

Ion Association in Polyvalent Symmetrical Electrolytes.

VIII. The Conductance of Calcium and Strontium *m*-Benzenedisulfonates in Methanol–Water and Acetone–Water Mixtures at 25°

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*The conductances of calcium and strontium m-benzenedisulfonates have been measured in methanol–water and acetone–water mixtures to 80% organic content. The data have been analyzed by use of the linearized Fuoss–Onsager theory to give Λ^0 , a_j , and K_A parameters. For both salts the $\log K_A$ vs. $[1/D]$ plots are linear and independent of the specific organic solvent. Although the a_j values for a given salt are essentially constant, the Walden product, $\Lambda^0\eta$, decreases drastically in the high organic content solvent mixtures. The marked contrast between these systems and the previously measured manganese *m*-benzenedisulfonate and $MnSO_4$ is discussed.*

The primary purpose of this series of papers has been to examine experimentally the relationship between ion–ion interactions and ion–solvent interactions in certain electrolyte solutions. Rather than concentrating our efforts on 1–1 electrolytes which have so dominated electrolyte solution research, we have concentrated on 2–2 electrolytes. This was done to increase the strength and specificity of ion–solvent interactions, and so, hopefully make them more tractable towards analysis. Much of the effort has been spent contrasting the behavior of $MnSO_4$, a rather typical 2–2 salt with an association constant of 133 in water with manganese *m*-benzenedisulfonate ($MnBDS$) which is essentially unassociated in water [$K_A \approx 4$].^{1–4} It was demonstrated that the conductance of the $MnBDS$ in water was described very well by the Fuoss–Onsager equation in the linearized form.⁵

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

This demonstrated the essential correctness of the Fuoss–Onsager approach, even when applied to high-charge electrolytes, in the concentration range where the theory can be assumed valid. The behavior of $MnSO_4$ and $MnBDS$ in the four solvent systems examined (dioxane–water, methanol–water, acetone–water, and Methyl Cellosolve–water) was quite specific for each solvent system. Both salts behaved very similarly in a given solvent system but each salt exhibited individual dependence on solvent composition in each of the four solvent systems. The solvent dependence could not be explicated on the basis of the continuum solvent model on which the Fuoss–Onsager

theory is based. Solvent specificity was normally exhibited both in the hydrodynamic parameter Λ^0 and in the thermodynamic parameter K_A .

In an attempt to examine the dependence of solution behavior on cation character magnesium, calcium, strontium, and barium *m*-benzenedisulfonates were examined in water.⁶ All four salts seemed essentially unassociated. However, an interesting peculiarity⁷ was re-emphasized in the analysis. The λ^0_+ values do not change monotonically with cation size but exhibit an inflection ($\lambda^0_{Mg} = 53.06$, $\lambda^0_{Ca} = 59.50$, $\lambda^0_{Sr} = 59.46$, and $\lambda^0_{Ba} = 63.64$). This seemed reasonable only if one assumed strong and specific prejudices about solvent coordination on the part of the alkaline earth cations. Analogous effects had been noted in the field of ion exchange where Ca–Sr separation factors were found to be drastically affected by solvent composition.⁸

Therefore, it seemed valuable to explore the behavior of Ca^{+2} and Sr^{+2} in mixed solvent systems. The BDS^{-2} salts were chosen because of their high solubility in mixed solvents. It was also hoped to examine the similarities and differences in specific solvent requirements of these nontransition element ions as contrasted to the Mn^{+2} and Cu^{+2} previously examined.

Experimental

The apparatus and the details of the experimental technique are given in ref. 6.

The $CaBDS$ and $SrBDS$ were prepared from purified $BaBDS$ by conventional cation-exchange techniques. The salts were purified by double recrystallization from conductivity water and dried to their anhydrous form at 110° under vacuum.

Analysis of Ca^{+2} or Sr^{+2} was performed by EDTA titration using eriochrome black T as an indicator.⁹ Total cation analyses were performed by conversion of the salt to H_2BDS by cation exchange followed by a differential titration of the acid solution on an automatic titrator.¹⁰

The water used for conductance was double distilled, the first distillation being from an alkaline $KMnO_4$ solution. Its conductance was always below 4×10^{-7} mho cm^{-1} .

