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Conductometric Determination of Ion-association Constants for Magnesium and Nickel Sulfates in Aqueous Solutions at Various Temperatures between 0°C and 45°C

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Thermodynamic equilibrium constants for the ion-association in aqueous solutions of magnesium and nickel sulfates were determined by electrical conductivity measurements at various temperatures between 0°C and 45°C. The standard Gibbs energy and the enthalpy and entropy for the reaction $M^{2+}+SO_4^{2-}\rightleftharpoons M^{2+}\cdot SO_4^{2-}$ (M: Mg or Ni) were then calculated from the temperature-dependence of the ion-association constants. The values obtained are as follows: $\Delta G°_{298}=-2.91$ kcal mol^{-1}, $\Delta H°=2.04$ kcal mol^{-1}, and $\Delta S°_{298}=16.6$ cal deg^{-1} mol^{-1} for $Mg^{2+}\cdot SO_4^{2-}$; and $\Delta G°_{298}=-3.10$ kcal mol^{-1}, $\Delta H°=1.27$ kcal mol^{-1}, and $\Delta S°_{298}=14.7$ cal deg^{-1} mol^{-1} for $Ni^{2+}\cdot SO_4^{2-}$.

Different values are sometimes obtained for the formation constant of a given ion-pair when different experimental methods are used in its determination. For example, the formation constant of the ion-pair $[Co(NH_3)_6]^{3+}\cdot X^-$ (X: Cl, Br, I, NO_3) as determined by the spectroscopic method is significantly smaller than that determined by the conductometric method.[1,2] It is, thus, important to study whether such a discrepancy in the thermodynamic constant is attributable to the different working principles of various methods or simply to experimental errors.

This paper will deal with the conductometric determination of ion-association constants for magnesium and nickel sulfates in aqueous solutions at temperatures from 0 to 45°C. Except for a few investigations, the determination of ion-association constants has mostly been done at one particular temperature (say, 25°C). The temperature dependence of ion-association constants, however, is important because the standard enthalpies and entropies of ion-association will provide more useful information concerning the interaction between the ions than the formation constants at some fixed temperature.[3] The thermodynamic quantities determined by the present study are compared with the values obtained by Nair and Nancollas[4,5] by emf measurements, and also with the theoretical values based upon the electrostatic model of ion-pairs.

Experimental

Magnesium and nickel sulfates of an analytical reagent grade were recrystallized twice from conductivity water at a temperature between 10 and 20°C and then dried at room temperature. The purity of the samples was examined by a conventional chemical analysis of the components; the analysis gave results which were in good agreement with the theoretical values (Found: Mg^{2+}, 9.82; SO_4^{2-}, 38.93; H_2O, 51.20% for $MgSO_4\cdot 7H_2O$ and Ni^{2+}, 20.95; SO_4^{2-}, 34.39; H_2O, 44.73% for $NiSO_4\cdot 7H_2O$).

Solutions of different concentrations were carefully prepared by using conductivity water of a specific conductivity lower than 2.4×10^{-7} ohm^{-1} cm^{-1} at 25°C in an atmosphere of purified nitrogen gas.

The electrical conductivities at different temperatures were measured by the apparatus shown in Fig. 1. The apparatus consisted of the following two parts: (a) a deviation-linear-bridge operated at 1000 Hz which detected the difference in conductance between a conductivity cell and a given standard,

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[1] N. Tanaka, Y. Kobayashi, and M. Kamada, This Bulletin, **40**, 2839 (1967).

[2] S. Katayama and R. Tamamushi, *ibid.*, **41**, 606 (1968).

[3] J. E. Prue, *J. Chem. Educ.*, **46**, 12 (1969).

[4] V. S. K. Nair and G. H. Nancollas, *J. Chem. Soc.*, **1958**, 3706.

[5] V. S. K. Nair and G. H. Nancollas, *ibid.*, **1959**, 3934.

