qquad \text{(XXXIII)}$$

$$K_{M^+Br^-} = \frac{[M^+][Br^-]\,\gamma_\pm^2}{[M^+Br^-]\,\gamma_{M^+Br^-}} \qquad \text{(XXXIV)}$$

$$K_{K^+Br^-} = \frac{[K^+][Br^-]\,\gamma_\pm^2}{[KBr]\,\gamma_{K^+Br^-}} \qquad \text{(XXXV)}$$

$$K_{M^+X^-} = \frac{[M^+][X^-]\,\gamma_\pm^2}{[M^+X^-]\,\gamma_{M^+X^-}} \qquad \text{(XXXVI)}$$

If it is possible to evaluate each of these constants separately, they should combine to give the

K' in equation (XXXII) directly. Comparison of the K' obtained in this manner with that obtained from solubility data by equation (XXX) should either lend support to the theory that ion-pair interchange accounts in large part for the solubility effects observed, or indicate that some other effect is occurring.

By means of conductance measurements using the Fuoss-Kraus treatment outlined in the preceding section the <u>thermodynamic</u> dissociation constants for these ion-pairs resulted. The solubility data give K values which are uncorrected for activity coefficients. This means that the K''s which are compared in the end are not exactly of the same form. A quantitative estimate of activity coefficients of ion-pairs in acetic acid would be required to judge exactly how well the K's compare. In any event the processes actually occurring may be demonstrated if we ignore the activity coefficients. At most this will introduce a small adjustment in the K values.

Activity Coefficients

In the treatment of solubility data described above, the activity coefficients of the ion-pairs are assumed to cancel out. Thus in the equilibrium constant expression

$$K' = \frac{[K^+X^-][M^+Br^-]\,\gamma_{K^+X^-}\,\gamma_{M^+Br^-}}{[K^+Br^-][M^+X^-]\,\gamma_{K^+Br^-}\,\gamma_{M^+X^-}}$$

or the equivalent form

$$K = K'[KBr]_0 = \frac{[KX]\,[MBr]\,\gamma_{KX}\,\gamma_{MBr}}{[MX]\qquad\gamma_{KBr}\,\gamma_{MX}}$$

the quotient

$$\frac{\gamma_{KX}\,\gamma_{MBr}}{\gamma_{KBr}\,\gamma_{MX}}$$

is set equal to unity.

From previous work (9) on solubilities of potassium bromide in the presence of salts with a common ion, where ion-interchange cannot occur, it is known that $[KBr] \neq [KBr]_0$ but differs from it by a relatively small amount. This particular simplification does not introduce any considerable error into the treatment.

The quotient $\gamma_{KX}\gamma_{MBr}/\gamma_{KBr}\gamma_{MX}$ cannot be evaluated from Griswold's work or from the experimental work presented in this thesis. It is nevertheless of some interest to know that there ~~is~~ are experimental data in the literature from which approximate values of this quotient may be obtained for one case. This is the quotient for sodium acetate as solvent salt. In this case the quotient becomes

$$\frac{\gamma_{KOAc}\,\gamma_{NaBr}}{\gamma_{KBr}\,\gamma_{NaOAc}}$$

These activity coefficients have been estimated in the following ways: γ KOAc from the freezing point depressions measured by Davidson and McAllister (18); γ NaOAc and γ NaBr from the freezing point depressions measured by Webb (11) and γ KBr from the solubility measurements of Griswald.

Where freezing point depression data were used, the j function of Lewis was calculated as

$$j = 1 - \frac{\vartheta}{\nu\lambda m} = 1 - \frac{\vartheta}{3.569m}$$

$-\vartheta$ is the freezing point depression

ν is the no. of particles per molecule of solute taken as 1

λ is the freezing point depression constant calculated as

$$\lambda = \frac{R T_0^2 M_1}{1000 L_0}$$

L_0 = 2757 calories per mole = heat of fusion

R = gas constant/mole = 1.98 cals.deg.

T_0 = melting point of acetic acid 289.79K.

M_1 = molecular weight of acetic acid 60.05

These data were obtained from Timmerman's "The Physical Constants of Pure Organic Compounds"(63).

The activity coefficient of the solute may be obtained by a graphical solution of the equation:

$$\ln \gamma = -\int_0^m j \, d\ln m - j + \frac{\alpha}{\nu}\int_0^m \frac{\theta}{m}\, d\theta$$

$$\alpha = \frac{1000}{R T_0^2 M_1}\left(b + c\theta\right)$$

$$b = \left(\frac{2L_0}{T_0} - \Delta C_p\right) \qquad c\theta \text{ term neglected}$$

$$\alpha = -7.051 \times 10^{-4}$$

ΔC_p = 8.94 cals./mole (from Timmerman's)

The first two terms on the right-hand side were found to be the only ones which contributed appreciably to $\ln \gamma$.

Where solubility data were used, the most dilute solution was used as a temporary standard. γ_s/γ_0 values were calculated and plotted as ordinates with the molality as abscissa. A graphical extrapolation was used to obtain γ_s/γ^* from this plot (42). From this, with $\gamma^* = 1$, activity coefficients of all the solutions at finite concentrations were calculated.

The results of these computations are conveniently summarized in the following table:

Table II

Σm	γ_{KOAc}	γ_{NaBr}	γ_{KBr}	γ_{NaOAc}	$\frac{\gamma_{KOAc}\gamma_{NaBr}}{\gamma_{KBr}\gamma_{NaOAc}}$
.010	1.000	1.20	.99	1.15	1.05
.015	1.002	1.14	.98	1.03	1.13
.018	1.002	1.09	.97	1.09	1.03
.020	1.002	1.09	.97	1.12	1.005
.022	1.004	1.09	.97	1.13	0.998
.025	1.006	1.09	.96	1.10	1.04

Although these activity coefficients are by no means precise the resultant quotient is fairly constant. The variation in the quotient in the region in which most measurements lie i.e. .018 to .025 molal is less than 4%. The quotient could not be evaluated in more concentrated solutions because of a lack of data.

If these figures do not completely vindicate the assumption that the quotient is unity, they at least show that such an assumption will not lead to an equilibrium constant differing significantly from that obtained by the use of activities.

The fact that solutions of these salts in acetic acid behave almost as ideal solutions ($\nu = k$) was noticed over sixty years ago by Raoult (43), Raoult and Recoura (44), and Beckmann (45).

Experimental

The experimental work reported in this thesis consists of two parts. The first and principal part consists of the measurement at 30°C. of the electrical conductance of solutions of the bromides, acetates, and formates of lithium, sodium, and potassium in anhydrous acetic acid. Concentrations ranging from about $1x10^{-5}$ to 1×10^{-2} molal were used in this part of the work.

For the second part of this investigation the solubility of potassium bromide at 30°C. in acetic acid solutions of lithium formate and of sodium bromide was determined. The first of these salts is, of course, a heteroionic solvent salt, the second has an ion in common with the solute salt. Concentrations of solvent salt ranging from about 1×10^{-3} to 3×10^{-2} molal were employed in this study.

Preparation of Salts

The salts used in this work were recrystallized twice from reagent quality salts, except for potassium bromide which was recrystallized three times. These salts were dried at 110°C. for a week. Several samples were identical with those used in a previous investigation (9). Their preparation was as follows: the acetates were prepared from commercial c.p. salts, crystallized from water, dried at 110°C., then pulverized and dried again at 190°C.; the sodium bromide was recrystallized from water, dried at 110°C. to remove the water of crystallization, and then dried at 150°C.; the potassium formate was recrystallized from water and dried at 110°C.; the sodium formate was prepared from c.p. sodium carbonate and c.p. formic acid (85%), crystallized twice and dried at 130°C.; the lithium acetate was recrystallized from the c.p. salt and dried at 110°C., then pulverized and dried again at 130°C. The salts were analyzed for purity by gravimetric methods. The bromides were precipitated as silver bromide and the acetates and formates were fumed with concentrated sulfuric acid to give the alkali metal sulfate. The components used were generally better than 99.5% pure.

Preparation of Anhydrous Acetic Acid

The anhydrous acetic acid used in this work was prepared from 99.5% commercial c.p. acetic acid. For the earlier work this acid was fractionated and analyzed for its water content by the freezing point method. Here the weight of acetic anhydride required was calculated from the factor of DeVisser (46)

$$Ac_2O = .028137\, w \Delta t$$

where w is the weight of impure acid

Δt is the difference between the freezing point of the acid and 16.60°C.

