The Temperature Dependence of the Conductivities and Ion-Association Constants of Potassium Nitrate and Potassium Perchlorate in Water

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The electric conductivities of potassium nitrate and potassium perchlorate in water have been measured at eleven temperatures from 0 to 50 °C and analyzed in order to obtain the ion-association constants and the limiting molar conductivities of these salts. It was found that the observed ion-association constants have a minimum value at 30 °C for KNO_3 and at 36 °C for $KClO_4$. Such a characteristic temperature dependence was considered to be due to the presence of specific short-range interactions within contact ion pairs, although the weak hydration of the ions seemed to help the formation of the contact ion pairs. The experimental standard enthalpies and entropies of ion association were discussed in comparison with the theoretical ones. The limiting molar conductivities of NO_3^- and ClO_4^- at each temperature were also evaluated and expressed as cubic equations of the temperature.

Potassium nitrate and potassium perchlorate have been known to be slightly associated in water.[1–4] It is of interest what interactions are concerned with their ion associations, since, from the electrostatic ion-association theories,[5,6] 1:1 electrolytes can be predicted to be almost completely dissociated in water. The detailed knowledge of the temperature dependence of their ion-association constants (K) should be useful in clarifing such a problem. At the present stage, however, we have no available information about this.

The limiting molar conductivities (λ^∞) of alkali metal ions and halide ions in water have been measured in detail at temperatures between 0 and 55 °C and expressed as cubic equations of the temperature.[7,8] However, the λ^∞ values of the nitrate ion and the perchlorate ion are known only for a few temperatures, although information on their temperature dependence would be valuable for the analysis of the conductivities of unsymmetrical electrolytes involving these anions and also for the investigation of the ion-solvent interactions in water.[8] For these reasons we performed conductivity measurements on aqueous solutions of potassium nitrate and potassium perchlorate at eleven temperatures between 0 and 50 °C and obtained the ion-association constants of KNO_3 and $KClO_4$ and the limiting molar conductivities of NO_3^- and ClO_4^- as a function of the temperature. On the basis of these results, we will discuss the character of the interactions between the ions.

Experimental

Materials. The potassium nitrate and potassium perchlorate (Wako Pure Chemical Industries, reagent-grade) were recrystallized twice from conductivity water and then air-dried at room temperature. The potassium perchlorate was then further dried at about 150 °C and kept over diphosphorus pentaoxide in a desiccator under reduced pressure. Small quantities of adsorption water (0.21 wt% for KNO_3 and 0.01 wt% for $KClO_4$) were found by the Karl-Fischer method with an AQ-5 Aquacounter of the Hiranuma Sangyo Co. and were corrected in the calculation of the concentrations of solutions.

Solutions. All the solutions were made by weight, and the molar concentration at each temperature was calculated by the use of the solution densities, which had been themselves estimated from those at 25 °C in the manner described previously.[9] The density measurements at 25 °C were carried out by using a vibrating-tube SS-D-200 twin-type densimeter of the Shibayama Scientific Co. Water purified by the use of Milli-Q Reagent-grade Water Systems of Japan Millipore was used for the preparation of the solutions. Its conductivity was always lower than 1×10^{-7} S cm^{-1} at 25 °C after the dissolved carbon dioxide had been removed. Ten solutions (from 0.0007 to 0.010 mol dm^{-3}) were examined.

Conductivity Measurements. The conductivity measurements were made with a Fuso 360 linear-bridge conductometer in the manner described previously.[10] The cell constant of the cell used was 0.13720 cm^{-1} at 25 °C. For the other temperatures, the change in the cell constant due to the thermal expansion of platinum and glass was corrected; it was regarded as −0.0014% for the elevation of 1 °C, which was estimated in the manner described by Robinson and Stokes.[8] The reproducibility of the conductivity measurements was within 0.03%, and the precision of the temperature measurements was ±0.003 °C. The accuracy of the temperature was ±0.01 °C.

