Conductometric Study of Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Perchlorates in Methanol–Ethylene Glycol Mixtures

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The ionic association constants of $M(ClO_4)_2$ (M=Co, Ni, Cu, Zn) were determined by conductometric measurements in methanol–ethylene glycol mixtures of 100, 80, 60, 40, 20, and 0 wt% methanol compositions at 5, 15, 25, 35, and 45 °C. The conductometric data were analyzed using a modified Fuoss and Edelson method. The association constant of an ion pair $M^{2+}ClO_4^-$, K_{1A}, was studied and thermodynamic functions, ΔH_{1A}° and ΔS_{1A}°, for that association were determined at 25 °C. Free-energy changes, ΔG_{1A}° $(=-RT\ln K_{1A})$, at 25 °C which slowly decreased with an increase in the ethylene glycol content in a solvent, are in good agreement with estimates from Fuoss' theory regarding ionic association. Values of both ΔH_{1A}° and ΔS_{1A}° were positive in many systems: *i.e.*, unfavorable enthalpy and favorable entropy changes, and those were obtained near to estimates from the Fuoss' theory in pure methanol, 100 wt%. However, there have been a few systems with a negative ΔH_{1A}° (Co, Ni, and Zn at 40 and 20 wt%, and Co at 0 wt%), contrary to theoretical expectations. These results are discussed from the standpoint of a changing solvation between M^{2+} and $MClO_4^+$. In all the solvents, moreover, the ΔH_{1A}° and ΔS_{1A}° values have been in a sequence according to Co<Ni<Cu>Zn. The results of limiting molar conductances, Λ_0, are discussed regarding Walden products.

Many problems concerning ionic solvation have been attracting the attention of chemists in various fields.[1] After taking some interest in the ionic associations between divalent metal cations and a perchlorate anion, we previously[2] made a study of various $M(ClO_4)_2$'s in methanol. In that study, conductometric data were treated using the Fuoss and Edelson method in which an ion-activity coefficient of M^{2+}, y_{2+}, was calculated using the Debye-Hückel second approximation in a manner different from the original paper. There, the Debye-Hückel limiting equation was used.[3] According to our calculation, the ionic association constant of $M^{2+}ClO_4^-$, K_{1A}, is about 10% less for the second approximation than for the limiting equation. The Fuoss and Edelson method was also established on the basis of the Onsager limiting equation. As done in the y_{2+}-calculation, it would therefore be more desirable to treat conductance data using an approximation involving the factor $1+\kappa a$ for moderate concentrations[4] than the Onsager limiting equation. Thus, using such a modified Fuoss and Edelson method, we have made a study of the ionic associations of Co(II), Ni(II), Cu(II), and Zn(II) perchlorates in methanol–ethylene glycol (EG) mixtures.

Both methanol and EG are amphiprotic nonaqueous solvents, but they are typical ionic media like water. The molecular volume of EG, which has a molecular structure that combines two methanol molecules, is less than twice that of methanol. The viscosity of EG is much larger than that of methanol. Their dielectric constants are also different from each other. Of course, methanol and EG resemble each other relatively, regarding their chemical properties as solvents. Therefore, research concerning their mixtures should yield good information concerning various solvent effects due to differences in physical properties: viscosity, dielectric constant, molecular volume, compressibility, *etc.*

Experimental

Materials. The preparation and purification of $M(ClO_4)_2\cdot 6H_2O$ salts were described previously.[2] Methanol and EG were dried over 3A molecular sieves and distilled fractionally. EG was distilled under a reduced pressure of 25 mmHg.† The electric conductivities of the purified methanol and EG were 1.5×10^{-7} and 1.6×10^{-8} S cm^{-1} at 25 °C, and the water contents were 0.023 and 0.024 wt%, respectively. The mixed solvents were prepared by weighing each solvent to an accuracy of $<\pm0.05\%$. All reagents were special grade materials (Wako).