A quantity of acetic anhydride (slightly in excess of the amount needed theoretically to react with all the water present) was added. This mixture was then allowed to reflux for at least two days. It was then fractionated through a four foot column packed with 1/4" glass beads, the portion going over at 116-118°C. being collected. Acid purified in this manner had a specific conductance of $3\text{-}4.5 \times 10^{-8}$ cm ohm^{-1} and a melting point of 16.60 ± .01°C. The lowest value of the specific conductance of acetic acid in the literature is .4 x 10^{-8} cm ohm^{-1}(32) while the accepted melting point is 16.60°C. For the later work a more convenient method of purification was used. In this method a quantity of 99.5% acetic acid is refluxed with acetic anhydride (excess) and benzene. After two days this is fractionated. The benzene forms an azeotrope with what water, if any, that remains in the mixture and distills over at 78°C. Following this the temperature of the column rises to 116°C. and the same fraction is cut as before. The acetic acid prepared by this method is found to have a specific conductance of 3-4 x 10^{-8}cm ohm^{-1}. The melting point of this acid is 16.60°C.

Constant Temperature Bath

Both the solubility studies and the conductance measurements in this work were made at 30°C. Since control of bath temperature is very important, especially for conductance measurements, the bath used here will be described in some detail. The bath proper consisted of a rectangular enameled cast iron tub approximately

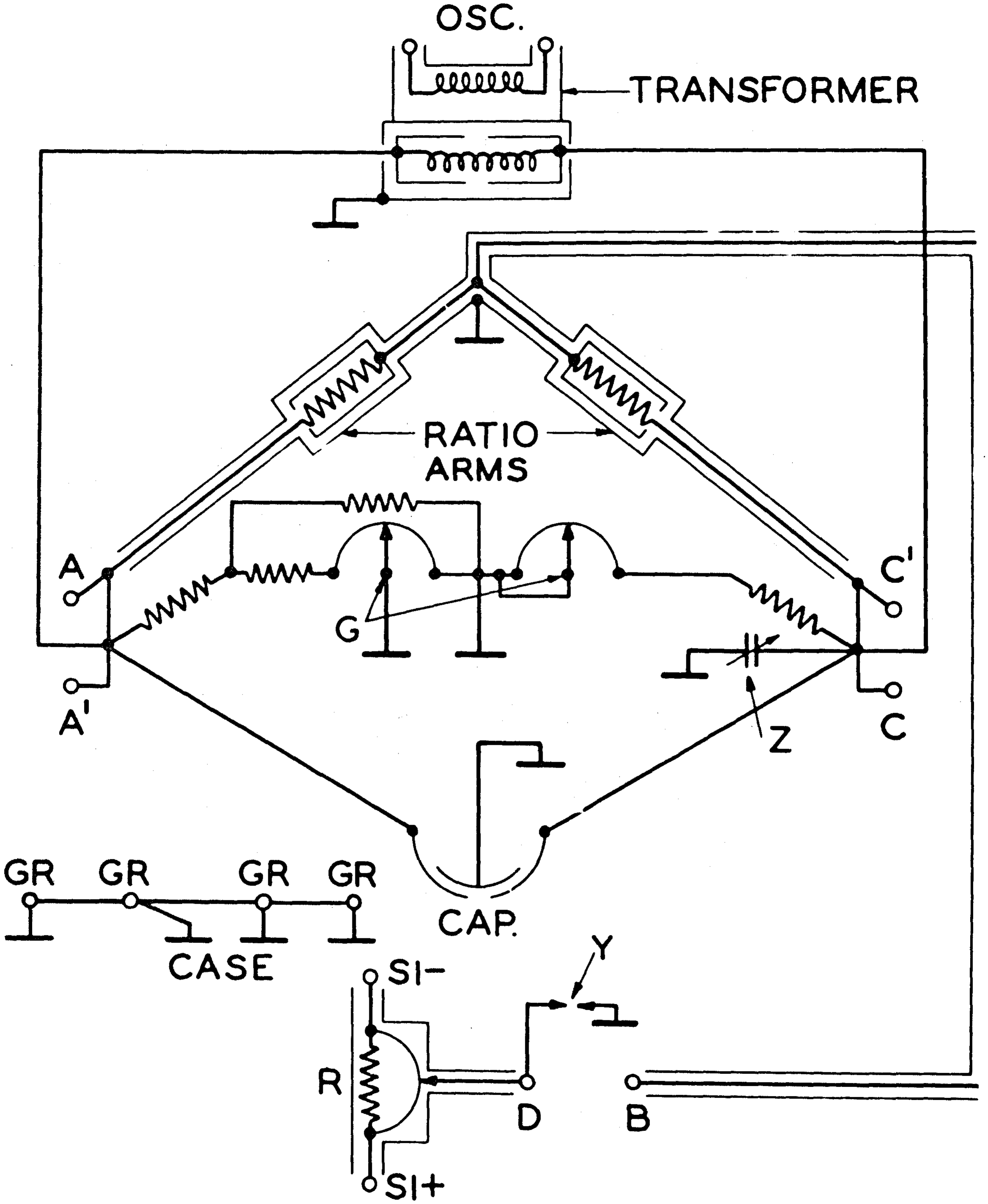
2' x 2' x 4'. It contained a stirrer-sample holder, made of stainless steel which kept the solubility samples submerged and tumbled them end over end until equilibrium was reached. A small oil bath, equipped with its own stirrer, was inserted to hold the conductivity cells (47). The main bath was heated by means of a 500 watt copper tube heater. Cooling coils, also of copper, were used continually in the summer. It was found that a slow trickle of cooling water was sufficient to keep the bath at constant temperature i.e. with the thermoregulator clicking intermittently. The actual thermoregulator was obtained from the American Instrument Company, Silver Springs, Maryland. The sensitivity of these thermoregulators is not greater than ± 0.02°C.

Since the average temperature coefficient of conductivity is 2%, this means that the error introduced by the fluctuation of the thermoregulator is of the order of ± 0.04%. This error is often the factor which limits the precision of conductivity measurement. Because of the very high resistances measured in the present work, and because of the bridge employed, however, temperature control turns out not to be the limiting factor in this case. The original setting of the mercury thermoregulator was made by comparison with a set of Anschutz thermometers previously calibrated at the National Bureau of Standards. When all the sources of error are taken into consideration the constant temperature bath probably had a temperature of 30°C. to within ± 0.05°C.

Conductance Studies

The Bridge The bridge used in these measurements was a Leeds and Northrup Model 1554-A-2. A diagram of this bridge is shown on the next page. Other equipment used with the bridge was: (1) a resistance box of 11,111.11 ohms, Leeds and Northrup Model 4750, (2) an oscillator which was capable of furnishing 500, 1000, or 2000 cycles per second, Leeds and Northrup Model 9842, (3) a large air capacitor of 1200 mmfd, Leeds and Northrup Model 1187, (4) an amplifier, Leeds and Northrup Model 9847 and (5) a pair of earphones.

With reference to the diagram, the additional resistance box of 11,111.11 ohms was connected between a ground and


OSC.
TRANSFORMER
RATIO
ARMS
A
A'
C'
C
G
Z
GR
GR
GR
GR
CASE
CAP.
Y
SI-
SI+
R
D
B

terminal A'. The conductivity cell as well as a 10,000.00 ohm standard resistance and the large air capacitor were connected between the same ground and C'. This allowed capacitance effects, originating in the conductivity cell, to be balanced out. It was found that the dial on the box corresponding to hundredths of an ohm could not be used. This was due to the presence of a large amount of electrical equipment in the vicinity of the bridge. The bridge was found to be very sensitive to the effects of running electrical equipment such as motors, the bath thermostat, etc. and ordinarily any equipment which could be, was momentarily shut off while the final balance of the bridge was made. A superficial analysis of the effect of errors in the bridge reading upon the calculated resistance of the cell and dial box in parallel ~~are~~ when balanced against a 10,000 ohm standard at all times may be readily made. From this information we may write

$$\frac{1}{R_{Std.}} = \frac{1}{R_{cell}} + \frac{1}{R_{box}}$$

$$\frac{1}{R_{std}} = 1.0000 \times 10^{-4} \text{ at all times}$$

$$\frac{d\,R_{cell}}{R^2_{cell}} + \frac{d\,R_{box}}{R^2_{box}} = 0$$

$$\frac{d\,R_{cell}}{R^2_{cell}} = -\frac{d\,R_{box}}{R^2_{box}}$$

or more conveniently

$$\frac{\delta R_{cell}}{\delta R_{box}} = -\frac{R^2_{cell}}{R^2_{box}}$$

From this we may readily show that an error of 0.1 ohm in the dial box reading will cause an error of 100 ohms in the cell reading if we take $R_{box} = 10^4$ and $R_{cell} = 10^6$. Thus while our box reading may be precise to .01% our cell resistance will have a precision of only .1%.

