Ion Association in Polyvalent Symmetrical Electrolytes. II. The Conductance of Manganese(II) Sulfate and MnBDS in Methanol–Water Mixtures

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The conductance of Mn *m*-benzene disulfonate (MnBDS) has been measured at 25° in mixtures ranging from 0 to 100% methanol; and MnSO₄ has been studied from 0 to 40% methanol. The data are analyzed using the extended Fuoss–Onsager theory and K_A, Λ^0 and a^0 parameters obtained. In marked contrast with MnSO₄, MnBDS is only very slightly associated in water (99.6 ± 0.6% unassociated at 3×10^{-3} molar). K_A is examined as a function of dielectric constant; and a^0 and the Walden product as functions of mole fraction methanol. The functional dependence of these parameters strongly reflects the non-ideality of the solvent mixture.

The degree of association of high-charge electrolytes such as CuSO₄ has been a bone of contention for many years. The actual association constants calculated from the data vary much more between workers than the precision of the individual sets of data would lead one to expect. Certain reasons for this have been emphasized recently. Prue[1a] has shown that the K_A calculated for CuSO₄ is very strongly dependent on the particular theory used and markedly dependent on the parameters used in the data fitting. A particularly thorny problem is posed by the a^0 (mean distance of closest approach) needed in both the extended Debye–Hückel and Onsager theories. Since there is no *a priori* way of fixing a^0, one must fit the data with at least the two parameters a^0 and K_A. Prue demonstrated in his fitting of some spectrophotometric data that a variety of sets of these two parameters would give equally good data fits. A second problem is exemplified by the recent theoretical work of Guggenheim.[2] He raises the basic question of whether one can rightfully expect any theory based on the Debye model to work for high-charge electrolytes. Guggenheim says that for a 2–2 salt, such a theory cannot work and goes on to revive the La Mer[3] treatment in slightly modernized form. A more complete critique of this work must await further investigation, but one certainly can quarrel with Guggenheim's introduction of further names (sociation, supersociation) into this already cluttered field.

In an attempt to clarify this problem experimentally we have initiated a broad program of measurements on high-charge electrolytes. The first paper in this series[4] demonstrated the properties of an interesting class of anions, the aryl polysulfonates. It was shown that copper *m*-benzene disulfonate (CuBDS) was a much less highly associated electrolyte than CuSO₄ and, that, in fact, the extended Fuoss–Onsager conductance theory[5] described the data very well without the intro-

duction of an association constant. This is not the same as saying that CuBDS is not associated in water. In order, then, to explore this type of anion further we have measured the conductances of MnBDS and MnSO₄ in methanol–water mixtures. The shift from Cu to Mn was made because of the other measurements under way that are more practical for Mn (e.s.r. and ultrasonic relaxation).

Experimental

The preparation of the MnBDS followed closely that outlined for CuBDS in ref. 4; the preparation of H₂BDS by ion exchange from pure BaBDS and a subsequent reaction with MnCO₃. The MnBDS was recrystallized from conductivity water and dried to a definite 3¹/₂ hydrate over CaCl₂. Mn analyses were done by standard oxidation–reduction techniques and BDS was found by ion-exchange titration.[4] MnSO₄ was recrystallized reagent grade dried to the definite monohydrate at 105°. Sulfate was determined by BaSO₄ precipitation.

The apparatus and *modus operandi* were described previously.[4] All solutions were made up in the flask cells by weight. Pycnometric densities were used for conversion to molarities. The methanol was purified by the standard techniques.[6] Since Mn(II) hydrolyzes less than Cu(II) it was found that the hydrolysis corrections needed in the previous work[4] were not necessary. The correction was smaller than the error in the equivalent conductance. In addition, the theoretical foundation of the correction in the methanol mixtures was somewhat uncertain.

Data Treatment.—Table I gives the equivalent conductance and concentration data for the two salts in the various solvent mixtures. Figure 1 shows the phoreograms of MnBDS in water and 20, 60 and 100% methanol mixtures. The water results are those to be expected from a completely or almost completely unassociated salt. That is, the experimental curve approaches the Onsager limiting tangent from above, crosses it and approaches Λ^0 from below. This "crossover" phenomenon, as discussed previously,[4] is a natural consequence of the form of the extended Fuoss–Onsager equation for unassociated electrolytes[5]

$$\Lambda = \Lambda^0 - SC^{1/2} + EC \log C + JC$$

where

Λ	= equivalent conductance
C	= molar concentration
S	= limiting slope
E, J	= extended law parameters (J including the ion-size correction).