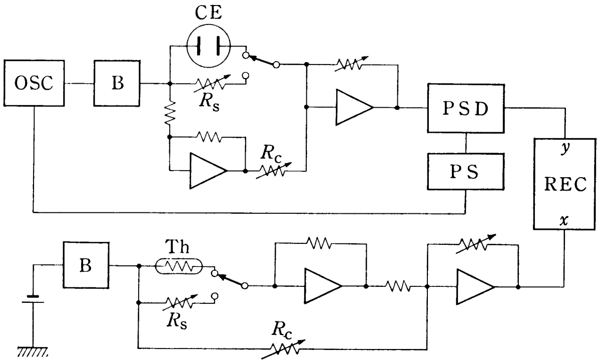

Fig. 1. Basic circuit of the apparatus for measuring conductance-temperature relationship: OSC, oscillator; B, buffer amplifier; CE, conductance cell; Th, thermistor; R_s standard resistance; R_c, variable resistance; PSD, phase-sensitive detector; PS, phase-shifter; REC, *x-y* recorder.

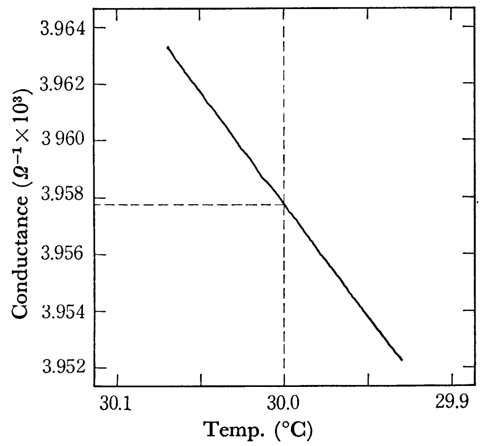

Fig. 2. Determination of conductance at a given temperature (30.0°C) from a conductance-temperature plot.

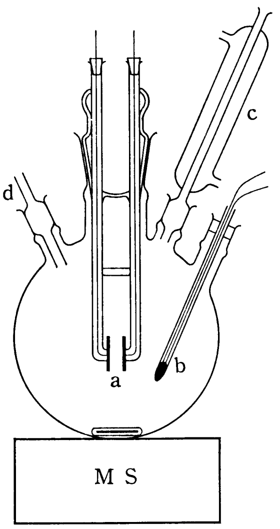

Fig. 3. Conductivity cell: a, platinized platinum electrodes; b, thermistor; c, condenser; d, nitrogen inlet; MS, magnetic stirrer.

and (b) a dc deviation-linear-bridge for temperature measurements using a thermistor. Both bridges were calibrated by the substitution method, using a precision decade resistance (Dekastat RS-624, Electro Scientific Industries; accuracy, ±0.005%). The conductance of a solution at a given temperature, T, was determined from the plot of the conductance against the temperature in the temperature range of $T\pm\Delta T$ (usually $\Delta T\simeq 0.05$°C), as is shown in Fig. 2. The details of the apparatus and the procedure will be reported elsewhere.

The conductivity cell used was a four-necked flask with a 300 cc capacity, as is shown in Fig. 3. After the air in the cell had been replaced with nitrogen gas through the inlet, d, the solution to be measured was poured into the cell. During the conductivity measurements, pure nitrogen gas was gently streamed over the surface of the solution, and the solution was stirred by a magnetic stirrer at a constant speed. The cell constant was determined to be 0.13729 $\mathrm{cm^{-1}}$ by using a standard potassium chloride solution. The reproducibility of the conductivity measurements was better than ±0.02%, and the sensitivity of the temperature measurements was ±0.003°C.