It must be remembered that the calculation is representative of the readings actually taken. In some instances a precision of 0.02% on the dial box or 0.2% on the cell was the greatest that could be obtained.

Conductance Cells

A great many conductance cells were made for the studies on conductivities. They are all of the design advocated by Jones and Bollinger (48) very slightly modified. Of those that were made only five showed themselves usable in the concentration ranges studied. These had cell constants ranging from 0.1 to 0.3 and were recalibrated several times (49)(50). The calibration procedure used was as follows: solutions of KCl in re-distilled water were prepared according to the directions of Jones and Bollinger (3); these standard solutions were then used to calibrate a cell with a high cell constant; a more dilute KCl solution was then prepared and its conductivity was measured in the cell previously calibrated; this solution was then used to calibrate cells with lower cell constants. It was found that it was necessary that the conductance cells be dried in a vacuum oven at 40-50°C. to prevent the cell constant from drifting. Cells dried at 110°C. subsequent to calibration showed a marked change in cell constant when recalibrated. The fact that dilute solutions of the salts studied had very high resistances ($\sim$1,000,000 ohms) demanded cell constants no higher than 0.15.

Preparation of Samples for Conductance Measurements

The solutions used in the conductance studies were prepared in the following manner. The dry salt (usually dried at 110°C. for 24 hours) was put into a weighing bottle and weighed. A sample of acetic acid was transferred to a weight burette in a dry box and subsequently weighed. Suitable portions of these were then transferred to a glass stoppered bottle in a dry box. The weighing bottle, weight burette and solution were subsequently removed from the dry box and all but the latter were weighed. The solution was usually shaken overnight on an automatic shaker, to insure complete solution. This solution was then transferred to a dry box and used to furnish a stock solution from which more dilute solutions were prepared. All transfers of acetic acid and of solution were performed in a dry box, dried with phosphorous pentoxide. The weights of the containers before and after transfer furnish information from which the molalities could be calculated. These molalities were later converted to concentration units by use of the density. For dilute solutions (below about $1 \times 10^{-3} m$) the density was assumed to be the same as the density of the acid at the temperature (30°C.). For the more concentrated solutions the density was computed by assuming the volume of the solution to be the same as that of the acid used, but taking the weight of the added salt into account. Since even the most concentrated solution used was quite dilute ($7 \times 10^{-2} m$) the corrections were ordinarily not more than 0.01% of the density of acetic acid alone.

Preparation and Analysis of Solubility Samples

The solubility samples were all prepared directly in ampules drawn from 8" Pyrex test tubes. A stock solution of a salt in acetic acid was prepared in a dry box. The weight of salt and acetic acid used was determined and the stock solution then put on a shaker to insure solution. A known weight of stock solution of the solvent salt, a known volume of acetic acid (delivered from a calibrated pipette), and an excess of solid potassium bromide were all added to the ampule. It was then sealed off with an oxygen torch, tested for leaks and, if none were found, was put on the rotating sample holder in a 30°C. bath. These samples were then allowed to equilibrate for 5 to 30 days before analysis (usually about 14 days). At the end of the settling period the tip of the ampule was broken and a pipette, whose tip was covered with filter paper, was inserted. The sample drawn up was immediately transferred to a tared weighing bottle and weighed. The material in the weighing bottle was then washed into a beaker and analyzed by the Volhard Method (5). When the solvent salt was not a bromide, this analysis gave the total potassium bromide directly, i.e. the solubility of the potassium bromide. Where the solvent salt was sodium bromide the total analytical concentration of bromide ion, together with the total weight of sample analyzed and the known ratio of acetic acid to sodium bromide in the initial solvent mixture were combined to yield values of potassium bromide concentration. This calculation is illustrated for NaBr:

If

x = weight of solvent in sample
y = weight of NaBr " "
z = weight of KBr " "
A = total weight of sample
k = ratio of HOAc/NaBr in sample
B = weight of bromide by Volhard Analysis

$$x + y + z = A$$
$$ky = x$$

$$\left[\frac{Br}{NaBr}\right] y + \left[\frac{Br}{KBr}\right] z = B$$

$$0.7765y + 0.6715z = B$$

Now

$$k = \frac{1000}{102.913\,m}$$

Solving these equations for y and z we get

$$y = \frac{\begin{vmatrix} A & 1 \\ B & .6715 \end{vmatrix}}{\begin{vmatrix} 1+k & 1 \\ .7765 & .6715 \end{vmatrix}} \; ; \qquad z = \frac{\begin{vmatrix} 1+k & A \\ .7765 & B \\ \cancel{B} & \cancel{.6715} \end{vmatrix}}{\begin{vmatrix} 1+k & 1 \\ .7765 & .6715 \end{vmatrix}}$$

Table III

Equivalent Conductance of Potassium Bromide Solutions at 30° C.

C molarity	Λ_c (ohms^{-1})
9.140×10^{-5}	1.281
2.247×10^{-4}	1.150
2.334×10^{-4}	1.107
3.525×10^{-4}	0.9075
3.661×10^{-4}	0.8737
4.498×10^{-4}	0.6785
6.173×10^{-4}	0.6006
9.614×10^{-4}	0.4861
1.190×10^{-3}	0.4422
1.332×10^{-3}	0.4203
2.338×10^{-3}	0.3240
7.607×10^{-3}	0.1954

