(m), 1433 (m), 1395 (m), 1366 (s), 1336 (w), 1311 (w), 1298 (w), 1239 (m), 1215 (s), 1204 (m), 1170 (m), 1128 (m), 1080 (m), 948 (m), and 882 cm^{-1} (m).

Anal. Calcd for $C_{21}H_{35}F$: C, 82.35; H, 11.44; F, 6.20. Found: C, 82.29; H, 11.38; F, 6.50.

Acknowledgment. We are grateful to Drs. L. Kaplan, K. Wilzbach, and M. Studier for their assistance in the mass spectrometric identification of the compounds prepared.

Electrical Conductance of Anhydrous Potassium, Magnesium, Cobalt, Nickel, Copper, and Zinc *m*-Benzenedisulfonates in Methanol at 25°

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Abstract: The equivalent conductivities of the K^+, Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} *m*-benzenedisulfonates have been measured in anhydrous methanol at 25°. The data for the 2:2 salts have been interpreted by the Fuoss–Kraus technique for determining the limiting equivalent conductance and association constant. The data for K_2-BDS have been analyzed by the Fuoss–Edelson technique obtaining the limiting conductance Λ_0 and therefore $\lambda^0{}_{1/2BDS^{2+}}$ from the known conductance of K^+ in methanol. The values of $\lambda^0{}_{1/2Me^{2+}}$ for Mg^{+2} and Zn^{2+} compare favorably with the data of Hartley and Raykes. With the so-determined values of Λ_0, the Fuoss–Onsager equation is fitted to the data as a two-parameter equation in the association constant K_A and collision diameter a. The sum of the Stokes hydrodynamic radii ($R_+{}^0 + R_-{}^0$) is of the same order of magnitude as a_J.

It is about 100 years since the pioneering measurements of ac electrical conductivity by Kolhrausch were performed in aqueous solutions of electrolytes. During this time the Onsager theory[2] at different levels of sophistication[3] has given a rather exhaustive microscopic picture of the phenomenon of conduction, at least in the diluted range. Other nonelectrochemical methods have been developed in the meantime, like nmr relaxation,[4] ultrasonic absorption, and other relaxation methods,[5] uv, visible,[6a] and Raman spectra.[6b] These techniques have offered intimate insights into the phenomena of solvent exchange in the first coordination sphere of the metal cation,[4] of the mechanism of ligand substitution during the process of complexation,[5] and of the coordination of ligands by the metal cation.[6]

While the above does reflect a harmonic development of a branch of science from the classical to the molecular approach, in nonaqueous solvents a strange state of affairs exists. Indeed, modern kineticists and spectroscopists have often applied their techniques to solutions of, say, transition metal ions in nonaqueous solvents.[7] However, the corresponding classical measurements like thermodynamical and transport ones are often lacking (perhaps due to the decline of electrochemistry in the current fashion list of scientific topics).

Still, the classical measurements are needed since they often give necessary and precise information like the degree of association and the activity of an electrolyte. It is enough to think of the dangers of neglecting association in arriving at any conclusion about the rate of exchange of the solvent around a particular cation.

If the anion that one must necessarily add participates in the first and even the second coordination sphere as a complexed or paired species,[7] the rate of exchange of the solvent can be dramatically altered. This may happen both because of a statistical effect of occupation of an exchange site or because the partial or total charge neutralization may effect the tightness by which the solvent is retained in the coordination shell around the metal cation.[8]

In an effort to avert the present situation and to rebalance our state of knowledge of the classical and nonclassical information of divalent ions in nonaqueous solvents, it has been decided in this laboratory to carry measurements of electrical conductance of Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} *m*-benzendisulfonates in methanol. The choice of the anion has been dictated by a parallel study by P-jump relaxation kinetics[9] and by the solubility ($\sim 5 \times 10^{-2}$ *M*) being high enough to carry a conductance study without difficulties. Methanol has been chosen as the natural starting point from water. The conductance of K_2BDS has also been measured in order to calculate the limiting conductance of the benzenedisulfonate anion in methanol.