Physical Properties of Solvents. The densities of solvents at 25 °C were determined using a vibrating densimeter (Model 01D, Sodev Inc., Sherbrooke, Canada), with chlorobenzene and methylcyclohexane as standards.[5] The accuracy of the measurements was $\pm2\times10^{-5}$ g cm^{-3}. The densities of pure methanol and EG at other temperatures were calculated using $v=v_0\,(1+\alpha_1 t+\alpha_2 t^2+\alpha_3 t^3)$, where v and v_0 are the volumes of the solvents at t and 0 °C, respectively. The α's are the thermal-expansion coefficients (α_1, α_2, and α_3 are 1.1342×10^{-3}, 1.3635×10^{-6}, and 0.8741×10^{-8} for methanol, and 0.5657×10^{-3}, 1.7074×10^{-6}, and 0.293×10^{-8} for EG, respectively).[6] Densities of the mixtures at temperatures other than 25 °C were also calculated based on the densities of pure solvents at corresponding temperatures and volume change rates of mixing. Then, it was assumed that the rates at 25 °C, which can be calculated based on densities of the mixtures at 25 °C, are equal to those at the other temperatures. The results are shown in Table 1.

Using an Ostwald viscometer, viscosities were measured in the usual way. Water was used as a standard substance.[7] The viscosity results are summarized in Table 2.

Measurements of dielectric constants were carried out by a resonance method at a frequency of 1 MHz. Constants for the standard methanol are cited from Albright and Gosting.[8] The results are shown in Table 3.

Temperatures were controlled within an accuracy and

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† 1 mmHg≈133.322 Pa.

TABLE 1. DENSITIES (g cm^{-3}) OF METHANOL–ETHYLENE GLYCOL MIXTURES AT 278.15—318.15 K

wt% Methanol	278.15 K	288.15 K	298.15 K[a]	308.15 K	318.15 K
100	0.8050	0.7958	0.78656	0.7772	0.7677
80	0.8606	0.8515	0.84226	0.8329	0.8234
60	0.9200	0.9111	0.90207	0.8929	0.8834
40	0.9835	0.9751	0.96639	0.9575	0.9484
20	1.0514	1.0436	1.03560	1.0273	1.0187
0	1.1237	1.1170	1.10996	1.1026	1.0949

a) Measured with the accuracy of <±2×10^{-5} g cm^{-3}.

TABLE 2. VISCOSITIES (cP: 1 cP=10^{-3} kg m^{-1} s^{-1}) OF METHANOL–ETHYLENE GLYCOL MIXTURES AT 278.15—318.15 K

wt% Methanol	278.15 K	288.15 K	298.15 K	308.15 K	318.15 K
100	0.7261	0.6244	0.5422	0.4742	0.4174
80	1.268	1.047	0.8746	0.7399	0.6339
60	2.371	1.865	1.499	1.223	1.016
40	5.098	3.756	2.853	2.222	1.768
20	13.08	8.782	6.213	4.530	3.433
0	43.48	26.10	16.74	11.27	7.929

These values involve the errors of at least ±0.14—0.28% caused by the accuracy of temperature.

TABLE 3. DIELECTRIC CONSTANTS OF METHANOL–ETHYLENE GLYCOL MIXTURES AT 278.15—318.15 K

wt% Methanol	278.15 K	288.15 K	298.15 K	308.15 K	318.15 K
100	36.88	34.70	32.66	30.74	28.92
80	38.30	36.20	34.05	32.06	30.22
60	39.84	37.70	35.49	33.53	31.69
40	41.37	39.14	36.88	34.75	32.92
20	43.25	40.93	38.58	36.42	34.53
0	45.52	43.01	40.57	38.35	36.37

These values involve the errors of at least ±0.04% caused by the accuracy of temperature.

precision of ±0.01 and ±0.0005 °C for density, ±0.05 and ±0.01 °C for viscosity, and ±0.05 and ±0.02 °C for the dielectric constant measurements, respectively.

Electric Conductances. The measurements were carried out with a Yanagimoto Model MY-8 conductivity outfit and a type C cell, which had a cell constant of 0.3801± 0.0006. This represents a mean value calibrated at 5, 15, 25, 35, and 45 °C with potassium chloride (Aldrich, 99.999% reagent).[9] All temperatures were controlled with an accuracy of <±0.1 °C using a Sharp TE-12K thermoelectric circulating system. The ClO_4^- concentrations, c, of the measured solutions were in the range of 1.5—20×10^{-4} M (M=mol dm^{-3}). When, therefore, a hexahydrated $M(ClO_4)_2$ solution of c=2×10^{-3} M was prepared, water of about 0.014 wt% was added to the solvents, inherently containing water of 0.023—0.024 wt%. However, this increase in water probably did not much affect our results and are negligible in comparison with other experimental errors. The measured solutions were prepared in an air-conditioned room (about 25 °C) and their molar concentrations were taken as those at 25.0 °C. Molarities at other temperatures were corrected using the densities of the corresponding temperatures.