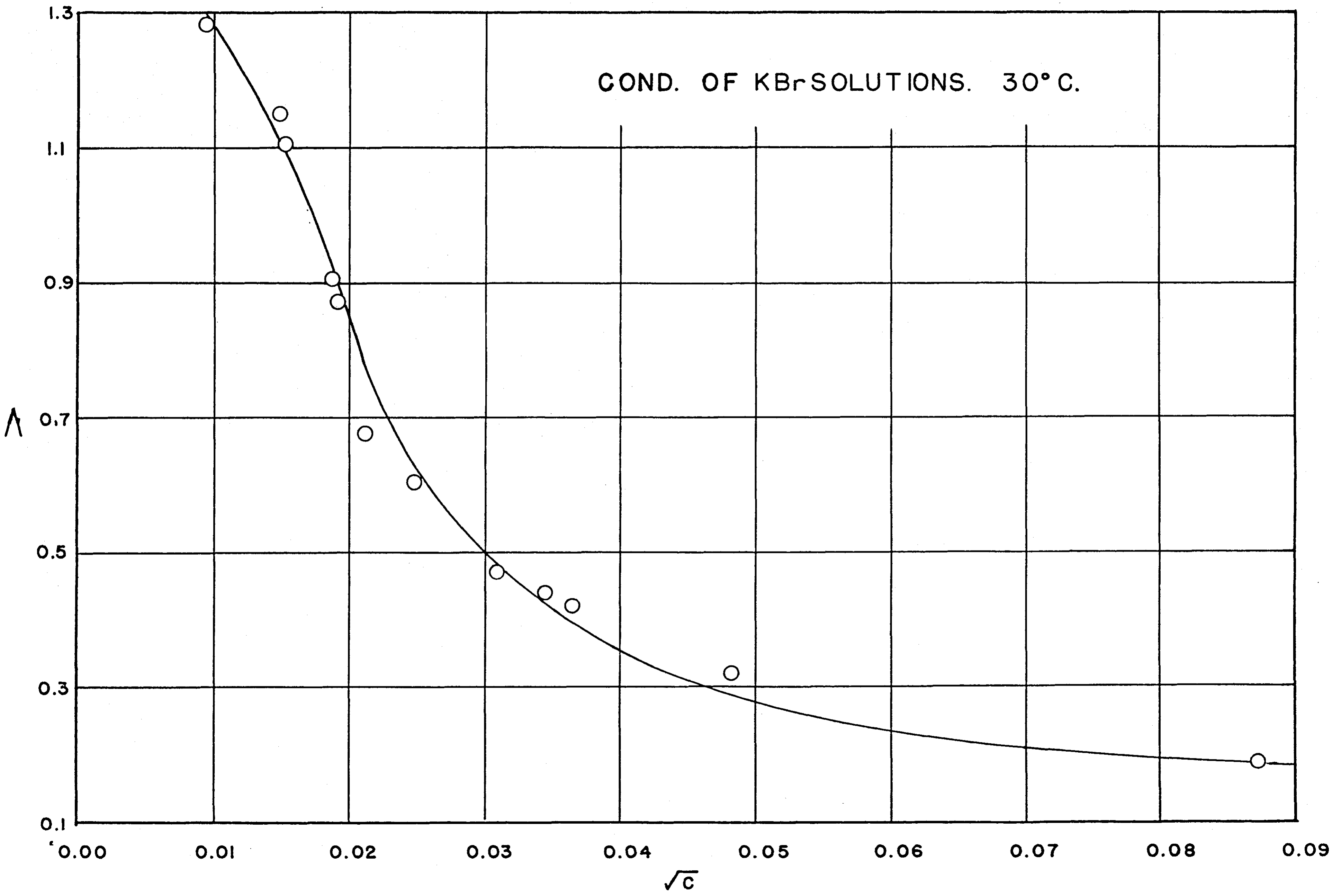

COND. OF KBr SOLUTIONS. 30° C.
Λ
1.3
1.1
0.9
0.7
0.5
0.3
0.1
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
√C

Table IV

Equivalent Conductance of Sodium Bromide at 30° C.

C molarity	Λ_c (ohm^{-1})
1.109×10^{-5}	6.789
5.596×10^{-5}	2.222
5.908×10^{-5}	2.245
1.382×10^{-4}	1.229
4.757×10^{-4}	0.7727
4.973×10^{-4}	0.6801
1.890×10^{-3}	0.5377
2.046×10^{-3}	0.5194

Table V

Equivalent Conductance of Lithium Bromide at 30° C.

C molarity	Λ_c (ohm^{-1})
2.177×10^{-5}	4.640
5.836×10^{-5}	3.170
1.146×10^{-4}	2.286
1.409×10^{-4}	2.269
1.440×10^{-4}	2.123
1.682×10^{-4}	2.067
1.861×10^{-4}	1.980
3.442×10^{-4}	1.496
3.681×10^{-4}	1.348
5.818×10^{-4}	1.198
6.583×10^{-4}	1.100
7.555×10^{-4}	0.9715
2.172×10^{-3}	0.6792
4.770×10^{-3}	0.5015
5.493×10^{-3}	0.4777

Table VI

Equivalent Conductance of Potassium Formate at 30° C.

C molarity	Λ_c (ohm^{-1})
8.069×10^{-5}	1.264
2.309×10^{-4}	0.7489
3.011×10^{-4}	0.5967
9.230×10^{-4}	0.3890
1.570×10^{-3}	0.3781
1.768×10^{-3}	0.2821
1.935×10^{-3}	0.2800
5.231×10^{-3}	0.1787
5.668×10^{-3}	0.1643
1.126×10^{-2}	0.1318
4.377×10^{-2}	0.1091

Table VII

Equivalent Conductance of Sodium Formate at 30°C.

C molarity	Λc (ohm)
1.250×10^{-4}	0.7534
2.583×10^{-4}	0.5371
3.616×10^{-4}	0.4264
5.349×10^{-4}	0.3748
1.327×10^{-3}	0.2457
1.617×10^{-3}	0.2323
1.170×10^{-3}	0.2251
1.905×10^{-3}	0.2116
9.841×10^{-3}	0.1080

Table VIII

Equivalent Conductance of Lithium Formate at 30°C.

C molarity	Λ_c (ohm^{-1})
4.010×10^{-4}	0.3863
4.838×10^{-4}	0.3466
5.723×10^{-4}	0.3087
5.960×10^{-4}	0.3040
6.686×10^{-4}	0.2912
6.783×10^{-4}	0.2831
8.500×10^{-4}	0.2549
4.354×10^{-3}	0.1182
5.769×10^{-3}	0.1080
1.074×10^{-2}	0.08333
2.117×10^{-2}	0.08425

Table IX

Equivalent Conductance of Potassium Acetate at 30°C.

C molarity	Λc ohm^{-1}
1.558×10^{-5}	3.640
2.882×10^{-5}	2.508
8.895×10^{-5}	1.706
1.066×10^{-4}	1.557
2.336×10^{-4}	1.014
2.462×10^{-4}	0.9972
3.321×10^{-4}	0.8699
3.901×10^{-4}	0.7965
1.046×10^{-3}	0.5118
2.509×10^{-3}	0.3539
3.474×10^{-3}	0.3069
3.872×10^{-3}	0.2961
4.460×10^{-3}	0.2816

Table X

Equivalent Conductance of Sodium Acetate at 30°C.

C molarity	Λ_c (ohm^{-1})
1.154×10^{-5}	4.082
3.597×10^{-5}	1.527
4.982×10^{-5}	1.316
5.550×10^{-5}	1.229
8.507×10^{-5}	1.032
1.004×10^{-4}	0.9158
2.277×10^{-4}	0.7417
1.034×10^{-3}	0.2787
1.173×10^{-3}	0.2664
1.663×10^{-3}	0.2221
2.150×10^{-3}	0.1603
6.448×10^{-3}	0.1569

Table XI

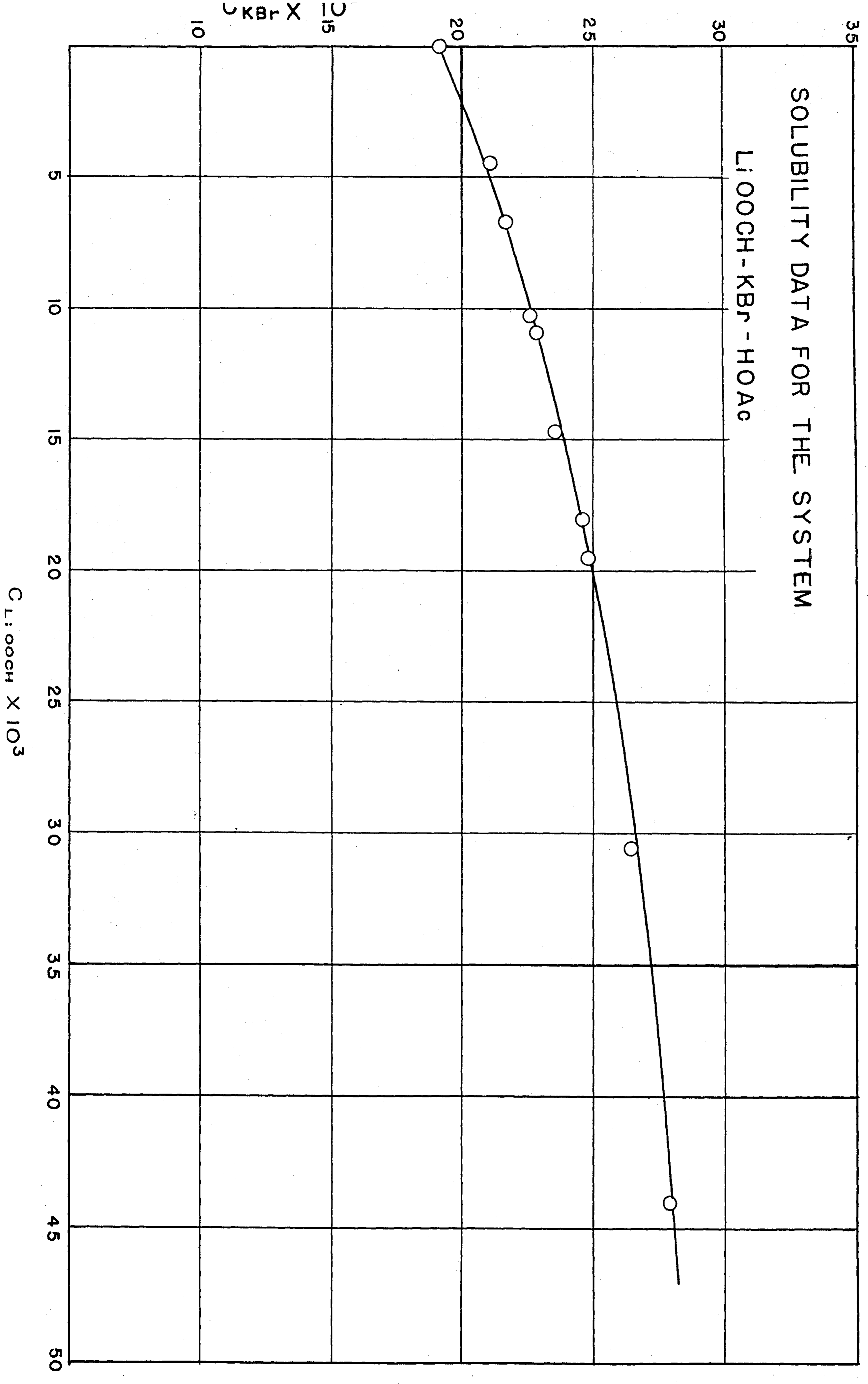
Equivalent Conductance of Lithium Acetate at 30°C.