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[1] This work is part of the thesis of R. Lovas in partial fulfillment for the requirements of the degree of Bachelor of Sciences, Polytechnic Institute of Brooklyn, 1970.

[2] L. Onsager, *Phys. Z.*, 28, 277 (1927).

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Table I

Salt	Temp, °C	Cation anal method	% cation Exptl	% cation Theor	Anion anal method	% anion Exptl	% anion Theor
MgBDS	85	Hydroxyquinolate	9.52	9.33	Cation exchange	90.53	90.67
CoBDS	120	α-Nitroso-β-naphthol	20.16	19.97	Cation exchange	79.77	80.03
NiDBS	110	Dimethylglyoxime	19.60	19.91	Cation exchange	80.48	80.09
CuBDS	70	Iodometry	20.86	21.20	Cation exchange	79.30	78.80
ZnBDS	70	Ferricyanide	21.31	21.68	Cation exchange	78.72	78.32

Experimental Section

The instrumentation, method, and procedure have been described elsewhere.[10] The only change, in order to improve the accuracy of the conductance values, was to prepare and analyze the stock concentrated solution by weight. A simple error analysis shows that when a concentration method is used the largest possible systematic error one can make is in the concentration analysis of the stock solution. After conversion of a weighted amount of the methanolic solution containing the BDS salt into the corresponding acid, this was analyzed by weight burets containing a Tham stock solution,[11] using a Beckmann expanded-scale pH meter as the sensor device. The final result was a factor expressing the moles of salt per gram of stock solution *in vacuo*. This was used to calculate the portions of salt added to the solution in the conductance cell. The conversion to the molarity scale was made for the solutions in the conductance cell by approximating the density of its solutions ($c < 50 \times 10^{-4}$ M) to that of the solvent. The cell used had a constant $K_c = 0.1143 + 4\ X_s$, where X_s is the specific conductance of the solution. All the operations like transfer of solvent and stock solution were performed in a drybox under a dry N_2 atmosphere.

Materials. Methanol (Baker ACS reagent) was purified by distillation in a 3-ft, all-Pyrex, Vigreux column over aluminum amalgam, collecting only the middle portion boiling at 64.5° (Karl Fisher and vpc analyses, performed just before the runs indicated less than 0.01% of water content in the methanol).

The salts were prepared by purifying *m*-benzenedisulfonic acid (K and K, technical grade) by decoloration with Norit-A decolorizing carbon neutral and converting it into BaBDS with $BaCO_3$. The $BaSO_4$ precipitate from the aqueous solution of BaBDS was filtered off. The solution was reduced in volume by heating and cooled, and the BaBDS was precipitated with distilled acetone (1:10, Metro scientific NF grade).

The BaBDS was redissolved in water. To this solution the metal sulfates (recrystallized twice from conductance water), in stoichiometric amounts, were added. The final solution was tested for lack of a excess either of Ba^{2+} or of SO_4^{2-} (after filtration of $BaSO_4$).

The metal BDS salts were recrystallized twice from acetone–water, air-dried, and then dried in a vacuum oven at 50×10^{-6} mm at temperatures less than 150° until, by analysis, they were dry.

These temperatures, checked by vapor chromatography for the release of water and absence of decomposition, are reported in Table I. The analyses of the anhydrous salts, stored in a vacuum dessicator over anhydrous $Mg(ClO_4)_2$, are also reported in Table I.

K_2BDS was prepared by reacting BaBDS with K_2CO_3 and filtering off the resulting $BaCO_3$. The solution was boiled down to a small volume and the salt precipitated from acetone–water. It was then recrystallized from conductance water three times, dried in air, and then dried in a vacuum oven at 75° and 50×10^{-6} mm. Analysis showed it to be anhydrous.

Results and Calculations

In Table II the results (expressed in equivalent conductance Λ (ohm^{-1} cm^2 equiv^{-1}) at the concentration c (M) studied for the various salts investigated) are reported. For the calculations the density of the solvent, $\rho = 0.7866$ g/cc, the dielectric constant, $D = 32.66$, and the viscosity, $\eta = 0.005445$ P, were used.