Since $EC \log C$ is always negative in the concentration range of interest ($\kappa a^0 < 0.2$) and JC always positive, the competition of these terms produces the crossover phenomenon. This was first predicted by Fuoss[5] and first observed in CuBDS.

Figure 2 shows the Λ' plots for MnSO₄ and MnBDS in water. The MnBDS exhibits only a slight curvature at the

$$\Lambda' = \Lambda + SC^{1/2} - EC \log C \qquad (1)$$
$$= \Lambda^0 + JC$$

(1) In part from a Ph.D. thesis submitted to the graduate school of The University of Michigan.

(1a) W. G. Davies, R. J. Otter and J. E. Prue, *Discussions Faraday Soc.*, **24**, 103 (1957).

(2) (a) E. A. Guggenheim, *Trans. Faraday Soc.*, **56**, 1159 (1960); (b) **55**, 1714 (1959).

(3) T. H. Gronwall, V. K. La Mer and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

(4) G. Atkinson, M. Yokoi and C. J. Hallada, *J. Am. Chem. Soc.*, **83**, 1570 (1961).

(5) (a) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957); (b) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959.
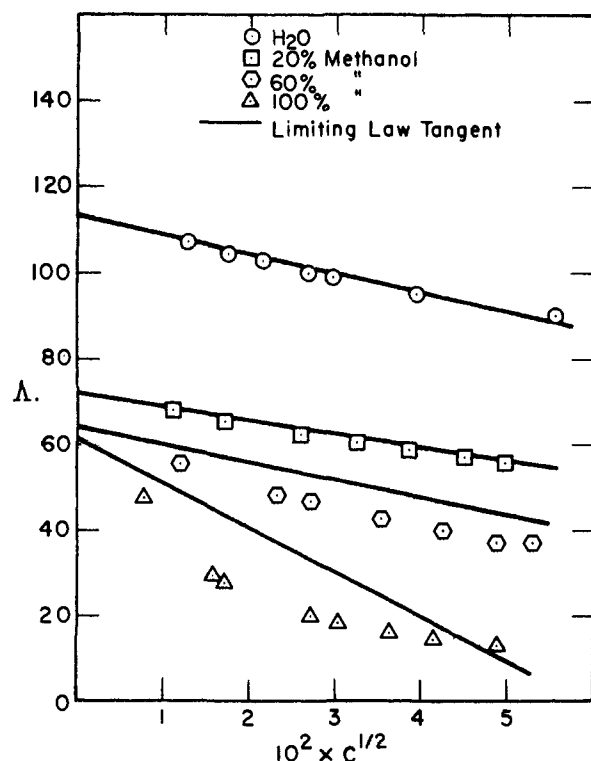
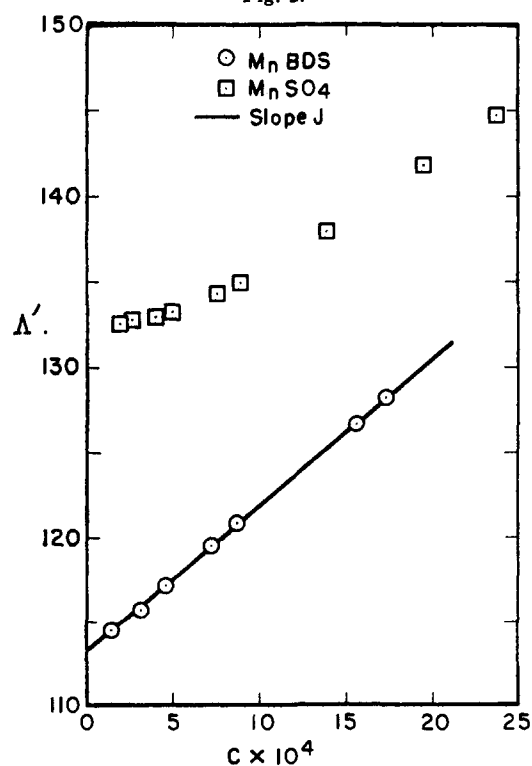(6) A. I. Vogel, "Practical Organic Chemistry, "2nd Ed., Longmans, Green and Co., London, 1951, p. 168.

Fig. 1.

Fig. 2.

high concentration end indicating possible slight association. For this case J can be replaced by $(J - K_A{}^2\Lambda f_\pm{}^2)^7$ where

K_A = association constant = $(1 - \alpha)/C\alpha^2 f_\pm{}^2$
α = fraction of ions associated
$f_\pm$ = mean activity coefficient

(7) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 3163 (1958).

