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Conductometric Study of Calcium(II), Strontium(II), and Barium(II) Perchlorates in Methanol-Ethylene Glycol Mixtures

Hidekazu Doe,* Hiroshi Ohe, Hiroyuki Matoba, Akio Ichimura, and Toyokichi Kitagawa
Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558
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The ion-association constants, K_{1A}, of an ion pair, $M^{2+}ClO_4^-$ (M=Ca, Sr, Ba), have been determined by conductometric measurements in methanol-ethylene glycol mixtures of 0, 20, 40, 60, 80, and 100 wt% of ethylene glycol at 5, 15, 25, 35, and 45 °C. The conductometric data were treated by an improved Fuoss and Edelson method. The thermodynamic functions of $\Delta H_{1A}^{\ominus}$ and $\Delta S_{1A}^{\ominus}$ have also been determined at 25 °C from the temperature dependence of K_{1A}. In 60—80 wt% of ethylene glycol the K_{1A} values of these metal perchlorates are similar to each other, since the characteristics of individual metal ions are probably depressed by the strong solvations of those cations. The results are discussed while considering the cation solvation and structure of a bulk solvent.

We studied the ion association of some divalent transition, post-transition and alkaline earth metal perchlorates in methanol and in methanol-ethylene glycol (EG) mixtures in order to determine the effect of solvation on ion associations.[1-3] Generally, an ion pair may exist not only as one type of contact structure (contact ion pair), but also as various types of solvent-separated structures in which the cation and/or anion remain solvated (solvent-separated ion pair).[4] Previous studies of Co(II), Ni(II), Cu(II), and Zn(II) in mixtures of methanol and EG have revealed a relation between the first ion-association constant, K_{1A}, and solvation. Thus, the K_{1A} values decrease with the addition of EG, which has a stronger ability for cation solvation than does methanol,[5] since the proportion of the contact ion pair is decreased by the high solvation ability of EG.[2] Another study of Ca(II), Sr(II), and Ba(II) in methanol showed that the alkaline earth metal ions are solvated more weakly than are the above-mentioned transition and post-transition metal ions, since their K_{1A} values are larger than those of the transition and post-transition metals.[3] This means that the solvation mode should widely change upon the addition of EG in systems of alkaline earth metals. It has thus been expected that studies of the alkaline earth metals in mixtures of methanol and EG will provide further information concerning the mode of solvation which affects ion association.

Experimental

The preparation and purification of $Ca(ClO_4)_2 \cdot H_2O$, $Sr(ClO_4)_2$, and $Ba(ClO_4)_2$ were described previously,[3] and the purification of methanol and EG was carried out in the same way as previously reported.[2] Purified methanol and EG have 1.5×10^{-7} and 1.6×10^{-8} S cm^{-1} the conductivities at 25 °C, and 0.023 and 0.024 wt% the water content, respectively. The physical properties of solvents as well as outlines of the instrumentation and measurement techniques were also described previously.[2,3] At 25 °C the dielectric constants of 0, 20, 40, 60, 80, and 100 wt% of EG were 32.66, 34.05, 35.49, 36.88, 38.55, and 40.57; their viscosities were 0.5422, 0.8746, 1.499, 2.853, 6.213, and 16.74×10^{-3} kg m^{-1} s^{-1}, respectively. About ten solutions in the concentration range 8×10^{-4}—1.2×10^{-3} mol dm^{-3} of $[M(ClO_4)_2]$ were examined at 5.00, 15.00, 25.00, 35.00, and 45.00±0.01 °C.[6]

Data Treatment

Considering only one equilibrium (Eq. 1) in a solution, where the formation of $M(ClO_4)_2$ is assumed to be negligible,

$$M^{2+} + ClO_4^- \rightleftarrows MClO_4^+ \ (K_{1A}) \tag{1}$$

conductance data were analyzed on the basis of Fuoss and Edelson theory.[7] Previously, the Fuoss and Edelson equation was modified by considering a finite-size ion.[2] In this study the previous equation was further improved, while considering a decrease in the ionic strength caused by the formation of $MClO_4^+$. The new equation can be expressed as

$$\Lambda F = \Lambda_0 - XK_{1A}/\Lambda_0, \tag{2}$$

where

$$X = cy_{2+}\Lambda F(\Lambda F - \Lambda_0/2),$$
$$F = [\{1 - \delta I^{1/2}/(1 + Ba\,I^{1/2})\}^{-1} + (\Lambda - \lambda_0)/2\Lambda]$$
$$/\{1 + (\Lambda_0 - \lambda_0)/2\Lambda_0\}.$$