Results and Discussion

The equivalent conductivities, Λ, for magnesium and nickel sulfates in aqueous solutions at various temperatures between 0 and 45°C are summarized in Table 1. The thermodynamic ion-association constants, K_A, for the reaction:

$$\mathrm{M^{2+} + SO_4{}^{2-} \rightleftharpoons M^{2+}\cdot SO_4{}^{2-}} \quad \text{(M: Mg and Ni)} \qquad (1)$$

were calculated from the conductivity data according to the Fuoss-Onsager conductance theory.[6,7]

The revised Fuoss-Onsager equation for the equivalent conductivity of an associated symmetrical electrolyte is:

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + Ec\gamma\log(c\gamma) + Jc\gamma - K_A c\gamma f^2\Lambda \qquad (2)$$

with:

$$K_A = \frac{1-\gamma}{c\gamma^2 f^2} \qquad (3)$$

where Λ_0 is the limiting equivalent conductivity; c, the molar concentration; γ, the degree of dissociation; f, the mean activity coefficient, and S, E, and J, theoretical coefficients. Introducing some new variables defined by the equations;

$$\Lambda' = \Lambda + S(c\gamma)^{1/2} - Ec\gamma\log(c\gamma) \qquad (4)$$

$$y = (\Lambda'-\Lambda_0)/c \qquad (5)$$

$$x = f^2\Lambda \qquad (6)$$

we can transform Eq. (2) into a simple form:

$$y = J - K_A x \qquad (7)$$

Equation (7) implies that if the variables x and y are known, the values of J and K_A can be determined by a plot of y against x (the y-x plot). The coefficient, J, is a function of the ion-size parameter, a, and is used for the evaluation of a.

The numerical analysis of the conductivity data given in Table 1 was carried out according to the method of successive approximation on the following bases:

(1) A preliminary value of Λ_0 is obtained by Owen's method of extrapolation,[8] and then a better value for Λ_0 is determined from the y-x plot.

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6) R. M. Fuoss, *J. Amer. Chem. Soc.*, **81**, 2659 (1959).

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

8) B. B. Owen, *J. Amer. Chem. Soc.*, **61**, 1393 (1939).

Table 1. Equivalent conductivities, Λ, of $MgSO_4$ and $NiSO_4$ in aqueous solutions at various temperatures

Temp. (°C)	Concentration [mol/l] 0.0002	0.0003	0.0004	0.0005	0.0007	0.0010	0.0015	0.0020	0.0025	0.0030
					($MgSO_4$)					
0	63.40	62.20	61.15	60.25	58.70	56.84	54.55	52.75	51.23	50.04
5	74.12	72.68	71.44	70.37	68.55	66.41	63.66	61.53	59.75	58.33
10	85.55	83.85	82.38	81.09	78.97	76.50	73.31	70.83	68.80	67.11
15	97.49	95.53	93.84	92.33	89.90	87.05	83.37	80.42	78.15	76.24
20	110.10	107.81	105.89	104.18	101.32	98.15	93.93	90.58	87.95	85.76
25	123.29	120.65	118.49	116.58	113.35	109.69	104.93	101.23	98.14	95.69
30	137.34	134.24	131.63	129.50	125.95	121.85	116.32	112.12	108.67	105.90
35	151.32	148.05	145.22	142.68	138.71	134.12	127.93	123.23	119.38	116.30
40	166.62	162.95	159.55	156.73	152.00	146.77	139.87	134.65	130.37	126.94
45	181.83	177.70	173.94	170.82	165.60	159.80	152.09	146.28	141.50	137.79
					($NiSO_4$)					
0	63.22	61.78	60.63	59.59	57.89	55.85	53.23	51.20	49.58	48.19
5	73.85	72.15	70.80	69.59	67.57	65.18	62.10	59.71	57.82	56.18
10	85.20	83.21	81.64	80.21	77.86	75.07	71.50	68.72	66.52	64.62
15	97.06	94.72	92.90	91.27	88.57	85.36	81.25	78.07	75.55	73.35
20	109.50	106.90	104.78	102.91	99.80	96.14	91.46	87.83	84.96	82.47
25	122.56	119.60	117.20	115.07	111.54	107.38	102.08	97.97	94.74	91.92
30	136.11	132.78	130.08	127.69	123.73	119.03	113.06	108.39	104.79	101.64
35	150.06	146.34	143.28	140.62	136.20	130.93	124.24	119.04	115.01	111.50
40	164.51	160.34	156.98	153.96	149.06	143.18	135.75	129.92	125.43	121.55
45	179.55	174.92	171.12	167.69	162.28	155.72	147.59	140.93	136.03	131.71