Table II. Concentration (M) and Equivalent Conductance (ohm^{-1} cm^2 equiv^{-1}) for the Electrolytes Investigated in Methanol at 25° [a]

Electrolyte	$c \times 10^4$	Λ	Electrolyte	$c \times 10^4$	Λ
K_2BDS	1.876_4	96.22_2	MgBDS	1.361_0	43.24_1
	4.262_8	88.61_5		3.271_0	31.62_9
	7.401_1	82.32_6		6.169_0	25.08_5
	9.949_9	78.91_2		10.66_9	20.54_0
	14.11_4	74.62_3		17.79_4	17.19_9
	17.79_9	71.77_0		25.22_1	15.31_3
			Co BDS (first run)	2.545_8	36.80_8
				5.805_2	27.42_8
				9.812_0	22.73_9
				11.71_0	21.38_7
				18.41_8	18.29_7
				34.23_8	15.03_9
CoBDS (second run)	2.986_4	34.75_6	NiBDS	0.6655_0	59.03_6
	6.887_4	25.77_8		2.493_4	38.83_1
	11.04_6	21.79_3		4.801_1	30.97_2
	13.99_9	20.08_7		8.241_3	25.65_4
	32.08_1	15.33_2		11.95_1	22.57_4
				16.61_4	20.22_0
				21.47_3	18.61_4
CuBDS	1.503_7	41.37_8	ZnBDS	1.902_7	40.42_6
	2.793_8	33.25_2		3.280_8	33.40_8
	4.432_2	28.14_3		4.749_1	29.26_7
	7.914_3	22.81_8		6.766_3	25.78_8
	13.10_6	19.08_0		9.325_1	23.03_2
	21.22_7	16.21_1		12.893_9	20.58_0
	26.56_0	15.10_1		15.932_0	19.16_2
	31.13_8	14.46_3			

[a] At least one figure in excess with respect to the sensitivity of the method is reported in the above. This is done in order to avoid round-off errors in future recalculations by others from these data.

The analysis of the data of Table II was first tried by the 1959 version of the Fuoss–Onsager equation[3a] (adapted to 2:2 salts) for associated electrolytes[10]

$$\Lambda = \Lambda_0 - S\sqrt{c\alpha} + Ec\alpha \log c\alpha + Jc\alpha - K_A c\alpha f_\pm{}^2\Lambda \quad \text{(I)}$$

where the symbols have their usual meaning.[10] During the analysis it became clear that no unique solutions were obtainable for the three parameters Λ_0, J, and K_A, given the large association and size of the competing terms $Ec\alpha \log c\alpha$ and $Jc\alpha$ at these dielectric constants (effective dielectric constant of $(32.66/4) \approx 8.2$ for a corresponding 1:1 electrolyte). Values of Λ_0 oscillating between 60 and 140 ohm^{-1} cm^2 equiv^{-1} could be imposed on the data with a very sluggish conversion or no conversion at all on a y–x plot. In fact, from Figure 1 it can be seen that the plot of Λ *vs.* $\sqrt{c}$ for ZnBDS resembles that of a weak electrolyte like acetic acid in water (the Λ_0 reported in Figure 1 has been calculated as shown below). Fuoss in his monograph[3a] warned against the insensitivity of the y–x procedure when K_A was larger than several thousand units. Under the circumstances, and in the absence of the knowledge of Λ_0, it is more convenient[3a] to drop the $Ec\alpha \log c\alpha$ and

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[10] S. Petrucci, P. Hemmes, and M. Battistini, *J. Amer. Chem. Soc.*, 89, 5552 (1967).

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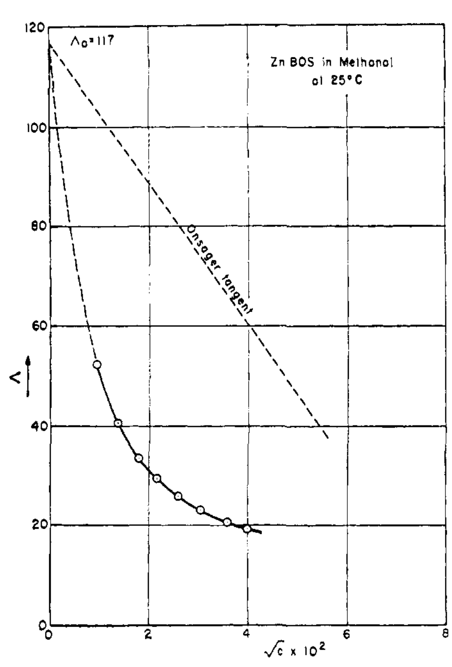

Figure 1. Plot of Λ *vs.* $\sqrt{c}$ for ZnBDS in methanol at 25°.

