Journal of Solution Chemistry, Vol. 3, No. 10, 1974

The Conductance of Divalent Ions in H_2O at 10 and 25°C and in D_2O

T. L. Broadwater[1,3] and D. F. Evans[2]

Received November 15, 1973; revised January 14, 1974

Precise conductance measurements are reported for potassium m-*benzenedisulfonate and ferricyanide, for calcium, strontium, barium, and manganese chloride, and for manganese and potassium sulfate in D_2O at 25°C. Measurements were also carried out in water at 10 and 25°C for all the salts with the exception of $K_3Fe(CN)_6$ at 10°C. Two runs are reported for sodium sulfate in water at 25°C. Limiting conductances of these ions are discussed in terms of solvent structural effects. The association constant for $MnSO_4$ is found to be the same in H_2O and D_2O.*

KEY WORDS: Conductance ; divalent salts ; H_2O ; D_2O ; ionic association.

1. INTRODUCTION

The conductance of monovalent ions has been extensively studied in water as a function of temperature and in heavy water.(1) This information has proved valuable in elucidating the effect of ions on water structure since the conductance can be unambiguously split into single-ion values at each temperature. In addition, the results can be extrapolated to infinite dilution where solvent structural effects are at a maximum per ion. At present there is a paucity of precise data on the temperature coefficient of conductance for divalent ions in aqueous solution. There is no information on the conductance of divalent ions in heavy water. We have determined the conductance of a number of divalent ions in light and heavy water in order to investigate the effect of these ions on water structure and have also determined the association constants for $MnSO_4$ in water at 25 and 10°C and in D_2O at 25°C.

---

[1] Department of Chemistry, Howard University, Washington, D.C. 20001.

[2] Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

[3] To whom correspondence should be addressed.

2. EXPERIMENTAL

The electrical components, conductance equipment, and procedures for carrying out a conductance run have been previously described.(2)

$MgCl_2$ was dried for two days in a vacuum oven at 90°C and stored in a desiccator over $CaCl_2$. Prior to a conductance run, the halide content of the salt was determined potentiometrically,(3) and the water content was determined by the Karl Fischer method.(4) Two different $CaCl_2$ salt samples were used for the conductance runs. One was recrystallized reagent grade salt and the other was made from the neutralization of $CaCO_3$ by hydrochloric acid. Both samples were dried at 300°C in a stream of nitrogen containing dry HCl. Reagent grade $BaCl_2$ and $SrCl_2$ were twice recrystallized from conductivity water and dried in a vacuum oven at 125°C.

After recrystallization, K_2SO_4 and Na_2SO_4 were partially dried in a vacuum oven at 110°C. The remaining water was removed by heating the salts in platinum crucibles: K_2SO_4 until the crystals sintered, and Na_2SO_4 to its fusion point. Neither salt was hygroscopic.

$MnSO_4$ and $MnCl_2$ were made by neutralizing $MnCO_3$ with the corresponding reagent grade acid. The resulting solutions were filtered through medium (porosity) glass filters, and crystals were formed by reducing the volume of water with a rotary evaporator. After two recrystallizations from conductivity water, the $MnSO_4$ was dried to the monohydrate in a vacuum oven at 110°C. $MnCl_2$ was partially dried in a vacuum oven at 110°C, and finally in a stream of nitrogen containing dry HCl at 250°C. The latter salt was hygroscopic.

Potassium ferricyanide was twice recrystallized and allowed to dry in the air. Potassium *m*-benzenedisulfonate (K_2BDS) was made by the method described by Atkinson.(5)

All of the salts were ground to a fine powder in an agate mortar, and the pH of a solution of each salt was checked with an expanded-scale pH meter (2 pH units full scale) to ensure that there were no acidic impurities, or that no hydrolysis correction was required.