Results and Discussion

Analysis of Conductivity Data. The observed molar conductivities (Λ)[11] were analyzed by assuming the ion association(ion-pair formation) of the salts in terms of the 1970 Fuoss-Justice equation,[12,13] with $E=E_1\Lambda^\infty-2E_2$:

$$\Lambda = \alpha[\Lambda^\infty - S(\alpha c)^{1/2} + E\alpha c\log(\alpha c) + J_1\alpha c - J_2(\alpha c)^{3/2}],$$

where S, E_1, E_2, J_1, and J_2 have the usual meanings and where α is the fraction of free ions. The values of the closest distance of approach of the ions(a) involved in J_1 and J_2 and the Debye-Hückel equation of the activity coefficient were assumed to be equal to 3.38 and 3.63 Å for KNO_3 and $KClO_4$ respectively. These values were estimated from the crystallographic radius of K^+ (1.33 Å)[8] and the effective radii of NO_3^- and ClO_4^- (2.05 and 2.30 Å respectively, estimated from the ionic partial molar volumes[14] by the use of Glueckauf's equation[10,15]). The ion-association constant (K) and the limiting molar conductivity (Λ^{∞}) were determined by the least-squares procedure, minimizing σ, where $\sigma^2=\sum[\Lambda(\mathrm{obsd})-\Lambda(\mathrm{calcd})]^2/(n-2)$. The details of the calculations have been described previously.[10]

Ion-Association Constants and Their Temperature Dependence. The values of K, Λ^{∞}, and σ obtained are summarized in Tables 1 and 2.[16] The values of K and Λ^{∞} at 25 °C are in practical agreement with the following values reported by Carman[2]: K=1.2—1.3 dm³ mol⁻¹ and Λ^{∞}=145.05 S cm² mol⁻¹ (a=3.46—3.83 Å) for KNO_3 and K=1.6 dm³mol⁻¹ and Λ^{∞}=140.65 S cm²mol⁻¹ (a=4.21 Å) for $KClO_4$. The experimentally obtained ion-association constants are larger than those predicted from the electrostatic ion-association theory[6], K=0.52 and 0.48 dm³ mol⁻¹ at 25 °C for a=3.38 and 3.63 Å respectively. The temperature dependence of the ion-association constant can be well characterized when log (K/dm³ mol⁻¹) values are plotted against t/°C, as shown in Fig. 1. That is, the experimental ion-association constant has a minimum value at a certain temperature, while the theoretical one[6] increases with an increase in the temperature: for example, K/dm³ mol⁻¹=0.46 (0 °C), 0.48 (10 °C), 0.50 (20 °C), 0.53 (30 °C), 0.56 (40 °C), and 0.59 (50 °C) for a=3.38 Å and 0.43 (0 °C), 0.45 (10 °C), 0.47 (20 °C), 0.49 (30 °C), 0.52 (40 °C), and 0.55 (50 °C) for a=3.63 Å.

Table 1. Experimental Ion-Asssociation Constants and Limiting Molar Conductivities of KNO_3 Obtained by Assuming a=3.38 Å

t	K	Λ^{∞}	σ
°C	dm³ mol⁻¹	S cm² mol⁻¹	S cm² mol⁻¹
0	1.28±0.09	80.57±0.02	0.0121
5	1.26±0.11	92.52±0.02	0.0163
10	1.25±0.11	104.98±0.02	0.0195
15	1.26±0.12	117.94±0.03	0.0264
20	1.21±0.11	131.30±0.03	0.0241
25	1.21±0.10	145.10±0.02	0.0172
30	1.20±0.10	159.30±0.02	0.0193
35	1.22±0.10	173.85±0.03	0.0204
40	1.22±0.10	188.74±0.03	0.0211
45	1.22±0.14	203.94±0.03	0.0265
50	1.25±0.19	219.44±0.05	0.0460

