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Temperature Dependence of Conductivities and Ion-Association Constants of Potassium Sulfate in Water

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Synopsis. From the temperature dependence of the ion-association constants between K^+ and SO_4^{2-} at 0 to 50 °C, the contact ion-pair formation and short-range interactions are discussed while considering the hydration of the anion. The limiting molar conductivities of SO_4^{2-} are expressed as a cubic equation of the temperature.

In a previous conductivity study[1] of $KClO_4$ and KNO_3 in water, we found that their ion-association constants have minimum values at certain temperatures between 0 and 50 °C. This phenomenon was explained as indicating the presence of specific interactions within contact ion pairs, the formations of which were considered to be helped by a weak hydration of the ions. The sulfate ion, one of the oxoacid anions, also has been known to associate with the potassium ion.[2] It is of interest to examine the temperature dependence of the ion-association constant between these ions, especially whether the specific interactions are characteristic of oxoacid anions.

Although a sulfate ion is one of the most usual types of inorganic anions, details concerning the temperature dependence of its limiting molar conductivity have not yet clarified.[3,4] In the present study, the precise conductivities of potassium sulfate in aqueous solutions were measured at eleven temperatures between 0 and 50 °C in order to clarify these problems.

Experimental

Materials. Potassium sulfate (Wako Pure Chemical Industries, reagent grade) was recrystallized twice from conductivity water and then air-dried at room temperature. It was further dried at about 150 °C and kept over diphosphorus pentaoxide in a desiccator under reduced pressure. This salt was confirmed to be anhydrous by the Karl-Fischer method with an AQ-5 Aquacounter of Hiranuma Sangyo Co. The quantity of adsorption water was less than 0.003 wt%.

Solutions. All solutions were made by weight and the molar concentration at each temperature was calculated by using the solution densities estimated from those at 25 °C (as previously described).[1,5] The conductivity of the water used[1] was always lower than 1×10^{-7} S cm^{-1} at 25 °C after dissolved carbon dioxide was removed. Eight solutions of 0.00025 to 0.0023 mol dm^{-3} were examined.

Measurements. Conductivity measurements were made with a Fuso 360 linear-bridge conductometer in a manner described previously.[1,5] The change of the cell constant (0.13720 cm^{-1} at 25 °C) with temperature was corrected to be regarded as −0.0014% for an elevation of 1 °C.[1] The reproducibility of conductivity measurements was within 0.05%. The precision of temperature measurements was ±0.003 °C and the accuracy of the temperature was ±0.01 °C.

Results and Discussion

Analysis of Conductivity Data. The observed molar conductivities, $\Lambda(K_2SO_4/2)$,[6] were analyzed by assuming the following ion-association (ion-pair formation) equilibrium between the ions, as made by Jenkins and Monk:[2]

$$K^+ + SO_4^{2-} \rightleftharpoons K^+SO_4^{2-}.$$

Representing the fraction of the free sulfate ion as α and the ionic molar conductivity as λ, we can express $\Lambda(K_2SO_4/2)$, based on the mixed rule, by

$$\Lambda(K_2SO_4/2) = \alpha[\lambda(K^+) + \lambda(SO_4^{2-}/2)] + (1-\alpha)[\lambda(K^+) + \lambda(K^+SO_4^{2-})]/2 = \alpha\Lambda_{12} + (1-\alpha)\Lambda_{11}/2,$$

where Λ_{12} and Λ_{11} correspond to the molar conductivities of hypothetical 1:2 and 1:1 electrolytes completely dissociated. In the present study Λ_{12} and Λ_{11} were expressed by means of the Robinson-Stokes equation[3] as follows:

$$\Lambda_{12} = [\lambda^\infty(K^+) + \lambda^\infty(SO_4^{2-}/2)] - S\sqrt{I}/(1+Ba\sqrt{I}) \quad (1)$$

and

$$\Lambda_{11} = [\lambda^\infty(K^+) + \lambda^\infty(K^+SO_4^{2-})] - S\sqrt{I}/(1+Ba\sqrt{I}), \quad (2)$$

where λ^∞ is the limiting molar ionic conductivity, a is the closest distance of approach of ions, S and B have their usual meanings[3] and I is the ionic strength, $I=c(1+2\alpha)$, where c is the molar concentration of the salt. According to the treatment of Jenkins and Monk,[2] the $\lambda^\infty(K^+SO_4^{2-})$ was approximated as $0.6\lambda^\infty(SO_4^{2-}/2)$ and S in Eqs. 1 and 2 were taken as those in hypothetical solutions for $\alpha=1$ and 0, respectively. The activity coefficients of the ions, y_i, were expressed by the Debye-Hückel equation involving a.[3] The values of a were assumed to be 3.66 Å, considering the crystallographic radius of K^+ (1.33 Å)[3] and the effective ionic radius of SO_4^{2-} (2.33 Å), which was estimated from its ionic partial molar volume by means of Glueckauf's equation.[1,5] The values of $\lambda^\infty(K^+)$ were obtained from the following cubic equation in which parameters had been given by Harned and Owen:[1,4]

$$\lambda^\infty(t\,°C) = \lambda^\infty(25\,°C) + a(t-25) + b(t-25)^2 + c(t-25)^3. \quad (3)$$

