Ion Association in Polyvalent Symmetrical Electrolytes. VII. The Conductance of Manganese(II) Sulfate and Manganese(II) *m*-Benzenedisulfonate in Methyl Cellosolve–Water Mixtures at 25°

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Abstract: The conductance of $MnSO_4$ has been measured in methyl cellosolve (MC)–water mixtures up to 55% MC, and the conductance of Mn(*m*)BDS up to 95% MC. All data were analyzed using the linearized Fuoss–Onsager equation to give $\Lambda°$, K_A, and a_J values. The behavior of these two salts in MC–water mixtures shows marked specific solvent effects. The results are compared with the previously obtained results in three other solvent mixtures. Some speculations are advanced as a start to a general explanation of the solvent effects.

In a series of recent papers we have examined the conductances of $MnSO_4$ and manganese *m*-benzenesulfonate (Mn(*m*)BDS) in dioxane–water,[1] methanol–water,[2] and acetone–water mixtures.[3] The data were analyzed using the Fuoss–Onsager equation[4] to give the three parameters of the theory, the limiting conductance at infinite dilution (Λ^0), the association constant (K_A), and the mean distance of closest approach (a_J). The purpose of the research is to examine ion–ion interactions in electrolyte solutions where ion–solvent interactions are large, and, in some cases, specific. We do not feel that in the limit of low concentrations and ions of low charge that the basic correctness of the Debye–Hückel–Onsager (DHO) model can be doubted. Its successes are too widespread and consistent. It is equally apparent that relationships such as Walden's rule ($\Lambda^0\eta$ = constant) and $K_A = K_A{}^0e^b$ ($b = e_1e_2/2aDkT$) are effective descriptions in the same conditions. Yet the large number of systems that are inadequately described by the DHO-based theories and the limited concentration range of the theories demand a more detailed view of ion–solvent interaction. A number of recent attempts to do this have been specifically directed toward given solvent systems.[5,6] Other attempts[7] have involved slight modifications of the DHO continuum solvent and have taken little account of the molecular character of the ion–solvent interaction. Most of these works have focused on 1:1 electrolytes where it was hoped that specific ion–solvent effects would be small. However, even as simple a salt as KCl exhibits nonclassical behavior in mixed solvent systems.[8] In this work on 2:2 electrolytes we are attempting to lay the classical foundation for a thorough experimental study of the relationsphip between ion–ion and ion–solvent interactions. $MnSO_4$ is a typical 2:2 salt, being somewhat associated in water ($K_A = 133$). Mn(*m*)BDS is essentially unassociated in water ($K_A \simeq 4$) and remains soluble in reasonably high concentrations of organic solvents. To conclude this phase of the classical studies we wanted to use an organic solvent that was known to show marked specific solvent effects. Ion-exchange separation work in mixed solvents had indicated that the cellosolves showed very marked solvent effects.[9] Therefore, we chose methyl cellosolve (MC), $CH_3OCH_2CH_2OH$, for this work.

Experimental Section

The experimental technique is described in a previous publication.[10] The Mn(*m*)BDS was a laboratory stock prepared as in the previous work.[1-3] It was dried over $CaCl_2$ at room temperature to the definite weighing form Mn(*m*)BDS·3.5H_2O. The $MnSO_4$ was CP material recrystallized twice from conductance water. Dried at 105°, it was used in the form $MnSO_4 \cdot H_2O$. This is a definite weighing form that is best kept in a desiccator over anhydrous $MnSO_4$.

The methyl cellosolve was dried over anhydrous Na_2CO_3 and distilled at atmospheric pressure. A redistillation was then carried out at 50 mm using a 30-plate fractionating column. The purity was checked by boiling point and refractive index. The water was purified by a double pass through a mixed-bed ion-exchange column.

The conductance apparatus used is a Leeds and Northrup Jones bridge with the necessary auxillary equipment. All measurements were made at 25° in a Leeds and Northrup standards oil bath controlled to ±0.001° with the temperature being checked with an NBS-calibrated Pt resistance thermometer. The conductances were measured in flask-type cells by the weight dilution technique. Since bright Pt electrodes were used, the resistance of each solution was measured at 1000, 2000, 3000, 5000, and 10,000 hertz and an extrapolation made to R_∞ by a R *vs.* $f^{-1/2}$ plot.

