On the Electrical Conductance of KCl in Various Solvent Mixtures at 25 ° C. Test of the Theoretical Equations

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Data of electrical conductance of KCl in various solvent mixtures are surveyed. It is pointed out that in some cases the present theoretical equations show some inadequacy.

The Fuoss-Onsager theoretical equation for the equivalent conductance of an unassociated electrolyte can be written ¹:

$$A = A_0 - S\sqrt{c} + Ec \log c + J_1c - FA_0c \quad (1)$$

where A_0 is the limiting conductance at infinite dilution and c is concentration expressed in equivalents per liter. S and E are the Onsager-Fuoss coefficients, both depending on the dielectric constant D , on the viscosity η_0 of the solvent and on the temperature T . J_1 is a coefficient depending upon the same parameters. It is also a function of the so called minimum approach distance a between the two oppositely charged ions. F is the Einstein viscosity coefficient for the solution. It can be neglected for ions that are of approximately the same size as the solvent molecules.

Eqn. (1) has recently been shown ² to hold for the KCl-water system up to $C = 0.012$ N.

If the electrolyte is partially associated to ion pairs *, the equation expressing the dependence of the equivalent conductance on the concentration becomes ¹:

$$A = A_0 - S\sqrt{c\gamma} + Ec\gamma \log(c\gamma) + J_1c\gamma - K_Ac\gamma^2A - FA_0c \quad (2)$$

K_A is the association constant, γ the degree of ionization, f the activity coefficient according to Debye-Hückel. (The constant K_A may, of course, be expressed in terms of γ and f , but is retained in the equation because of the convenience in numerical calculation).

* In this paper only ionophores ³ like KCl *etc.* are considered, not ionogenes ³ like acetic acid, *etc.*

In other words, eqn. (1) is a two-parameter equation and can be written in the general form:

$$\Lambda = f(\Lambda_o, a)$$

since D , η_o and T are properties which are directly measured by independent methods. Similarly, eqn. (2) is a three-parameter equation:

$$\Lambda = f'(\Lambda_o, a, K_A)$$

This means that the above equations are considered to give satisfactory results only when the experimental Λ - c data can be fitted to the equations giving reasonable and consistent values for the parameter Λ_o , a , and K_A if different from zero.

During the last years, eqns. (1) and (2) have been used to analyze conductance-concentration data of large ions, such as tetramethyl- and tetraethyl-ammonium picrate ⁴, in several solvent mixtures. For such systems the theoretical equations were generally consistent with the experimental data. For KCl in water, eqn. (1) gave an a value of 3.07 Å² which is in good agreement with the crystallographic distance of 3.14 Å. Kay ⁵ has used eqns. (1) and (2) to analyze data found in the literature for KCl (and other salts) in water at various temperatures, in alcohol at 25°C, and in liquid ammonia at -34°C. The analysis for the KCl data gave agreement with the crystallographic distance especially for solutions in water and in methanol.

Eqns. (1) and (2) are derived on the basis of a model considering the ions as discrete particles moving in a continuous medium. The molecular structure of the solvent and the interaction between ions and solvent molecules are thus not taken into account. This model would be expected to show some inadequacy especially for the smaller ions (such as alkali and halide ions) in highly viscous solvents and in mixed solvents with strong interaction between the solvent components. Some research work has been done to clarify this point. For example, conductance measurements have been made for KCl in water-glycerol ⁶ and in water-ethylene glycol ⁷ mixtures, with dielectric constants in the range 80 to 40. Analysis of these experimental data by means of eqn. (1) gave values for a in the range 3.3 to 3.8, that is, values in reasonable agreement with the crystallographic distance.

However, when the values of Λ_o for these systems were considered, a positive deviation in the Walden product, compared to the water value, was noticed ^{6,7}. This was tentatively explained ⁷ by taking into account the ion-solvent interactions. Indeed it has to be kept in mind that when dealing with limiting values of electrical conductance, every peculiar behaviour must result from ion-solvent interactions. The ion-ion interactions are negligible at zero limiting concentrations.

On Fig. 1 the product of the limiting conductance and the solvent viscosity, $\Lambda_o\eta_o$, is plotted as a function of the dielectric constant.

The system KCl-water-glycerol is shown on curve 1. The Walden product corresponding to $D = 78.5$ is the limiting value for pure water. The last point to the right on curve 1 is the value of $\Lambda_o\eta_o$ in pure glycerine. The KCl-water-glycol system is plotted on curve 2. It is seen that $\Lambda_o\eta_o$ greatly increases from water to glycerol, and also increases from water to glycol.

Fig. 1. Walden product *versus* D , for potassium chloride in various solvent mixtures: (1) Water-glycerol; (2) Water-glycol; (3) Water-methanol; (4) Water-methylcellosolve. (5) Circles: Methanol-butanol; Squares: Methanol-methylcellosolve. (6) Water-dioxane.

This increase of $\Lambda_0\eta_0$ with decreasing dielectric constant is contrary to the general behaviour noticed by Fuoss for many electrolyte solutions⁸. The data for KCl in water-methanol mixtures⁹ (curve 3) show this decrease for smaller values of D , but the curve passes through a slight maximum.