(2) The starting approximation for γ is given by the classical Onsager equation:

$$\gamma_1 = \Lambda/[\Lambda_0 - S(c\cdot\Lambda/\Lambda_0)^{1/2}] \qquad (8)$$

and higher approximations for the degree of dissociation, γ_i ($i=2, 3, \cdots$), are calculated by:

$$\gamma_i = \Lambda/[\Lambda_0 - S(c\gamma_{i-1})^{1/2} + Ec\gamma_{i-1}\log(c\gamma_{i-1}) + Jc\gamma_{i-1}] \qquad (9)$$

(3) The mean activity coefficient, f, is estimated by means of the Debye-Hückel equation:

$$\log f = \frac{-Az^2\sqrt{I}}{1+Ba\sqrt{I}} \qquad (10)$$

where z ($z=|z_+|=|z_-|$ for a symmetrical electrolyte) is the charge number; I, the ionic strength, and A and B, the theoretical coefficients.

All the calculations were performed on a FACOM 270-20/30 computer using a FORTRAN program.

Table 2 summarizes the values of Λ_0, K_A, and a thus determined for $MgSO_4$ and $NiSO_4$ at different temperatures. The K_A-values for $NiSO_4$ were larger than those for $MgSO_4$ at each temperature, while the temperature-coefficient of K_A for $NiSO_4$ was smaller than that for $MgSO_4$. The ion-size parameters for $NiSO_4$ and $MgSO_4$ were about 6 Å at temperatures ranging from 0 to 45°C. In Table 2, the present results are compared with the K_A values (shown in parentheses) obtained by Nair and Nancollas[4,5] using the emf method.

The standard enthalpy of association, $\Delta H°$, was determined from the linear plots of $\log K_A$ against T^{-1}, as is shown in Fig. 4, according to the relation:

$$d\ln K_A/d(1/T) = -\Delta H°/R \qquad (11)$$

The standard Gibbs energy and the standard entropy of association, $\Delta G°$ and $\Delta S°$, were calculated by means of the well-known thermodynamic equations:

Table 2. Limiting equivalent conductivities, Λ_0, ion association constants, K_A, and ion-size parameter, a, of $MgSO_4$ and $NiSO_4$ in aqueous solutions at various temperatures

Temp. (°C)	Λ_0	K_A	a[Å]
		($MgSO_4$)	
0	68.15	103±1 (92±12)	5.59
5	79.75	108±1	5.71
10	92.15	116±2	5.87
15	105.15	121±2	5.95
20	118.90	129±2 (160±17)	6.09
25	133.30	135±2 (179±12)	6.18
30	148.70	147±5 (222±5)	6.29
35	164.15	151±3 (248±16)	6.30
40	181.20	167±4 (281±15)	6.33
45	198.05	175±3 (312±54)	6.33
		($NiSO_4$)	
0	68.40	156±3 (121±6)	5.86
5	80.00	162±3	6.06
10	92.40	168±3 (151±5)	6.14
15	105.40	176±4 (174±4)	6.33
20	119.10	183±3	6.38
25	133.45	187±3 (211±16)	6.28
30	148.40	191±3	6.22
35	163.90	201±3 (247±8)	6.30
40	180.00	209±4	6.31
45	196.85	217±3 (289±23)	6.27

(The values of K_A obtained by Nair and Nancollas from the emf measurement are shown in parentheses)