The analyses of the solutions were checked with two different techniques. In the first, excess EDTA solution is added to the Mn^{+2} solution and the excess EDTA titrated with standard Mg^{+2} solution to an eriochrom black T end point. In the second, the Mn^{+2} solution is converted to the corresponding acid using an analytical ion-exchange column in the H^+ form. The acid solution is then titrated with standard NaOH using a Metrohm E336 potentiograph and a differential end point.

Results

The conductance data are given in Table I. The conductances and concentrations are not corrected for hydrolysis. Preliminary calculations showed that such corrections are within experimental error. The upper limit of organic content in the solvent was set by the impracticality of using very dilute stock solutions needed because of low salt solubility. All data were analyzed using the Fuoss–Onsager equation in the

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(1) G. Atkinson and C. J. Hallada, *J. Am. Chem. Soc.*, **84**, 721 (1962).

(2) C. J. Hallada and G. Atkinson, *ibid.*, **83**, 3759 (1961).

(3) G. Atkinson and S. Petrucci, *ibid.*, **86**, 7 (1964).

(4) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959.

(5) A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, **67**, 1722 (1963).

(6) A. D'Aprano and R. M. Fuoss, *ibid.*, **67**, 1704 (1963).

(7) H. L. Curry and W. R. Gilkerson, *J. Am. Chem. Soc.*, **79**, 4021 (1957).

(8) S. Petrucci, *Acta Chem. Scand.*, **16**, 760 (1962).

(9) H. Kakihana, private communication.

(10) G. Atkinson and S. Petrucci, *J. Phys. Chem.*, **67**, 337 (1963).

Table I.[a] Experimental Data

$C \times 10^4$	Λ	$C \times 10^4$	Λ
	MnSO$_4$		
20.14% MC		30.13% MC	
1.0278	73.979	0.4459	59.908
2.4098	69.447	1.3203	56.799
3.5135	66.637	2.5034	51.899
4.9519	63.739	3.7858	48.433
6.4330	61.407	5.3387	45.381
8.4753	58.694	7.5717	42.214
13.949	53.629	10.303	39.394
39.90% MC		49.95% MC	
1.2908	41.230	0.8838	30.077
2.2732	37.316	2.1419	24.208
3.7090	33.604	3.6025	20.798
5.5444	30.497	5.2756	18.443
7.5799	28.102	7.5541	16.382
9.9741	26.037	10.590	14.600
12.600	24.338	14.270	13.154
15.992	22.670	17.737	12.180
54.93% MC			
0.7334	24.602		
1.7650	19.256		
2.7239	16.753		
4.2534	14.391		
5.9153	12.796		
8.2270	11.344		
10.400	10.401		
13.004	9.5660		
15.432	8.9700		
	Mn(m)BDS		
10.07% MC		20.10% MC	
1.7846	79.144	1.3263	63.211
4.1278	76.359	3.7382	60.287
6.6497	74.319	6.0630	58.434
9.6466	72.502	8.1794	56.886
12.440	71.144	10.262	55.919
15.783	69.807	12.962	54.688
18.657	68.824	16.299	53.652
22.160	67.768		
	Mn(m)BDS		
29.87% MC		40.25% MC	
2.1225	47.281	1.2538	39.425
4.9008	44.947	2.8216	37.502
7.7907	43.352	4.8094	35.915
13.071	41.330	6.9568	34.657
18.859	39.785	10.115	33.226
24.281	38.675	14.377	31.806
28.876	37.904	20.096	30.428
33.677	37.215		
49.82% MC		59.96% MC	
1.6178	31.879	1.1353	27.781
4.8249	28.902	2.1213	26.026
9.0113	26.766	3.8892	23.981
15.278	24.838	5.9234	22.442
21.327	23.606	8.5805	21.052
27.317	22.709	11.0896	20.097
33.542	21.974	13.4239	19.391
38.715	21.474		
70.13% MC		80.08% MC	
1.2298	22.327	1.2021	14.340
3.4351	18.279	2.7779	11.041
5.6851	16.278	6.1850	8.4718
8.4291	14.784	9.6800	7.3031
11.058	13.814	12.978	6.6400
14.242	12.960	17.778	6.0138
16.968	12.401	23.285	5.5435
19.962	11.906	28.889	5.2106
22.896	11.507		
25.697	11.186		
90.01% MC		94.97% MC	
0.9336	4.2408	3.5991	0.64796
2.3112	2.8533	11.078	0.41770
3.8634	2.3262	18.839	0.35353
6.4414	1.8994	29.158	0.31862
9.4679	1.6374	41.811	0.30155
12.906	1.4638	51.644	0.29590
18.660	1.2939	59.613	0.29473
22.202	1.2279		
25.350	1.1805		
28.286	1.1443		

