Conductivity of Manganese(II) Sulfate in Aqueous Solution at Various Temperatures

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Synopsis. The molar conductivity of manganese(II) sulfate, $MnSO_4$, in aqueous solution was measured in a temperature range of 10—45 °C. The acquired data were analyzed by the Quint–Viallard equation, and the resulting ion association constant, K_A, was used in the Bjerrum equation to determine the contact ion size, R_B. The limiting ionic molar conductivity λ_0 (1/2 Mn^{2+}) for the manganese ion at 15, 25, 35, and 45 °C are 40.8, 53.1, 65.2, and 79.8 S cm² mol⁻¹, respectively. The resulting thermodynamic properties for the ion association reaction are: $\Delta G^\circ_{298}=-13.5$ kJ mol^{-1}, $\Delta H^\circ=7.91$ kJ mol^{-1}, and $\Delta S^\circ_{298}=74.1$ J K^{-1} mol^{-1}.

Though the conductivity of manganese(II) sulfate in aqueous solutions at 25 °C has been the subject of extensive works,[1—4] its molar conductivity in aqueous solutions at other temperatures has never been studied. We previously measured the molar conductivity of iron(II) sulfate at various temperatures.[5] In this paper, the measurement was extended to manganese(II) sulfate in a temperature range of 10—45 °C. The temperature dependence of the ionic molar conductivity of divalent metal ions in aqueous solution is discussed in terms of the ion size.

Experimental

Reagent grade $MnSO_4$ was repeatedly recrystallized and purified in the usual manner. Preparation and purification of $MnSO_4$ were conducted under nitrogen atmosphere. Conductivity water was prepared by distilling water three times, and then allowed to pass very slowly through a mixed bed ion-exchange resin shortly before use.

All the measurements were made under nitrogen atmosphere. Conductivities were measured at a frequency of 1 kHz with a linear type bridge[6] in a temperature range of 10—45 °C, with the temperature controlled to ±0.005 °C. The conductivity cell was equipped with a platinized platinum electrode, and the cell constant was 0.99877±0.00001 cm^{-1} at 25 °C. No detectable change in the cell constant was observed over the temperature range of 10—45 °C.

On starting each run, nitrogen gas was passed gently through the conductivity water in the cell for about 20 min, and the conductivity of water was measured equilibrium value, which was less than 1.1×10^{-7} S cm^{-1}. The concentration of the sample solution was determined gravimetrically by the weight buret technique. A stock solution was poured from the weight buret into the cell without opening the cell to prevent contamination from CO_2 in the air. About 30 min was required for the reading of resistance to reach an equilibrium value. The measured resistance exhibited little drift with time after the thermal equilibration.

Results and Discussion

The molar conductivities, Λ, measured as a function, of concentration, c, in the temperature range 10—45 °C are given in Table 1. Using the successive approximation method, the conductivity data were analyzed in terms of the Quint–Viallard equation, Eq. 1.[17]

Table 1. Conductivity Data for Aqueous $MnSO_4$ Solution at Various Temperatures[a)]

10 °C		15 °C		20 °C		25 °C	
10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ
7.0245	77.189	9.9630	84.416	4.3636	103.12	3.7170	116.95
10.002	74.397	15.637	79.725	9.4219	95.633	9.7315	106.40
11.567	73.156	19.093	77.487	17.459	88.221	17.162	98.560
23.943	66.246	29.092	72.507	31.619	80.205	30.909	89.536
31.665	63.342	33.679	70.708	45.109	75.135	40.123	85.348
48.021	58.830	46.776	66.569	60.210	70.901	52.789	80.863
60.123	56.313	51.372	65.365	81.108	66.422	71.573	75.803
						86.157	72.671

30 °C		35 °C		40 °C		45 °C	
10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ
8.4681	119.31	9.0125	130.17	9.6862	140.79	17.345	140.63
13.212	112.70	13.601	123.23	13.205	134.90	25.751	131.40
21.098	105.02	25.084	111.81	23.561	122.95	37.398	122.43
31.631	97.942	36.495	104.42	34.236	114.81	49.623	115.49
43.809	92.071	45.501	99.995	46.347	108.10	58.981	111.29
63.146	85.354	57.643	95.208	57.671	103.22	67.376	108.00
82.418	80.382	65.987	92.456	69.131	99.162	75.368	105.24
		80.963	88.269			86.572	101.83

a) c/mol dm^{-3}; Λ(1/2$MnSO_4$)/S cm² mol^{-1}, molar conductivity.