The acetone¹¹ and methanol¹² were purified as pre-

(1) C. J. Hallada and G. Atkinson, *J. Am. Chem. Soc.*, **83**, 3759 (1961).

(2) G. Atkinson and C. J. Hallada, *ibid.*, **84**, 721 (1962).

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

(4) G. Atkinson and H. Tsubota, *ibid.*, in press.

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

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

(7) T. Shedlovsky and A. S. Brown, *J. Am. Chem. Soc.*, **56**, 1066 (1934).

(8) H. Tsubota and H. Kakihana, private communication.

(9) G. Schwarzenbach, "Complexometric Titrations," Methuen and Co., Ltd., London, 1957.

(10) Potentiograph E 336, Metrohm, Ltd., Herisau, Switzerland.

(11) References for acetone–water (see ref. 3 for purification) are: (a) densities ("International Critical Tables," Vol. 3, p. 112); (b)

Table I^a

$C \times 10^4$	Λ	$C \times 10^4$	Λ	$C \times 10^4$	Λ	$C \times 10^4$	Λ
A. Methanol-Water Data				40.04% methanol		50.05% methanol	
CaBDS				1.0127	59.850	0.9482 ₀	59.554
10.09% methanol		20.08% methanol		2.3002	57.293	1.9130	56.985
1.2334	88.697	0.8660 ₀	74.283	3.9160	55.109	3.4132	54.249
2.3629	86.550	1.9317	72.317	5.5774	53.429	5.4466	51.643
3.6025	84.750	3.2880	70.543	7.3654	51.985	8.1416	49.161
4.9234	83.544	4.6517	69.160	9.2078	50.660	11.338	46.996
7.2747	81.218	6.4174	67.713	11.532	49.368	14.080	45.535
9.3321	79.616	8.4962	66.341	13.835	48.291	18.061	43.839
11.758	78.054	10.270	65.351	60.02% methanol		80.03% methanol	
29.96% methanol		40.04% methanol		0.8912 ₅	59.521	0.6662 ₅	65.100
3.5892	61.218	0.5822 ₀	61.649	1.8475	56.121	1.8691	55.093
7.4699	57.990	1.5443	59.308	3.1938	52.863	2.7052	51.072
13.268	54.968	2.6753	57.402	4.1780	50.227	3.5612	48.035
18.939	52.945	4.0236	55.682	6.5567	47.858	4.4508	45.579
26.487	50.955	5.6299	54.138	8.3440	46.056	6.0684	42.221
34.153	49.417			10.297	44.455	8.4010	38.828
41.622	48.218			12.928	42.716	10.401	36.689
49.903	47.125			B. Acetone-Water Data			
56.874	46.312			CaBDS			
50.05% methanol		60.02% methanol		29.97% acetone		59.91% acetone	
1.0247	58.916	0.8639 ₀	60.364	1.1762	70.160	0.9868 ₅	60.550
2.2801	56.030	1.7715	57.220	2.0276	68.367	2.0799	53.750
3.4852	54.081	2.9541	54.321	2.9171	66.896	3.5290	48.394
4.9820	52.224	4.0428	52.321	4.3132	65.084	5.7464	43.398
7.1840	50.106	5.8058	49.834	6.1415	63.181	7.6528	40.483
10.074	48.019	8.7763	46.825	7.7083	61.877	9.6767	38.195
13.210	46.278	10.930	45.186	9.6686	60.507	12.095	36.094
17.399	44.470	13.905	43.375	12.344	58.977	15.114	34.082
80.03% methanol		40.06% methanol		79.45% acetone			
1.5834	57.896	1.2881	58.238	0.9585 ₀	28.261		
3.1773	50.577	2.8283	55.692	2.1945	20.460		
4.4436	46.960	4.5436	53.732	3.7344	16.554		
6.0623	43.665	6.9853	51.674	5.7911	13.899		
7.6037	41.304	10.113	49.735	8.0395	12.211		
9.5481	39.000	13.881	47.949	10.705	10.927		
12.288	36.550	18.640	46.249	13.929	9.8860		
15.317	34.508	23.436	44.922	16.837	9.2185		
SrBDS				SrBDS			
5.12% methanol		10.09% methanol		29.97% acetone		59.91% acetone	
1.1592	97.974	0.7206 ₅	89.207	0.8313 ₅	69.186	0.8996 ₀	59.718
2.2854	95.734	2.0964	86.390	1.8739	66.747	2.4711	50.439
3.6567	93.783	3.4311	84.558	3.1810	64.626	4.3921	44.641
5.5702	91.721	5.2486	82.681	4.8671	62.594	6.3876	40.875
7.6125	89.991	7.4809	80.862	6.8531	60.703	8.6450	37.919
10.059	88.326	10.422	79.001	8.8993	59.184	10.981	35.676
12.725	86.817	13.799	77.263	11.269	57.727	13.384	33.890
15.742	85.368	17.050	75.884	13.902	56.393	16.989	31.830
18.928	84.069			79.45% acetone			
20.08% methanol		29.96% methanol		0.4639 ₂	36.131		
1.0160	73.162	0.8752 ₀	65.573	1.4231	23.829		
2.7827	70.288	1.7311	63.976	3.2957	17.085		
4.7450	68.206	3.3670	61.721	5.6068	13.815		
7.3601	66.170	4.9499	60.131	8.2177	11.874		
10.057	64.549	6.9938	58.513	10.472	10.802		
12.827	63.199	11.072	56.107	12.560	10.072		
16.767	61.624	15.155	54.319				
20.296	60.458	20.065	52.652				
		23.291	51.758				
		25.965	51.100				