D_2O (Atomic Energy Commission normal O^{18} content) was distilled using a vigreux column and stored in glass containers under nitrogen. The specific conductance of the solvent was considerably improved by passing it through a resin column just before it flowed into the cell during the filling process. The resin had previously been equilibrated with several batches of D_2O over a six-month period.(6) The D_2O was reclaimed following the conductance runs by distillation under nitrogen. The preparation of conductance grade H_2O has been described previously.(6)

3. RESULTS AND DISCUSSION

Higher-valent symmetrical electrolytes can be analyzed in terms of the Fuoss–Onsager conductance theory(7,8) [Eq. (1)] by simply dividing the dielectric constant by $[Z_A \cdot Z_B]$ and the viscosity by $[Z_A \cdot Z_B]^{1/2}$.(9)

$$\Lambda = \Lambda_0 - S(C\gamma)^{1/2} + E(C\gamma)\log(C\gamma) + J(C\gamma) - K_A C\gamma f^2 \Lambda \qquad (1)$$

Unsymmetrical electrolytes can be analyzed by setting $\gamma = 1$, $K_A = 0$, and making suitable changes in the functions α, β, κ, and b which are contained in the S, E, and J terms of Eq. (1). These functions are given for a 1:1, 2:1, and 3:1 electrolyte in Table I, and the values of C (mole-liter^{-1}) and Λ (cm^2-equiv^{-1}-ohm^{-1}) are recorded in Table II.

The density at each concentration, needed to convert to a molar basis, was calculated from the relationship $d = d_0 + A\bar{m}$, where d and d_0 are the density of solution and solvent, respectively, and $\bar{m}$ is the concentration of salt in moles per kilogram of solution. The density increment constant A (given in Table II) was determined for each electrolyte from a measurement carried out on the solution following a conductance run in water at 25°C, and the same value was also used at 10°C in water and in D_2O.

Values of the dielectric constant, viscosity (poise), and density, respectively, of the solvents used were: H_2O (10°C), 83.96, 0.01306, 0.99973; H_2O (25°C), 78.37, 0.008903, 0.99707; D_2O (25°C), 78.06, 0.01096, 1.10449.(1) The

Table I. Values of α, β, κ, and b Needed in the Analysis of Unsymmetrical Electrolytes

	1:1	2:1[a]	3:1[a]
α	$\frac{820{,}400}{(\varepsilon T)^{3/2}}$	$\frac{Q(11.8271)}{1 + (Q)^{1/2}} \cdot \alpha_{11}$	$\frac{P(25.0941)}{1 + (P)^{1/2}} \cdot \alpha_{11}$
β	$\frac{82.501}{\eta(\varepsilon T)^{1/2}}$	$2.5981 \cdot \beta_{11}$	$4.9024 \cdot \beta_{11}$
κ	$\frac{(50.29 \times 10^8)}{(\varepsilon T)^{1/2}}$	$\sqrt{3} \cdot \kappa_{11}$	$\sqrt{6} \cdot \kappa_{11}$
b	$\frac{0.0016708}{(\varepsilon T)}$	$2 \cdot b_{11}$	$3 \cdot b_{11}$

[a] The following equations were used to calculate Q and P:

$$Q = \frac{2}{3(1 + \lambda_0/\Lambda_0)} \qquad P = \frac{3}{4(1 + 2\lambda_0/\Lambda_0)}$$

where Λ_0 is the limiting equivalent conductance of the salt and λ_0 is the limiting equivalent conductance of the univalent ion.

Table II. Equivalent Conductances of Inorganic Salts

10^4C	Λ	10^4C	Λ
H_2O, 25°C			
$MnSO_4 \cdot H_2O$		$K_2BDS \cdot H_2O$	
$10^7\kappa^\circ = 1.01$	$A = 0.159$	$10^7\kappa^\circ = 1.53$	$A = 0.193$
(Run 1, Sample 1)		1.211	130.45
1.252	124.27	2.072	129.50
2.906	119.13	2.930	128.73
4.254	115.99	4.063	127.96
6.141	112.44	5.323	127.22
8.254	109.21	7.292	126.25
11.597	105.11	9.279	125.44
15.492	101.32	11.668	124.58
		14.821	123.62
		18.866	122.57
		25.308	121.17
$MnSO_4 \cdot H_2O$		$MgCl_2$	
$10^7\kappa^\circ = 1.21$	$A = 0.159$	$10^7\kappa^\circ = 1.46$	$A = 0.078$
(Sample 2)		0.449	128.52
1.090	125.60	0.663	128.05
2.321	121.23	0.944	127.55
4.011	116.91	1.239	127.13
6.297	112.57	1.442	126.90
8.553	109.19	1.812	126.50
12.737	104.27	2.408	125.99
17.600	99.89	3.176	125.40
24.261	95.29	3.800	125.00
33.788	90.33	4.406	124.65
47.986	84.96	5.372	124.11
		6.259	123.65
		7.116	123.28
		7.939	122.93
		9.273	122.45
		10.553	122.02
$K_3Fe(CN)_6$		Na_2SO_4	
$10^7\kappa^\circ = 0.75$	$A = 0.209$	$10^7\kappa^\circ = 1.84$	$A = 0.130$
2.063	164.94	(Run 1)	
3.583	162.21	3.405	125.24
5.412	159.64	4.131	124.77
8.080	156.74	6.280	123.44
11.483	153.93	7.888	122.66
16.609	150.42	10.918	121.31
21.997	147.58	14.050	120.16
		16.750	119.28