Table 2. Experimental Ion-Asssociation Constants and Limiting Molar Conductivities of $KClO_4$ Obtained by Assuming a=3.63 Å

t	K	Λ^{∞}	σ
°C	dm³ mol⁻¹	S cm² mol⁻¹	S cm² mol⁻¹
0	1.80±0.12	77.52±0.02	0.0174
5	1.73±0.10	89.18±0.02	0.0164
10	1.68±0.10	101.36±0.02	0.0189
15	1.64±0.10	114.04±0.03	0.0207
20	1.61±0.10	127.17±0.03	0.0244
25	1.57±0.08	140.70±0.03	0.0235
30	1.56±0.08	154.64±0.03	0.0264
35	1.55±0.09	168.93±0.04	0.0301
40	1.56±0.10	183.56±0.04	0.0347
45	1.58±0.13	198.53±0.05	0.0413
50	1.59±0.11	213.75±0.05	0.0427

The experimental log K values can be reproduced well by a full line shown in Fig. 1 using this equation:

$$\log K = p(t - t_{\mathrm{min}})^2 + \log K_{\mathrm{min}}, \qquad (1)$$

where the values of p, t_{min}, and K_{min} are as given in Table 3. This equation is similar to that used by Harned and Embree[17,18] for the temperature dependence of the dissociation constants of such weak acids as acetic acid. The p values in Table 3 are near to the usual one, 5×10^{-5} K⁻², for the acid-dissociation constants reported by Harned and Embree.[17,18] The standard enthalpy and entropy of ion association (ΔH° and ΔS°), which can be estimated by the use of Eq. 1, are shown for several temperatures in Tables 4 and 5. These values are smaller than the theoretical ones,[6] as shown in the same tables. Their deviation becomes remarkable with a decrease in the tempera-

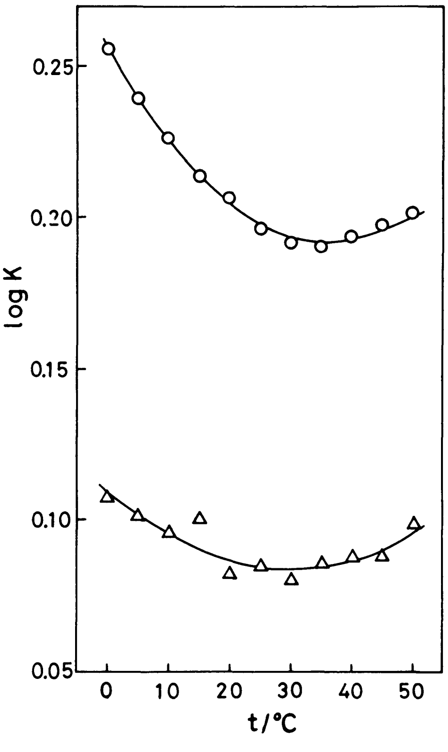

Fig. 1. Temperature dependence of ion-association constants of KNO_3 (△) and $KClO_4$ (○).

ture. Negative or small $\Delta H°$ values mean that exothermic interactions exist between the ions and become dominant at temperatures below t_{min}.

Although one may consider that the ion associations of KNO_3 and $KClO_4$ are due only to the weakness of the hydration of NO_3^- and ClO_4^-, this explanation is not necessarily adequate for the following reason. The hydration of I^- is supposed to be weaker than that of NO_3^- because of its more positive hydration free energy at 25 °C.19) However, the ion-association constant between K^+ and I^- is 0.6_4 $dm^3\,mol^{-1}$ (a=4.5 Å, t=25 °C) smaller than that of KNO_3, and it decreases with the decrease in the temperature in the range from 5 to 55 °C.20) This temperature dependence differs from that observed in the present study, although it is in agreement with the prediction from the electrostatic ion-association theory.6)

Table 3. Values of Parameters in Eq. 1 Representing the Temperature Dependence of the Ion-Association Constants

Salt	$p\times10^6$	t_{min}	$\log K_{min}$
	K^{-2}	°C	
KNO_3	2.88	29.9	0.084
$KClO_4$	5.10	35.6	0.192