Data Treatment

Conductometric data were treated using a modified Fuoss and Edelson method. According to the original method,[3] only the ionic equilibrium was considered:

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

Then they derived the following equation based on the Onsager limiting law:

$$\Lambda F = \Lambda_0 - XK_{1A}/\Lambda_0 \qquad (2)$$

where

$$X = cy_{2+}\Lambda F(\Lambda F - \Lambda_0/2)$$
$$F = \{(1-\delta c^{1/2})^{-1} + (\Lambda_0 - \lambda_0)/2\Lambda\}/\{1 + (\Lambda_0 - \lambda_0)/2\Lambda_0\}$$

where Λ and Λ_o are the molar and the limiting molar conductances of $1/2\,M(ClO_4)_2$, respectively. λ_o and c are the limiting molar conductance of ClO_4^- and the total concentration of ClO_4^-, respectively. The symbol δ is Onsager's slope divided by Λ_o. In previous papers,[2,10] the ion activity coefficient of M^{2+}, y_{2+}, was calculated using the Debye-Hückel second approximation (Eq.3) with an ion-size parameter, a, of 6 Å:[2]

$$\log y = -Az_i^2 I^{1/2}/(1 + BaI^{1/2}) \qquad (3)$$

The Fuoss and Edelson function, F (in Eq. 2), has been calculated by us using Eq. 4 in which $\delta c^{1/2}/(1+BaI^{1/2})$ is used instead of $\delta c^{1/2}$:

$$F = [\{1 - \delta c^{1/2}/(1 + BaI^{1/2})\}^{-1} + (\Lambda_0 - \lambda_0)/2\Lambda]/$$
$$\{1 + (\Lambda_0 - \lambda_0)/2\Lambda_0\} \qquad (4)$$

I indicates the ionic strength: I=1.5×c.

λ_o is 70.1 S cm^2 mol^{-1} in methanol at 25.0 °C.[11] Since, however, we had no data regarding the λ_o's at other conditions, solvents and temperatures, we calculated them on the basis of a value of 70.1. Briefly speaking, they were determined proportionally to mean Λ_o values of $Co(ClO_4)_2$, $Ni(ClO_4)_2$, and $Zn(ClO_4)_2$ at the respective conditions. The evaluation procedure of λ_o and the thermodynamic functions, $\Delta H_{1A}^{\ominus}$ and $\Delta S_{1A}^{\ominus}$, have been described in more detail elsewhere.[2]

Results and Discussion

Limiting Molar Conductances. The result of limiting molar conductances (Table 4) will be scrutinized *via* the Walden product, $\Lambda_o\eta$. Plots of the $\Lambda_o\eta$ of $Zn(ClO_4)_2$ are shown in Fig. 1 as functions of the wt% composition of methanol. As shown in this figure, there are three characteristics of the $\Lambda_o\eta$'s for all the $M(ClO_4)_2$'s. 1) $\Lambda_o\eta$ increases upon going from

Table 4. Limiting molar conductances ($S\,cm^2\,mol^{-1}$) of $1/2\,M(ClO_4)_2$ and ClO_4^- in methanol-ethylene glycol mixtures at 278.15—318.15 K