On these assumptions, the $\lambda^\infty(SO_4^{2-}/2)$ and the ion-association constant,

$$K = (1-\alpha)/[c\alpha(1+\alpha)y_{2-}],$$

were determined by a least-squares procedure, minimizing σ, where $\sigma^2=\sum[\Lambda(\text{obsd})-\Lambda(\text{calcd})]^2/(n-2)$. Further details of the calculation have been described

Table 1. Ion-Association Constants (K) and Limiting Molar Ionic Conductivities (λ^∞)

t	K	$\lambda^\infty(SO_4^{2-}/2)$	$\lambda^\infty(K^+)$	σ
°C	$dm^3\ mol^{-1}$	$S\ cm^2\ mol^{-1}$	$S\ cm^2\ mol^{-1}$	$S\ cm^2\ mol^{-1}$
0	8.1±0.6	41.55±0.04	40.72	0.0342
5	7.8±0.6	48.49±0.04	46.72	0.0343
10	7.9±0.5	55.80±0.03	53.03	0.0277
15	8.0±0.4	63.47±0.03	59.61	0.0246
20	8.1±0.4	71.50±0.03	66.44	0.0291
25	8.2±0.4	79.84±0.04	73.50	0.0331
30	8.4±0.4	88.54±0.04	80.76	0.0381
35	8.6±0.5	97.54±0.06	88.20	0.0535
40	8.6±0.5	106.81±0.08	95.79	0.0703
45	9.0±0.6	116.52±0.09	103.52	0.0870
50	9.4±0.8	126.52±0.13	111.35	0.1231

Table 2. Experimental and Theoretical Values of Standard Enthalpy and Entropy of Ion Association at Several Temperatures (a=3.66 Å)

	Experimental		Theoretical[a]	
t	ΔH°	ΔS°	ΔH°	ΔS°
°C	$kJ\ mol^{-1}$	$J\ K^{-1}\ mol^{-1}$	$kJ\ mol^{-1}$	$J\ K^{-1}\ mol^{-1}$
5	−0.2±1.7	16.6±6.2	2.71	26.9
15	1.1±0.9	20.9±3.3	3.27	28.9
25	2.4±0.7	25.7±2.3	3.86	30.9
35	4.0±1.0	30.9±3.5	4.49	33.0
45	5.8±2.2	36.5±7.0	5.16	35.2

a) Ref. 9.

previously.[1,5]

Ion-Association Constants and Their Temperature Dependence. The obtained values of K, $\lambda^\infty(SO_4^{2-}/2)$ and σ are shown in Table 1 together with the used values of $\lambda^\infty(K^+)$.[7] The results at 25 °C are in practical agreement with those of Jenkins and Monk:[2] K=9 $dm^3\ mol^{-1}$ and $\lambda^\infty(SO_4^{2-}/2)=79.9_8\ S\ cm^2\ mol^{-1}$.[8] The values of K are apparently comparable to the theoretical ones:[9] $K/dm^3\ mol^{-1}$=7.75 (0 °C), 8.08 (10 °C), 8.48 (20 °C), 8.93 (30 °C), 9.45 (40 °C), and 10.05 (50 °C) for a=3.66 Å. However, as shown in Fig. 1, the difference in the temperature dependence between the theoretical and experimental values is found, especially at lower temperatures, even if the scattering of the experimental values is taken into consideration. The full line fitted to the log K values in Fig. 1 was drawn by using the following equation:[1]

$$\log K = p(t - t_{\min})^2 + \log K_{\min}, \tag{4}$$

with $p=(3.9\pm0.8)\times10^{-5}\ K^{-2}$, $t_{\min}=6.4\pm3.7$ °C, and $\log K_{\min}=0.899\pm0.001$ (obtained by a least-squares calculation). The standard enthalpy and entropy of ion association, ΔH° and ΔS°, were estimated by the use of Eq. 4 and are shown for several temperatures in Table 2, compared with the theoretical values.[9] The experimental and theoretical values (ΔH° and ΔS°) are close to each other at higher temperatures. However, the experimental values deviate more with decreasing temperature.

