Investigations on Association of Ions. I.

The Influence of Association of Ions on the Activity of the Ions at Intermediate Degrees of Association

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A. INTRODUCTORY SURVEY

The modern theory for the strong electrolytes explains their properties in terms of the electrical forces between the ionic charges, without assuming any formation of un-dissociated molecules. This conception, which was founded by Bjerrum, Hertz, Milner, and further developed by Brønsted, Lorenz and Schreiner, has recently been crowned by the beautiful works of Debye and co-workers[1].

In my opinion several of the difficulties which beset this theory have been caused by the fact that, so far, too little attention has been paid to the association of ions caused by inter-ionic forces between the electrical charges of the ions.

The effect of the inter-ionic forces must be that oppositely charged ions are more often found in the proximity of each other than is the case with ions of like charge. In order to obtain an idea of the importance of this phenomenon of association, it is necessary to calculate its order of magnitude.

Let us calculate the probability H that an ion of the i-th kind is present at a distance between r and $r + dr$ from a chosen ion of the k-th kind and forms with this an ion pair, in which the distance between the electrical charges is r.

For dilute solutions and for small values of r we can write:

$$H = \frac{Nc_i}{1000} \cdot 4\,\pi\, r^2\, dr \cdot e^{\frac{\varphi}{k\,T}} \qquad (1)$$

in which c_i is the molarity and $Nc_i/1000$ the number of ions of the i-th kind per cc.; $4\,\pi\, r^2\, dr$ is the volume of a spherical shell with the radii r and $r + dr$; φ is

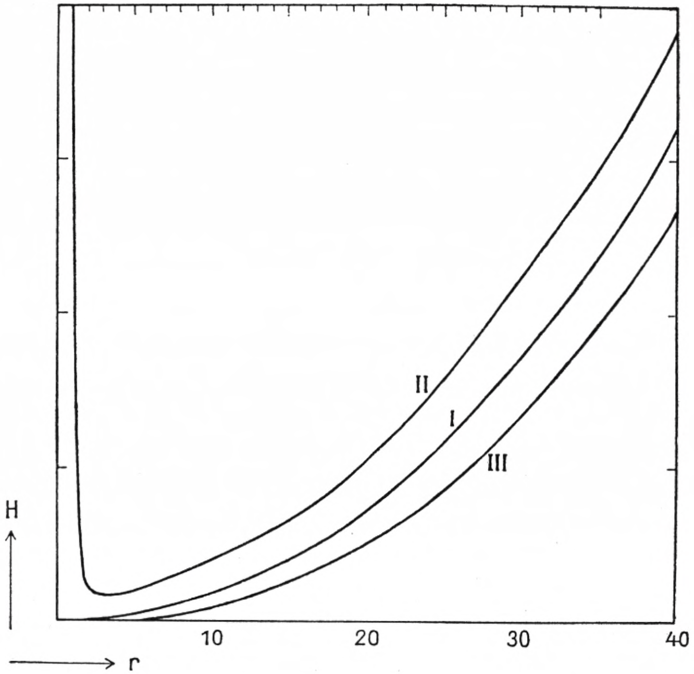

Fig. 1. Frequency (H) of ion pairs with internal distance r as a function of r (monovalent ions in water at 18° C, r small compared with the mean distance between the ions in the solution).

the work required for separating the two ions, and $e^{\frac{\varphi}{kT}}$ is a factor which according to Boltzmann, expresses the extent to which the electrical forces favour the configuration in question. If the solvent is considered as a homogeneous medium with a dielectric constant of D, it follows from Coulomb's law that

$$\varphi = -\frac{z_i \; z_k \; \varepsilon^2}{D \cdot r} \qquad (2)$$

It is presupposed here that the ions are spheres with the charges placed centrally. The valencies of the ions, z_i and z_k, are considered positive or negative, according to whether the ions are positively or negatively charged.

From fig. 1 it is seen how, for monovalent ions in water at 18° C, the ion pairs present are distributed over the range of different ionic distances, according to equations 1 and 2, H being in this case expressed as a function of r. Curve 1 shows the number of ion pairs if no electrical forces were present ($\varphi = 0$). Curve 3 shows the frequency of ion pairs composed of like charged ions (φ negative). The occurrence of ion pairs of this kind is of course considerably more rare than it would be if no electrical forces were present. Finally, curve 2, the most important and most interesting, shows that the number of ion pairs composed of oppositely charged ions first decreases with diminishing distance, then passes a minimum and finally increases rapidly.