Table II. Continued

10^4C	Λ	10^4C	Λ
	H_2O, 25°C		
$MnCl_2$		$CaCl_2$	
$10^7\kappa^\circ = 1.93$	$A = 0.112$	$10^7\kappa^\circ = 1.18$	$A = 0.104$
1.238	125.92	(Sample 2)	
2.705	124.58	1.255	132.28
5.062	123.13	2.693	130.98
7.415	122.00	4.642	129.81
11.073	120.71	6.959	128.72
15.005	119.61	9.753	127.66
19.021	118.60	13.609	126.43
23.953	117.54	18.244	125.19
30.900	116.27	25.496	123.64
		33.155	122.29
		38.746	121.42
$CaCl_2$		K_2SO_4	
$10^7\kappa^\circ = 1.93$	$A = 0.104$	$10^7\kappa^\circ = 2.64$	$A = 0.153$
(Run 2, Sample 1)		3.102	148.57
1.509	131.90	4.843	147.21
6.044	128.84	6.170	146.29
9.502	127.47	8.223	145.17
14.031	126.13	10.671	144.01
19.499	124.78	13.519	142.84
26.469	123.36	16.370	141.81
33.760	122.10	18.859	140.99
47.324	120.19	21.513	140.19
		26.542	138.83
		34.128	137.07
Na_2SO_4		$SrCl_2$	
$10^7\kappa^\circ = 5.71$	$A = 0.130$	$10^7\kappa^\circ = 1.82$	$A = 0.144$
(Run 2)		1.214	132.63
3.005	125.43	3.222	130.88
4.573	124.34	7.564	128.68
5.986	123.52	13.357	126.64
8.622	122.21	20.007	124.89
10.726	121.28	29.215	123.00
13.754	120.17	39.612	121.31
16.718	119.22	48.878	120.06
19.204	118.50		
20.678	118.11		
22.344	117.68		

Table II. Continued

10^4C	Λ	10^4C	Λ
H_2O, 25°C			
$CaCl_2$		$BaCl_2$	
$10^7\kappa^\circ = 1.00$	$A = 0.104$	$10^7\kappa^\circ = 2.38$	$A = 0.190$
(Run 1, Sample 1)		1.209	136.96
1.233	132.28	3.284	135.02
2.814	130.81	6.661	133.15
4.638	129.87	10.587	131.53
6.994	128.66	15.824	129.88
9.659	127.65	21.672	128.38
13.985	126.28	27.517	127.15
19.398	124.92	34.215	125.93
26.792	123.40	44.270	124.38
37.040	121.65		
H_2O, 10°C			
$CaCl_2$		$MnSO_4 \cdot H_2O$	
$10^7\kappa^\circ = 0.52$	$A = 0.104$	$10^7\kappa^\circ = 0.75$	$A = 0.159$
2.268	92.11	2.755	83.42
5.305	90.69	4.704	80.52
9.439	89.46	7.899	76.99
14.279	88.48	11.743	73.86
23.839	86.93	16.847	70.66
39.955	85.14	21.903	68.18
44.051	84.72	27.428	65.97
53.952	83.92	35.360	63.39
		43.589	61.23
$BaCl_2$		K_2SO_4	
$10^7 = 0.39$	$A = 0.190$	$10^7\kappa^\circ = 0.72$	$A = 0.153$
1.302	96.48	0.866	107.74
4.185	94.85	2.398	106.12
7.611	93.66	4.067	105.03
12.771	92.37	6.227	104.04
19.492	91.13	9.124	102.95
26.716	90.04	13.310	101.71
63.182	88.89	18.026	100.56
49.113	87.62	23.120	99.50
		30.269	98.23
		38.692	96.99