wt% Methanol	278.15 K	288.15 K	298.15 K	308.15 K	318.15 K
			$Co(ClO_4)_2$		
100	98.6±0.13	114.0±0.10	130.7±0.14	149.0±0.10	169.3±0.22
80	64.4±0.09	77.0±0.10	90.5±0.09	105.5±0.12	122.2±0.20
60	38.0±0.07	47.5±0.08	57.9±0.09	69.6±0.12	82.8±0.17
40	19.72±0.02	26.24±0.03	33.7±0.05	42.4±0.08	52.4±0.12
20	8.27±0.02	12.03±0.03	16.65±0.04	22.3±0.07	28.9±0.09
0	2.605±0.002	4.314±0.003	6.61±0.006	9.68±0.01	13.60±0.02
			$Ni(ClO_4)_2$		
100	99.2±0.13	114.7±0.08	131.5±0.12	150.0±0.16	170.6±0.17
80	64.13±0.03	76.9±0.05	90.6±0.07	106.0±0.10	123.0±0.14
60	39.3±0.05	49.2±0.05	60.2±0.09	72.7±0.10	86.7±0.17
40	20.13±0.04	26.8±0.06	34.5±0.07	43.4±0.10	53.7±0.13
20	8.43±0.01	12.26±0.02	17.01±0.03	22.80±0.04	29.7±0.06
0	2.69±0.005	4.48±0.008	6.89±0.014	10.10±0.02	14.19±0.02
			$Cu(ClO_4)_2$		
100	97.6±0.16	113.2±0.20	130.1±0.23	149.4±0.31	171.4±0.45
80	63.2±0.12	75.8±0.15	89.6±0.18	105.3±0.21	123.0±0.21
60	37.2±0.07	46.8±0.09	57.4±0.12	69.5±0.16	83.2±0.30
40	19.37±0.04	25.93±0.04	33.5±0.06	42.4±0.07	52.7±0.10
20	8.29±0.02	12.15±0.03	16.9±0.05	22.9±0.05	30.2±0.06
0	2.666±0.004	4.43±0.007	6.85±0.010	10.12±0.014	14.36±0.02
			$Zn(ClO_4)_2$		
100	95.9±0.09	110.9±0.11	127.1±0.13	145.0±0.16	164.5±0.19
80	62.7±0.15	75.1±0.17	88.4±0.22	103.2±0.27	119.6±0.31
60	36.9±0.06	46.1±0.08	56.3±0.09	67.9±0.10	81.0±0.12
40	19.45±0.03	25.85±0.04	33.2±0.05	41.7±0.07	51.3±0.11
20	8.30±0.01	12.08±0.02	16.72±0.03	22.39±0.04	29.14±0.04
0	2.637±0.004	4.38±0.005	6.74±0.008	9.88±0.012	13.90±0.02
			ClO_4^- [a]		
100	52.9	61.2	70.1[b]	80.1	90.9
80	34.5	41.3	48.6	56.8	65.8
60	20.7	26.0	31.7	38.3	45.6
40	10.7	14.3	18.3	23.1	28.4
20	4.51	6.57	9.09	12.2	15.9
0	1.43	2.38	3.66	5.37	7.54

a) Calculated according to the procedure in the text. b) Ref. 11.

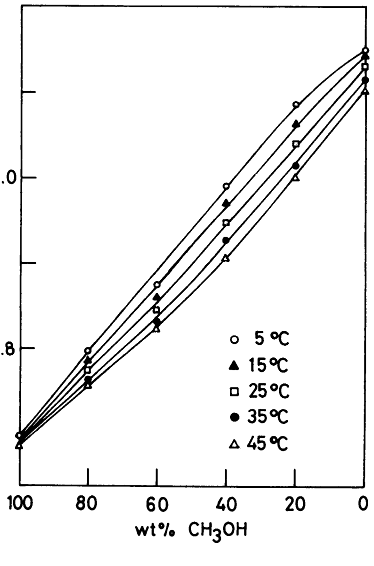

Fig. 1. The plots of Walden products of $Zn(ClO_4)_2$ against wt% of methanol at various temperatures.

methanol to EG; from 100 to 0 wt%, ($\Lambda_0\eta$'s of EG are about 1.6 times as large as those of methanol). 2) $\Lambda_0\eta$'s of all the systems except Cu in methanol decrease with an increase in temperature: negative temperature coefficients of $\Lambda_0\eta$. 3) The negative temperature coefficient (characteristic 2) is most significant at 40 wt% (in the 40 wt% mixture, $\Lambda_0\eta$'s at 5 °C are 1.06—1.09 times as large as those at 45 °C). Molar ionic conductances of these divalent metal ions are larger than those of hydrophilic structure-making ions like Li^+ and Na^+ in methanol. Probably the primary solvation shells of the M^{2+}'s are relatively firm and considerably structured in methanol.[2] We think the same situation can also be established in EG. Therefore, the M^{2+} must move with only the primary solvation shell in the solvents and the effect of the secondary solvation appears to be very small. The size of the primary solvated ion is expected to be smaller in EG than in methanol because of the high solvating power of EG.[12] Thus, this is probably a cause of