C molarity	Λ_c (ohm^{-1})
2.718×10^{-5}	3.022
3.980×10^{-5}	2.275
4.910×10^{-5}	1.651
2.058×10^{-4}	0.7387
2.687×10^{-4}	0.6375
6.365×10^{-4}	0.3817
7.722×10^{-4}	0.3035
1.448×10^{-3}	0.2234
1.716×10^{-3}	0.2225
3.387×10^{-3}	0.1606

Table XII

Solubility of Potassium Bromide in Lithium Formate-Acetic Acid Solutions

$C_{molality}$	$S_{molality}$	K
0	0.01837	---
4.432×10^{-3}	0.02100	3.84×10^{-3}
6.389×10^{-3}	0.02169	3.59×10^{-3}
10.19×10^{-3}	0.02256	2.93×10^{-3}
10.71×10^{-3}	0.02283	3.18×10^{-3}
14.65×10^{-3}	0.02353	2.76×10^{-3}
17.95×10^{-3}	0.02473	3.54×10^{-3}
18.42×10^{-3}	0.02487	3.54×10^{-3}
30.43×10^{-3}	0.02657	3.02×10^{-3}
43.96×10^{-3}	0.02799	2.69×10^{-3}

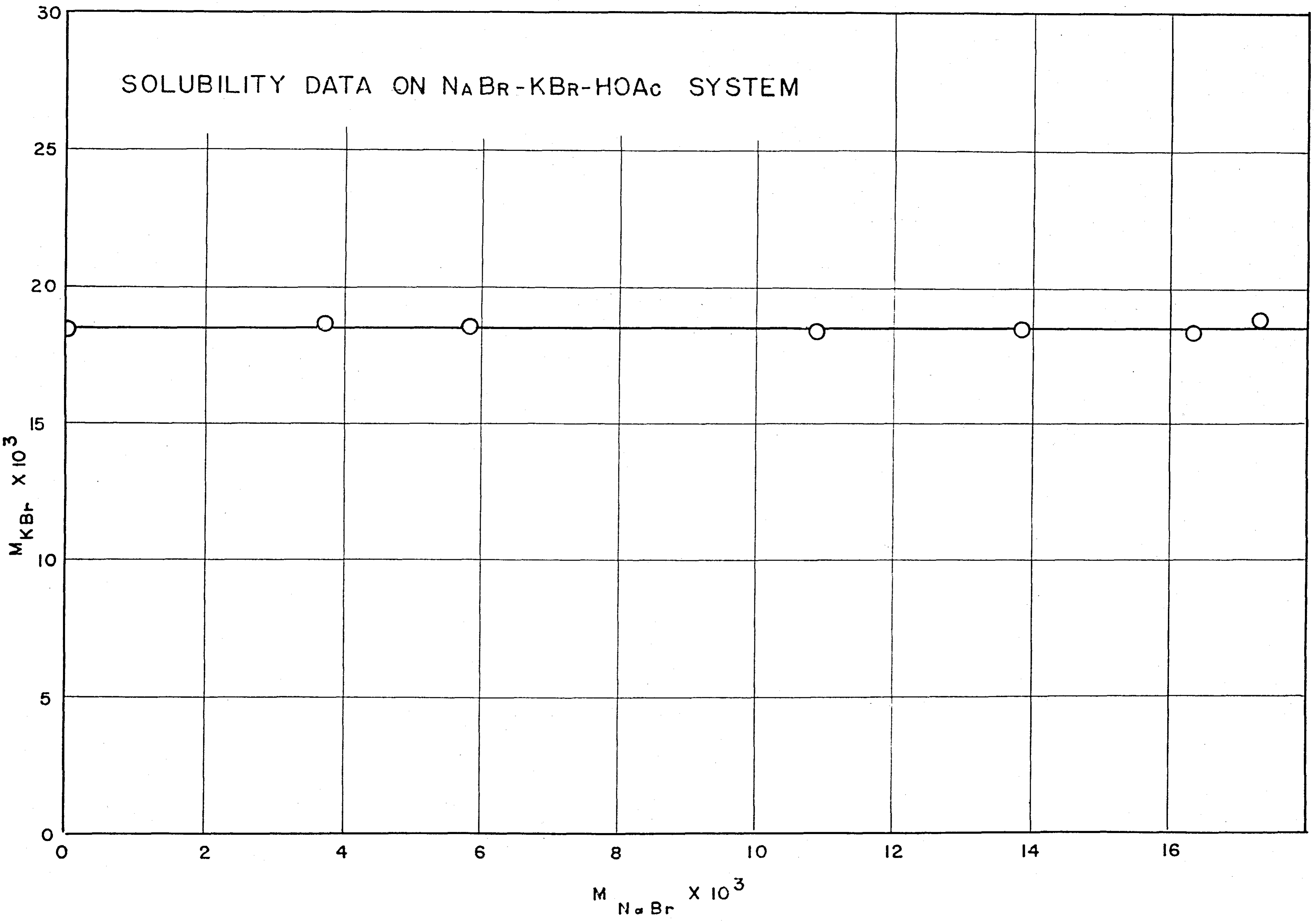

SOLUBILITY DATA FOR THE SYSTEM

LiOOCH-KBr-HOAc

Table XIII

Solubility of Potassium Bromide in Sodium Bromide-Acetic Acid Solutions

$C_{molality}$	$S_{molality}$
0	0.01837
3.785×10^{-3}	0.01862
5.829×10^{-3}	0.01858
1.087×10^{-2}	0.01844
1.385×10^{-2}	0.01850
1.639×10^{-2}	0.01832
1.732×10^{-2}	0.01890