Table II. Continued

10^4C	Λ	10^4C	Λ
H_2O, 10°C			
$MnCl_2$		$SrCl_2$	
$10^7\kappa^\circ = 0.63$	$A = 0.117$	$10^7\kappa^\circ = 0.61$	$A = 0.144$
1.315	87.61	2.949	91.73
3.373	86.40	5.123	90.93
6.113	85.43	8.773	89.90
9.447	84.54	12.679	89.05
13.788	83.63	17.662	88.14
18.140	82.87	23.390	87.29
25.598	81.81	31.368	86.30
34.086	80.81	45.081	84.95
42.526	79.98		
55.528	78.89		
$K_2BDS \cdot H_2O$		$MgCl_2$	
$10^7\kappa^\circ = 2.71$	$A = 0.193$	$10^7\kappa^\circ = 0.81$	$A = 0.078$
0.820	92.54	0.411	89.75
2.165	91.42	0.792	89.55
3.932	90.49	1.495	98.82
6.153	89.64	2.176	88.33
9.660	88.66	2.984	87.92
15.002	87.50	3.686	87.58
22.886	86.20	4.263	87.25
32.078	85.03	5.938	86.73
33.041	84.92	7.468	86.27
		9.191	85.83
		10.729	85.38
		12.193	85.02
D_2O, 25°C			
K_2SO_4		$MnSO_4 \cdot H_2O$	
$10^7\kappa^\circ = 0.67$	$A = 0.153$	$10^7\kappa^\circ = 2.33$	$A = 0.179$
1.065	124.63	1.884	98.98
2.266	123.36	3.806	94.72
4.090	122.04	6.574	90.38
6.443	120.73	10.944	85.49
9.762	119.30	15.569	81.66
14.412	117.70	21.875	77.71
19.582	116.27	28.311	74.57
27.613	114.24	36.559	71.38
36.547	112.76	45.567	68.59
37.851	112.54		

Table II. Continued

10^4C	Λ	10^4C	Λ
D_2O, 25°C			
$MnCl_2$		$SrCl_2$	
$10^7\kappa^\circ = 1.75$	$A = 0.117$	$10^7\kappa^\circ = 1.34$	$A = 0.144$
2.984	100.44	1.901	108.10
6.890	99.27	4.292	106.61
12.427	97.83	7.043	105.44
18.384	96.69	11.477	104.11
26.410	95.34	17.138	102.79
34.746	94.18	25.888	101.18
43.947	93.11	34.837	99.93
		46.982	98.50
$K_2BDS \cdot H_2O$		$BaCl_2$	
$10^7\kappa^\circ = 0.78$	$A = 0.193$	$10^7\kappa^\circ = 0.97$	$A = 0.234$
0.694	108.41	3.733	110.67
1.813	107.18	6.952	109.31
3.909	105.79	10.971	108.02
6.478	104.65	16.223	106.71
9.639	103.51	21.556	105.63
13.301	102.53	28.283	104.48
17.118	101.67	35.400	103.44
22.816	100.60	44.316	102.33
31.692	99.23		
$CaCl_2$		$K_3Fe(CN)_6$	
$10^7\kappa^\circ = 2.55$	$A = 0.104$	$10^7\kappa^\circ = 1.28$	$A = 0.255$
1.265	108.16	1.706	135.72
3.921	106.51	3.302	133.14
6.247	105.50	5.439	130.70
9.131	104.50	8.086	128.35
14.129	103.18	10.843	126.39
19.422	102.02	14.135	124.45
27.300	100.67	18.283	122.41
37.628	99.25	23.837	120.16
48.010	98.10	31.349	117.71

conductance parameters resulting from this analysis are shown in Table III along with the limiting ionic conductances for the divalent ions. The values of λ° for the monovalent ions were taken from the literature.(1)

Analysis of the data for unsymmetrical electrolytes in terms of the Fuoss–Onsager conductance theory is open to considerable debate since a satisfactory conductance theory has not been formulated for this class of electrolytes. It has been shown that empirical equations containing a log and linear terms are correct for describing the conductance behavior.(10) Equation (1) should, therefore, be satisfactory for extrapolating to infinite dilution, but the concentration dependence does not have theoretical significance.