$$\Lambda=\gamma[\Lambda_0-Sc^{1/2}\gamma^{1/2}+Ec\gamma\log c\gamma+J_1c\gamma-J_2c^{3/2}\gamma^{3/2}]. \quad (1)$$

Here

$$K_A=(1-\gamma)/c\gamma^2f_\pm^2, \quad (2)$$

$$-\log f_\pm=Ac^{1/2}\gamma^{1/2}/(1+B\mathring{a}c^{1/2}\gamma^{1/2}), \quad (3)$$

where c is the concentration, γ the degree of dissociation, K_A the ion association constant, $f_\pm$ the mean ionic activity coefficient given by the Deby–Hückel theory,[8] and $\mathring{a}$ the ion size parameter. The coefficients S, E, J, A, and B contain solvent properties, and J_1 and J_2 are functions of the ion size parameter $\mathring{a}_{J2}$.

In the analysis, the ion size parameters appearing in the J_1 and $f_\pm$ terms were fixed at the Bjerrum's distance, q. The best-fit $\mathring{a}_{J2}$ values for J_2 were calculated by minimizing the value of $\sigma\Lambda$ defined by

$$\sigma\Lambda=[\Sigma(\Lambda_{calcd}-\Lambda_{obsd})^2/(N-3)]^{1/2}, \quad (4)$$

where N is the number of experimental points.[9] The results are given in Table 2.

Table 2. Conductivity Parameters for Aqueous $MnSO_4$ Solution at Various Temperatures[a)]

t/°C	Λ_0	$\mathring{a}_{J2}$	K_A	$\sigma\Lambda$	R_B
10	91.6±0.1	11.7±0.1	234±1	0.02	4.0
15	104.6±0.1	11.8±0.1	249±2	0.02	4.0
20	118.3±0.1	11.8±0.1	259±1	0.02	4.0
25	133.1±0.1	11.8±0.1	277±1	0.04	3.9
30	147.6±0.1	11.8±0.1	291±1	0.03	3.9
35	163.2±0.1	11.8±0.1	307±1	0.03	3.9
40	179.3±0.1	11.8±0.1	324±1	0.03	3.9
45	196.1±0.2	11.9±0.1	337±2	0.04	3.8

a) $\Lambda_0(1/2MnSO_4)$/S cm² mol⁻¹, limiting molar conductivity. $\mathring{a}_{J2}$/Å, ion size parameter for J_2 term. K_A/dm³ mol⁻¹, ion association constant. $\sigma\Lambda$/%, relative standard deviation in Λ. R_B/Å, contact ion size for the Bjerrum's equation.

When a conductivity equation containing the $c^{3/2}$ term as in Eq. 1 is applied, the fitting of the data is generally better.[5,9] If an ion association is represented by the Bjerrum's equation, Eq. 5, the contact ion size, R_B(Å), can be calculated from the K_A value given by Eq. 2;[5,10]

$$K_A(\text{calcd})=\frac{4\pi N}{1000}\int_{R_B}^{q}r^2\exp(e^2/r\,DkT)\mathrm{d}r. \quad (5)$$

The results for R_B are also given in Table 2.

As can be seen in Table 2, Λ_0 and K_A tend to increase with raising temperature. This is also the case for other sulfates of divalent transition metal ions ($FeSO_4$,[5] $CoSO_4$,[3] $NiSO_4$,[3] and $ZnSO_4$[3]). Among these sulfates, $MnSO_4$ exhibits the smallest Λ_0 value and the largest K_A value while $ZnSO_4$ exhibits the greatest Λ_0 value and the smallest K_A value.