SOLUBILITY DATA ON NaBr-KBr-HOAc SYSTEM

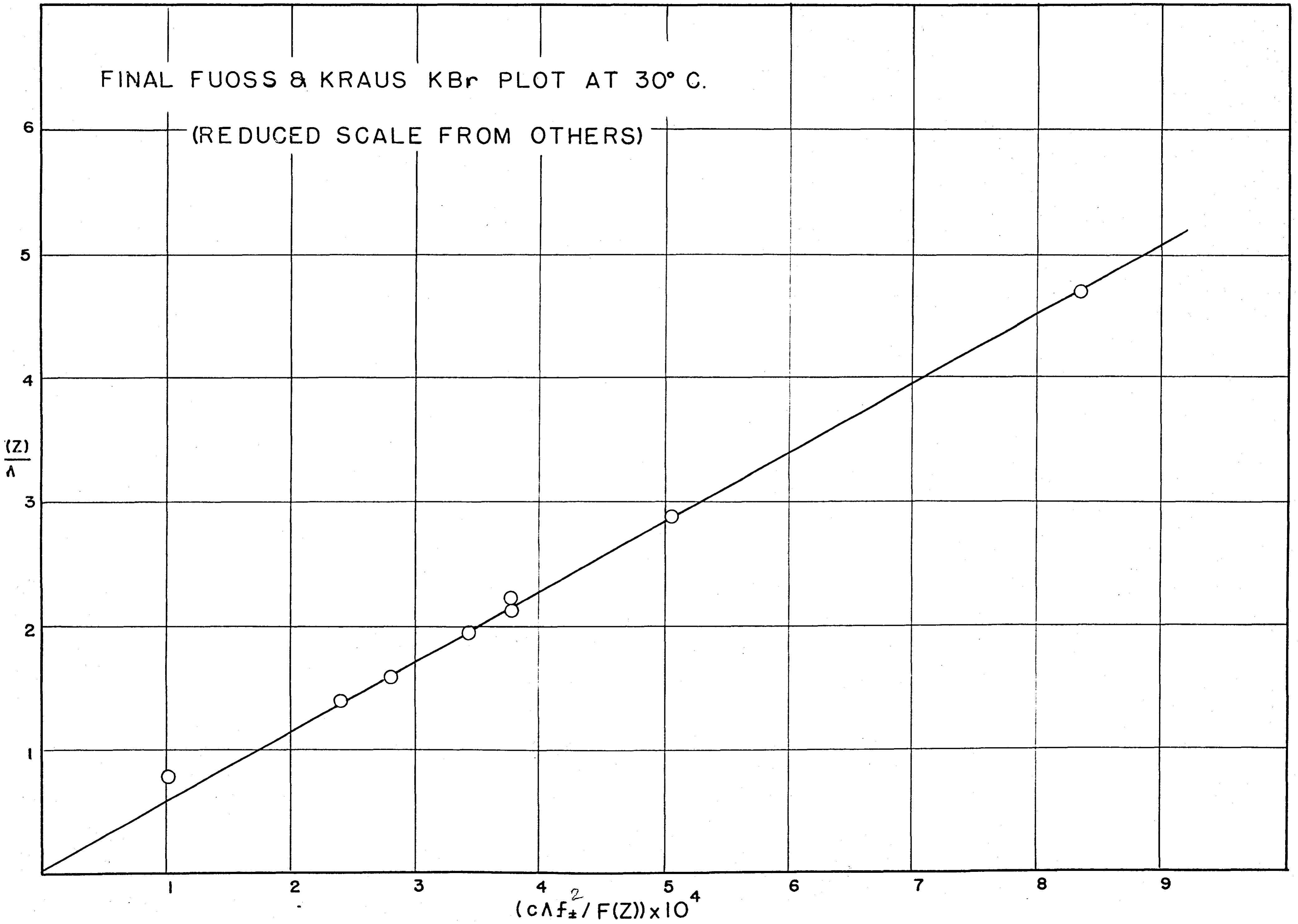
Discussion

The results of the conductance measurements show a variation of equivalent conductance with concentration which is characteristic of weakly dissociated solutes. Qualitatively, at least, the relations are typical of those previously observed with other solvents of moderately low dielectric constant. It seemed worthwhile, therefore, to undertake a Fuoss-Kraus treatment of the data. The data so used ~~is~~ are expressed in terms of molarity. Values of the limiting equivalent conductance, Λ_0 , were accordingly obtained for each salt by the method of successive approximations outlined in the Theoretical section. A typical final set of values used in this treatment is given for KBr in Table XIV. The corresponding plot is shown following the table. From a large-scale plot of this kind the intercept could be obtained and Λ_0 calculated. This value, together with the slope of the line then made it possible to get a value of the ion-pair dissociation constant for each salt. The results of these computations rounded to two significant figures are presented in Table XV.

Table XIV

Figures for final Fuoss and Kraus plot on KBr

$\frac{F(z)}{\Lambda}$	$\frac{c\Lambda\overset{?}{y}^{2}}{F(z)}$ x 10^4
2.888	5.036
2.141	3.752
2.248	3.729
1.591	2.794
4.649	8.345
1.954	3.400
1.414	2.363
0.761	1.000



FINAL FUOSS & KRAUS KBr PLOT AT 30° C.

(REDUCED SCALE FROM OTHERS)

Table XV

Limiting Equivalent Conductances and Dissociation Constants of the Salts Studied Conductometrically

Salt	Λ_0	$K_{molarity}$
KBr	41	1.1×10^{-7}
NaBr	37	1.37×10^{-7}
LiBr	29	7.21×10^{-7}
KOOCH	35	1.05×10^{-7}
NaOOCH	31	6.5×10^{-8}
LiOOCH	23	8.64×10^{-8}
KOAc	24	3.60×10^{-7}
NaOAc	20	2.13×10^{-7}
LiOAc	13	6.0×10^{-7}

An examination of the values of Λ_0 in the table shows that Kohlrausch's law of additivity of ionic conductances at infinite dilution must be obeyed. Thus

$$\Lambda^0_{KBr} - \Lambda^0_{NaBr} = \Lambda^0_{KOAc} - \Lambda^0_{NaOAc} = \Lambda^0_{KOOCH} - \Lambda^0_{NaOOCH} = 4$$

Similarly

$$\Lambda^0_{KBr} - \Lambda^0_{KOAc} = 17$$

$$\Lambda^0_{NaBr} - \Lambda^0_{NaOAc} = 17$$

$$\Lambda^0_{LiBr} - \Lambda^0_{LiOAc} = 16$$

Thus, except for lithium acetate, the values of Λ^0 obtained here are all self-consistent with respect to Kohlrausch's law.

In order to obtain values of limiting ionic conductances it is necessary, of course, to have values of transference numbers for the ions in at least one of the salts. Davidson and Lanning (52) determined transference numbers of sodium and acetate ions in sodium acetate solutions in acetic acid at 30°C. over a concentration range of .35 to .89 molal. From their data one may readily obtain t_0^+ and t_0^- values by an extrapolation to infinite dilution. These values, combined with the data collected in this thesis were used to calculate limiting ionic equivalent conductances for all the ions. For this the equations used were:

$$t_0^+ \Lambda_0 = \lambda_0^+$$

$$t_0^- \Lambda_0 = \lambda_0^-$$

The results of these calculations are presented in Table XVI. In many cases further information may be obtained from these limiting ionic equivalent conductances. The ionic mobilities may be directly calculated from the value of the limiting ionic equivalent conductance $\lambda_0^{\pm}$ and the value of the faraday (F).

$$\lambda_0^+ = u_0^+ F$$

$$\lambda_0^- = u_0^- F$$

$$F = 96{,}500 \text{ coulombs equivalent}^{-1}$$

Under certain conditions further information may be obtained from these ionic mobilities. It can be shown that

$$u_0^{\pm} = \frac{z_{\pm} e E}{300 P_f}$$

where P_f is the viscous resistance of the medium. Stokes law enables us to write

$$P_f = 6 \pi r_i \eta$$

where η is the viscosity of the medium here taken as 1.006 x 10^{-3} poise and r_i the radius of the ion. By combining our equations we arrive at

$$r_i = 7.966 \times 10^{-12} \frac{z}{u_i}$$

Under suitable conditions this relationship will furnish a method for the determination of the ionic radii. The values of the ionic radii obtained by this method are all somewhat larger than those obtained from the equilibrium constant. They are listed in Table XVI. It is most reasonable to

Table XVI

Ion	$\lambda_0^{\pm}$	u cms sec^{-1}	r_{vis}	$r_{crystal}$
K^+	14	1.45×10^{-4}	5.5 A	1.19
Na^+	10	1.04×10^{-4}	7.7 A	0.88
Li^+	2	2.07×10^{-5}	38 A	0.48
Br^-	27	2.80×10^{-4}	2.8 A	1.60
$OOCH^-$	21	2.18×10^{-4}	3.7 A	----
OAc^-	10	1.04×10^{-4}	7.7 A	----

conclude that Stoke's law holds fairly well.

It is of interest to note that the order of decreasing mobility of the three cations considered in the present investigation is $K^+ > Na^+ > Li^+$, the same order as in water. As in the latter case, this reversal in order may probably be attributed to different degrees of solvation increasing in the order indicated.

The values of ion-pair dissociation constants given in Table XVII indicate that the salts involved do indeed exist very largely in acetic acid as ion-pairs with only very low concentrations of free ions present. For instance, the concentration of free ions in a 0.01 molar solution of KBr is $3.3 \times 10^{-5} m$. The effect of long-range interaction among ions in this solvent would thus appear to be much smaller than has generally been assumed.

Attention may be called to the fact that the order of decreasing dissociation constant for the acetates is LiOAc > KOAc > NaOAc . Since these compounds are bases in acetic acid this order should represent their relative basic strengths. Previous work by Kolthoff and Willman (32)(33) does not agree with this. The order obtained by these investigators is KOAc > NaOAc > LiOAc. This work used indicator methods.