If q represents the ionic distance corresponding to the minimum frequency in this association curve (curve 2), the position of the minimum can be found by a simple calculation:

$$q = \frac{\varepsilon^2 z_i z_k}{2 DkT} \tag{3}$$

As is easily seen, the work of separating two oppositely charged ions being this distance apart is equal to $2kT$. That means *that the energy necessary for separating the ion pair is four times as great as the average kinetic energy per degree of freedom.*

In water at 18° C, the minimum for monovalent ions lies at $q = 3.5$ Ångström (Å $= 10^{-8}$ cm). Hence, ions, which are so large that the sum of the ionic radii exceeds 3.5 Å, will associate into pairs only to an inconsiderable extent; but in the case of smaller ions, the association will become more and more marked with diminishing radii.

Ions, such as K^+ and Cl^-, are so large that their charges cannot come closer to each other than 3.5 Å. For this reason the association in water does not play any important rôle for these ions. In the case of smaller ions or ions of the same size, but polyvalent, the inter-ionic forces will, even in water, produce a considerable association and in non-aqueous solvents with a small dielectric constant the association into smaller or larger groups may be very great.

Let us tentatively affirm *that ion pairs, with an internal distance of less than that corresponding to the minimum, are to be denoted as associated and all other ion pairs as free.* Naturally this distinction between free and associated ions is rather arbitrary. The association phenomena induced by the Coulomb forces between the charges of the ions do not display the discontinuity which is in general considered characteristic for chemical processes. While it is possible clearly and unambiguously to state the degree of dissociation in the thermic dissociation of hydrogen iodide into iodine and hydrogen, because transitional forms between un-dissociated and dissociated molecules are not present in finite concentrations (at least, this has so far been considered as correct — compare however Lewis and Randall[2]), the problem is quite a different one in the present case, where transitional forms between free and associated ions appear in finite amounts, *although in the smallest number, when the line of distinction is placed at the minimum of the frequency curve.*

The theory of Debye and Hückel does not pay sufficient attention to the presence of associated ions in general. This is connected with the fact that Debye and Hückel in their differential equation, had to substitute $\frac{\varphi}{kT}$ for $\sinh \frac{\varphi}{kT}$ in order to carry through the integration. Since at the present moment, it seems impossible to integrate the unsimplified equation, an attempt will be made in the paper presented here, to achieve a somewhat more accurate, even if not completely exact, calculation of the degree of association and its effect upon the activity of the ions.

For very dilute solutions and small degrees of association, a simple integration of equation 1 from a to q ($a =$ the sum of the ionic radii) will give the degree of association.

For higher concentrations, the mass-action law is used in the determination of the degree of association. From a thermodynamic point of view, it is permissible to apply this law to the equilibrium between associated and free ions, provided suitable expressions for the activity of these particles are introduced.

It was supposed that the association is exclusively binary, and the activity of the product of association was put equal to its concentration. For the free ions an activity coefficient was taken into account, calculated according to Debye and Hückel for ions with a diameter q (corresponding to the minimum of the association curve), and at the same concentration of ions as that of the free ions.

By subtracting the calculated degree of association from 1, and multiplying by the above mentioned activity coefficient for the free ions after Debye-Hückel, the required composite activity coefficient f is found.

The details of these calculations are dealt with in the special part of this paper.

Fig. 2 shows the result of such calculations. The dependence of the activity coefficient f for the ions on the ion concentration c at different ion diameters is here given, partly according to the older Debye-Hückel formulae (fully drawn curves) and partly according to the new calculation (dashed curves).

For monovalent ions, with a diameter equal to or greater than 3.52 Ångström in the solvent water, associated ions are excluded by definition, and the new curves coincide with those of Debye-Hückel. Even at an ionic diameter down to 1.76 Å, the two systems of curves follow each other approximately. But with further decrease of the ionic diameter greater differences appear: the Debye-Hückel curves slowly converge towards a limiting curve corresponding to the ionic diameter $= 0$ Å, while the new curves clearly demonstrate a strongly increasing diminution of the activity coefficient f with decreasing size of the ion.

Besides the dashed curve for the ion diameter $a = 1.01$ Å, another has been drawn of alternating dashes and dots. This curve has been calculated by considering only ions with a distance of less than 1.76 Å as associated and all other ions as free. The small difference between the results of the two different methods of calculation shows, as also was to be expected, that the choice of distinction between free and associated ions can be made rather arbitrarily.