Table 5. Ionic association constants, K_{1A} (M^{-1}), of $M(ClO_4)_2$ in methanol–ethylene glycol mixtures at 278.15-318.15 K

wt% Methanol	278.15 K	288.15 K	298.15 K	308.15 K	318.15 K
		$Co(ClO_4)_2$			
100	151±7	167±4	194±6	225±4	264±8
80	153±6	160±6	166±5	174±6	193±8
60	117±8	117±8	114±7	117±8	123±10
40	92±5	85±6	78±6	75±7	78±10
20	79±7	70±8	64±9	53±12	50±12
0	61±2	64±3	55±3	54±4	52±5
		$Ni(ClO_4)_2$			
100	131±3	147±4	170±5	202±6	245±6
80	126±2	138±4	152±4	170±5	194±7
60	110±5	118±4	124±6	138±6	155±9
40	89±9	87±10	80±9	76±10	83±11
20	80±6	71±5	69±7	68±6	66±8
0	63±7	83±7	87±9	86±8	85±7
		$Cu(ClO_4)_2$			
100	143±7	166±8	201±9	257±11	336±15
80	126±8	141±9	160±9	191±9	229±9
60	86±7	95±8	107±8	124±9	137±16
40	51±7	58±6	64±7	69±7	79±8
20	54±8	56±9	63±9	77±8	99±7
0	64±5	69±6	77±5	87±5	100±6
		$Zn(ClO_4)_2$			
100	109±5	120±5	144±6	173±6	203±7
80	119±10	129±11	138±12	154±13	171±13
60	89±6	88±7	87±7	91±6	102±6
40	88±6	82±6	79±6	71±6	63±8
20	93±7	83±7	76±6	69±8	67±6
0	69±5	77±4	80±4	79±4	81±4

characteristic 1. In a previous work regarding methanol systems, a brief description concerning negative temperature coefficients was made using the thermal expansion of a solvated ion.[2] However, these coefficients are too negative in EG-rich solvents to be explained in terms of thermal expansion. According to a well known structure effect,[13] ClO_4^- (a typical structure-breaking ion) can exhibit a large negative temperature coefficient for the Walden product in EG-rich solvents, if EG is a highly structured solvent in comparison with methanol. If so, this could also be applied to an explanation of characteristic 1.

On the other hand, we think that the large negative temperature coefficients of $\Lambda_0\eta$ in EG-rich solvents might be closely related to the density, the molecular volume, and/or the compressibility of the solvents. Methanol has a larger molecular volume for its molecular structure (*cf.* introduction) and has a much higher compressibility than EG. That is to say, methanol is expected to have loose interactions and wide spaces among methanol molecules in comparison with EG. Hence, it appears that a change in the size of a solvated ion exerts a larger influence on $\Lambda_0\eta$ in dense EG than in methanol. In connection with an explanation of characteristic 1, it may be further inferred that the primary solvated M^{2+}, which moves as a single kinetic unit, exhibits a structure-breaking effect in dense and viscous (probably highly structured) EG. As shown in the density data (Table 1), mixed solvents of methanol-EG have negative excess volumes of mixing. The maximum volume decrease occurs at 40 wt%. Analogically, this may be a cause of the characteristic 3. As another cause of characteristic 3, we think that the sizes of solvated ions in the mixtures increase with a temperature increase because the proportion of methanol and EG molecules in the sheath of solvation (and/or the structure of the sheath) varies with temperature.

Ionic Association Constants. The results of K_{1A} are summarized in Table 5. Before a discussion regarding them, it is necessary to describe the difference between the previous[2] and the present results for pure methanol: in the previous study we took no account of the $1+\kappa a$ term in the conductance equation. Because the $1+\kappa a$ term has been introduced in the conductance equation of the present study (Eq. 4), the present K_{1A}'s have become larger than the previous ones though there are no changes in the order of magnitude of K_{1A}. The present values are 1.84 ($Co(ClO_4)_2$ at 45 °C) −2.45 ($Zn(ClO_4)_2$ at 5 °C) times larger than previous ones. These ratios seem to be larger, the smaller K_{1A} is, and to be smaller, the higher the temperature is. Similar results were obtained for K_{1A} of alkaline-earth metal perchlorates. Some of these have been reported elsewhere.[14]