^a Concentrations are in moles/l. and conductances in (ohm cm.⁻² equiv.)⁻¹; organic solvent composition is in wt. %.

viously described. The solvent mixture parameters were taken from the literature.

viscosities (*ibid.*, Vol. 5, p. 22); (c) dielectric constants (P. S. Albright, *J. Am. Chem. Soc.*, **59**, 2098 (1937)).

(12) For methanol-water (see ref. 1 for purification) see H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolyte Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958.

Results and Calculations

Table I gives the experimental results. All data are reported to one more place than their probable error justifies so that recalculation will not be plagued by "rounding-off" errors.

The data were analyzed by the linearized Fuoss-

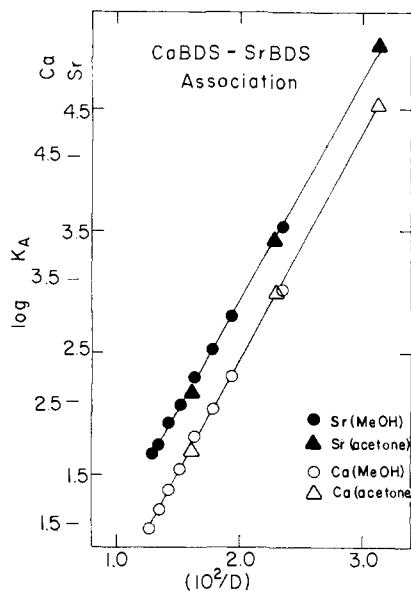


Figure 1.

Onsager equation in the form for associated electrolytes¹³

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

where Λ^0 is the equivalent conductance at infinite dilution, C is the molar concentration, γ is the degree of dissociation, K_A is the association constant, S , E , and J are Fuoss-Onsager parameters, and f_{\pm} is the mean ionic activity coefficient. No viscosity correction was made because of the lack of actual viscosity data. The concentration range was kept low enough so that terms of order higher than C would not interfere with the analysis.

The actual data treatment was done by hand using the "Y-X" method¹⁴ with occasional refinement by the Δ_K or Δ_J methods¹⁵ when these seemed justified. The data were also processed using an IBM 7090 computer with a program involving a "brute force" three-dimensional, three-parameter [Λ^0 , A_J , K_A] fit. Both techniques gave identical results for the more associated salt-solvent systems. The computer technique, however, was much more sensitive to small experimental errors in the systems where K_A was small.

Table II summarizes the derived parameters.