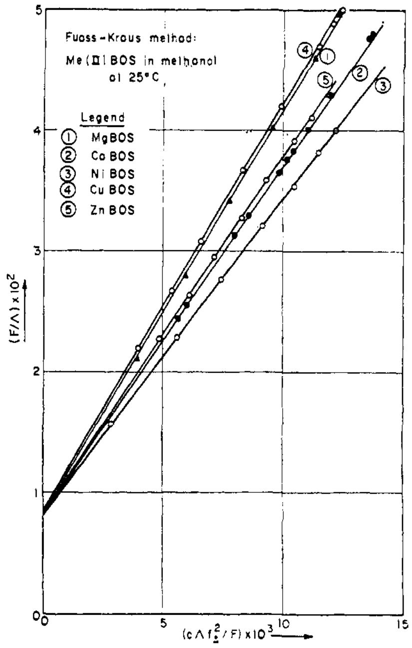

Figure 2. Fuoss–Kraus plot for $Me^{II}BDS$ in methanol at 25°.

$Jc\alpha$ terms, reducing the conductance equation to a two-parameter expression in Λ_0 and K_A. The Fuoss–Kraus[12] or Shedlovsky method[13] may be conveniently used up to association constants of the order of $K_A \approx 10^5\ M^{-1}$.

The Fuoss–Kraus method[12] consists of plotting (F/Λ) *vs.* $(c\Lambda f_{\pm}^2/F)$ according to the function

$$\frac{F}{\Lambda} = \frac{1}{\Lambda_0} + \frac{c\Lambda f_{\pm}^2}{F}\left(\frac{K_A}{\Lambda_0^2}\right) \tag{II}$$

where $F = {}^4/_3 \cos^2 [{}^1/_3 \cos^{-1}(-3^{3/2} z/2)]$, $f_{\pm}^2$ is the limiting Debye–Hückel function for the activity coefficients, and $z = (S/\Lambda_0^{3/2})(C\Lambda)^{1/2}$. Values of the function F have been tabulated[14] for useful ranges of the variable z. Consequently, a plot of F/Λ *vs.* $(C\Lambda f_{\pm}^2/F)$ will determine $(1/\Lambda_0)$ and (K_A/Λ_0^2) as intercept and slope, respectively, whence Λ_0 and K_A simultaneously.

By starting with an arbitrary value of Λ_0, say 100 $ohm^{-1}\ cm^2\ equiv^{-1}$, to calculate the function z, a cycle of approximations can be performed until convergence of Λ_0 and K_A. In our case a computer program was used. In Figure 2, the final plots of the quantity F/Λ *vs.* $(c\Lambda f_{\pm}^2/F)$ are reported for the five electrolytes investigated. In Table III the results for Λ_0 and K_A are also reported. In order to have an assessment of the reliability of the method used, the Kohlrausch rule has been used as a check of the above results for the two cases for which the value of the limiting mobility of the cations in methanol is known,[15] namely, Mg^{2+} and Zn^{2+}.

In order to have an evaluation of the value of λ_-^0 for the BDS^{2-} ion the data for K_2BDS reported above have been treated by the Fuoss–Edelson[16] technique. This method consists in evaluating the Λ_0 and K_{A_1} for an unsymmetrical electrolyte of the type M_2A, for instance. K_{A_1} refers to the equilibrium

$$M^+ + A^{2-} \rightleftharpoons MA^-$$

while the equilibrium leading to the neutral species M_2A is neglected. Because of the presence of the conducting species MA^-, one has to consider $\lambda^0_{MA^-}$. It is approximated to $\lambda^0_{MA^-} \approx 0.5\lambda^0_{1/2A^{2-}}$. Other approximations are introduced, such as the activity coefficient equality, $f_{M^+} \approx f_{MA^-}$, and the single ionic coefficient $f_{A^{2-}}$ introduced through the Debye–Hückel limiting law.