The limiting ionic molar conductivity, $\lambda_0(1/2\ Mn^{2+})$ =53.1 S cm² mol⁻¹, for Mn^{2+} at 25 °C is in good agreement with the literature value: 53.1 S cm² mol⁻¹ by Broadwater and Evans[11] and 53.2 S cm² mol⁻¹ by Hallada and Atkinson,[12] with the value $\lambda_0(1/2\ SO_4^{2-})$= 80.0 S cm² mol⁻¹.[8] Althogh the ion size parameter $\mathring{a}_{J2}$ is relatively large, reflecting the nature of the adjustable parameter, R_B has a reasonable value (the sum of the ionic crystal radii is ≈3.4 Å [13]).

The λ_0's for the Mn^{2+} ion at a series of temperatures are given in Table 3 together with those for other divalent ions; these were calculated using the Λ_0 values for $CaSO_4$[3] and the λ_0 values for the Ca^{2+} ion at 15, 35, and 45 °C.[8] As is evident in Table 3, the limiting molar conductivities for a series of divalent transition metal ions show a similar increase with a rise in the temperature. The value of λ_0^{2+} generally increases from Mn^{2+}

Table 3. Limiting Ionic Conductivity of Several Divalent Ions in Aqueous Solution at Various Temperatures

t/°C	$\lambda_0(1/2M^{2+})$[a)]					
	SO_4^{2-}	Mn^{2+},[b)]	Fe^{2+},[c)]	Co^{2+},[d)]	Ni^{2+},[d)]	Zn^{2+},[d)]
15	63.8	40.8	41.2	41.1	41.6	41.7
25	80.0[e)]	53.1	53.8	52.8	53.5	54.3
35	98.0	65.2	69.1	65.1	65.9	67.1
45	116.3	79.8	—	80.1	80.6	82.2
R_c[g)]	2.58[f)]	0.97	0.92	0.89	0.83	0.88
$r(M^{2+}-OH_2)$[h)]		2.20	2.12	2.08	2.04	2.08

a) $\lambda_0(1/2M^{2+})$/S cm² mol⁻¹, limiting ionic molar conductivity. b) This work. c) Ref. 5. d) Ref. 3. e) Ref. 8. f) Ref. 14. g) R_c/Å, crystal ionic radius (as octahedron).[13] h) $r(M^{2+}-OH_2)$/Å, distance of $M^{2+}-OH_2$.[15]

Table 4. Thermodynamic Parameters for Ion Association in Aqueous Solution

Reaction	$K_{A(298)}$	$\Delta G^\circ_{(298)}$	ΔH°	$\Delta S^\circ_{(298)}$
	dm³ mol⁻¹	kJ mol⁻¹	kJ mol⁻¹	J K⁻¹ mol⁻¹
$Mn^{2+}\cdot SO_4^{2-}$,[a)]	277	−13.5 ±0.1	7.91±0.03	74.1±0.3
$Fe^{2+}\cdot SO_4^{2-}$,[b)]	247	−13.7 ±0.1	9.72±0.05	78.5±0.4
$Co^{2+}\cdot SO_4^{2-}$,[c)]	178	−12.80±0.04	5.00±0.30	59.8±1.2
$Ni^{2+}\cdot SO_4^{2-}$,[c)]	187	−12.97±0.04	5.18±0.16	60.9±0.6
$Zn^{2+}\cdot SO_4^{2-}$,[c)]	165	−12.65±0.04	8.65±0.34	71.4±1.3

a) This work. b) Ref. 5. c) Ref. 3.

to Zn^{2+} except for Fe^{2+} at 35 °C. In particular, this trend is conspicuous at elevated temperatures of 35 and 45 °C.

From Mn^{2+} to Ni^{2+}, the order of the λ_0^{2+} value is opposite to those of the crystal ionic radii and the size of the first hydration sphere revealed by X-ray diffraction on the aqueous solutions.[15] This may suggest that the ionic mobility is inversely proportional to the crystal ionic radii of divalent transition metal ions and of the hydrated ion size.

The $\log K_A - 1/T$ plot to obtain ΔH^0 or ΔS^0 exhibits a good linearity. The resulting thermodynamic constants for the ion association reaction are given in Table 4 together with those of other sulfates. It is seen that the parameters for $Mn^{2+} \cdot SO_4^{2-}$ are similar in magnitude to those for the sulfate ion pairs compared.

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