Here, Λ and Λ_0 are the molar and the limiting molar conductances of $1/2M(ClO_4)_2$, respectively; λ_0 and c are the limiting molar conductance and the total concentration of ClO_4^-, respectively; I is the ionic strength, $I=2[M^{2+}]+c/2$; δ is the Onsager's slope for a 2:1 electrolyte divided by Λ_0; and y_{2+} is the ion activity coefficient of M^{2+}, which is calculated by the Debye-Hückel second approximation:

$$\log y = -Az_i^2 I^{1/2}/(1 + Ba I^{1/2}). \tag{3}$$

Here, a is an ion-size parameter which is assumed to be 5 Å for Sr^{2+} and Ba^{2+} or 6 Å for Ca^{2+}.[8,9] The dependence of the K_{1A} value on a was somewhat described elsewhere; as shown in Table 4 of Ref. 3, the K_{1A} values at 5 Å are smaller by about 3% than those at 6 Å (this percentage increases a little with a decrease in K_{1A}).

A calculation was carried out using an iterative procedure until the Λ_0 value became constant.[1] In every iteration, the I value was calculated by another iterative procedure so that the values of F and y_{2+} could be evaluated. The K_{1A} values from this new calculation are larger by 5—8% than those from the previous one.

The limiting molar conductance of $MClO_4^+$, $\lambda_0(MClO_4^+)$, is assumed to be half of that of $1/2M^{2+}$, $\lambda_0(1/2M^{2+})$, in Eq. 2: that is, $\lambda_0(MClO_4^+)=0.5\,\lambda_0(1/2\,M^{2+})$. In order to check this assumption, the K_{1A} values were calculated at $\lambda_0(MClO_4^+)=0.6\,\lambda_0(1/2M^{2+})$. The K_{1A} values at $\lambda_0(MClO_4^+)=0.6\,\lambda_0(1/2M^{2+})$ were larger by 4—8% than those at $\lambda_0(MClO_4^+)=0.5\,\lambda_0(1/2M^{2+})$. These differences are comparable to the standard deviations of K_{1A} and increase with an increase in K_{1A}.

Results and Discussion

The values of Λ_0 and K_{1A} are summarized in Tables 1 and 2, respectively. It is natural that the Λ_0 values decrease with the addition of EG because of the extremely high viscosity of EG. The Walden products for the salts, $\Lambda_0\eta$, show the same three characteristics as do those of the transition and post-transition metal perchlorates (as an example, see Fig. 1 in Ref. 2): 1) the values in EG are about 1.6-times larger than those in methanol; 2) the values have a negative temperature dependence, except in methanol (the dependence is very small in methanol); and 3) the maximum temperature dependence appears around 60 to 80 wt% of EG. Qualitative discussions concerning them were previously carried out.[2] According to recent theories concerning dielectric friction,[10-12] these characteristics should at least be partly caused by

Table 2. Ion-Association Constants, K_{1A}/M^{-1}, of $MClO_4^+$ in Methanol-Ethylene Glycol Mixtures at 278.15—318.15 K

EG wt%	278.15K	288.15K	298.15K	308.15K	318.15K
			$CaClO_4^+$		
0	187±11	226±11	274±12	333±12	414±13
20	112±9	123±9	137±9	157±9	177±10
40	109±10	115±10	124±10	136±11	153±11
60	93±5	93±6	100±6	108±6	117±7
80	86±7	90±7	95±6	98±7	101±5
100	96±14	114±14	124±16	130±16	131±15
			$SrClO_4^+$		
0	247±10	301±11	374±13	463±15	590±22
20	144±9	160±9	177±10	201±10	249±15
40	80±8	89±8	101±9	116±9	137±9
60	67±4	72±4	79±5	87±6	100±6
80	88±6	92±6	90±6	97±6	98±6
100	54±4	64±5	70±5	73±6	76±6
			$BaClO_4^+$		
0	313±13	387±15	478±17	592±20	751±24
20	147±8	162±11	191±8	216±7	241±6
40	121±8	134±9	153±10	180±10	205±10
60	68±13	70±16	72±17	79±19	80±21
80	73±9	66±10	68±10	77±10	74±12
100	81±11	89±10	94±10	93±10	98±10

Table 1. Limiting Molar Conductances, $\Lambda_0/(S\,cm^2\,mol^{-1})$, of $1/2M(ClO_4)_2$ in Methanol-Ethylene Glycol Mixtures at 278.15—318.15 K