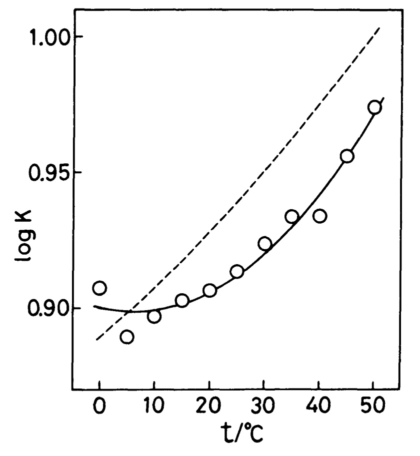

Fig. 1. Temperature dependence of the ion-association constants: experimental (○) and theoretical (----) values.

The temperature dependence of K between K^+ and SO_4^{2-} is similar to that for KNO_3 and $KClO_4$, for which the K values were considerably larger than the theoretical ones and became minimum at higher temperatures: 30 °C for KNO_3 and 36 °C for $KClO_4$.[1] These results have been explained as indicating the presence of specific short-range interactions within the contact ion pairs of which formations were helped by the weak hydration of the ions.[1] The present results can be explained by considering the relatively strong hydration of SO_4^{2-} compared to that of NO_3^- and ClO_4^-.[10] The appearance of $t_{\min}$ may suggest the presence of short-range interactions within contact ion pairs,[11] as observed for KNO_3 and $KClO_4$.[1] The lower $t_{\min}$ is due to the relatively large energy requirement for the partial release of hydration water molecules around SO_4^{2-} by the contact ion-pair formation. The not so large values of K (in spite of the possibility of the presence of specific interactions) is due to a strong hydration of SO_4^{2-}, which hinders contact ion-pair formation. A similar hydration effect has been found concerning the ion association between Na^+ and SO_4^{2-}, of which the K value, $6._7$ dm^3 mol^{-1},[2] is relatively small compared to that for K^+. This has been attributed to a stronger hydration of Na^+ than of K^+.[10]

The Temperature Dependence of Limiting Molar Conductivities of SO_4^{2-}. Equation 3 was used to represent the temperature dependence of $\lambda^\infty(SO_4^{2-}/2)$. The parameters were determined to be as follows: $\lambda^\infty(25\,°C)=79.83$ S cm^2 mol^{-1}, $a=1.7027$ S cm^2 mol^{-1} K^{-1}, $b=6.70\times10^{-3}$ S cm^2 mol^{-1} K^{-2}, and $c=-5.4\times10^{-6}$ S cm^2 mol^{-1} K^{-3}. By using Eq. 3 with these parameter values, the experimental $\lambda^\infty(SO_4^{2-}/2)$ could be reproduced with an average deviation of ±0.03 S cm^2 mol^{-1}.

References

1) H. Yokoyama and T. Ohta, *Bull. Chem. Soc. Jpn.*, **61**, 3073 (1988).

2) I. L. Jenkins and C. B. Monk, *J. Am. Chem. Soc.*, **72**, 2695 (1950).

3) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London (1959), Chaps. 4, 6, and 7 and Appendixes.

4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York (1958), p. 233.

5) H. Yokoyama, *Bull. Chem. Soc. Jpn.*, **57**, 1304 (1984); H. Yokoyama and M. Nishimura, *ibid.*, **58**, 1094 (1985).

6) The table of the observed molar conductivities are deposited as Document No. 8836 at the Office of the Editor of Bull. Chem. Soc. Jpn.

7) The values of K are somewhat dependent on the assumptions for $\lambda^\infty(K^+SO_4^{2-})$ and a: for example, we obtain $K(25\,°C)/\mathrm{dm^3\,mol^{-1}}=7.8\pm0.4$ by assuming $\lambda^\infty(K^+SO_4^{2-})=0.5\lambda^\infty(SO_4^{2-}/2)$ and 8.8 ± 0.4 by assuming $a=4.16$ Å. However, the following discussion in this study is qualitatively unaltered.

8) Obtained from the analysis with the Onsager limiting equation;[3] we can obtain $K=8.5\pm0.9$ dm^3 mol^{-1} and $\lambda^\infty(SO_4^{2-}/2)=79.85\pm0.06$ S cm^2 mol^{-1} with the Robinson-Stokes equation by reanalyzing their data in the concentration range examined in the present study.

9) H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 1770, 3002 (1975); although the theoretical equation of the ion-association constant has been derived for symmetrical electrolytes, it was assumed to be also applicable to unsymmetrical electrolytes.

10) Y. Marcus, "Ion Solvation," John Wiley & Sons, New York (1985), Chap. 5.

11) About half of ion pairs are presumed to be contact ion pairs, since the formation constants of separated ion pairs are theoretically estimated as follows: 3.9, 4.4, and 5.0 dm^3 mol^{-1} at 0, 25, and 50 °C, respectively,[9] where the closest distance of approach was taken as 6.4_2 Å equal to the sum of 3.66 and 2.7_6 Å (diameter of water molecule).