Literature data for appropriate unsymmetrical and symmetrical divalent salts have been recalculated using Eq. (1) and the solvent properties given above. The resulting parameters are shown in Table IV. Comparison of the data in Tables III and IV shows good agreement in Λ_0 except for $MnSO_4$ and $CaCl_2$. The literature value for $MnSO_4$(11) is higher than our value by almost one conductance unit. The limiting ionic conductance for Mn^{++} can be obtained from our data through two independent routes: from $\Lambda_0(MnCl_2) - \lambda_0(Cl^-) = 52.3$ and $\Lambda_0(MnSO_4) - \lambda(SO_4^=) = 52.1$. This close agreement suggests that our value is to be preferred. Our value for $CaCl_2$ is 0.7 conductance units lower than those reported by Shedlovsky(12) and Gordon.(13) The reason for this discrepancy is not clear, but we did use two salt samples prepared in different ways and obtained good agreement. Furthermore, no acidic impurities were found.

The ratio of the limiting ionic conductance-viscosity product for the divalent ions in water at 25°C to those in water at 10°C and in D_2O are shown in Table V. For monovalent ions, the change of $\lambda_0\eta$ in water with temperature has been shown to be a sensitive probe for water structure effects.(1) For the alkali and halide ions with a large surface-to-charge ratio, $(\lambda_0\eta)10/(\lambda_0\eta)25$ is greater than unity and such ions behave as structure breakers. For ions with either a small surface-to-charge ratio or with large hydrophobic surfaces, the temperature dependence of $\lambda_0\eta$ is positive or almost zero and such ions behave as structure makers. For the alkaline earth ions, the Walden-product ratio is essentially unity except for Ba^{++} ion. This constant value for the smaller alkaline earth ions is consistent with a small surface-to-charge ratio and strong electrostrictive hydration similar in behavior to that observed for the Li^+ ion.(1)

The net structure-breaking ability of the barium ion probably results from a mismatch of its hydrated water molecules with those involved in normal water structuring. It is interesting to note that the Na^+ and Ba^{++} ions have the same-surface-to-charge ratio and the same temperature effect on mobility, the temperature coefficient of $\lambda_0\eta$ being 1.02_1 and 1.02_2, respectively. The value of $\lambda_0\eta$ of the Mn^{++} ion, which has a crystallographic

Table III. Conductance Parameters for the Inorganic Salts

Salt	Solvent	Temp.	Λ_0	$\mathring{a}$	σ	$\lambda_0(\pm)^a$	K_A
$K_2BDS \cdot H_2O$	H_2O	10	93.99 ± 0.03	4.07 ± 0.07	0.06	(−)40.91)	
		25	133.18 ± 0.03	4.09 ± 0.06	0.05	(−)59.63	
	D_2O	25	110.01 ± 0.04	4.05 ± 0.08	0.08	(−)48.61	
$MgCl_2$	H_2O	10	90.92 ± 0.04	3.90 ± 0.23	0.07	(+)36.59	
		25	130.00 ± 0.03	3.97 ± 0.18	0.08	(+)53.61	
$CaCl_2$	H_2O	10	94.76 ± 0.05	4.18 ± 0.06	0.08	(+)40.43	
		25	135.27 ± 0.07	4.49 ± 0.11	0.13	(+)58.88	
		25	135.32 ± 0.06	4.45 ± 0.08	0.12	(+)58.93	
		25	135.21 ± 0.10	4.40 ± 0.11	0.16	(+)58.82	
	D_2O	25	110.70 ± 0.05	4.14 ± 0.07	0.10	(+)47.87	
$SrCl_2$	H_2O	10	94.88 ± 0.07	4.47 ± 0.13	0.12	(+)40.55	
		25	135.65 ± 0.08	4.16 ± 0.08	0.14	(+)59.26	
	D_2O	25	111.03 ± 0.04	4.15 ± 0.06	0.08	(+)48.20	
$BaCl_2$	H_2O	10	98.55 ± 0.04	4.00 ± 0.06	0.06	(+)44.22	
		25	139.89 ± 0.04	3.99 ± 0.05	0.07	(+)63.50	
	D_2O	25	114.95 ± 0.06	4.07 ± 0.07	0.09	(+)52.12	
$K_3Fe(CN)_6$	H_2O	25	172.03 ± 0.10	3.07 ± 0.04	0.15	(−)98.48	
	D_2O	25	140.83 ± 0.08	3.10 ± 0.03	0.13	(−)79.43	
$MnSO_4 \cdot H_2O$	H_2O	10	91.28 ± 0.12	4.46 ± 0.14	0.08	(+)35.24	103 ± 5
		25	132.28 ± 0.05	6.28 ± 0.18	0.03	(+)52.30	172 ± 4
		25	132.46 ± 0.23	4.71 ± 0.21	0.25	(+)52.48	136 ± 8
	D_2O	25	106.92 ± 0.16	4.51 ± 0.15	0.14	(+)41.46	136 ± 7
K_2SO_4	H_2O	10	109.12 ± 0.09	2.61 ± 0.14	0.18	(−)56.04	
		25	153.53 ± 0.03	2.94 ± 0.04	0.05	(−)79.98	
	D_2O	25	126.86 ± 0.04	2.82 ± 0.05	0.09	(−)65.46	
$MnCl_2$	H_2O	10	89.63 ± 0.05	4.09 ± 0.07	0.10	(+)35.30	
		25	128.73 ± 0.03	4.44 ± 0.05	0.05	(+)52.34	
	D_2O	25	104.39 ± 0.21	4.69 ± 0.30	0.30	(+)41.56	