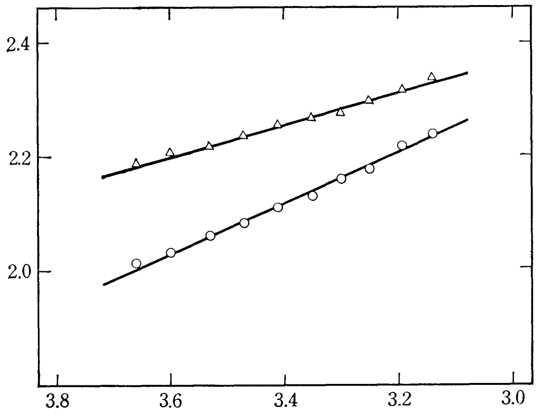

Fig. 4. Plots of log K_A against T^{-1} for magnesium sulfate (○) and nickel sulfate (△).

Table 3. Standard Gibbs energy, enthalpy, and entropy of ion-pair formation of $Mg^{2+} \cdot SO_4^{2-}$ and $Ni^{2+} \cdot SO_4^{2-}$

Ion-pair	ΔG°_{298} [kcal mol^{-1}]	ΔH° [kcal mol^{-1}]	ΔS°_{298} [cal deg^{-1} mol^{-1}]
$Mg^{2+} \cdot SO_4^{2-}$	−2.91	2.04	16.6
	(−3.07)	(4.84)	(26.2)
$Ni^{2+} \cdot SO_4^{2-}$	−3.10	1.27	14.7
	(−3.16)	(3.31)	(21.7)

(The values obtained by Nair and Nancollas from the emf measurement are shown in parentheses)

$$\Delta G^\circ = -RT \ln K_A \tag{12}$$

and:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{13}$$

The values of ΔG°, ΔH°, and ΔS° for the association reaction (1) are given in Table 3, in which the values of Nair and Nancollas are also presented (in parentheses). Qualitatively, the present results show a tendency similar to those of Nair and Nancollas[4,5] obtained by the emf measurements. Quantitatively, however, the values of ΔH° and ΔS° obtained from the conductivity data are significantly smaller than those determined from the emf data.

It seems worthwhile to compare the experimental values of ΔH° and ΔS° with those theoretically predicted from the electrostatic model of ion-pairs. According to Fuoss' theory of electrostatic interaction, the ion-pair association constant, K_A, is given by this equation:[3,9]

$$K_A = \bar{v} e^b \tag{14}$$

with

$$\bar{v} = \frac{4\pi L a^3}{3000}, \quad b = \frac{|z_+ z_-| e^2}{\varepsilon a k T}$$

where z_+ and z_- are the charge numbers of the cation and anion respectively, where ε is the dielectric constant, and where the other symbols have their usual meaning. Provided $\bar{v}$ is independent of the temperature, we obtain the following expressions for ΔH° and ΔS° from Eq. (14):[3]

$$\Delta H^\circ = -RTb\left(1 + \frac{d \ln \varepsilon}{d \ln T}\right) \tag{15}$$

and:

$$\Delta S^\circ = R \ln \bar{v} - Rb\left(\frac{d \ln \varepsilon}{d \ln T}\right) \tag{16}$$

With the values of $d \ln \varepsilon / d \ln T = -1.37$ for water at 25°C and $a = 6$ Å as determined from the conductivity data (see Table 2), Eqs. (15) and (16) give the theoretical values of $\Delta H^\circ = 1.05$ kcal mol^{-1} and $\Delta S^\circ = 14.4$ cal deg^{-1} mol^{-1} for the ion-pair formation of $M^{2+} \cdot SO_4^{2-}$ (M: Mg and Ni) at 25°C. These theoretical values are reasonably close to the experimental values we give in Table 3; this suggests that the electrostatic interaction exerts a dominant influence on the ion-pair formation of $Mg^{2+} \cdot SO_4^{2-}$ and $Ni^{2+} \cdot SO_4^{2-}$.

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[9] R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y. (1959), Chap. XVI.