

mole for the $\text{H}-\text{C}_3\text{H}_6$ reaction, and adjusted the A -factor for this reaction to give $k_p = 4.8 \times 10^{11}$ mole $^{-1}$ cc. sec. $^{-1}$ at 31°. The result thus obtained was used to estimate the Arrhenius parameters summarized in Table III, where the results in reference 9 are also included for comparison. The present

values for both A and E are lower in all three reactions. The source of this discrepancy is not clear.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

Ion Association in Polyvalent Symmetrical Electrolytes. IV. The Conductance of MnSO_4 and MnBDS in Dioxane-Water Mixtures

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The conductance of $\text{Mn } m$ -benzene disulfonate (MnBDS) has been measured in mixtures from 0 to 40% dioxane; and MnSO_4 has been studied from 0 to 25% dioxane. The data are analyzed using the Fuoss-Onsager theory and K_A , Λ^0 and a_j parameters obtained. As was found in the previous work on these salts in methanol-water mixtures, MnBDS is far less associated in water than MnSO_4 . a_j and the Walden product ($\Lambda^0\eta$) are constant for both salts over the solvent range examined and the same as found in the methanol-water mixtures. However, the K_A 's found in the dioxane-water mixtures are uniformly lower than those found in the methanol-water mixtures of the same dielectric constant. It also is found that the $\log K_A$ vs. $1/D$ plot for only MnSO_4 in dioxane-water mixtures is in very good agreement with the Fuoss-Bjerrum theory of ion-pairing. Various speculations on the solvation of the ions involved are advanced to tentatively explain these results.

Recent work on the conductance of high-charge electrolytes³⁻⁵ has demonstrated the existence of 2-2 salts that are only very slightly associated in water. These substances, the Cu(II) and Mn(II) salts of m -benzene disulfonic acid and the Cu(II) salt of 4,4'-biphenyldisulfonic acid follow the Fuoss-Onsager theoretical predictions exactly and yield very reasonable values of the conductance parameters Λ^0 and a_j . One of these salts MnBDS has been examined in methanol-water mixtures from 0 to 100% methanol; and as a comparison, MnSO_4 was examined in the same solvent mixtures. It was found that in the range 0 to 0.25 mole fraction methanol both salts exhibited a constant value of a_j (the ion size parameter) and the Walden product, $\Lambda^0\eta$. In addition, the plots of $\log K_A$ vs. $1/D$ were linear for both salts in this range. Unfortunately, solubility problems prevented the extension of the measurements much past this range for MnSO_4 . For MnBDS , where the measurements could be made to 100% methanol, it was found that a_j and $\Lambda^0\eta$ deviated strongly from the low methanol concentration values when X_{MeOH} was greater than 0.25. It also was shown that the association constants in this high methanol content range were not consistent with the low range values. All of these deviations were tentatively correlated with the extreme deviations of the methanol-water solvent mixtures from ideality.

In an attempt to further clarify this problem and to further determine the association of these salts, measurements have been made in dioxane-water mixtures covering the same dielectric constant range.

Experimental

The preparation, purification and analysis of the Mn(II) salts have been described previously⁴ as have the apparatus and modus operandi.³ All solutions were made up by weight in flask-type conductance cells. Pycnometric densities were used for conversion to the molarity scale. The dioxane was purified by the standard procedures⁶; and the physical constants of the dioxane-water mixtures used in the calculations were those given by Fuoss.⁷ Hydrolysis corrections were not used because their calculated size fell within the experimental errors of Λ determination.

Data Treatment.—Table I gives the equivalent conductance and concentration data for the two salts in the various solvent mixtures. The phoreograms of the two salts in the different solvent mixtures are so similar to those shown previously⁴ as to make their portrayal superfluous.

For the treatment of the data the Fuoss-Onsager equation in the form for associated electrolytes was used. We again have ignored the viscosity correction which has been proposed by Fuoss since its contribution to 2-2 salt conductances is unknown.

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

where the symbols are explained in references 4 and 7, (particularly 4, for 2-2 salt treatment).

For the actual analysis of the association we have adopted the Fuoss "y-x" method and have used the Debye-Hückel extended equation to calculate the activity coefficients, f_{\pm} . The calculation has been programmed for the IBM 704 computer so that maximum utilization of data can be achieved. Fuoss defines

$$\Lambda' = \Lambda + SC_i^{1/2} - EC_i \log C_i \quad (2)$$

$$\Delta\Lambda = \Lambda' - \Lambda^0 \quad (3)$$

$$y = \Delta\Lambda/C_i \quad (C_i = \alpha C) \quad (4)$$

and

$$x = f_{\pm}^2\Lambda \quad (5)$$

Then

$$y = J - K_A x \quad (6)$$

The computer first evaluates an approximate α from

$$\alpha^1 = \frac{\Lambda}{\Lambda^0 - S(\Lambda/\Lambda^0)^{1/2}C^{1/2}} \quad (7)$$

(6) C. A. Kraus and R. A. Vingee, *ibid.*, **56**, 513 (1934).