[a] The limiting ionic conductances are preceded by a plus (+) sign to indicate the value for a cation or by a minus (−) sign to indicate an anion.

Table IV. Conductance Parameters for Salts Taken from the Literature

Salt	Temp.	Λ_0	$\mathring{a}$	σ	$\lambda_0(\pm)^a$	Ref.
$MgCl_2$	25	129.73 ± 0.05	4.29 ± 0.06	0.15	(+)53.34	*c*
$CaCl_2$	15	108.60 ± 0.05	4.10 ± 0.07	0.09	(+)47.18	*d*
	25	136.10 ± 0.03	4.23 ± 0.05	0.11	(+)59.71	*c*
	25	136.15 ± 0.07	4.00 ± 0.06	0.12	(+)59.76	*d*
	35	165.91 ± 0.10	4.11 ± 0.08	0.16	(+)73.69	*d*
	45	197.52 ± 0.11	4.06 ± 0.07	0.18	(+)88.62	*d*
$SrCl_2$	25	136.01 ± 0.06	4.25 ± 0.08	0.12	(+)59.62	*c*
$BaCl_2$	25	140.22 ± 0.03	4.07 ± 0.05	0.10	(+)63.83	*c*
K_2BDS	25	133.46 ± 0.09	4.00 ± 0.09	0.24	(−)59.91	*e*
$MnSO_4{}^b$	25	133.05 ± 0.17	4.73 ± 0.26	0.14	(+)53.09	*e*
K_2SO_4	25	153.49 ± 0.02	2.7 ± 0.13	0.04	(−)79.94	*f*
	25	154.31 ± 0.02	1.4 ± 0.17	0.04	(−)80.76	*g*
Na_2SO_4	25	130.14 ± 0.02	3.2 ± 0.1	0.01	(−)79.94	*f*
$K_3Fe(CN)_6$	25	174.11 ± 0.03	0.66 ± 0.09	0.04	(−)100.56	*g*
	25	171.70 ± 0.04	3.00 ± 0.04	0.12	98.15	*h*

[a] Limiting cation conductances are preceded by a (+) sign, anions by a (−) sign.

[b] $K_A = 119 \pm 8$.

[c] Ref. 12.

[d] Ref. 13.

[e] Ref. 14.

[f] Ref. 11.

[g] G. S. Hartley and G. W. Donaldson, *Trans. Faraday Soc.* **23**, 457 (1937).

[h] J. C. James and C. B. Monk, *Trans. Faraday Soc.* **46**, 1041 (1950).

Table V. Conductance-Viscosity Product Ratios for Divalent Ions in Water at 10 and 25°C and in Heavy Water

Ion	$(\lambda_0)\eta 10/(\lambda_0\eta)25$	$(\lambda_0\eta)D_2O/(\lambda_0\eta)H_2O$
Mg^{++}	1.00	—
Ca^{++}	1.00	1.00
Sr^{++}	1.00	1.00
Ba^{++}	1.02	1.01
Mn^{++}	0.996	0.98
$SO_4^{=}$	1.03	1.01
$BDS^{=}$	1.00	1.00
$Fe(CN)_6^{-3}$	—	0.99

radius of 0.80 Å intermediate between Mg^{++} (0.65 Å) and Ca^{++} (0.99 Å), also show a small temperature dependence, decreasing as the temperature decreases.

For the anion, the symmetrical sulfate ion appears to be a structure breaker. The BDS anion shows no net effect, probably reflecting a cancellation between the effect of the two sulfonate end groups by an opposing effect around the hydrocarbon framework.