TABLE I (a)

MnBDS in 100% MeOH		MnBDS in 80% MeOH	
10^4C	Λ	10^4C	Λ
0.5876	47.57	1.8569	56.49
2.4879	29.56	2.4658	53.89
2.9312	27.89	3.1599	51.55
7.3039	19.95	4.9331	47.21
9.1328	18.36	7.8202	42.63
13.162	16.09	15.397	36.33
17.249[a]	14.62	19.477[a]	34.30
23.867[a]	13.08	22.646[a]	33.03

MnBDS in 60% MeOH		MnBDS in 40% MeOH	
1.4611	55.78	1.6284	55.73
5.4190	48.27	5.9389	51.04
7.4454	46.95	13.119	47.07
12.403	42.74	17.769	45.39
18.031	40.15	22.640	44.00
23.729[a]	38.27	27.530[a]	42.88
28.084[a]	37.13	32.809[a]	41.87
		39.418[a]	40.80

MnBDS in 30% MeOH		MnBDS in 20% MeOH	
2.0449	58.48	1.2249	67.96
5.0302	55.71	2.9912	65.58
9.1027	53.14	6.7493	62.52
14.352	50.89	10.498	60.53
18.989	49.40	14.879	58.75
24.685[a]	47.95	20.221	57.04
		24.799[a]	55.91

MnBDS in 10% MeOH		MnBDS in H₂O	
1.7387	82.85	1.6202	107.02
4.5360	79.45	3.0881	104.39
10.182	75.51	4.5834	102.71
16.903	72.55	7.2762	100.12
21.694	70.94	8.7987	99.03
25.843[a]	69.81	15.667	95.04
29.480[a]	68.89	17.335	94.35
		30.710	89.82
		50.255[a]	85.66

MnSO₄ in 40% MeOH		MnSO₄ in 30% MeOH		MnSO₄ in 20% MeOH	
2.2748	52.11	0.9595	66.96	2.0589	75.45
4.5601	45.72	2.6435	60.47	5.8421	67.25
6.6662	42.00	6.1582	53.04	11.814	60.13
8.7040	39.38	9.9216	48.32	17.857	55.58
10.716	37.32	12.869	45.69	23.318	52.60
		16.531	43.15	28.154[a]	50.48

MnSO₄ in 10% MeOH		MnSO₄ in H₂O	
1.3726	97.22	2.0134	122.84
5.0088	88.44	2.6134	121.39
10.598	80.81	3.2881	119.89
17.950	74.56	5.0626	115.98
24.324	70.73	8.9728	109.94
29.461[a]	68.24	13.945	104.54
		19.570	100.00
		23.732	97.14
		31.411	93.02

[a] For completeness of data these points are included. However, the validity of applying theoretical calculations to them is questionable, since at these concentrations $\kappa a^0 > 0.2$. All concentrations are in moles/liter.

and a K_A evaluated from the last few points on the Λ' plot. The MnSO₄ curve has the typical "S" shape of an appreciably associated electrolyte. As can be seen the measurements must be extended to low concentrations to obtain

TABLE II

Salts	Solvent	D	Λ^0	$K_A \times 10^{-3}$	a^0(cond.) (Å.)	a^0(Bjerrum) (Å.)	$\Lambda^0\eta$
MnBDS	H₂O	78.48	113.35	(0.045)	5.4	...	1.01
	10% MeOH	74.21	88.3	.08	5.4	13.1	1.02
	20% MeOH	70.01	72.1	.16	5.8	13.9	1.01
	30% MeOH	65.55	63.9	.21	5.5	14.8	0.98
	40% MeOH	60.92	60.8	.56	5.7	15.7	.97
	60% MeOH	51.71	64.1	5.13	8.2	7.8	.90
	80% MeOH	42.60	74.2	14.9	7.3	7.4	.75
	100% MeOH	32.64	61.6	81.7	8.0	7.2	.33
MnSO₄	H₂O	78.48	133.22	1.33	5.0	5.4	1.19
	10% MeOH	74.21	104.9	2.37	5.2	4.6	1.21
	20% MeOH	70.01	85.8	4.39	5.8	4.1	1.20
	30% MeOH	65.55	74.7	8.81	8.0	3.7	1.14
	40% MeOH	60.92	68.9	17.1	8.2	3.7	1.10

a realistic view of the salt. In this case if only the points above 10^{-3} molar are used a Λ^0 of 129 is obtained. This is over 4Å units lower than the correct value.