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

(1) Department of Chemistry, University of Maryland, College Park, Maryland.

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

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

(5) M. Yokoi and G. Atkinson, *ibid.*, **83**, 4367 (1961).

TABLE I^a
MEASURED EQUIVALENT CONDUCTANCES

(A) MnSO ₄					
Dioxane, 5% 10°C		Dioxane, 10% 10°C		Dioxane, 15% 10°C	
2.5436	109.49	2.0338	98.85	1.7955	85.16
3.0623	107.16	5.3590	90.52	3.1304	83.79
6.4510	100.22	8.6953	85.08	6.5431	76.13
8.3348	98.00	12.259	80.79	10.053	70.97
11.093	93.92	26.460	70.51	13.586	67.21
14.791	90.14			17.161	63.71
20.130	85.94			23.292	60.22
24.351	83.26				
Dioxane, 20% 10°C		Dioxane, 25% 10°C			
3.2800	69.16	2.9289	61.78		
5.6592	63.64	6.2320	53.51		
9.2369	57.50	14.876	43.53		
16.919	50.13	18.305	41.28		
28.752 ^b	43.85	21.025	39.74		
		24.926 ^b	37.94		
(B) MnBDS					
Dioxane, 5% 10°C		Dioxane, 10% 10°C		Dioxane, 15% 10°C	
1.0330	94.97	1.5509	86.58	1.0379	74.57
2.8948	92.02	2.5295	85.08	3.4139	71.59
6.2067	88.70	4.0017	83.26	5.9255	69.38
9.2874	86.47	7.6010	80.04	9.4294	67.10
14.355	83.77	12.737	76.92	12.229	65.72
16.523	82.84	15.046	75.86	14.466	64.76
		19.949	73.92		
		26.258	71.97		
Dioxane, 20% 10°C		Dioxane, 30% 10°C		Dioxane, 40% 10°C	
1.9092	69.40	3.2349	56.00	1.6927	46.01
4.7130	65.44	5.0887	53.18	3.7865	41.24
7.4401	62.65	6.7143	51.37	6.9113	37.30
14.911	58.13	8.4049	49.52	9.8937	34.92
18.546	56.70	13.234	46.58	12.911	33.20
25.866 ^b	54.48	18.088	44.54	15.904	31.78

^a Concentration in moles/liter. ^b $\kappa a_J > 0.2$, data not used in analysis.

using a Λ^0 estimated from the phoreogram. It then operates on equations 2-6 and does a least squares treatment on (6). It finds a new α from K_A and repeats the calculation until $\alpha_{(in)} = \alpha_{(out)}$. In all rounds of computation but the first the approximation

$$\alpha = \frac{\Lambda}{\Lambda^0 - S(C\alpha)^{1/2} + E(C\alpha) \log(C\alpha) + J(C\alpha)} \quad (8)$$

is used.

The computer performs this series of calculations for a set of Λ^0 values calculating a fitting parameter for the $y-x$ line for each Λ^0 , originally using 1 or 2 Λ^0 unit increments. It then selects the Λ^0 which gives the best fit and repeats the whole calculation with smaller increments of Λ^0 . This process is continued until the increments are only 0.01 Λ^0 units. At this point the computation stops and the machine prints out the "best" K_A , Λ^0 , J and a_J (ion size parameter) for the data. It concludes its work by printing out the original (Λ , C) input, the Λ 's calculated from the "best fit" parameters and the α and f_{\pm} for each concentration. The average machine time for the calculation is 2 minutes.

For the cases where K_A is quite small (MnBDS in high D mixtures); the above calculation procedure is not very good, and a randomness is observed in the "best fit" parameters. In these cases the "y-x" method is supplemented by the Λ_J or Λ_K methods.⁸ These are methods that supplement the "y-x" method by assuming certain consistencies in the given electrolytes behavior over the solvent mixture

range. For example, if it appears that the $\log K_A$ vs. $1/D$ plot is linear from the low D data analysis, then we may extrapolate a K_A value in the high D range. Then define

$$\Lambda_K = \Lambda' + K_A(C\alpha)f_{\pm} \Lambda \quad (9)$$

$$= \Lambda^0 + J(\alpha C)$$

The Λ_K vs. $C\alpha$ plot gives us J (and a_J) and Λ^0 . On the other hand if a_J seems to be a constant then we may use and plot

$$\Lambda_J = \Lambda' - J(C\alpha) \quad (10)$$

$$= \Lambda^0 - K_A(C\alpha)f_{\pm}^2 \Lambda$$

$$= \Lambda^0 - K_A X$$

Λ_J vs. X to obtain Λ^0 and K_A . Both of these methods have utility but depend on additional assumptions (or extrapolations) that are not always desirable or correct.