Table 4. Experimental and Theoretical Values of Standard Enthalpy and Entropy of Ion Association Obtained for KNO_3 with a=3.38 Å

t	Experimental $\Delta H°$	Experimental $\Delta S°$	Theoretical6) $\Delta H°$	Theoretical6) $\Delta S°$
°C	$kJ\,mol^{-1}$	$J\,K^{-1}\,mol^{-1}$	$kJ\,mol^{-1}$	$J\,K^{-1}\,mol^{-1}$
5	−2.1±1.3	−5.7±4.8	2.54	2.9
15	−1.4±0.7	−3.0±2.5	3.06	4.7
25	−0.5±0.5	0.0±1.8	3.61	6.6
35	0.5±0.8	3.4±2.7	4.19	8.5
45	1.7±1.7	7.0±5.4	4.80	10.5

Table 5. Experimental and Theoretical Values of Standard Enthalpy and Entropy of Ion Association Obtained for $KClO_4$ with a=3.63 Å

t	Experimental $\Delta H°$	Experimental $\Delta S°$	Theoretical6) $\Delta H°$	Theoretical6) $\Delta S°$
°C	$kJ\,mol^{-1}$	$J\,K^{-1}\,mol^{-1}$	$kJ\,mol^{-1}$	$J\,K^{-1}\,mol^{-1}$
5	−4.6±0.5	−12.0±1.6	2.53	2.2
15	−3.3±0.3	−7.5±0.9	3.05	4.0
25	−1.8±0.2	−2.4±0.6	3.59	5.9
35	−0.1±0.3	3.3±0.9	4.17	7.8
45	1.9±0.6	9.6±1.9	4.78	9.8

The exothermic interactions between the ions are considered to be specific interactions within contact ion pairs, independent of the macroscopic properties of a solvent such as the dielectric constant. The negative $\Delta S°$ values at lower temperatures suggest that the specific interactions require steric restrictions for the formation of contact ion pairs. The local charges of oxygen atoms are presumed to play an important role in such interactions within the contact ion pairs. The slightly large values of K and t_{min} of $KClO_4$ compared with those of KNO_3 mean that the specific interactions of K^+ with ClO_4^- are stronger than those with NO_3^-. This may be due to the relatively weak hydration of ClO_4^-19) and also to the difference in the number of oxygen atoms of the anions.

The nitrate and perchlorate ions have been known to associate also with the other alkali metal ions.2) Their ion-association constants increase with the ionic radii of the cations in the following sequences: $K(NaNO_3)<K(KNO_3)K(CsNO_3)$ and $K(KClO_4)<K(RbClO_4)<K(CsClO_4)$.21) This may indicate that the formation of the contact ion pairs depends also on the ease of the release of the hydration water molecules of the cations, since the ion-association constants increase with a decrease in the hydration power of the alkali metal ions.19)

The Temperature Dependence of the Limiting Molar Conductivities of NO_3^- and ClO_4^-. Harned and Owen represented the temperature dependence of the limiting molar conductivities (λ^∞) of alkali metal ions and halide ions between 5 and 55 °C by means of this cubic equation:7)

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

The values of $\lambda^\infty(K^+)$ were calculated with this equation and then used to evaluate those of $\lambda^\infty(NO_3^-)$ and $\lambda^\infty(ClO_4^-)$ at the temperatures between 0 and 50 °C from $\Lambda^\infty(KNO_3)$ and $\Lambda^\infty(KClO_4)$. By using the resulting values, the parameters, a, b, c, and $\lambda^\infty(25\,°C)$, for NO_3^- and ClO_4^- were determined; they are summarized in Table 6. With these parameter values, the experimental values of $\lambda^\infty(NO_3^-)$ and $\lambda^\infty(ClO_4^-)$ can be reproduced by the use of Eq. 2 within an accuracy of 0.01 $S\,cm^2\,mol^{-1}$.

Table 6. Values of Parameters in Eq. 2 Representing the Temperature Dependence of the Limiting Ionic Molar Conductivities

Ion	$\lambda^\infty(25\,°C)$	a	$b\times10^3$	$c\times10^6$
	$S\,cm^2\,mol^{-1}$	$S\,cm^2\,mol^{-1}\,K^{-1}$	$S\,cm^2\,mol^{-1}\,K^{-2}$	$S\,cm^2\,mol^{-1}\,K^{-3}$
NO_3^-	71.60	1.3670	3.776	−3.5
ClO_4^-	67.20	1.3159	3.833	−5.9

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