Therefore for such salts (in this work, MnBDS in over 20% methanol and all MnSO₄ work) the approximate method is no longer accurate and a more nearly complete treatment must be used. We have adopted the Fuoss "$y-x$" method since it is most closely related to the theory and needs no additional parameters beyond K_A, a^0 and Λ^0. For a complete outline of this method see reference 7. However a brief outline is given. Let

$$\Lambda = \Lambda^0 - S(\alpha C)^{1/2} + E\alpha C \log \alpha C + J\alpha C - K_A\Lambda f_{\pm}^2\alpha C \quad (2)$$

and

$$\log f_{\pm} = -\frac{S_f(\alpha C)^{1/2}}{1 + A(\alpha C)^{1/2}} \quad (3)$$

where

$$A = \frac{a^0\kappa}{C^{1/2}} \times 10^{-8} \quad \text{(extended Debye–Hückel law)}$$

α is found by

$$\alpha_1 = \frac{\Lambda}{\Lambda^0 - S\left(\frac{\Lambda}{\Lambda^0}\right)^{1/2}C^{1/2}}$$

$$\alpha_2 = \frac{\Lambda}{\Lambda^0 - S(C\alpha_1)^{1/2} + EC\,\alpha_1 \log C\alpha_1 + JC\alpha_1}$$

$$\vdots$$

$$\alpha_n,$$

until $\alpha_{n-1} = \alpha_n$. Now define

$$\Delta\Lambda = \Lambda' - \Lambda^0 \quad (4)$$

$$y = \frac{\Delta\Lambda}{C\alpha} \quad (5)$$

and

$$x = f_{\pm}^2\Lambda \quad (6)$$

Then eq. 2 becomes

$$y = J - K_Ax \quad (7)$$

In a series of successive approximations values of a^0 and Λ^0 are introduced into the above equations until eq. 7 is the best fit straight line. The a^0 then obtained from J must be compatible with the a^0 introduced into that round of approximation. Since this is an extremely tedious procedure, it was programmed for the IBM 704 computer and all data were processed in this manner.

Table II gives the final parameters obtained. Complete tables of the S, E, J parameters for these salts in the different solvent mixtures (and for different a^0 values) are available from the senior author on request.

Discussion of Results

In an attempt to analyze the data further, log K_A was plotted versus $1/D$ for the two salts[8] and is shown as Fig. 3. Both sets of data exhibit some curvature at low D but seem quite linear in approaching the pure water value. As can be seen

(8) R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc., **79**, 3304 (1957).

from the figure and Table II the extrapolated value for MnSO₄ in water is quite close to the value obtained by the approximate method. Since the association is so slight for the MnBDS in the high D range, the "$y-x$" method is not as accurate, but a value for K_A of MnBDS in water can be obtained from the log K_A plot by assuming it to be linear in the high D range. This method gives a K_A of 4.5_0 corresponding to an α of 0.995 at a concentration of 3×10^{-3} molar. Because of the uncertainty in the extrapolation the error in this α could be as large as ± 0.006 so that a finite value for K_A need not be inconsistent with the previous assumption that MnBDS is unassociated in water.
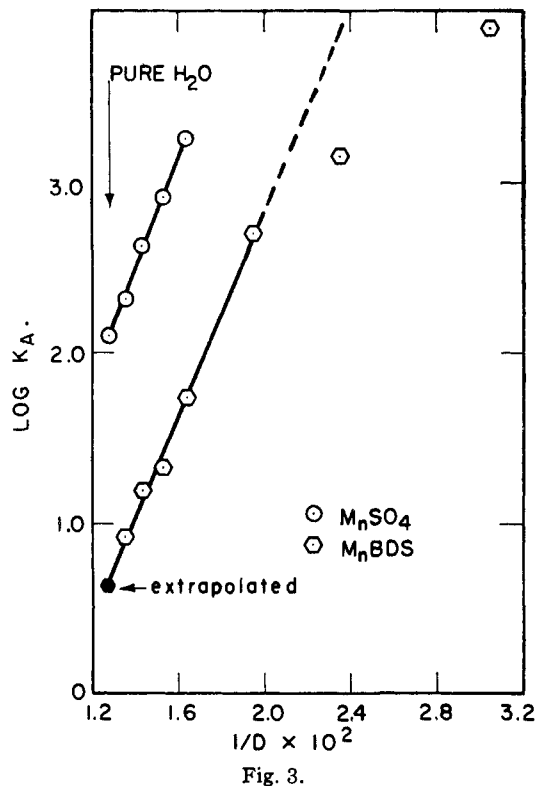

Fig. 3.