In the data discussed here the "y-x" method was used exclusively. The data for the MnBDS in 5 and 10% dioxane then were refined using the Λ_K method.

The parameters found using these treatments as well as the recalculated values of the previous work in methanol-water systems⁴ are given in Table II.

Discussion of Results

The following consistencies should be pointed out immediately:

1. Over the D range covered a_J is a constant for a given salt in either solvent mixture (within experimental error).

2. Over the D range covered $\Lambda^0 \eta^0$, the Walden product, is a constant for a given salt regardless of solvent mixture.

At this point, however, consistencies become harder to find. Figure 1 shows $\log K_A$ vs. $1/D$ plots for both salts in both solvent mixtures.⁹ The plots are all straight lines but it is quite obvious that for a given salt K_A is not just a function of D . For both MnSO₄ and MnBDS the K_A in the methanol mixtures is greater than that in the dioxane mixtures at the same D . The simple equation proposed by Fuoss¹⁰ is obviously not able to explain this phenomenon. A more sophisticated approach

$$K_A = \left(\frac{4\pi N_A a^3}{3000} \right) \exp(e^2/aDkt) \quad (11)$$

has been suggested by Gilkerson¹¹ who proposed the equation:

$$K_A = \left(\frac{4\pi N_A a^3}{3000} \right) \exp[(e^2/aD - E_s)/kT] \quad (12)$$

where E_s is a term describing a specific ion-solvent interaction. However, in contrast to the cases described by Fuoss and Sadek,⁸ our E_s is a function of D (and, so, a function of the mole fraction organic component).

In the case of a_J for MnSO₄, the average value for the salt in the two solvent mixtures is 5.05 Å. If we calculate an a_K from the slope of the $\log K_A$ vs. $1/D$ plot in dioxane, we obtain $a_K = 4.98$ Å. This is good enough agreement so that we can say that the MnSO₄-dioxane system is described by the Fuoss-Bjerrum approach. Why, then does the MnSO₄-methanol system deviate from this description? Since a_J is essentially the same for the two systems, we feel that a simple viscosity effect is not a likely cause. The simplest tentative explanation must involve a difference in solvation

(9) The high methanol content points from ref. 4 have been omitted because of the drastic change of parameters noted in this previous article.

(10) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

(11) W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).

(8) H. Sadek and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 4507 (1959).

TABLE II
 SUMMARY OF CONDUCTANCE PARAMETERS

Organic, %	MnSO ₄		CH ₃ OH-H ₂ O ^a		Dioxane-H ₂ O		MnBDS		CH ₃ OH-H ₂ O ^a	
	Δ ⁰	K _A	Δ ⁰	K _A	Δ ⁰	K _A	Δ ⁰	K _A	Δ ⁰	K _A
0	133.22	133	133.22	133	113.35	(4.5)	113.35	(4.5)	113.35	(4.5)
5	122.2	201			100.4	6.6				
10	109.6	242	104.9	237	92.6	10	88.3	8.0		
15	99.5	409			80.0	16.0				
20	88.2	804	85.8	439	77.6	26.4	72.1	15.9		
25	81.0	1156								
30	74.7	881	67.8	96.2	63.9	33.3		
40	68.9	1710	55.0	588	60.8	56.0		
60					64.1	513		
a _j	4.98 ± 0.29 ^b		5.12 ± 0.22		6.16 ± 0.41		6.02 ± 0.35			
a _k	4.98		3.20		4.86		3.18			
Δ ⁰ η	1.17 ± 0.02		1.17 ± 0.04		0.989 ± 0.022		0.982 ± 0.016			

^a Recalculated from ref. 4 using new computer program.

^b All variations given are average deviations. There are no

apparent trends. of the salt in the two solvent systems. Why, then, is Δ⁰η the same for both systems? It seems that Δ⁰η and a_j describe the behavior of separated ions where the continuum model is tenable while K_A must depend on the short range interactions and a more specific effective solvation.