A qualitatively similar change in the Walden product has been noticed for $\text{Et}_4\text{N-picrate}$ in the same three solvent systems as above^{10,20}. This confirms that these deviations depend upon the solvent and not upon a property of KCl.

A slight maximum in the Walden product is also noticed in the system KCl-water-dioxane¹¹ (curve 6 on Fig. 1).

Fuoss⁸ has presented an explanation for the decrease in Walden product with decreasing dielectric constant, according to which the actual viscosity around an ion will be different from the bulk viscosity of the solvent due to an ion-solvent relaxation effect. The actual viscosity η , according to Fuoss can be expressed by the equation:

$$\eta = \eta_0 \left(1 + \frac{B}{R_\infty^2 D} \right) \quad (3)$$

where B is a constant, and R_∞ is the hydrodynamic radius of the ion in a hypothetical medium of infinite dielectric constant.

The increase of the Walden product in water-glycerol, water-glycol and in some of the water-methanol mixtures has been ascribed⁷ to the formation of H-bonded solvent complexes. Indeed the anomalous deviation in the Walden product seems to increase with the potential number of H-bonds between

the solvent molecules (*cf.* Fig. 1). This was expressed⁷ by a negative term introduced into eqn. (3):

$$\eta = \eta_0 \left(1 + \frac{B}{R_\infty^2 D} - \frac{f(h)}{R_\infty^2 D} \right) \quad (4)$$

where $f(h)$ is an implicit unknown function of the H-bonds. Indeed in the Walden product, we multiply A_0 (that is a quantity inversely proportional to the actual viscosity, η , in the vicinity of the moving ion) by the macroscopic viscosity, η_0 , of the solvent. If eqn. (4) is correct, it could explain the increase of the Walden product from methanol to glycerol at the same D as shown in Fig. 1. The situation for curve 6 is somewhat different, dioxane being only a H-bond acceptor.

In order to check the hypothesis on which eqn. (4) is based, some further work has recently been carried out by Accascina *et al.*¹², and some of the preliminary results are reported in Table 1 and are incorporated in Fig. 1 for comparison. Curve 4 shows the Walden product for KCl in water-methylcellosolve, while curve 5 is valid for methanol-methylcellosolve and for methanol-butanol. (All the data were analyzed by eqn. (1) assuming the Einstein coefficient equal to zero. No association was noticeable in a trial analysis applying eqn. (2). Details, experimental and final results will be published soon).

It can be seen from Fig. 1 that for water-methylcellosolve the behaviour is similar to the water-methanol mixtures as expected. The non-aqueous mixtures (curve 5) show apparent ideal behaviour with respect to the Walden rule. This is probably due to the weak interaction between the alcohols compared to the water mixtures. The values for the Walden product in the non-aqueous solvent mixtures were analyzed¹² in terms of the semiempirical equation given by Fuoss⁸:

$$R^\pm D = A + R_\infty^\pm D \quad (5)$$

where

$$R^\pm = (Fe/6\pi)(1/\lambda_0^\pm \eta_0) \quad (6)$$

$R^\pm$ is the hydrodynamic radius of the K^+ and Cl^- ions, respectively, and $\lambda_0^\pm$ their limiting ionic conductance. F is the Faraday, and e the charge of the electron. The transport number of K^+ in the mixtures was assumed constant and equal to the value in methanol at zero concentration¹³. The slopes of the $R^\pm D$ versus D plots gave the radius sum $(R_\infty^+ + R_\infty^-) = 5.7$ Å in methanol-methylcellosolve, and 5.5 Å in methanol-butanol mixtures. These values are much greater than the crystallographic distance. On the other hand, Fuoss¹¹ has found $(R_\infty^+ + R_\infty^-) = 1.688$ Å for KCl in water-rich dioxane mixtures. This is approximately one half of the crystallographic distance.

This again means that eqn. (5) does not hold in these cases where we have H-bonds between the solvent molecules. Possibly if the $f(h)$ function of eqn. (4) could be found, it would solve the enigma.

Fuoss¹¹ has proposed an alternative approach: When the ions are of the same size as the solvent molecules, the possibility of a slippage of the ions into

Table 1. Conductance and related data for potassium chloride in various mixed solvents ¹². First four columns: Experimental data. Last three columns: Calculated values.