EG wt%	278.15K	288.15K	298.15K	308.15K	318.15K
			$Ca(ClO_4)_2$		
0	99.1±0.3	115.2±0.3	132.3±0.3	150.9±0.4	171.8±0.4
20	62.2±0.1	74.5±0.2	88.1±0.2	103.1±0.2	119.3±0.2
40	37.2±0.1	46.6±0.1	57.2±0.1	69.1±0.2	82.3±0.2
60	19.33±0.02	25.77±0.04	33.38±0.05	42.19±0.06	52.12±0.08
80	8.24±0.02	12.06±0.02	16.87±0.03	22.68±0.04	29.53±0.04
100	2.66±0.01	4.43±0.02	6.88±0.03	10.12±0.04	14.21±0.06
			$Sr(ClO_4)_2$		
0	95.9±0.2	111.5±0.3	128.2±0.4	146.8±0.4	167.2±0.6
20	63.7±0.1	76.5±0.2	90.4±0.2	105.8±0.2	123.1±0.4
40	37.10±0.07	46.53±0.09	57.2±0.1	69.2±0.1	82.4±0.2
60	19.32±0.03	25.85±0.04	33.52±0.06	42.33±0.08	52.4±0.1
80	8.46±0.01	12.38±0.02	17.27±0.03	23.25±0.03	30.32±0.04
100	2.650±0.003	4.400±0.006	6.83±0.01	10.04±0.02	14.10±0.02
			$Ba(ClO_4)_2$		
0	101.8±0.3	118.3±0.3	135.9±0.4	155.0±0.5	176.3±0.6
20	63.3±0.1	75.9±0.2	90.0±0.1	105.1±0.1	121.1±0.1
40	37.88±0.08	47.59±0.09	58.6±0.1	71.1±0.1	84.9±0.2
60	19.59±0.07	26.2±0.1	33.9±0.2	42.8±0.2	52.9±0.3
80	8.48±0.02	12.38±0.03	17.29±0.04	23.32±0.06	30.40±0.09
100	2.799±0.009	4.65±0.01	7.20±0.02	10.55±0.03	14.88±0.04

dielectric friction, even if there is not a big difference in the static dielectric constants of methanol and EG. However, we can not estimate such a contribution here, since we do not know all of the solvent properties necessary for an estimation.

The Walden product for each ion gives more useful information. However, since all of the values of $\lambda_0(ClO_4^-)$ were not available, they were calculated under some assumption[2] since they were needed in calculations of Λ_0 and K_{1A}. Our limiting molar conductance data of each ion, therefore, are not suitable for any detailed discussion of the Walden product.

Figure 1 shows a plot of the K_{1A} value against the wt% of EG in comparison with that of the $Zn(ClO_4)_2$ system, as a representative of the transition and post-transition metals. As shown in this figure, the tendency of the K_{1A} values is substantially similar to that of the transition and post-transition metals. The K_{1A} values of the alkaline earth metal perchlorates, however, significantly decrease with an increase in the EG content of the solvent from 0 to 20 wt%; those values at 20 wt% are already close to the K_{1A} value of $Zn(ClO_4)_2$. Furthermore, there is almost no difference regarding the K_{1A} values at 60—80 wt%. These results mean that the specific properties of each metal ion hardly appear in the K_{1A} values in the EG-rich solvents, since strong cation solvation considerably masks such properties.[13] That is, these facts support the idea that solvent-separated ion-pairs are dominant in EG rich solvents.[2]

The thermodynamic functions at 25 °C are summarized in Table 3 and are compared with those of $Zn(ClO_4)_2$ in Fig. 2. The values of the alkaline earth

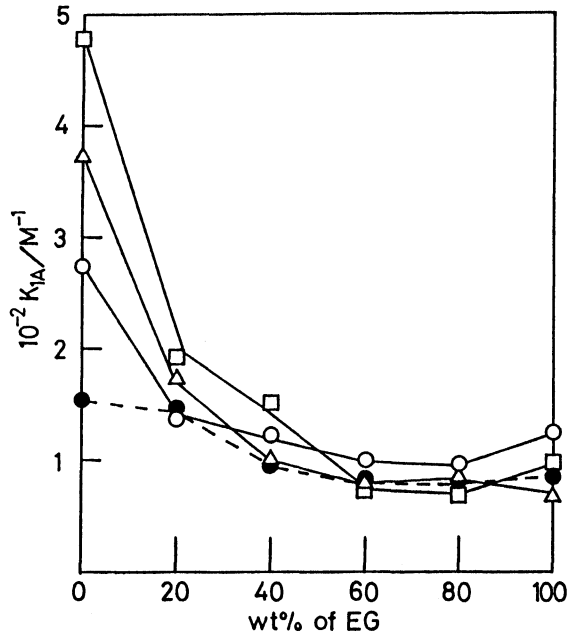

Fig. 1. Ion association constants of the metal(II) perchlorates at 298.15 K: (○) Ca, (△) Sr, (□) Ba, (●) Zn.