Support for this speculation can be derived from an examination of the electron spin resonance (e.s.r.) spectra of Mn(II) in these two systems. It is well established that the e.s.r. spectra of Mn(II) is extremely sensitive to the immediate surroundings of the ion.¹²⁻¹⁴ In some recent theoretical work Berry¹⁵ has investigated the dependence of the e.s.r. line width of Mn(II) on various solution parameters. We have applied this work to the determination of the K_A of MnSO₄ and MnBDS in these solvent mixtures¹⁶; and have demonstrated that we obtain the same K_A by conductance and e.s.r. for MnSO₄ and MnBDS in dioxane-water mixtures. It is also quite clear from the Mn(II) line width in these mixtures that the unassociated Mn(II) species over the whole solvent range investigated is the Mn(H₂O)₆²⁺ ion. In an attempt to apply the same technique to the methanol-water system an immediate problem was encountered. It became quite clear that a usable spectrum could only be obtained in the very low or very high methanol range. The spectra in the intermediate range was so broad as to be unusable. The simplest conclusion to be drawn is that there is definite replacement of water by methanol in the first coordination sphere of the Mn(II) ion. We are currently applying the technique to other similar systems and attempting a more quantitative approach to the solvation effect. It should be possible to study the ultraviolet-visible spectra of the solution and by the crystal field approach obtain corroborative evidence.¹⁷

When we examine the MnBDS results another problem intrudes. The Fuoss-Bjerrum line cal-

culated using the average a_j (6.08 Å.) falls below the experimental dioxane line. Therefore, we cannot say that the Fuoss-Bjerrum treatment accurately describes the system as in the MnSO₄ case. This presumably is due to the peculiar charge characteristics of the BDS anion. This is

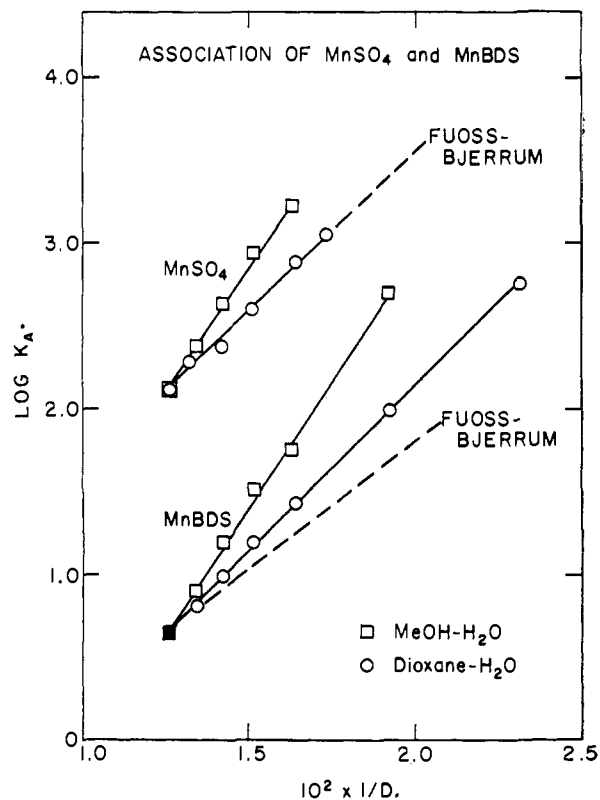


Fig. 1.

not a simple divalent ion but has a bolaform charge distribution. Its interaction with the solvent and cation then can be expected to be different, as witness the essentially unassociated character of MnBDS in water. If we express the log K_A plot by

$$\log K_A = \log K_A^0 + B/D \quad (13)$$

we can still see a great similarity between the behavior of the two salts

(12) M. Cohn and J. Townsend, *Nature*, **173**, 1090 (1954).

(13) B. R. McGarvey, *J. Phys. Chem.*, **61**, 1232 (1957).

(14) B. M. Kozyrev, *Discussions Faraday Soc.*, **19**, 135 (1955).

(15) R. S. Berry, Molecular Spectroscopy Meeting, Columbus, Ohio, May, 1960 (in preparation).

(16) G. Atkinson and J. E. Bauman, presented at 139th American Chemical Society meeting, St. Louis, April 1961 (in preparation).

(17) E.g., L. J. Heidt, G. F. Koster and A. M. Johnson, *J. Am. Chem. Soc.*, **80**, 6471 (1958).

$$\text{MnSO}_4[B_{(\text{MeOH})} - B_{(\text{diox})}] = 109.0$$

$$\text{MnBDS}[B_{(\text{MeOH})} - B_{(\text{diox})}] = 106.0$$

That is, even though the dioxane baseline does not seem as good for the MnBDS, yet the difference between the dioxane and methanol results is essentially the same for the two salts.