Table III. Results of the Fuoss–Kraus and of the Fuoss *y*–*x* Analysis[a]

Electrolyte	Λ_0, ohm^{-1} cm^2 $equiv^{-1}$	K_A (Fuoss–Kraus), M^{-1}	K_A (*y*–*x*), M^{-1}	$J \times 10^{-3}$, cm	$a \times 10^8$, cm
MgBDS	120.5	48,500	46,000	200	13.5
CoBDS	123.5	44,400	41,700	200	12.9
NiBDS	120.5	37,300	35,300	200	13.4
CuBDS	119	47,900	45,000	200	13.9
ZnBDS	117	39,700	37,300	193	13.4

[a] Limiting conductance and association constant for the 2:2 electrolytes investigated in methanol at 25°. (The limiting conductances are precise to about ±1%, the association constants to about ±5%.) The parameters *J* and *a* have been obtained from the *y*–*x* analysis. The values of *a* are precise within $\pm 1 \times 10^{-8}$ cm.

Despite all these approximations the method gives useful results especially reliable for Λ_0. It consists of using the equation

$$\Lambda^* = \Lambda_0 - \chi\frac{K_{A_1}}{\Lambda_0} \tag{III}$$

Plotting Λ^* *vs.* χ, Λ_0 is obtained from the intercept and K_{A_1}/Λ_0 from the slope, whence K_{A_1} is obtained.

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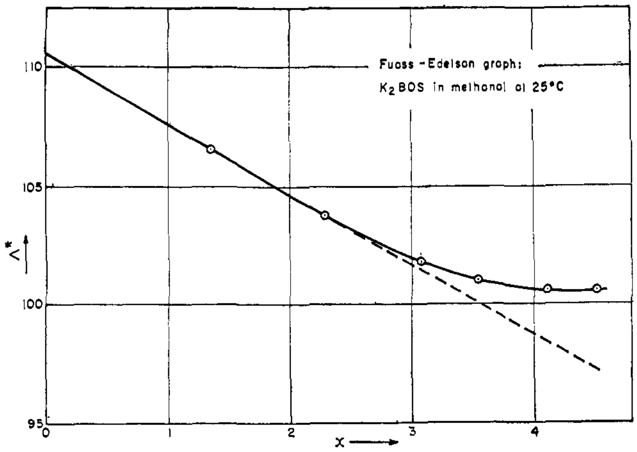

Figure 3. Fuoss–Edelson plot for K_2BDS in methanol at 25°.

In the above, $\Lambda^* = \Lambda_0\gamma_1$ and

$$\gamma_1 = \frac{\Lambda}{\Lambda_0}\left[\frac{1}{1 + \lambda^0{}_{1/2A^{2-}}/2\Lambda_0}\right]\left[\frac{1}{1 - (S_{12}/\Lambda_0)\Gamma^{1/2}} + \frac{\lambda^0{}_{1/2A^{2-}}}{2\Lambda}\right]$$

where S_{12} is the Onsager conductance coefficient for a 1:2 electrolyte

$$S_{12} = \frac{1.98 \times 10^6}{(DT)^{3/2}}\frac{q^*}{1 + \sqrt{q^*}}|Z_1Z_2|\Lambda_0 + \frac{29.16}{\eta(DT)^{1/2}}(|Z_1| + |Z_2|)$$

and Γ is the ional concentration, $\Gamma \cong 3N\gamma_1 \cong 3N$. In the above, $\chi = Nf_A = \Lambda^*(\Lambda^* - 0.5\Lambda_0)$, where N is the concentration in equivalents/liter.

Starting from a preliminary value of Λ_0 obtained through a free-hand extrapolation from a Λ–$\sqrt{c}$ plot a series of approximations are performed in order to evaluate Λ^* and χ. The final plot of Λ^* *vs.* χ is shown in Figure 3. The results are $\Lambda_0 = 110.5$ ohm^{-1} cm^2 equiv^{-1} and $K_A \cong 320$ M^{-1}. The plot becomes nonlinear if the concentration is increased because of the failure of the approximations involved in the theory and the onset of the association of the M_2A species.