In an earlier section of this thesis it was pointed out that the Bjerrum-Fuoss-Kraus theory yields the following relation involving the ion-pair dissociation constant

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

With K known, it is easy to get the corresponding value of the definite integral, $Q(b)$. From this, in turn, the parameter b may be obtained. Since b is related to the distance of closest approach parameter, a, through the relation

$$b = \frac{\epsilon^2}{DkTa}$$

values of a may be calculated. Results of these

Table XVII

Ionic Radii from the Bjerrum Theory

Salt	K	$Q(b)$	$\log Q(b)$	b	a
LiOOCH	8.64×10^{-8}	7.69×10^{3}	3.886	20.7	4.40 A
KOAc	3.60×10^{-7}	1.85×10^{3}	3.267	19.0	4.79
LiBr	7.21×10^{-7}	9.22×10^{2}	2.965	18.0	5.06
KOOCH	1.05×10^{-7}	6.33×10^{3}	3.801	20.6	4.42
KBr	1.096×10^{-7}	6.07×10^{3}	3.783	20.5	4.44
LiOAc	6.0×10^{-7}	1.1×10^{3}	3.045	18.3	5.0
NaOOCH	6.5×10^{-8}	1.0×10^{4}	4.009	21.3	4.3
NaOAc	2.13×10^{-7}	3.12×10^{3}	3.494	19.5	4.67
NaBr	1.37×10^{-7}	4.85×10^{3}	3.686	19.2	4.59

calculations are given in Table XVII. These values appear to be of reasonable magnitude. In view of solvation effects it is not surprising that the calculated distances for the bromides, for example, are larger than the sums of the crystal radii.

Solubility Studies

It is to be noted that a heteroionic solvent salt produces a pronounced increase in solubility while a salt with a common ion has little effect. The common ion effect seems to be absent in this solvent. This fact is illustrated in the data for the effect of sodium bromide on the solubility of potassium bromide, which shows no evidence of a decrease in potassium bromide concentration when sodium bromide is added. The assumption that ion-pair exchange occurs, together with the assumption that the free ion concentrations are small and that the γ's of the ion pairs are constant, leads in the case of a heteroionic solvent salt to

$$K' = \frac{\Delta S^2}{S_0(C - \Delta S)}$$

The K' values for lithium formate, collected in this thesis, confirm the constancy of K'. It can also be seen that in the case of a solvent salt with a common ion the ion-pair exchange cannot affect the solubility. The data on sodium bromide-potassium bromide mixtures presented here confirms this.

It is of some interest to consider another mechanism which will also furnish an equilibrium constant of exactly the same form as equation (XXXI). The conditions under which such a mechanism may occur will be explicitly stated below. If one assumes that all solutes in solution are present predominantly as triple ions we may consider the following equilibria. For pure solutions of KBr or MX we may write

$$\left\{\begin{array}{l} K^+ + K^+Br^- \rightleftharpoons K^+Br^-K^+ \\ Br^- + K^+Br^- \rightleftharpoons Br^-K^+Br^- \end{array}\right.$$

$$\left\{\begin{array}{l} M^+ + M^+X^- \rightleftharpoons M^+X^-M^+ \\ X^- + M^+X^- \rightleftharpoons X^-M^+X^- \end{array}\right.$$

The equilibria are assumed to be displaced far to the right. If we add a moles of MX to a solution saturated with KBr the following reactions may occur

$$\mathrm{KBrK} + \mathrm{MXM} \rightleftharpoons \mathrm{KBrM} + \mathrm{MXK}$$

$$\mathrm{BrKBr} + \mathrm{XMX} \rightleftharpoons \mathrm{BrKX} + \mathrm{BrMX}$$

for these reactions we may write an equilibrium constant

$$K = \frac{[\mathrm{KBrM}][\mathrm{MXK}][\mathrm{BrKX}][\mathrm{BrMX}]}{[\mathrm{KBrK}][\mathrm{MXM}][\mathrm{BrKBr}][\mathrm{XMX}]}$$

If we now write

$$[\mathrm{KBrK}] = [\mathrm{BrKBr}] = \frac{S_0}{3}$$

$$[\mathrm{MXM}] = [\mathrm{XMX}] = \frac{a - \Delta S}{3}$$

$$[\mathrm{MXK}] = [\mathrm{KBrM}] = [\mathrm{BrMX}] = [\mathrm{BrKX}] = \frac{\Delta S}{4}$$

Then

$$K = \frac{\left(\frac{\Delta S}{4}\right)^4}{\left(\frac{S_0}{3}\right)^2 \left(\frac{c - \Delta S}{3}\right)^2}$$

$$K'' = \left(\frac{\Delta S^2}{c - \Delta S}\right)^2$$

So if the above conditions were to hold, the particular combination of factors

$$\frac{\Delta S^2}{c - \Delta S}$$

would be a constant. The conditions for this mechanism are quite stringent (also unlikely). While ion triplets of the type KBrK and BrKBr are probably present in nearly equal amounts, such triplets as MXK and XKBr would hardly be expected to be present in equal amounts. It seems probable that under conditions such that ion triplets were present in relatively high proportion, other ion multiples might very well be also, so that the reactions would be much less definite than those written above. The absence of minima in the $\Lambda - c$ curves, in the light of present theories, makes it very doubtful that a significant proportion of triple ions is present.

The calculation of equilibrium constants for the solubility equations, from ion-pair dissociation constants obtained from conductivity data can be illustrated by considering the situation when sodium formate is the solvent salt. In this case the solubility constant is written

$$K = K'S_0 = \frac{[K^+OOCH^-][NaBr^-]}{[Na^+OOCH^-]}$$

$$K' = \frac{[K^+OOCH^-][Na^+Br^-]}{[K^+Br^-][Na^+OOCH^-]}$$

But if we use the dissociation constants of these ion-pairs we may write

$$K' = \frac{K_{K^+Br^-} K_{Na^+OOCH^-} [K^+][Br^-][Na^+][OOCH^-]}{K_{K^+OOCH^-} K_{Na^+Br^-} [K^+][Br^-][Na^+][OOCH^-]}$$

The actual concentration of the ions is seen to cancel out.

$$K' = \frac{K_{K^+Br^-} \; K_{Na^+OOCH^-}}{K_{K^+OOCH^-} \; K_{Na^+Br^-}} = \frac{(1.096 \times 10^{-7})(6.5 \times 10^{-8})}{(1.05 \times 10^{-7})(1.37 \times 10^{-7})} -$$

$$K' = 0.50$$

From this and the fact that

$$K' S_0 = K$$

we may write (with $S_0 = 0.01837$)

$$K = (.50)(0.01837) = 9.2 \times 10^{-3}$$

The K from solubility data alone is 10×10^{-3}. The other K values are tabulated below.

Table XVIII

The Solubility Equilibrium Constants

Salt	K from soly. data	K from cond. data
LiOOCH	3.2×10^{-3}	2.25×10^{-3}
LiOAc	2.6×10^{-3}	4.65×10^{-3}
NaOOCH	10×10^{-3}	9.20×10^{-3}
NaOAc	12×10^{-3}	8.7×10^{-3}

These equilibrium constants are important because they show that in all probability the mechanism proposed by Griswold to account for the change in solubility is the correct one. The actual form used by Griswold can be derived on other bases. One such method assumes merely that most of the ions are present as ion-triplets instead of assuming, as Griswold does, that most of the ions are paired. The work presented in this thesis shows that such a situation is highly unreasonable.

Other Methods for the Determination of the Dissociation Constant

An independent determination of the ion-pair dissociation constants by a method not involving conductivity would certainly be very desirable. A search of the literature showed that other methods commonly used for this purpose in aqueous solutions stood only a small chance of success in acetic acid. Some of the methods which have been used to investigate this type of problem are:

1. Molar refraction studies (53)(54)(55)(56)

2. Raman Spectra (57)(58)(59)
3. Rotation of the Plane of Polarization in a Magnetic Field (60)~~(61)~~(61)

There is one serious difficulty which is common to all of the methods other than the conductometric method. This is that all these methods require that solutions of the components studied must be available in relatively pure form. Thus in the equilibrium

$$A^+ + B^- \rightleftharpoons A^+B^- \text{(ion-pair)}$$

one must have solutions of free A^+ and B^-, and of A^+B^- for comparison. Since free ions appear to be present to such a small extent in all acetic acid solutions of electrolytes, this condition cannot be fulfilled directly. It may be possible to establish the properties of such solutions indirectly, but the manner in which this is done will always be somewhat arbitrary.