Table 3. Thermodynamic Functions of Ion Association of $M^{2+}ClO_4^-$ at 298.15 K

EG wt%	$\Delta H_{1A}^{\ominus}$/kJ mol^{-1}	$\Delta S_{1A}^{\ominus}$/J K^{-1} mol^{-1}	$\Delta G_{1A}^{\ominus}$/kJ mol^{-1}
		$CaClO_4^+$	
0	14.6±1.1	96±4	−13.9±0.11
20	8.6±1.6	70±6	−12.2±0.16
40	6.3±1.9	61±6	−12.0±0.20
60	4.5±1.4	53±4	−11.4±0.15
80	2.9±1.6	48±5	−11.3±0.17
100	5.3±3.1	58±10	−12.0±0.31
		$SrClO_4^+$	
0	16.1±0.9	103±3	−14.7±0.09
20	9.9±1.4	76±5	−12.8±0.14
40	9.9±2.0	72±7	−11.5±0.21
60	7.4±1.4	61±5	−10.8±0.16
80	2.1±1.4	45±5	−11.2±0.16
100	5.8±1.8	55±6	−10.5±0.19
		$BaClO_4^+$	
0	16.1±0.9	105±3	−15.3±0.09
20	9.3±1.0	75±3	−13.0±0.10
40	10.0±1.4	75±5	−12.5±0.16
60	3.3±5.3	47±18	−10.6±0.58
80	1.6±3.3	41±11	−10.5±0.36
100	2.8±2.7	47±9	−11.3±0.27

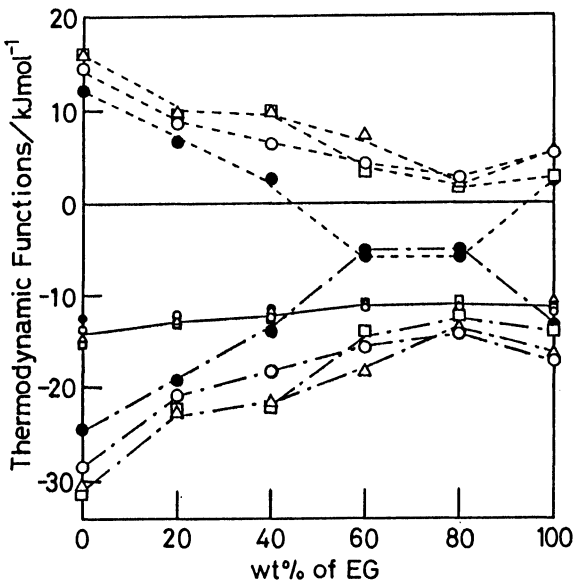

Fig. 2. Thermodynamic functions of ion associations of the metal(II) perchlorates at 298.15 K: (○) Ca, (△) Sr, (□) Ba, (●) Zn; (——) $\Delta G_{1A}^{\ominus}$, (----) $\Delta H_{1A}^{\ominus}$, (— · —), $-T\Delta S_{1A}^{\ominus}$.

metal perchlorates also exhibit similar tendencies to those of $Zn(ClO_4)_2$. In detail, however, the $\Delta H_{1A}^{\ominus}$ values of $Zn(ClO_4)_2$ are smaller than those of the alkaline earth metal perchlorates, and are even negative at 60—80 wt%. It is expected that the $\Delta H^{\ominus}$ value of ion association is negative if the ions are rigid and associate in a Coulombic interaction in a dielectric

continuum media. There are several theories regarding ion association which stand on the above assumption.[14,15] The theories, however, give positive $\Delta H^{\ominus}$ values in many solvents, since the theoretical equation for $\Delta H^{\ominus}$ contains the $1+\partial \ln \varepsilon/\partial \ln T$ term (ε is the solvent dielectric constant); thus, the experimental value of $\partial \ln \varepsilon/\partial \ln T$ makes the theoretical $\Delta H^{\ominus}$ value positive, contrary to the expectation.

The theoretical $\Delta H^{\ominus}$ values of any ion pair are positive in methanol, EG, and their mixtures, since their $\partial \ln \varepsilon/\partial \ln T$ values are smaller than -1 around room temperature. On the other hand, many experimental $\Delta H^{\ominus}$ values for water[16-18] and methanol[2,3] are also positive. This agreement between the experimental and theoretical $\Delta H^{\ominus}$ values may mean that the temperature dependence of ε, $\partial \ln \varepsilon/\partial \ln T$, represents how much the ion solvation is weakened by ion association. Regarding the negative value of $\Delta H^{\ominus}$, there are two explanations which consider the participation of a specific covalent interaction in the ion-association reaction. The first is that the covalent interaction somewhat works between ions; if so, the binding enthalpy between the ions is sufficiently negative to compensate for the positive contribution from the weakening of ion solvation. In this case, $\Delta G^{\ominus}$ of the ion association should have a large negative value (a large K value) and should depend on the kind of ion.