[a] Concentrations are in moles/l. and conductances in (ohm cm^2 equiv)$^{-1}$. C and Λ are reported to one more place than the authors feel is significant so that rounding off errors can be avoided in recalculation.

linearized form

$$\Lambda = \Lambda^0 - SC^{1/2}\gamma^{1/2} + EC\gamma \log C\gamma + JC\gamma - K_A f_{\pm}^2 \Delta\gamma C$$

where the symbols have been previously defined. The analysis was carried out with an IBM 7090 computer by a three-dimensional least-squares technique using Λ^0, K_A, and a_J as free parameters. An extended Debye–Hückel equation was used to calculate $f_{\pm}$, the mean activity coefficient. The most recent revision of the conductance theory[11] has not yet shown itself to be superior to the above form for our purposes. No viscosity correction was applied because of the lack of actual viscosity data. The concentrations were kept quite low so that contributions from terms of order higher than C would be small. The derived parameters are given in Table II. The solvent properties used in the data analysis are from the literature: densities, viscosities, and dielectric constants.[12]

Table II. Calculated Parameters

MC, %	D	$10^2\eta$	Λ^0	$\Lambda^0\eta$	K_A	a_J, A
			MnSO$_4$			
0	78.54	0.893	133.2_2	1.19	133	5.1
20.14	69.4	1.517	80.7	1.26	524	6.0
30.13	64.6	1.890	67.0	1.27	1,390	7.8
39.90	58.6	2.311	53.0	1.22	2,720	8.3
49.95	52.2	2.691	44.0	1.18	7,860	9.3
54.93	49.2	2.811	39.0	1.10	12,800	8.4
			Mn(m)BDS			
0	78.54	0.093	113.35	0.99_1	(4.5)	6.1
10.07	74.0	1.179	84.5	1.00	12	5.8
20.10	69.6	1.517	67.3	1.02	30	5.9
29.87	64.7	1.873	54.5	1.02	60	6.2
40.25	58.4	2.319	42.9	1.00	164	6.7
49.82	52.3	2.701	36.0	0.97_2	328	6.5
59.96	46.0	2.891	32.3	0.93_4	860	7.3
70.13	39.2	2.875	30.0	0.86_3	3,120	6.9
80.08	32.2	2.607	29.0	0.75_6	18,700	6.7
90.01	25.3	2.137	30.1	0.64_2	198,000	6.4
94.97	21.4	1.816	29.6	0.53_8	1,930,000	6.3

(11) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **66**, 1722 (1962); **67**, 621, 628 (1963); **68**, 1 (1964).

(12) F. Accascina, *et al.*, *Scienza e Tecnica*, **4**, 32 (1960).

Discussion of Results

Figure 1 compares the association constants for $MnSO_4$ in the four different solvent mixtures examined so far. The MC results present a different behavior than the other three mixtures. In the high D mixtures the K_A's are slightly higher. However, at $D \simeq 67$ there is a distinct inflection point, and in the low D portion of the plot the line is parallel to the earlier dioxane line. This distinct change in slope and an analogous change in the methanol–water system[13] point to rather strong specific solvent effects that reflect the strongly nonideal behavior of the solvent system.[12] These effects are also apparent in the a_J values which rise rapidly from the H_2O value. For some reason the nonideality is much less apparent in the Walden product which is shown in Figure 2. It would normally be expected that the thermodynamic nonideality of K_A would be reflected in hydrodynamic nonideality of $\Lambda^0\eta$.

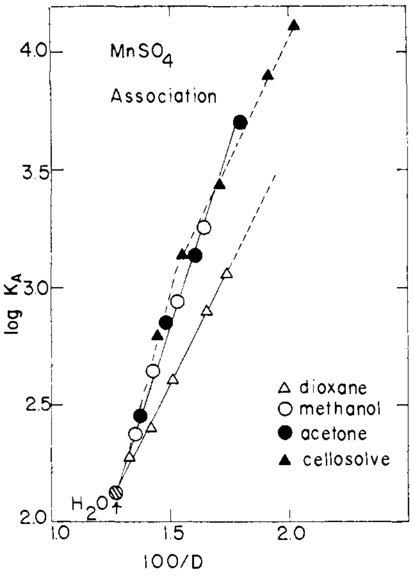

Figure 1.