By means of fig. 2 it is possible to obtain an impression of the effect of the

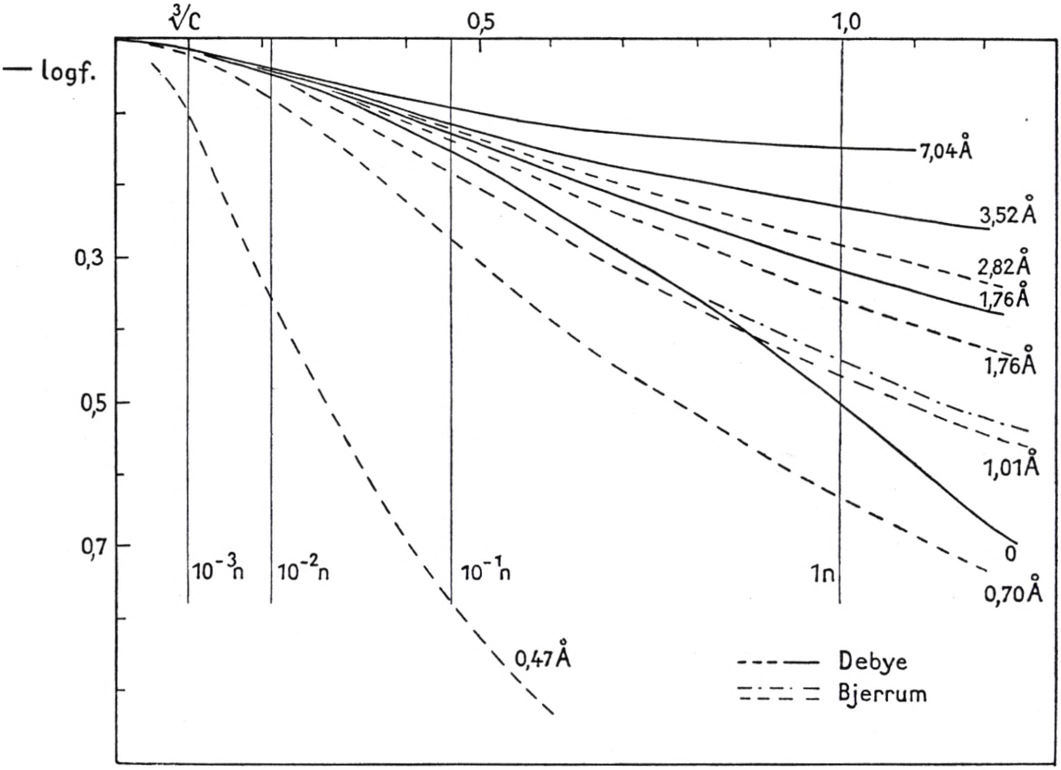

Fig. 2. Relation between activity coefficient (f) and ionic concentration (c) for monovalent ions of different size in water at 18° C.

simplification (sinh $\frac{\varphi}{kT} = \frac{\varphi}{kT}$), introduced by Debye and Hückel in their differential equation. It is seen that under unfavorable circumstances this simplification can lead to a considerable distortion of the results.

The validity of the formulae presented depends upon the supposition that only binary association occurs, that means that aggregates composed of three or more ions are not present in significant amounts. As long as the binary association is not large and the solution is dilute this supposition can be maintained. However, it is necessary to be careful, especially if the cation and anion are of different valencies.

In order to get an impression of the order of magnitude of the ternary association, the following considerations are put forward.

Let $[M^+]$ and $[S^-]$ denote the molar concentrations of the ions M^+ and S^-, and [MS] and $[MS_2^-]$, the molar concentrations of the association products MS and MS_2^-, and let us suppose that the solution is so dilute that "the volume of association" of the S^--ions constitutes only a small fraction K of the total volume of the solution. By the volume of association is here understood the volume in the vicinity of the S^--ions inside which the M^+ can be considered as associated with S^-. The following expression is then obtained:

$$\frac{[MS]}{[M^+]} = Ke^{\frac{\varphi}{kT}}, \tag{4}$$

φ denoting the mean value of the work of separation of the two ions inside the association volume.