This is probably enough speculation for the amount of data at hand. Before invoking the fickle aid of specific solvation effects further, data in a greater variety of solvent mixtures must be obtained. The aid of e.s.r. and ultraviolet-visible spectroscopy must be further enlisted; and an experimental attack on the problem of the viscosity correction must be made.

The authors feel, however, that a good case for the important role of selective solvation has been

made. Moreover, the fact that a Mn(II) ion is very particular about its immediate surroundings should not be too amazing. The great recent success in the solution of the problems of transition metal chemistry by ligand field theory is based on this idea. In examining the solution chemistry of such ions, then, we can and should draw on the facts and techniques of the coordination chemists.

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Preparation and Infrared Studies of Metal Complexes Containing the Zwitterion Ligand Betaine, $(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{COO}^-$

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The reactions of the metal ions Co(II), Co(III), Ni(II), Cu(II) and Zn(II) with the zwitterion, betaine, $(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{COO}^-$, have been studied. Coordination compounds of these metal ions have been prepared and their infrared spectra in the 2–15 μ region have been assigned. Comparison of the infrared spectra of these metal complexes with those of betaine and betaine hydrochloride reveals that the carboxylate ion antisymmetric stretching vibration at about 1630 cm^{-1} is retained, which in turn indicates that the resonance of the carboxylate group is maintained. The infrared spectra of metal complexes containing the monodentate betaine zwitterion are compared with those of the complexes of other amino acids such as glycine and alanine, previously reported, in which the amino acid ligands act as bidentate mononegative ions. The complexes, $[\text{Co}(\text{NH}_3)_5\{(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{COO}^-\}](\text{ClO}_4)_3$ and $[\text{Co}(\text{NH}_3)_4\{(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{COO}^-\}_2](\text{ClO}_4)_3$, also have been prepared and the observed absorption bands of their infrared spectra have been assigned.

Introduction

In marked contrast to the extensive work that has been carried out on the preparation and studies of metal complexes in which the coordinating groups are neutral molecules (*e.g.*, H_2O , NH_3) or negative ions (*e.g.*, Cl^- , CN^-), relatively few investigations have been reported on metal complexes containing zwitterion ligands¹ and positive ion ligands.² The preparation and study of these latter two types of coordination compounds are being investigated in this Laboratory, and in this paper we report the preparation and infrared studies of some transition metal complexes with the simplest of the betaine zwitterion ligands namely $(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{COO}^-$, which is in fact the betaine of glycine. The betaines are capable of donating methyl groups to other amino acids (transmethylation) and are also of considerable biological interest.

Coordination compounds of metal ions with the betaines should consist of the negative part of the zwitterion ligand orientated towards the central positive metal ion and the positive part orientated away from the metal ion. The resulting complex

ion, which would have the net charge of the metal ion, then should be comprised of this ion surrounded by a sphere of negative charge and this in turn surrounded by a sphere of positive charge. Hence compounds containing zwitterion ligands coordinated with metal ions would be expected to show the general well-known properties associated with the more common type of coordination compound.

Experimental

Preparation of Compounds.—Betaine monohydrate, $(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{COO}^- \cdot \text{H}_2\text{O}$ was supplied by K. and K. Laboratories, Inc., and was used without further purification.

Betaine (anhydrous) $(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{COO}^-$ was prepared by heating the monohydrate to 110° in an oven. Its infrared spectrum showed the complete absence of water.

Tetrakis-(betaine)-Cu(II)-Perchlorate, $[\text{Cu}\{(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{COO}^-\}_4](\text{ClO}_4)_2$.—To a solution of 2 g. (0.0171 mole) of betaine monohydrate, $(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{COO}^- \cdot \text{H}_2\text{O}$, in 30 ml. of absolute ethanol was added dropwise with stirring 1.6 g. (0.0043 mole) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 30 ml. of absolute ethanol. After standing, the deep blue crystals which formed were filtered, washed with absolute ethanol and dried in air. Recrystallization was effected by dissolving in the minimum amount of water followed by the addition of absolute ethanol. After about 5 hr. the crystals which formed were collected on a glass filter, washed with absolute ethanol and dried *in vacuo* over phosphoric anhydride. The crystals dissolve in water, but the original deep blue color immediately changes to the light blue color characteristic of aqueous solutions of the Cu(II) ion.

(1) F. Lions, B. S. Morris and E. Ritchie, *J. Proc. Roy. Soc. N. S. Wales*, **76**, 294 (1942).

(2) See for example, J. C. Bailar, Jr., Ed., "Chemistry of the Coordination Compounds," Reinhold Publishing Corporation, New York, N. Y., 1956, p. 533.