From the value of Λ_0 and from the known value of the limiting conductance of K^+ in methanol,[17] $\lambda^0{}_{K^+} = 52.4$, one can calculate $\lambda^0{}_{1/2BDS^{2-}} = 58.1$. Then, adding the limiting values of conductance[15] of Mg^{2+} and Zn^{2+}, $\lambda^0{}_{1/2Mg^{2+}} \cong 60$ and $\lambda^0{}_{Zn^{2+}} \cong 59.5$, one has $\Lambda^0{}_{1/2MgBDS} = 118.1$ and $\Lambda^0{}_{1/2ZnBDS} = 117.6$, which compare favorably with the quantities reported in Table III, given the sensitivity of the Fuoss-Kraus and of the Fuoss-Edelson methods for the present case ($\pm 1\%$).

In order to investigate the effect of having neglected the E and J terms in the conductance equation, a calculation of a y–x type, using eq I, was tried. By imposing the now determined Λ_0, the quantity y can now be calculated from

$$y = \frac{\Lambda' - \Lambda_0}{c\alpha} = J - K_Af_\pm{}^2\Lambda = J - K_Ax \qquad \text{(IV)}$$

where $\Lambda' = \Lambda + S\sqrt{c\alpha} - Ec\alpha \log c\alpha$. Plotting y *vs.* x, J and K_A are obtained as slope and intercept. This is shown in Figure 4; the results are reported in Table III. It may be seen that the differences between the calculated K_A from the Fuoss-Kraus method[12] and the ones from eq IV are within few per cent. The values of the parameter a, the collision distance between ions,[3a] are also reported in Table III.

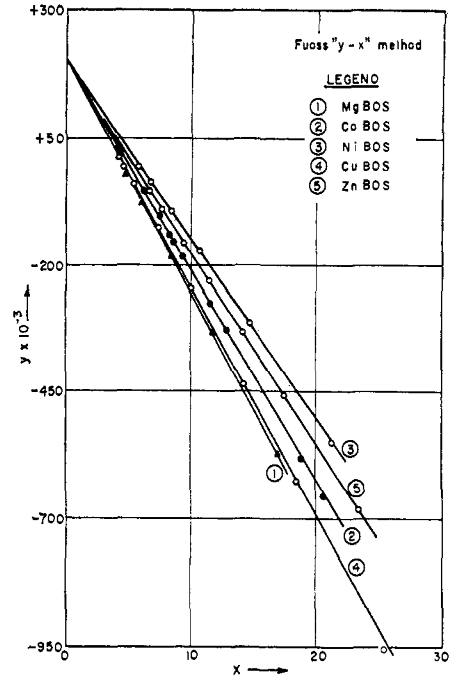

Figure 4. Fuoss y–x plot for $Me^{II}BDS$ in methanol at 25°.

Discussion

From the determined values of Λ_0 and $\lambda^0{}_{1/2BDS^{2-}}$, it is possible to calculate the limiting conductance for the various cations investigated. The accuracy of the cation mobilities so determined is estimated to be about $\pm 2\%$. This is not unreasonable considering the sensitivity of the methods used to determine Λ_0 and the extreme strains imposed on the conductance theories (for 2:2 electrolytes at this dielectric constant).

The $\lambda^0{}_{1/2Me(II)}$ are reported in Table IV together with the Stokes hydrodynamic radii calculated through the relation

Table IV. Ionic Limiting Equivalent Conductance and Stokes Hydrodynamic Radii for the Electrolytes Investigated in Methanol