Because of its much greater solubility the Mn(m)BDS could be examined in much higher MC concentrations. Figure 3 compares the log K_A *vs.* $1/D$ plots for the four solvent systems. The MC plot is completely analogous to the corresponding $MnSO_4$ plot with the inflection point occurring at the same D. With the more soluble Mn(m)BDS three out of four of the solvent mixtures show these inflections. Figure 4 compares the Walden products in the four systems. In this case there is a very drastic fall off in $\Lambda^0\eta$ as we go to the high MC content mixture, implying a definite change in ion solvation. However, an examination of the a_J values shows nothing but a random scattering around an average value (6.4 A) only slightly larger than the average for the other solvent systems (acetone, 6.1 A; methanol, 6.0 A; dioxane, 6.2 A).

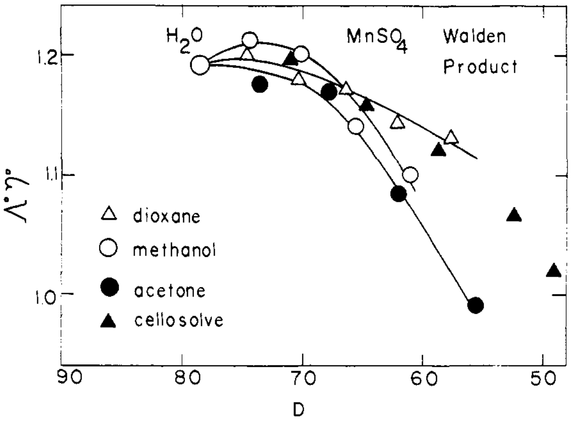

Figure 2.

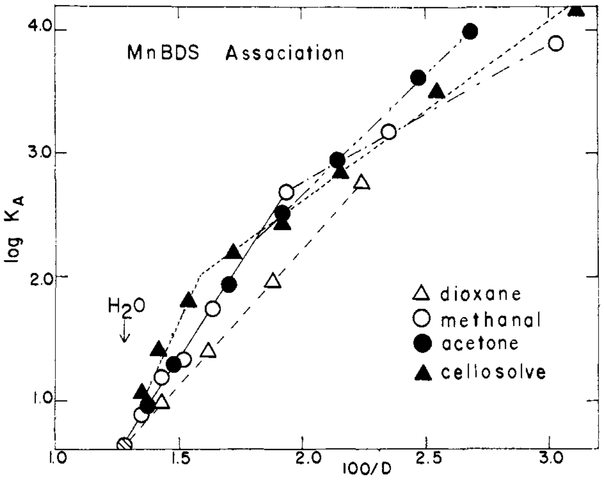

Figure 3.

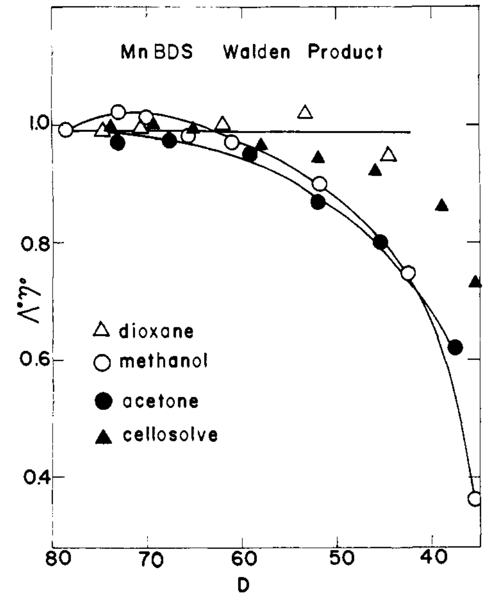

Figure 4.

At the present time we do not feel capable of analyzing in detail the perplexing individualistic behavior exhibited by these two Mn^{+2} salts in the four different solvent mixtures. Our original choice of 2:2 salts was made so as to encourage strong and specific ion–solvent interactions. The results have been embarrassingly rich in this respect. However, we do want to suggest the general approach to the complete analysis of such a problem.