In the case of spherical ions with the charge in the centre the work of separation for the second S^--ion in MS_2^- will be only half of the corresponding work for the first, presupposing that both ions are at the same distance from M^+, but diametrically opposite, and that the ions can not be deformed. With some approximation we may therefore put:

$$\frac{[MS_2^-]}{[MS]} = Ke^{\frac{1}{2}\frac{\varphi}{kT}}. \tag{5}$$

From equations 4 and 5 it can be estimated under which circumstances it is possible to neglect the ternary association for the binary. If, for example, in a 0.1 molar solution of certain monovalent ions in water at 18° C the degree of binary association is 0.2 and if we put K equal to 0.0014, equation 4 gives the value of 179 for $e^{\frac{\varphi}{kT}}$. From equation 5 furthermore follows that the concentration of the ternary product of association is 0.019 times that of the binary, i. e. only a few parts per mil.

If the valency of one of the ions is greater than that of the other, the circumstances are somewhat less favourable, as compared with the case of ions with valencies of the same value. Considering for example, the association of monovalent ions with a trivalent ion, the work of separation for the second ion (same assumptions as above) is not $\varphi/2$, but $\varphi \cdot 5/6$. If the degree of binary association of the trivalent ion in 0.01 mol. solutions is 0.2, then the degree of ternary association of the same ion is calculated to 0.02.

From equations 4 and 5 it follows in general that in sufficiently dilute solutions the importance of the ternary association is small as compared with the binary. From equations 4 and 5 we get namely:

$$\frac{[MS_2^-]}{[M^+]} = \left(\frac{[MS]}{[M^+]}\right)^2 \cdot e^{-\frac{1}{2}\frac{\varphi}{kT}}. \tag{6}$$

If the degree of binary association expressed by $\frac{[MS]}{[M^+]}$ is in itself small, the degree of ternary association calculated from equation 6 and measured by $\frac{[MS_2^-]}{[M^+]}$

is even smaller. If the degree of binary association in a dilute solution is still so great that $\frac{[MS]}{[M^+]}$ is about 1 then, according to equation 4, $e^{\frac{\varphi}{kT}} >> 1$ (since in dilute solution $K << 1$.). Consequently, following equation 6, the degree of ternary association will also be small.

The comparison, in the special part of this paper, between the new calculations and the experimental data shows that, in general by taking the ionic association into account, a striking agreement between observation and calculation is obtained. It is true that a satisfactory agreement may also be obtained by applying the formulae of Debye and Hückel, but the superiority of the new method is evident from the more reasonable values for the ionic dimensions obtained in this way.

In the following table 1, some calculated ionic dimensions are given as the distances of nearest approach of the ionic charges (Ångström).

Table 1. Ionic dimensions (distances of nearest approach in Å), calculated from the activity coefficients.

In water :

	KIO_3 $NaIO_3$	KNO_3	KCl	NaCl	K_2SO_4	$MgSO_4$ $CdSO_4$ $CuSO_4$	$BaCl_2$	La- $(NO_3)_3$
New calculation	1.33	1.57	3.40	4.02	3.8	4.2	5.8	6.4
Debye & Hückel	0	0.43	3.40	4.02	2.69	3.0		4.97

In alcohols :

New calculation: In CH_3OH 4.1–6.5. In C_2H_5OH 2.4–7.8.

It is evident that the new calculations has made the figures for the ionic dimensions more probable. Especially the values for iodates and nitrates are more reasonable than the earlier, impossible, small values.

Against the view put forward in this paper, the objection can be raised that we possess only little information about the laws of force prevailing under conditions where small ions are close to each other, and that the assumptions made concerning this question are not very convincing. It is therefore not without interest to emphasize that the *f*-curves will remain approximately the same, even if Coulomb's law is invalid in the neighbourhood of the ions, and even if the ions cannot be considered as spheres with the charge in the centre. The ionic dimensions, ascribed to the different curves, however, will no longer be the true dimensions, but only represent effective dimensions, i. e. such dimensions as must be assigned to spherical ions with a central charge in order that they, under the influence of the assumed laws of force, show the properties of the actual ions under the prevailing conditions.

In reality, however, the calculated dimensions of the ions are quite reasonable, and we may therefore conclude that the assumptions made have been justified. Naturally this does not imply that the ions of the strong electrolytes do not become at all deformed or that Coulomb's law of force is strictly valid in the vicinity of the ions, but only that these assumptions give, in this case, useful approximations.

By the methods applied here a distinction can be made between the influence of the forces between remote ions (which can be calculated according to Debye and Hückel) and the influence of the forces between adjacent ions. The latter forces are only little known. In spite of this, the dependence of their influence upon concentration can be calculated fairly exactly on the basis of the thermodynamic principles in the law of mass action.