Electrolyte	$\lambda_+{}^0$, ohm^{-1} cm^2 equiv^{-1}	$\lambda_-{}^0$, ohm^{-1} cm^2 equiv^{-1}	$R_+{}^0 \times 10^8$, cm	$R_-{}^0 \times 10^8$, cm	$(R_+{}^0 + R_-{}^0) \times 10^8$, cm
K_2BDS	(52.4)	58.1	2.88	5.2	8.1
MgBDS	62.4	58.1	4.8	5.2	10
CoBDS	65.4	58.1	4.6	5.2	9.8
NiBDS	62.4	58.1	4.8	5.2	10
CuBDS	60.9	58.1	4.9	5.2	10.1
ZnBDS	58.9	58.1	5.1	5.2	10.3

$$R_\pm = \frac{|Z_\pm|Fe}{1800\pi}\frac{1}{\lambda_\pm{}^0\eta} \qquad \text{(V)}$$

The values of R_+ of the order of 5 Å strongly suggest that the hydrodynamic entity moving is the solvated metal cation. The diameter of a molecule of methanol

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(17) J. P. Butler, H. I. Shiff, and A. R. Gordon, *J. Chem. Phys.*, 19, 752 (1951).

can be taken to be 4 Å.[18] The crystal radius of the metal cations investigated are of the order of 1 Å.[19] Therefore, the found $R_+ \approx 5$ Å seems to reflect the first solvation shell of the cations moving with them, possibly with an octahedral geometrical arrangement.

Next, the significance of the parameters a_J reported in Table III is discussed. The need of a $J_{3/2}c^{3/2}$ term in the conductance equation has been disputed,[20] and the identification of a_J with the Bjerrum distance q has been claimed[20a] and debated,[21] where

$$q = |Z_1Z_2|e^2/2DkT$$

for the minimum approach of the free ions. It is interesting to notice that in our case $q = 34.3$ Å. Therefore, the $J_{3/2}$ coefficient should be of such size as to force J to become much larger in order to fit the conductance data with $a_J = q$. Having dropped in our case the $J_{3/2}c^{3/2}$ term from the conductance equation, it remains in doubt whether a_J still retains any precise physical significance.

Comparison between the sum of the hydrodynamic radii $R_+^0 + R_-^0$ (Table IV) and a_J could, however, suggest that a_J may represent the sum of two solvated ionic radii, since $(R_+^0 + R_-^0)$ and a_J are of the same order of magnitude as in the original postulation of the theory.[3a]

A parallel kinetic investigation in this laboratory[9] by relaxation techniques indicates, for these 2:2 electrolytes in methanol, a multistep process of complexation. Indeed it could be argued, by conductance theory alone, that a continuum could not be assumed as a valid model for the association of these systems. If one believes a_J to represent the distance of approach of free ions, then substituting a_J in the Fuoss function[22] ($a_J = 13.5$ on the

$$K_F = \frac{4\pi Na^3}{3000} \exp\left(\frac{|Z_1Z_2|e^2}{aDkT}\right) \qquad \text{(VI)}$$

average) one may evaluate $K_F = 979\ M^{-1}$, much less than the determined $K(\Lambda)$ that is of the order of 40,000 M^{-1}.

On the other hand, if one would force the Fuoss function[22] to reproduce $K(\Lambda)$, the calculated a would be $a_K \cong 6.2$, much less than a_J.

Assuming a two-step mechanism from the kinetic evidence[9] of the existence of a multistep process of association

$$\underset{c_1}{\mathrm{Me^{2+} + BDS^{2-}}} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{c_2}{\mathrm{Me^{2+}(MeOH)_{\mathit{x}}}}$$

$$\mathrm{BDS^{2-}} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{c_3}{\mathrm{MeBDS}}$$

one has[5]

$$K_\Sigma^{-1} = K(\Lambda) = K_{21}(1 + K_{32}) \qquad \text{(VII)}$$

where K_Σ^{-1} is the overall association constant, $K_{21} = k_{12}/k_{21}$, and $K_{32} = k_{23}/k_{32}$. Setting the Fuoss function[22] to describe properly only the first step of the association, where a continuum seems still a reasonable model, one can calculate

$$K_{32} = \frac{K(\Lambda)}{K_F} - 1$$

Therefore, K_{32} becomes of the order of 40. Since[5] $K_{32} = c_3/c_2$, this also indicates the ratio between contact-associated species and solvated ion pairs, if the above scheme is correct.

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(19) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

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