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(13) H. Tsubota and G. Atkinson, to be published.

It has been demonstrated[14–16] that ion association in $MnSO_4$, $MgSO_4$, and many similar systems takes place in three distinct steps in water.

$$\overset{①}{M^{+2}(aq) + X^{-2}(aq)} \overset{I}{\rightleftharpoons} \overset{②}{[M^{+2}WWX^{-2}]} \overset{II}{\rightleftharpoons}$$

$$\overset{③}{[M^{+2}WX^{-2}]} + W \overset{III}{\rightleftharpoons} \overset{④}{[M^{+2}X^{-2}]} + W$$

Here ②, ③, and ④ are different ion-pair states differing only in the number of water molecules between the ions, and ④ is the contact ion pair. In this three-step process only step I, the diffusion-controlled approach of the completely hydrated ions, can be described adequately in terms of the macroscopic dielectric constant and viscosity. In fact, the equilibrium constant for step I is identical with that calculated from the Bjerrum equation[17] using a distance equal to the sum of the ion radii plus two water diameters.

Steps II and III are strongly dependent on the individual ions. In the cases that have been analyzed completely, the controlling factor seems to be the rate of exchange of solvent molecules on the ions. The interesting fact appears that the forward rates of steps II and III are independent of each other. The only reasonably thorough examination of the effect of an additional solvent was our work on $MnSO_4$ in dioxane–water and methanol–water mixtures.[18] Here it was found that the specific solvent effects noted in the conductance work appear only in steps II and III. Unfortunately, we were unable to go to the high methanol content beyond the inflection point. The detailed analysis of these inner solvent release steps must take account of specific numbers and types of solvent molecules and a detailed understanding of the kinetics of solvent exchange. These are presently under detailed study in a number of laboratories.

Further examination of step I by ultrasonic techniques can lead to further understanding of ion hydrodynamics. The forward and reverse rates are diffusion controlled and describable by the Debye diffusion theory.[19] As the interaction energy is classically coulombic, the measured rates can be used to give information on the hydrodynamics of ion approach.

The solvent mixtures examined in this series of papers (dioxane–water, methanol–water, methyl cellosolve–water, acetone–water) are all nonideal mixtures involving strong hydrogen-bond donors and acceptors. This adds an extra complication to an already complex situation. Can we use the properties of such solvent mixtures to understand the abrupt changes noted on our log K_A *vs.* $(1/D)$ plots? A recent paper[20] revived an approach that promises some first-order aid. Andreae and his co-workers have characterized the nonideal ultrasonic absorption, compressibility, and excess volume in terms of simple equilibria such as

$$R\text{-}OH + nH_2O \rightleftharpoons R\text{-}OH(OH_2)_n$$

Preliminary calculations using the equilibrium constants reported by Andreae, *et al.*, give a qualitative explanation of the differences in solvent character shown by our conductance results. For example, as we go from pure water past mole fraction 0.25 methanol we go from a region describable as a water structure containing water–alcohol complexes to a region whose basic structure is set by the complexes. The above approach is certainly only a crude approximation to such strong interaction systems. Yet in the absence of a more complete theory of such liquid mixtures, it could be of great aid in our understanding.

Acknowledgments. The authors express their gratitude to the U. S. Atomic Energy Commission for their support of this work under Contract AT-(40-1)-2983. They also express their appreciation for the support of the University of Maryland Computer Science Center, and to Mr. David Ebdon and Mr. Bert R. Staples.

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(14) M. Eigen and K. Tamm, *Z. Elektrochem.*, **6**, 107 (1962).

(15) M. Eigen and L. De Maeyer in "Investigations of Rates and Mechanisms of Reactions, Part II, Interscience Publishers, Inc., New York, N. Y., 1963, Chapter XVIII.

(16) G. Atkinson, S. K. Kor, and S. Petrucci, *Proc. Inst. Elec. Electron. Engrs.*, **53**, 1355 (1965).

(17) N. Bjerrum, *Kgl. Danske Videnskab. Selskab.*, **7**, No. 9 (1926).

(18) G. Atkinson and S. K. Kor, *J. Phys. Chem.*, **69**, 128 (1965).

(19) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

(20) J. Andreae, *et al.*, *Acustica*, **15**, 74 (1965).