The K_{1A} values (Table 5) will be discussed *via* the

Table 6. Thermodynamic functions of ionic association of $M^{2+}ClO_4^-$ at 298.15 K

wt% Methanol	Co	Ni	Cu	Zn	Fuoss[a]
		$\Delta H_{1A}^{\ominus}$(kJ/mol)			
100	10.7±0.7	11.7±0.6	16.1±1.1	12.1±1.0	11.6
80	4.1±1.0	8.0±0.6	11.2±1.2	6.7±1.9	10.6
60	0.9±1.6	6.3±1.1	9.1±2.2	2.6±1.6	9.4
40	−3.3±2.2	−1.9±2.8	7.7±2.6	−6.0±2.3	9.1
20	−8.8±4.1	−2.8±2.2	11.6±2.9	−6.0±2.0	8.4
0	−4.3±1.7	4.2±2.3	8.2±1.6	2.4±1.4	7.8
		$\Delta S_{1A}^{\ominus}$ (J/(K mol))			
100	79±2	82±2	98±4	82±3	81
80	56±3	69±2	80±4	64±7	76
60	43±6	62±4	69±7	46±5	70
40	25±7	30±9	60±9	16±8	68
20	5±14	26±7	73±10	16±7	63
0	20±6	51±8	64±5	44±5	59
		$\Delta G_{1A}^{\ominus}$ (kJ/mol)			
100	−13.1±0.04	−12.7±0.07	−13.1±0.10	−12.3±0.10	−12.7
80	−12.7±0.08	−12.5±0.07	−12.6±0.14	−12.2±0.21	−12.1
60	−11.7±0.16	−12.0±0.13	−11.6±0.19	−11.1±0.19	−11.5
40	−10.8±0.19	−10.9±0.29	−10.3±0.26	−10.8±0.19	−11.1
20	−10.3±0.37	−10.5±0.23	−10.3±0.36	−10.7±0.20	−10.5
0	−9.9±0.13	−11.1±0.24	−10.8±0.16	−10.9±0.13	−9.9

a) Calculated by Fuoss' theory at a distance of closest approach of 6 Å.[15]

influences of the following three variables: metal element, solvent composition, and temperature. Regarding the influences from different metal elements, there are few remarkable characteristics. According to a discussion in a previous paper,[2] these metal ions make relatively firm primary solvation shells in methanol, probably much more in EG. Therefore, it is thought that specific properties of the metal ions hardly appear in the K_{1A} values. We have to get more information concerning ionic association in order to understand the small and vague variations in K_{1A}.

The K_{1A} values tend to decrease with an increase in the EG content of the solvent; the tendency is the stronger the higher the temperature is. It is sure that such a decrease in K_{1A} is partly due to an increase in the dielectric constants of EG-rich solvents. If, however, this decrease is observed more carefully, it is found that the K_{1A} values decrease sharply up to 40 wt%, but slightly and irregularly between 40 and 0 wt% for all the salts. This can not be interpreted by the increase in dielectric constants. However, it might be explained by a view that a change in the composition and/or structure of the M^{2+} solvation shell caused by the ionic association depresses the stabilization of ion pairs M^{2+}(solvated)ClO_4^- in mixed solvents.

The temperature influence, according to the results of $\Delta H_{1A}^{\ominus}$ at 25 °C (Table 6), is complicated, but interesting. Curves of $\ln K_{1A}$ plotted as a function of T^{-1}, $d(\ln K_{1A})/d(T^{-1})=-\Delta H_{1A}^{\ominus}/R$, have various shapes in the present systems. Though there are some interesting characteristics regarding the shapes of these lines, we have too little information to discuss them here. The results of $\Delta S_{1A}^{\ominus}$ and $\Delta G_{1A}^{\ominus}$ at 25 °C are also summarized in Table 6, and their values are compared with theoretical values calculated using Fuoss' theory concerning ionic association with at the distance of closest approach (6 Å).[15] The previous results for methanol (the previous K_{1A}'s were smaller than the present ones) are compared with values calculated for a distance of 7.4 Å. This is an estimation for an ion pair $M(CH_3OH)_6^{2+}ClO_4^-$ perfectly separated by a primary solvation shell of M^{2+}.[2]