While in the calculations so far mentioned, it has been sufficient to take into account the binary association, it is necessary also to consider the higher association types in *solvents with very small dielectric constants*. If that is done, there is in my opinion, a possibility of explaining the characteristic phenomena, observed in these solvents, by means of the inter-ionic forces only.

In this connection, I think especially of the high molecular weights found cryoscopically by Walden, and of the anomalous properties of the molar conductance at high electrolyte concentrations, discussed in details by Kraus.

Probably it will also be possible in many cases to explain the absorption of small ions on large, highly charged *colloidal ions*, by means of the inter-ionic electrical forces alone. The osmotic and conductometric behaviour of large colloidal ions offer a very interesting field for investigation, in which the consideration of ionic association promises new results. In fused salts and in ionic lattices we find systems of the highest degree of association which in part have already been dealt with in a way similar to that implied in our association hypothesis.

In later publications I hope to be able to return to these phenomena and their explanation by inter-ionic forces.

The introduction of a degree of association brings the new conceptions nearer to the classical ideas involving an incomplete dissociation. The similarity is especially pronounced at higher degrees of association. This association explains why in earlier works often useful, if not completely exact, pictures were obtained by introducing the degree of dissociation in the classical sense.

The difference between the old and the new view is, however, still considerable. Firstly, even at high association, the classical clarity of distinction between free and bound ions is missing in our picture. As previously mentioned the definition of free and associated ions by means of the minimum of the association curve is somewhat arbitrary. Secondly, according to the new point of view the ions are supposed to enter the association products without essential alteration of their properties, a point that is inconsistent with the classical conception of un-dissociated molecules, composed of chemically bound ions.

Modern views on strong electrolytes are often briefly characterized as the hypothesis of 100 per cent dissociation of strong electrolytes. The marked phenomena of association, mentioned above, so characteristic for many solutions of strong electrolytes, make this definition less appropriate. I would prefer to speak about a 100 per cent ionization of strong electrolytes. This definition can be used not only for solutions, but also for solids. According to this definition, potassium chloride is even in the crystalline state a strong electrolyte.

The fundamental property of strong electrolytes is not the freedom of their ions. This freedom can be much restricted as in the crystals of potassium chloride. The essential point is that the oppositely charged ions can be in close contact without reacting chemically with one another, indeed without any considerable change of their properties. The typical strong electrolyte, is an electrolyte consisting of rigid and unchangeable ions. This picture has been in the centre of the discussions during recent years, and an attempt has been made to deduce all the properties of electrolytes from the properties of such ions by means of the inter-ionic forces.

By comparing the theory of the typical strong electrolytes with experiments on real electrolytes it can be seen how far it is justifiable, in the theory for strong electrolytes, to neglect ionic deformation.

It must still be considered an open question, whether it is possible to maintain a sharp distinction between associated ions and ions which are chemically bound to each other. From the *physicist's* point of view, it may be natural to assume a *gradual transition* from association products in which the ions are but slightly deformed, through intermediary steps with increasing deformation, to true chemical compounds. The *chemist*, on the other hand, will be inclined to maintain the existence of a *discontinuity* in the formation of the chemical compound between the ions.

In a future paper this important question will be dealt with in further detail. On this occasion, I would only like to stress the fact that the properties of a great number of electrolytes in solution are strong evidence that their ions are not, or only to a small degree, chemically bound, and that *deformation is even but little pronounced*. The clearest indication of this fact is the independence of the salt concentration shown by so many ionic properties, among which the colour of the ions may be especially mentioned (Hantzsch[3] and Bjerrum[4]). This constancy of colour is so convincing because here we deal with a property that is quite sensitive to changes in constitution. The recent, very exact investigations on light absorption that we owe to Ebert and v. Halban[5] have on the whole confirmed the older investigations, although some small corrections were found in several cases.

Table 2. The degree of association α for monovalent ions in water at 18° C. (q = 3.52 Å).