It is of some interest to note that studies by Bernstein and co-workers (62) showed that in aqueous solutions neither monatomic ions nor aggregates corresponding to ion-pairs (i.e. any electrovalent "bonds") were found to give any Raman lines. This would indicate that a Raman study of the particular equilibria studied in this thesis would probably be unsuccessful.

Summary

1. Solubility studies on the systems lithium formate-potassium bromide and sodium bromide-potassium bromide have been carried out in acetic acid at 30°C. The solubility of potassium bromide increases considerably in solutions of lithium formate but not in solutions of sodium bromide.

2. The equivalent conductances and the limiting equivalent conductances and dissociation constants of the formates, acetates, and bromides of lithium, sodium, and potassium in acetic acid have been determined.

3. The equilibrium constant expressions representing the effect of certain salts on the solubility of potassium bromide in acetic acid have been evaluated by an independent method and satisfactory agreement obtained.

4. The validity of the hypothesis of exchange among ion-pairs has been examined. This hypothesis has been shown to be capable of explaining qualitatively and quantitatively the behavior of the solutions examined. The equilibrium constants for the ion-pair exchange calculated from solubility data for this and other systems

have been found to agree reasonably well with constants calculated from individual ion-pair equilibrium constants.

5. Both conductivity measurements and the solubility data indicate that electrolytes in HOAc solution exist predominantly in the form of ion-pairs.

Bibliography

(1) Robinson, A. L., J. Phys. Chem. <u>32</u>, 1089 (1928)

(2) Seward, R. P., and Hamblett, C. H., J. Am. Chem. Soc. <u>54</u>, 554 (1932)

(3) Scholl, A. W., Hutchison, A. W., and Chandlee, G. C., J. Am. Chem. Soc. <u>55</u>, 3081 (1933)

(4) Kraus, C. A., and Seward, R. P., Trans. Farad. Soc. <u>23</u>, 488 (1927)

(5) Walden, P., "Molekulargrosen in Losungen" Theodore Steinkopf, Dresden and Leipzig (1923)

(6) Bjerrum, N., Danske Videnskabernes Selskab <u>7</u>,(1926)

(7) Fuoss, R. M., and Kraus, C. A., J. Am. Chem. Soc. <u>55</u>, 476 (1933)

(8) Fuoss, R. M., J. Am. Chem. Soc. <u>57</u>, 488 (1935)

(9) Griswold, E., Unpublished work

(10)Noyes, A., and Baxter,W., J. Am. Chem. Soc. <u>47</u>, 2122 (1925)

(11)Webb, T. J., J. Am. Chem. Soc. <u>48</u>, 2263 (1926)

(12)Williams,J.., J. Am. Chem. Soc. <u>51</u>,1112 (1929)

(13)Hansen,L.., and Williams,J.., J. Am. Chem. Soc. <u>52</u>, 2759 (1930)

(14) Kraus, C. A., and Seward, R. P., J. Phys. Chem. 32, 1294 (1927)

(15) Seward, R. P., J. Am. Chem. Soc. 56, 2610 (1934)

(16) Davidson, A. W., J. Am. Chem. Soc. 50, 1890 (1928)

(17) Davidson, A. W., J. Phys. Chem. 34, 1215 (1930)

(18) Davidson, A. W., and McAllister, W. H., J. Am. Chem. Soc. 52, 507 (1930)

(19) Davidson, A. W., Chem. Reviews 8, 175 (1931)

(20) Davidson, A. W., and Griswold, E., J. Am. Chem. Soc. 53, 1341 (1931)

(21) Davidson, A. W., and Holm, V., Univ. Kansas Sci. Bul. 21, 463 (1933)

(22) Davidson, A. W., and Chappell, W., J. Am. Chem. Soc. 55, 4524 (1933)

(23) Davidson, A. W., and Chappell, W., J. Am. Chem. Soc. 55, 3531 (1933)

(24) Davidson, A. W., and Geer, H. A., J. Am. Chem. Soc. 55, 642 (1933)

(25) Davidson, A. W., and Griswold, E., J. Am. Chem. Soc. 57, 423 (1935)

(26) Griswold, E., and Olsen, F. V., J. Am. Chem. Soc. 59, 1894 (1937)

(27) Griswold, E., Ash, A., and MacReynolds, L., J. Am. Chem. Soc. 67, 372 (1945)

(28) Griswold, E., and Van Horn, W., J. Am. Chem. Soc. 67, 763 (1945)

(29) Hutchison, A. W., and Chandlee, G. C., J. Am. Chem. Soc. 53, 2881 (1931)

(30) Weidner, B. V., Hutchison, A. W., and Chandlee, G. C., J. Am. Chem. Soc. 56, 1285 (1934)

(31) Weidner, B. V., Hutchison, A. W., and Chandlee, G. C., J. Am. Chem. Soc. 60, 2877 (1938)

(32) Kolthoff, I. M., and Willman, A., J. Am. Chem. Soc. 56, 1007 (1934)

(33) Kolthoff, I. M., and Willman, A., J. Am. Chem. Soc. 56, 1014 (1934)

(34) Grenwall, T., LaMer, V., and Sandved, K., Physik. Zeit. 29, 358 (1928)

(35) Halpern, O., J. Chem. Phys. 2, 85 (1934)

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

(37) Fuoss, R., Trans. Farad. Soc. 30, 967 (1934)

(38) Fuoss, R., Chem. Rev. 17, 27 (1935)

(39) Fuoss, R., and Kraus, C. A., J. Chem. Phys. 2, 386 (1934)

(40) Glasstone, S., "Textbook of Physical Chem." 2nd Ed., D. Van Nostrand Co., New York (1946)

(41) Fowler, R. H., and Guggenheim, E. A., "Statistical Thermodynamics" Cambridge University Press, Cambridge (1947)

(42) Klotz, I., "Chemical Thermodynamics" Prentice-Hall, New York (1950) p. 296

(43) Raoult, F. M., Ann. Chem. Phys. (6) 2, 72 (1884)

(44) Raoult, F. M., and Recoura, A., Z. Physik. Chem. 5, 424 (1890)

(45) Beckmann, E., Z. Physik. Chem. 57, 136 (1907)

(46) DeVisser, L. E. O., Rec. trav. chem. 12, 101 (1893), 17, 182 (1898)

(47) Jones, G., and Josephs, R. C., J. Am. Chem. Soc. 50, 1049 (1928)

(48) Jones, G., and Bollinger, G. M., J. Am. Chem. Soc. 53, 411 (1931)

(49) Jones, G., and Bradshaw, B. C., J. Am. Chem. Soc. 55, 1780 (1933)

(50) Glasstone, S., "Introduction to Electrochemistry" D. Van Nostrand Co., New York (1942) Ch. II

(51) Kolthoff, I. M., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis" MacMillan, New York (1943) p. 573

(52) Davidson, A. W., and Lanning, W., J. Am. Chem. Soc. 61, 147 (1939)

(53) Fajans, K., Zeit. Physik. Chem. A137, 361 (1928)

(54) Fajans, K., and Gressmann, M. L., Zeit. Physik. Chem. A146, 311 (1930)

(55) Kohner, H., and Gressmann, M. L., Zeit. Physik. Chem. A144, 143 (1929)

(56) Luhdemann, R., Zeit. Physik. Chem. B29, 133 (1935)

(57) Rao, N. R., Indian J. Physics 14, 143 (1940)

(58) Rao, N. R., Indian J. Physics 17, 357 (1943)

(59) Redlich, O., and Bigeleisen, J., J. Am. Chem. Soc. 66,13 (1944)

(60) Okazaki, A., Mem. Ryojun Coll. Eng. 9, 13, 101 (1936), 10, 89, 115 (1937)

(61) Redlich, O., Chem. Rev. 39, 345 (1946)

(62) Bernstein, H. J., Romans, R. G., Howden, O. H., and Martin, W. H., Trans. Roy. Soc. Can. III, 33, 49 (1936)

(63) Timmermans, J., "The Physical Constants of Pure Organic Compounds", Elsevier Pub. Co., New York (1950)