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

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Synopsis. The molar conductivity of iron(II) sulfate, $FeSO_4$, in water was measured in the temperature range 10—35 °C. Data were analyzed by the Quint-Viallard equation, and the resulting ion association constant, K_A, was applied to the Bjerrum equation to determine the contact ion size, R_B. The limiting ionic molar conductivity of iron(II) at 25 °C is $\lambda_0(1/2Fe^{2+})=53.8$ S cm^2 mol^{-1}. Thermodynamic properties of ion association reactions are $\Delta G^\circ_{298}=-13.7$ kJ mol^{-1}, $\Delta H^\circ=9.7$ kJ mol^{-1}, and $\Delta S^\circ_{298}=78.0$ J K^{-1} mol^{-1}.

Divalent metal sulfates have long been utilized as the most typical 2 : 2 type of electrolytes for the study of aqueous electrolyte solutions.[1—6] Regarding iron(II) sulfate, however, precise conductivity data of its aqueous solution are not available, except the work of Demassieux and Fedroff[3] at 25 °C. Conductivity data for the other iron(II) salts are not available either in the literature. This is probably because the salts undergo oxidation markedly on exposure to atmospheric oxygen. Thus we attempted to redetermine molar conductivities of iron(II) sulfate in aqueous solution at several temperatures by avoiding oxidation as carefully as possible.

Experimental

The preparation and purification of $FeSO_4$ were conducted in nitrogen atmosphere. A reagent grade $FeSO_4$ was recrystallized from water by adding a small amount of ethanol. The purified salt was dried at room temperature to obtain crystals of heptahydrate. The crystals were pulverized before use. Conductivity water was prepared by distilling water three times, and the distilled water was allowed to pass through a mixed bed ion-exchange resin shortly before use.

Measurements were made at a frequency of 1 kHz with a linear type bridge,[7] temperature variation being ±0.003 °C. The conductivity cell was equipped with a platinized electrode, and the cell constant was 0.99074±0.00001 cm^{-1} at 25 °C. No detectable change in the cell constant was observed in the temperature range 10—35 °C.

On starting each run, a nitrogen gas stream was bubbled gently through the conductivity water in the cell for about 30 to 40 min, and the conductivity of the water was measured after it reached an equilibrium value, which was less than 1.0×10^{-7} S cm^{-1}. The concentration (10^{-4} to 10^{-3} mol dm^{-3}) of $FeSO_4$ was adjusted by direct dissolution of pulverized specimen into the cell by utilizing Hawes-Kay's cup-dropping device[8] in an atmosphere of nitrogen. The variation in conductivity of the solution with time was 0.02% or less in 5 h after the preparation of the solution.

Results and Discussion

Conductivity data of aqueous solutions in the temperature range 10—35 °C are given in Table 1.

The conductivity data were analyzed by the Quint-Viallard conductivity theory in the form of Eq. 1:[9]

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

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

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

where c is the concentration, γ is the degree of dissociation, K_A is the ion association constant, and $f_\pm$ is the mean ionic activity coefficient given by the extended Debye-Hückel theory of Eq. 3.[10] In Eq. 3, A and B depend upon solvent properties, and $\mathring{a}$ is the ion size

Table 1. Conductivity Data in Aqueous Solutions at Various Temperatures[a)]

10 °C		15 °C		20 °C	
10^4c	Λ	10^4c	Λ	10^4c	Λ
5.0500	81.447	3.5268	93.939	4.7768	104.15
9.5538	76.985	8.8480	87.161	8.5492	98.752
14.698	73.280	13.435	83.170	13.372	93.882
22.439	69.175	19.425	79.411	18.778	89.898
31.680	65.496	28.362	75.186	28.739	84.400
43.811	61.890	38.008	71.836	39.230	80.262
25 °C		30 °C		35 °C	
10^4c	Λ	10^4c	Λ	10^4c	Λ
5.5040	114.81	3.8277	132.38	4.0641	145.82
9.9449	108.22	8.3249	123.31	9.6007	133.80
14.446	103.40	13.478	116.32	15.528	125.76
21.856	97.592	20.955	109.43	22.871	118.71
29.661	92.999	32.964	101.69	33.314	111.56
45.036	86.622	49.691	94.615	45.505	105.43

a) c/mol dm^{-3}; $\Lambda(1/2FeSO_4)$/S cm^2 mol^{-1}, molar conductivity.