Discussion of Results

Table II shows that, except for the highest acetone content system, a_J is constant for a given salt regardless of solvent composition. The scatter of a_J values around their average seems a consequence of the extreme sensitivity of the data treatment to the value of J for high charge type electrolytes.

Figure 1 gives the conventional Fuoss plot of $\log K_A$ vs. $(1/D)$ for the systems examined. What is surprising here is the placidity with which these systems follow the predicted straight-line behavior for a given solvent system. It is also quite apparent that the two solvent systems give identical $\log K_A$ dependence on $(1/D)$ for a given salt. These features are in very

(13) See ref. 5, Chapter XVII; and G. Atkinson, *et al.*, *J. Am. Chem. Soc.*, **83**, 1570 (1961).

(14) R. M. Fuoss, *ibid.*, **80**, 3163 (1958).

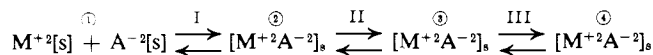
(15) R. M. Fuoss, *ibid.*, **81**, 2659 (1959).

Table II. Calculated Parameters

% organic material (w./w.)	D	Λ^0	$\Lambda^0\eta$	K_A	a_J , Å.
CaBDS. Methanol-Water					
0	78.48	119.4	1.07	[28.8]	6.3
10.09	74.17	93.7	1.09	40.7	6.2
20.08	69.97	78.0	1.09	59.1	6.6
29.96	65.57	71.0	1.09	87.1	6.1
40.04	60.90	63.1	1.02	131	5.5
50.05	56.34	64.2	1.01	267	6.0
60.02	51.69	66.7	0.935	497	6.8
80.03	42.59	78.0	0.784	2540	7.3
CaBDS. Acetone-Water					
29.97	61.91	75.5	1.03	122	6.3
59.91	43.48	76.0	0.798	2,510	7.4
79.45	31.84	97.0	0.608	105,000	15.1
SrBDS. Methanol-Water					
0	78.48	119.0	1.06	[5.1]	6.2
5.12	76.29	103.2	1.06	46.8	6.1
10.09	74.17	93.0	1.08	56.7	5.9
20.08	69.97	77.3	1.08	84.1	5.6
29.96	65.57	71.0	1.09	119	6.2
40.04	60.90	64.4	1.04	194	6.2
50.05	56.34	64.7	1.04	341	5.9
60.02	51.69	66.3	0.930	625	7.0
80.03	42.59	80.0	0.804	3420	8.8
SrBDS. Acetone-Water					
29.97	61.91	73.6	0.999	151	6.3
59.91	43.48	74.5	0.782	2,560	7.5
79.45	31.84	95.0	0.596	107,000	18.0

marked contrast with the highly individual behavior noted for $MnSO_4$ and $MnBDS$.¹⁻⁴ They also contrast strongly with the behavior of $CuBDS$ in methanol-water mixtures.¹⁶ We believe that this marked difference between the Cu^{+2} and Mn^{+2} salts on one hand and the Ca^{+2} and Sr^{+2} salts on the other must be sought in a more intimate picture of the ion association process.

It has been conclusively shown^{17,18} that the ion association process in 2-2 salts such as $MnSO_4$ is a three-step process describable by the diagram



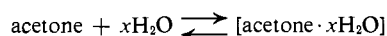
In this process only step I can be readily described by a classical continuum theory. It is the diffusion-controlled approach of ions with complete first solvation spheres. Steps II and III exhibit marked specific solvent effects not describable in terms of macroscopic solvent parameters such as dielectric constant.¹⁸ States two, three, four are ion-pair states differing only in the number and arrangement of solvent molecules between the ions with state four being, most probably, a contact ion pair. We showed¹⁸ that, in the case of $MnSO_4$ both in dioxane-water and methanol-water mixtures, the K_A measured by conductance counted all three ion-pair states as nonconducting species. The interaction of the three ion-pair states and their different solvent dependences make a complete analysis of the problem impossible at this time. This is particularly true because of the need to consider the coupling

(16) M. Yokoi, *et al.*, *Nippon Kagaku Zasshi*, **85**, 89 (1964).

(17) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 93, 107 (1962).