According to the results of $\Delta H_{1A}^{\ominus}$ (Table 6), only $Cu(ClO_4)_2$ has a tendency different from the other $M(ClO_4)_2$. The $\Delta H_{1A}^{\ominus}$'s of $Cu(ClO_4)_2$ (except in pure methanol) are in good agreement with the theoretical values if their errors are considered. On the other hand, the $\Delta H_{1A}^{\ominus}$'s of $M(ClO_4)_2$ (except $Cu(ClO_4)_2$) have common characteristics. $\Delta H_{1A}^{\ominus}$'s at 100 wt% are in good agreement with theoretical values. These rapidly decrease with an increase in the EG content of the solvent until 40—20 wt% (where the composition goes to 0 wt%: pure EG, those get to increase reversely). It is especially noteworthy that the $\Delta H_{1A}^{\ominus}$ values at 40—20 wt% are negative (the electrostatic theory of ionic association never gives a negative value to $\Delta H_{1A}^{\ominus}$).[2] If the positive value of $\Delta H_{1A}^{\ominus}$ (and/or the positive value of $\Delta S_{1A}^{\ominus}$) is explained by the fact that a solvation of M^{2+} is weakened by the ion pairing of $M^{2+}ClO_4^-$, the small $\Delta H_{1A}^{\ominus}$, including the negative one, (and the small $\Delta S_{1A}^{\ominus}$) in EG rich solvents will probably mean that the degree of the weakening of the M^{2+} solvation is small because of the high solvating power of EG. The very small values of $\Delta H_{1A}^{\ominus}$ at 40—20 wt% may also be explained by the view that the enthalpic instabilization of a M^{2+} solvation attended by $M^{2+}ClO_4^-$ ion pairing is depressed due to the change in the composition and/or the structure of the solvation shell (simultaneously an entropic stabilization is depressed considerably). On the other hand, the positive $\Delta H_{1\text{A}}^{\ominus}$ of Cu probably has some relation to a Jahn-Teller distortion of its solvation shell,[2] though we can not present a detailed discussion now.

As mentioned in the discussion regarding $K_{1\text{A}}$, the $\Delta G_{1\text{A}}^{\ominus}$ values of all the $\text{M(ClO}_4)_2$ are similar to each other, and are in good agreement with the theoretical values. That is to say, because $\Delta S_{1\text{A}}^{\ominus}$ mutually complements $\Delta H_{1\text{A}}^{\ominus}$ for $\Delta G_{1\text{A}}^{\ominus}$, the results of $\Delta S_{1\text{A}}^{\ominus}$ will also support the above discussion for the results of $\Delta H_{1\text{A}}^{\ominus}$. Moreover, it is very interesting that the values of both $\Delta H_{1\text{A}}^{\ominus}$ and $\Delta S_{1\text{A}}^{\ominus}$ have been in the sequence of $\text{Co}<\text{Ni}<\text{Cu}>\text{Zn}$ in all the solvents. In order to understand this, it will be necessary to make further investigations.

In conclusion, the primary solvated M^{2+} moves as a single kinetic unit and the secondary solvation only gives small effects on the Walden products of M^{2+} in the solvents. The size of the primary solvated M^{2+} will be smaller in EG-rich solvents than in methanol because of the high solvating power of EG. In EG-rich solvents, furthermore, the primary solvated M^{2+} may be rather a structure breaker. Thus, the Walden products of $\text{M(ClO}_4)_2$ probably result in the large values for EG-rich solvents. A strong solvation of M^{2+} with EG also causes a small $\Delta H_{1\text{A}}^{\ominus}$. We thus suggest that the $\Delta H_{1\text{A}}^{\ominus}/\Delta G_{1\text{A}}^{\ominus}$ ratio increases with an increase in the solvating power of a solvent. In mixed solvents, especially in 40 or 20 wt%, it seems that the composition and/or structure of the solvation shell of M^{2+} varies with temperature and/or with the ionic association. If so, such a variation in the solvation shell must cause the large negative temperature coefficients of the Walden products, and must cause the small $\Delta H_{1\text{A}}^{\ominus}$ and $\Delta S_{1\text{A}}^{\ominus}$ (and also maybe the slightly small $\Delta G_{1\text{A}}^{\ominus}$ as a result of complementarity between $\Delta H_{1\text{A}}^{\ominus}$ and $\Delta S_{1\text{A}}^{\ominus}$). The negative temperature coefficients of the Walden products may also result from the fact that ClO_4^- is a structure-breaking ion.

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