When an ion pair has a small negative $\Delta G^{\ominus}$ value, in spite of a negative $\Delta H^{\ominus}$ value, such as $Zn^{2+}ClO_4^-$ at 60—80 wt% (see Fig. 2), it is inferred that a specific covalent interaction acts on the primary solvation of the ion (the second explanation). In the case of $Zn^{2+}ClO_4^-$, the primary solvation of Zn^{2+} is probably very rigid due to the specific interaction between Zn^{2+} and solvent molecules, perhaps representing EG chelation of Zn^{2+}. If so, such tight Zn^{2+} solvation can not be loosened by ion association as much as expected from the $\partial \ln \varepsilon/\partial \ln T$ value of the solvent. Consequently, it makes the $\Delta H_{1A}^{\ominus}$ value small and even sometimes negative. On the other hand, the $-\Delta G_{1A}^{\ominus}$ value should be small because the ion pair Zn^{2+} (solvent)ClO_4^- separated by the primary solvation shell of Zn^{2+} is bound by the Coulomb force. According to the Fuoss' theory,[14] its $\Delta G_{1A}^{\ominus}$ values are very close to the theoretical values at a=6 Å; the theoretical $\Delta G_{1A}^{\ominus}$ values at 25.0 °C were -12.7, -12.1, -11.5, -11.1, -10.5, and -9.9 kJ mol^{-1} at 0, 20, 40, 60, 80, and 100 wt% of EG.[2] If Zn^{2+}(MeOH)ClO_4^- is completely separated by the van der Waals radius of a MeOH molecule, the a value is estimated at about 7.4 Å.[1] It is the distance most separated by one methanol molecule. Therefore, if a part of a ClO_4^- ion falls into a hollow among solvent molecules in the primary solvation shell, it is not unreasonable that a=6 Å, although a may depend on the solvent composition.

In the case of alkaline earth metal perchlorates, it is thought that a solvent-separated ion pair is still dominant in EG-rich solvents, since their $\Delta G_{1A}^{\ominus}$ values are near to the theoretical values at a=5 or 6 Å. However, it is expected that their primary solvation shells are not so rigid as Zn^{2+}'s. This means that solvations of alkaline earth metal ions are more weakened by ion association than that of Zn^{2+}. This directly affects the $\Delta H_{1A}^{\ominus}$ values of the alkaline earth metal perchlorates, and makes it larger than those of $ZnClO_4^+$. It also causes larger $\Delta S_{1A}^{\ominus}$ values for them than those of $ZnClO_4^+$ (see Fig. 2).

Some particular results have been obtained at 60—80 wt% of EG: for example, the maximum temperature dependence of the Walden products for the salts, the minimum K_{1A} values which least depend on the kind of the metal ion, and the minimum $\Delta H_{1A}^{\ominus}$ and $\Delta S_{1A}^{\ominus}$ values. In order to understand these results, we must consider not only the mode of solvation but also the condition of a bulk solvent, especially in the case of a partly structured hydrogen-bonding solvent. Jimenez et al.[19] reported that the maximum negative excess volume of mixing of methanol and EG appears in 60—70 wt% of EG and that it is bigger than those of the other normal alcohols with longer chains and EG. There may be two contradicting explanations for this fact: 1) the hydrogen-bonding structures of methanol and of EG (especially EG may be highly structured because the typical structure-breaking ClO_4^- has a very large Walden product in EG)[20,21] are partially destroyed by mixing, and 2) a mixture of methanol and EG which has an interpenetrating structure through hydrogen bonds is closely packed.

The Walden products of the salts at 60—80 wt% exhibit the highest negative temperature dependence, as already mentioned. This probably means that a solvent of 60—80 wt% is highly structured, since the Walden product of the typical structure-breaking ClO_4^- usually shows a negative temperature dependence in a structured solvent.[22] That is, this supports explanation 2; it is also consistent with the results of $\Delta H_{1A}^{\ominus}$, as follows. In a highly structured solvent related to explanation 2, the structure which is partly destroyed by ClO_4^- is probably recovered by ion association with ClO_4^-, so that the $\Delta H_{1A}^{\ominus}$ values are smaller at 60—80 wt% of EG than are other mixtures which include pure methanol and EG.

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