Figure 4 shows the Walden product ($\Lambda^0\eta$, where η is solvent viscosity) and a^0 for MnBDS plotted versus mole fraction methanol. The a^0 values exhibit a large jump between 40 and 60% methanol going from an average value of 5.6 Å. to a value
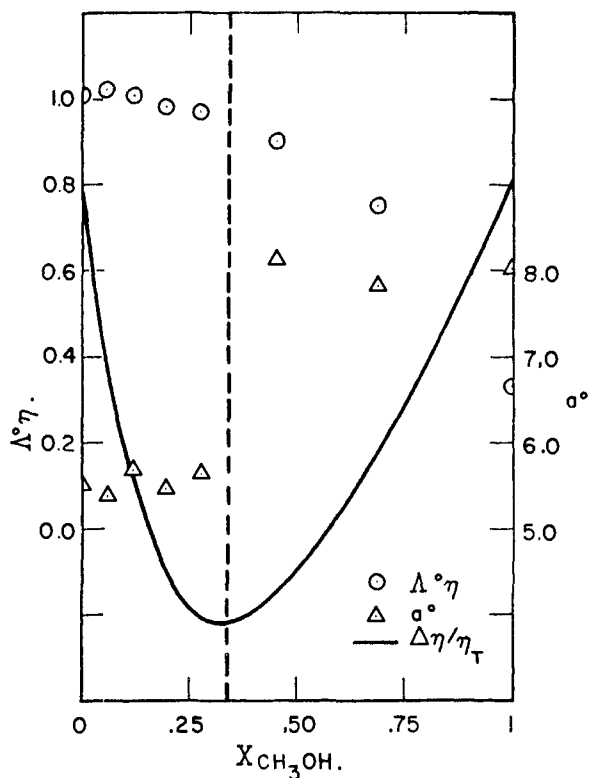
Fig. 4.

of 7.8 Å. A usual explanation for this type of behavior[9] has been the neglect of an Einstein viscosity correction. We have applied an empirical correction of this type but have found that the correction needed to keep a^0 even fairly constant is almost 20 Λ^0, corresponding to approximately 2000 in the J term. It seems to us very rash to add such a large correction until actual viscosity data are available for these systems. This is particularly true in view of the recent interest in the term so far neglected, $(O)C^{7/2}$. When the viscosity data become available, then it will be possible to reanalyze these data with both a viscosity and $C^{7/2}$ correction in a more honest manner.

The Walden product also exhibits a sharp falling off at a mole fraction of about 0.3. Without attempting further analysis at this time, we can still say that both $\Lambda^0\eta$ and a^0 are reflecting the non-

(9) Ref. 5b, Chapts. 15 and 17.

ideality of the methanol–water solvent system. To emphasize this we have included a plot of the relative viscosity of the solvent mixture on Fig. 4 noting that both $\Lambda^0\eta$ and a^0 exhibit their strange behavior past the point corresponding to the minimum in the viscosity curve (a mole fraction corresponding to about 3 waters/methanol). Similar behavior has been noted previously for some salts in methanol–water mixtures,[10] and a tentative explanation has been proposed.[11] Unfortunately the additional data needed to do an interpretation along the lines suggested by Fuoss are not yet available to us. It was not possible to repeat the above analyses for the $MnSO_4$ data because of the low solubility of this salt in mixtures greater than 40% methanol. Even before this point the $\Lambda^0\eta$ and a^0 do not behave quite regularly. It should also be noted on Fig. 3 that the log K_A plot for the MnBDS exhibits a break which corresponds to that noted for the other parameters.

The final column in Table II gives the Bjerrum a^0 values calculated from the measured K_A values.[12] There is, quite obviously, no simple relationship between the two sets of values except that the Bjerrum a^0's reflect the non-linearity of the MnBDS log K_A plot also.

Preliminary work on the same two salts in dioxane–water mixtures has been completed and will be published soon. In this more ideal solvent system, the above irregularities are not apparent. We are presently investigating some other solvent systems and attempting to find K_A's for these salts by other, non-conductance, methods.

In conclusion we can only reiterate that MnBDS like CuBDS is essentially unassociated in water in marked contrast to $MnSO_4$ and that the Fuoss–Onsager theory works remarkably well in the analysis of conductance data of these high-charge electrolytes.

(10) F. Accascina, A. D'Aprano and R. M. Fuoss, J. Am. Chem. Soc., 81, 1059 (1959).
(11) R. M. Fuoss, Proc. Natl. Acad. Sci. U. S., 45, 807 (1959).
(12) N. Bjerrum, Kgl. Danske Vidensk. Selskab., 7, No. 9 (1926).