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

of the ion-pair formation process with H-bonding processes in the mixed solvent. Andreae and co-workers¹⁹ have shown the necessity of considering the process



and have been able to deduce tentative values of x and K_{eq} for such processes. This chemical formulation of solvent mixture nonideality lacks the formal elegance of the more physical approaches yet promises to add greatly to our chances of solving the solvent-dependence problem.

Figure 2 shows the Walden product for the systems examined. The Walden product behaves in an ideal fashion for both salts in the low organic range, then starts decreasing drastically. Thus even a system that exhibits apparent ideal behavior for K_A need not exhibit ideality in its hydrodynamic parameters.

Acknowledgments. The authors acknowledge the support of the United States Atomic Energy Com-

(19) See J. Lamb, "Dispersione ed Assorbimento del Suono nei Processi Molecolari," Academic Press, Inc., New York, N. Y., 1963, p. 101.

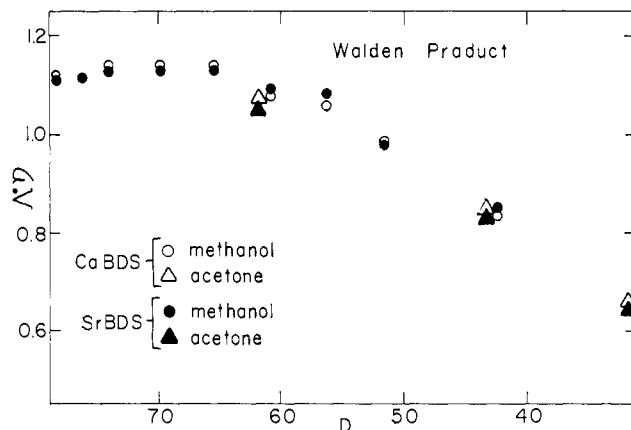


Figure 2.

mission under Contract AT-[40-I]-2983 during the course of this research. They would also like to express their appreciation to Mr. Bert R. Staples and Mr. David W. Ebdon for their aid in the computer calculations.

A Criterion for Reliability of Formation Constants of Weak Complexes

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Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa. Received September 14, 1964

A critical examination of the use of the Benesi-Hildebrand or Scott equations to obtain K and ϵ for weak complexes emphasizes the obvious: namely, the most accurate values for formation constants of a complex are obtained when the equilibrium concentration of the complex is of the same order of magnitude as the equilibrium concentration of the more dilute component. For complexes measured by the Benesi-Hildebrand method or one of its many variations, this condition requires that the donor concentration in the most concentrated solution must be greater than about $0.1(1/K)$. If it is less than this value, then the Benesi-Hildebrand plot will give zero intercept, and the Scott plot will give zero slope, within the experimental error, even though K may be moderately large and ϵ is finite. An examination of a few examples, selected at random from the literature, illustrates the application of this criterion to weak complexes for which experimental conditions are such that they either fail or just barely satisfy the criterion, suggesting strongly that the reported values of K are not significant.

Introduction

Although a healthy skepticism regarding the existence of weak complexes existed in the early years of the history of electron donor-acceptor complexes, the tendency in recent years has been to accept their existence

much more readily. In fact there are now several examples in the literature of complexes for which the experimental evidence for their existence leaves much to be desired. Certainly, if there were not a good reason from theory to expect a complex between anthracene and iodine, we should hate to accept evidence such as that presented recently¹ as proof that the complex really exists.

This remark applies with equal force to a number of other recent reports of "complex formation." To single out just one other paper, we may consider the report of complex formation between CCl_4 and aromatic donors.² In view of the importance of the question of existence of some of these interesting complexes, and in view of the number of studies of these difficult borderline cases, it would seem desirable to analyze critically the method of study, in order to determine its reliability.

The existence of the complex is deduced from the analysis of some change in the absorption spectrum of the mixture when compared to the spectrum of the individual components. From a study of these changes as a function of the concentration of the components, the values of the equilibrium constant K and molar absorptivity ϵ can be determined separately. Some

(1) J. Peters and W. B. Person, *J. Am. Chem. Soc.*, **86**, 10 (1964).

(2) R. Anderson and J. M. Prausnitz, *J. Chem. Phys.*, **39**, 1225 (1963).