Comparison of the ratios of the conductance-viscosity product for H_2O and D_2O is consistent with these conclusions and with the behavior observed for the monovalent ions in the two solvents. This interpretation differs somewhat from that of Greyson, who measured the heats of transfer of ions from H_2O to D_2O and concluded that, in addition to Ba^{++} ion, Ca^{++} and Sr^{++} ions also exhibited slight structure-breaking characteristics. Such behavior is similar to that observed for the tetraethylammonium ion in aqueous solution. This ion apparently sits on the borderline between structure making and breaking ions, and consequently different types of measurements are sensitive to different aspects of ion–solvent interactions.

The concentration dependence for $MnSO_4$ can be accurately evaluated by the Fuoss–Onsager equation since it is a symmetrical salt. The upper concentration limit for which the equation can be used depends upon the charge on the ions, their distance of closest approach, the temperature, and the dielectric constant. Preliminary calculations, assuming $\mathring{a} = 5$ Å, gives 50×10^{-4} *M* at 25°C. Analyzing several runs over different concentration ranges, however, gave consistent parameters only below a concentration of 30×10^{-4} *M*. This is in accord with the findings of Atkinson(14) and Fuoss(15) for 2:2 electrolytes.

At 25°C the association constant determined was 160 ± 8 and $\mathring{a} = 5.8 \pm 0.5$. The values at 10°C in water were $K_A = 121 \pm 5$ and $\mathring{a} = 5.0 \pm$

0.2. This gives a value for ΔH° for the association process of 3.2 ± 0.9 kcal-mole^{-1}, in good agreement with the value of 3.4 ± 0.3 kcal-mole^{-1} reported by Nair and Nancollas$^{(16)}$ from emf measurements. For D_2O at 25°C, K_A = 156 ± 6 and $\mathring{a}$ = 5.1 ± 0.2. Thus, no difference is seen in the association of this salt in D_2O as compared to H_2O in accordance with what has been observed for 1:1 electrolytes.$^{(17)}$

ACKNOWLEDGMENT

This work was supported by Contract No. 14-01-001-1281 and 14-30-2615 with the Office of Saline Water, U.S. Department of the Interior.

REFERENCES

1. R. L. Kay and D. F. Evans, *J. Phys. Chem.* **70**, 2325 (1966).
2. D. F. Evans and T. L. Broadwater, *J. Phys. Chem.* **72**, 1037 (1968). For more detailed information see T. L. Broadwater, Ph.D. Dissertation, Case Western Reserve University, 1968.
3. V. J. Shiner and M. L. Smith, *Anal. Chem.* **28**, 1043 (1956).
4. E. G. Almy, W. C. Griffin, and C. S. Wilcox, *Ind. Eng. Chem. Anal. Edition* **12**, 392 (1940).
5. G. Atkinson, M. Yokoi, and C. J. Hullada, *J. Am. Chem. Soc.* **83**, 1570 (1961).
6. C. G. Swain and D. F. Evans, *J. Am. Chem. Soc.* **88**, 383 (1966).
7. R. M. Fuoss and F. Accascina, *Electrolytic Conductance* (Interscience Publishers, Inc., New York, 1959).
8. R. L. Kay, *J. Am. Chem. Soc.* **82**, 2099 (1960).
9. J. E. Lind, Jr., and R. M. Fuoss, *J. Phys. Chem.* **66**, 1749 (1962).
10. T. Shedlovsky and A. S. Brown, *J. Am. Chem. Soc.* **56**, 1066 (1934); H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd ed. (Reinhold Publishing Corp., New York, 1958), pp. 207–208.
11. I. L. Jenkins and C. B. Monk, *J. Am. Chem. Soc.* **72**, 2645 (1950).
12. T. Shedlovsky and A. S. Brown, *J. Am. Chem. Soc.* **56**, 1066 (1934).
13. G. C. Benson and A. R. Gordon, *J. Phys. Chem.* **13**, 470 (1965).
14. G. Atkinson and H. Hallada, *J. Am. Chem. Soc.* **83**, 3759 (1961).
15. R. M. Fuoss and J. E. Lind, Jr., *J. Phys. Chem.* **66**, 1749 (1962).
16. V. S. K. Nair and G. H. Nancollas, *J. Chem. Soc.*, 3934 (1959).
17. R. L. Kay and D. F. Evans, *J. Phys. Chem.* **69**, 4216 (1965).