KCl in water-methylcellosolve mixtures						
w % methyl- cellosolve	<i>D</i>	$\eta_0 \times 10^2$ (poises)	A_0	$A_0\eta_0$	$J_1 \pm \Delta J_1$	$a \pm \Delta a$ (cm.10 ⁻⁸)
15.25	71.20	1.380	104.7 ₆	1.446	127 ± 11	2.5 ± 0.2
29.07	64.25	1.923	76.0 ₂	1.462	137 ± 5	2.9 ± 0.1
50.40	52.10	2.695	49.5 ₇	1.336	161 ± 3	3.05 ± 0.05
60.23	45.85	2.885	42.6 ₃	1.230	179 ± 4	2.82 ± 0.06
70.10	38.90	2.865	38.0 ₀	1.089	257 ± 3	2.88 ± 0.04
80.17	32.00	2.595	35.4 ₂	0.919	438 ± 3	3.04 ± 0.02
90.47	24.70	2.105	34.7 ₁	0.731	943 ± 5	3.18 ± 0.02
KCl in methanol-methylcellosolve						
w % methyl- cellosolve	<i>D</i>	$\eta_0 \times 10^2$ (poises)	A_0	$A_0\eta_0$	$J_1 \pm \Delta J_1$	$a \pm \Delta a$ (cm.10 ⁻⁸)
20.13	30.75	0.648	88.49	0.573	1 363 ± 14	2.26 ± 0.04
39.71	28.12	0.767	74.15	0.573	1 512 ± 7	2.32 ± 0.02
50.75	25.02	0.938	61.41	0.576	1 768 ± 15	2.43 ± 0.03
80.00	21.05	1.178	48.87	0.576	2 167 ± 11	2.22 ± 0.02
90.06	18.80	1.344	42.29	0.568	2 824 ± 12	2.52 ± 0.02
KCl in methanol — <i>n</i> -butanol						
w % butanol	<i>D</i>	$\eta_0 \times 10^2$ (poises)	A_0	$A_0\eta_0$	$J_1 \pm \Delta J_1$	$a \pm \Delta a$ (cm.10 ⁻⁸)
5.22	31.87	0.572	99.70	0.570	1 335 ± 6	3.07 ± 0.02
9.01	31.10	0.600	95.12	0.570	1 322 ± 11	2.93 ± 0.03
20.06	29.40	0.668	85.19	0.569	1 400 ± 11	2.99 ± 0.02
29.76	27.62	0.746	75.83	0.566	1 489 ± 10	3.02 ± 0.02

the holes of the liquid may be taken into consideration. According to Sutherland¹⁴, this can be accounted for by replacing the coefficient 6π in the Stokes equation by 4π . For the KCl water-dioxane mixtures the value of $(R_{\infty}^+ + R_{\infty}^-)$ is thereby changed from 1.688 Å to 2.53 Å. This latter value is in better accordance with the crystallographic distance than the former.

However, the use of the Sutherland assumption is not consistent with the model on which the equations (1), (2) are based.

Next, some remarks will be added concerning partially associated electrolytes and in particular the correlation between K_A , D and a . Denison and Ram-

sey assumed that an ion pair is only formed when the two ions are in close contact; then the K_A -data obtained from eqn. (2) should fit into the equation^{15,16}:

$$K_A = K_o \exp (e^2/aDkT) \quad (7)$$

According to this equation, the association for a certain electrolyte should depend only on the dielectric constant of the solvent (and on the temperature). This is experimentally in accord with some system; *e.g.*, for the large and spherical ions of tetrabutylammonium tetraphenylborate¹⁷, the results for K_A agree rather well with eqn. (7). On the other hand, for a large number of systems eqn. (7) does not hold, as pointed out already by Harned and Owen¹⁸ for pure solvents, and corroborated by some observations for methylammonium picrate in pure solvents and in water-dioxane^{19,4a}.

Furthermore, the slope of the $\log K_A$ versus $1/D$ plot (for different compositions of the same mixed-solvent system) in some cases gives an a value far from any expected one²⁰. For example, in the case of the system KCl-water-dioxane¹¹, the $\log K_A$ versus $1/D$ plot is not even linear. If a straight line is tentatively drawn through the points, the resulting a value is about 6.7 Å. This is more than twice the expected value. The same type of curvature in the $\log K_A$ versus $1/D$ graph has been noticed for tetrabutylammonium picrate, -iodide and -nitrate in nitrobenzene-carbon tetrachloride mixtures²¹. (Recent spectrophotometric results for the ionization constants of some acids in water-dioxane mixtures²² show the same concave downward curvature in the pK versus $1/D$ plot. Although these results are for ionogenes, they may be taken to indicate that the deviations in question do not depend on the method of measurement). Here again, the deviation between theory and experiment in all probability is due to the neglect of ion-solvent interactions in the theory.

The interaction between solvent and solute may tentatively be taken into account, as proposed by Gilkerson²³, by introducing into eqn. (7) a factor $\exp (-E_s/kT)$. According to Gilkerson, E_s is an energy due to the ion-dipole interaction and is proportional to the dipole moment of the solvent. Thus, for a mixed solvent, E_s would be expected to vary with the composition (that is, with the dielectric constant) of the mixture.

Finally, it should be mentioned that the introduction of the $a(0) c^{1/2}$ term^{20b} into eqns. (1) and (2) and the use of the Sandved-LaMer activity coefficients²⁴ would probably avoid trends in the a_f sets of data¹¹. These refinements in the calculations look important, especially when the dielectric constant is low or when dealing with 2-2 or 3-3 electrolytes.

This brief survey of the present state of the conductance theory indicates that in a modern approach, short range ion-solvent forces should be taken into account quantitatively. However, this implies a change of the present model.

Acknowledgements. Thanks are expressed to the *Italian Research Council* for research support through a NATO fellowship and to Prof. Kai Grjotheim, Head of the Institute of Inorganic Chemistry, for his kind hospitality.

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Received October 26, 1961.