	Sum of the ionic radii:					
	2.82 Å	2.35 Å	1.76 Å	1.01 Å	0.70 Å	0.47 Å
0.0001 *M*	0	0	0	0	0.001	0.027
0.0002 –	0	0	0	0	0.002	0.049
0.0005 –	0	0	0	0.002	0.006	0.106
0.001 –	0	0.001	0.001	0.004	0.011	0.177
0.002 –	0.002	0.002	0.003	0.007	0.021	0.274
0.005 –	0.002	0.004	0.007	0.016	0.048	0.418
0.01 –	0.005	0.008	0.012	0.030	0.083	0.529
0.02 –	0.008	0.013	0.022	0.053	0.137	0.632
0.05 –	0.017	0.028	0.046	0.105	0.240	0.741
0.1 –	0.029	0.048	0.072	0.163	0.336	0.804
0.2 –	0.048	0.079	0.121	0.240	0.437	0.854
0.5 –	0.090	0.140	0.204	0.360	0.568	0.901
1 –	0.138	0.206	0.286	0.457	0.651	0.928
2 –	0.204	0.289	0.383	0.554	0.725	0.946

Table 2a. Values of —log f according to Bjerrum for monovalent ions in water at 18° C. (q=3.52 Å)

	Sum of the ionic radii:					
	2.82 Å	2.35 Å	1.76 Å	1.01 Å	0.70 Å	0.47 Å
0.0001 *M*	0.005	0.005	0.005	0.005	0.005	0.017
0.0002 –	0.007	0.007	0.007	0.007	0.008	0.028
0.0005 –	0.011	0.011	0.011	0.012	0.013	0.059
0.001 –	0.015	0.016	0.016	0.017	0.020	0.098
0.002 –	0.022	0.022	0.023	0.025	0.030	0.157
0.005 –	0.034	0.035	0.036	0.040	0.053	0.262
0.01 –	0.047	0.048	0.050	0.057	0.081	0.360
0.02 –	0.064	0.066	0.070	0.085	0.121	0.474
0.05 –	0.095	0.100	0.107	0.133	0.200	0.637
0.1 –	0.127	0.135	0.146	0.188	0.278	0.769
0.2 –	0.164	0.179	0.198	0.255	0.371	0.907
0.5 –	0.230	0.251	0.282	0.366	0.516	1.092
1 –	0.285	0.317	0.360	0.463	0.635	1.244
2 –	0.351	0.395	0.447	0.574	0.760	1.387

SUMMARY

According to modern views, an electrolyte belongs to the class of *strong electrolytes* if its ions do not combine chemically under the conditions considered.

Since in general the mutual interaction between the ions of strong electrolytes does not give rise to pronounced deformations, it would seem natural to apply the term *ideal strong electrolyte* to an electrolyte composed of ions which cannot be deformed. It is the properties of such a type of electrolyte, which are dealt with theoretically in most of the recent papers on strong electrolytes, and which have also been studied in this paper.

The electrical forces between the ionic charges of an ideal strong electrolyte must cause a considerable association of ions in many cases. It is possible to predict that this association of ions must be especially great in the case of small ions and ions with high valencies. Furthermore it can be foreseen that it will be larger in non-aqueous solvents with a small dielectric constant than in water. This association can be considered as a purely physical process. Its existence makes it more correct to speak about 100 per cent ionization than about 100 per cent dissociation in the case of strong electrolytes.

In weak association, the ions will mainly associate in pairs, in stronger association — especially at higher concentrations — ternary and higher complexes are also formed to a considerable extent. In the present paper, the intermediary states of association have been studied, where it is sufficient to consider binary association. The effect of the association on the activity of the ions has especially been studied.

It is shown that the formulae derived by Debye and Hückel for the calculation of ionic activity from ionic concentration and size, do not give a good approximation in the case of small ions or ions with high valencies, and a method for obtaining more exact values has been developed.

The new values for the activity coefficients (f) for different ionic concentrations are given for monovalent ions in water at 18° C in table 2a, and in fig. 2 these new values can be compared with the old ones.

By means of a simple transformation, table 2a can be used for all solutions of electrolytes. The activity coefficient possesses, namely, the same value in all solutions for which the expressions

$$c\left(\frac{z_1 z_2}{DT}\right)^3 \quad \text{and} \quad a\,\frac{DT}{z_1 z_2}$$

have the same values ($c =$ mean molar ionic concentration, $D =$ dielectric constant, $T =$ abs. temperature, z_1 and z_2 the valencies of the two ions and a the sum of their ionic radii, indicating the distance between the charges, when the ions are in mutual contact).

On the basis of the available experimental material the sums of the ionic radii were determined for some electrolytes in water and in methyl and ethyl alcohol, using the above described principle (see table 1).

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