Table 2. Conductivity Parameters of $FeSO_4$ in Aqueous Solutions at Various Temperatures[a)]

T/°C	Λ_0	$\mathring{a}_{J2}$	K_A	$\sigma\Lambda$	R_B
10	93.1±0.3	12.6±0.2	201±4	0.06	4.3
15	105.0±0.1	11.4±0.1	215±3	0.06	4.3
20	119.4±0.1	11.4±0.2	231±3	0.05	4.2
25	133.8±0.1	11.5±0.1	247±2	0.05	4.1
30	150.4±0.2	11.3±0.1	264±3	0.08	4.1
35	167.1±0.1	11.4±0.1	281±3	0.07	4.0

a) $\Lambda_0(1/2\ FeSO_4)$/S cm^2 mol^{-1}, limiting molar conductivity. $\mathring{a}_{J2}$/Å, ion size parameter for the J_2 term. K_A/dm^3 mol^{-1}, ion association constant. $\sigma\Lambda$/%, relative standard deviation in Λ. R_B/Å, contact ion size for Bjerrum's equation.

Table 3. Limiting Molar Conductivity of Ions in Aqueous Solutions at 25 °C[a)]

Ion(M^{2+})	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$\lambda_0(1/2M^{2+})$	53.1[c)]	53.8[b)]	52.8[d)]	53.5[d)]	53.9[e)]	54.3[d)]

a) $\lambda_0(1/2M^{2+})$/S cm^2 mol^{-1}, limiting ionic molar conductivity. b) This work. c) Ref. 14. d) Ref. 4. e) Ref. 5.

Table 4. Thermodynamic Properties for Ion Association Reaction in Aqueous Solutions

Reaction	$K_{A\,298}$	ΔG°_{298}	ΔH°	ΔS°_{298}
	$dm^3\,mol^{-1}$	$kJ\,mol^{-1}$	$kJ\,mol^{-1}$	$J\,K^{-1}\,mol^{-1}$
$Fe^{2+}\cdot SO_4^{2-}$ a)	247	$-13.7\ \pm0.1$	9.72 ± 0.05	78.5 ± 0.4
$Co^{2+}\cdot SO_4^{2-}$ b)	178	-12.80 ± 0.04	5.00 ± 0.30	59.8 ± 1.2
$Ni^{2+}\cdot SO_4^{2-}$ b)	187	-12.97 ± 0.04	5.18 ± 0.16	60.9 ± 0.6
$Zn^{2+}\cdot SO_4^{2-}$ b)	165	-12.65 ± 0.04	8.65 ± 0.34	71.4 ± 1.3

a) This work. b) Ref. 4.

parameter. The coefficients J_1 and J_2 are functions of ion size parameter $\mathring{a}_{J2}$, and S, E, and J contain solvent properties.[10] The ion size parameters appearing in the J_1 and $f_{\pm}$ terms were fixed as equal to Bjerrum's q values, and the best fit $\mathring{a}_{J2}$ values for J_2 were calculated.[11] Table 2 shows the best fit parameters at the minimum value of $\sigma\Lambda$. $\sigma\Lambda(\%)$ is defined as

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

where N is the number of experimental points.

When a conductivity equation containing a $c^{3/2}$ term is applied, the fitting of the data is generally better, but the ion size parameter $\mathring{a}_{J2}$ for the 2:2 type electrolyte is usually as large as 10—20 Å. In the present work $\mathring{a}_{J2}$ of 11—13 Å was obtained.[11] If one assumes the validity of Bjerrum's Eq. 5, the contact ion size R_B can be calculated from the resulting K_A:[12,13]

$$K_A(\text{calcd})=\frac{4\pi N}{1000}\int_{R_B}^{q} r^2\exp(e^2/rDkT)\,dr. \qquad (5)$$

The results are also given in Table 2. The parameters, Λ_0 and K_A increase with increasing temperature. The limiting molar conductivity of Fe^{2+} ion at 25 °C is obtained as $\lambda_0\,(1/2\ Fe^{2+})=53.8\ S\,cm^2\,mol^{-1}$ by subtracting the value $\lambda_0\ (1/2SO_4^{2-})=80.0$ of SO_4^{2-} ion from the Λ_0 value.[10] Demassieux and Fedroff's data[3] give λ_0 $(1/2Fe^{2+})=49.8$. Table 3 shows a comparison with other divalent transition metal ions. The ion size parameter $\mathring{a}_{J2}$ has a relatively large value, more than 10 Å, whereas R_B has a substantially reasonable value (the sum of the ionic crystal radii is ≈3.3 Å).[15] The log K_A-$1/T$ plot gives a good linearity. The resulting thermodynamic properties of ion association reaction are shown in Table 4 with data of other sulfate solutions. It can be seen that the properties of $Fe^{2+}\cdot SO_4^{2-}$ are in parallel with those of the other sulfates, though the absolute values are a little larger than the others. The positive ΔS° has been considered as due to the decreased orientation of water molecules when the ion-pair forms.[16]

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