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# Specific coordination phenomena of alkaline earth metal ions with aromatic sulfonate ions in alcohols and binary solvents of acetonitrile–alcohols



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# ABSTRACT

The specific interactions between alkaline earth metal ( $Mg^{2+}$ ,  $Ca^{2+}$ , or  $Ba^{2+}$ ) and *p*-toluenesulfonate ( $L^{-}$ ), 1,5naphthalenedisulfonate  $(L^{2-})$ , or 1,3,6-naphthalenetrisulfonate  $(L^{3-})$  ions (from the tetraethylammonium salt of  $L^{-}$ ,  $L^{2-}$ , or  $L^{3-}$ ) have been examined by means of UV-visible spectroscopy in primary alcohols (from methanol to hexanol) as well as in the binary acetonitrile-alcohols (MeCN-MeOH, MeCN-EtOH), ethanol-methanol (EtOH-MeOH) and methanol-water (MeOH-H<sub>2</sub>O) solvents. The precipitation of non-charged species (e.g.  $ML^0$ ) and the successive re-dissolution of the precipitates, with increasing concentration of  $M(ClO_4)_2$ . have revealed the formation of cationic charged species or "reverse coordinated" species, M<sub>2</sub>L<sup>2+</sup>, even in the protic media as well as in the aprotic solvent MeCN. The solubility products  $(K_{sp})$  and the "reverse coordination" constants  $(2M^{2+} + L^{2-} = M_2L^{2+}, K_{2(-2)} = [M_2L^{2+}] / [M^{2+}]^2 [L^{2-}])$  have been evaluated. In ethanol, both phenomena of the precipitation of ML<sup>0</sup> and the successive re-dissolution to produce  $M_{2}L^{2+}$  are observed for Ca<sup>2+</sup> + or  $Ba^{2+}$ , but not for  $Mg^{2+}$ . In butanol, the interaction between  $Mg^{2+}$  and the  $L^{2-}$  causes the complete precipitation of MgL<sup>0</sup> ( $pK_{sp} = 10.39$ ) and also the successive re-dissolution of Mg<sub>2</sub>L<sup>2+</sup> ( $\log K_{2(-2)} = 8.08$ ). Even in methanol, the interaction between  $Ba^{2+}$  and  $L^{2-}$  results in precipitation  $(\log K_{sp} = 8.28)$  and the "reverse coordinated" species,  $Ba_2L^{2+}$  ( $\log K_{2(-2)} = 5.58$ ). The interaction of  $Ba^{2+}$  with  $L^-$  or  $L^{3-}$  causes no precipitation in methanol; however, in all the other alcohols, it results both in precipitation (BaL<sub>2</sub> or Ba<sub>3</sub>L<sub>2</sub>) and the "reverse coordinated" species,  $BaL^+$  or  $Ba_2L^+$ . The formulation for the formation constants  $(K_{2(-3)})$  for  $M^{2+}$  and  $L^{3-}$  is newly presented and the constants  $(2Ba^{2+} + L^{3-} \Rightarrow Ba_2L^+, K_{2(-3)} = [Ba_2L^+] / [Ba^{2+}]^2 [L^{3-}])$  are evaluated in ethanol and propanol as well as in the binary EtOH-MeOH solvents, up to 70% (v/v) MeOH. The donicities toward  $M^{2+}$  of the media have been related to the  $pK_{sp}$  and "reverse coordination" constants for L<sup>-</sup>, L<sup>2-</sup> and L<sup>3-</sup>

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# 1. Introduction

The association modes of metal ions and anions in various solvents have acquired great attention due to their extensive use in many areas of fundamental research, e.g. the evaluation of major physicochemical properties of solution [1], mechanistic studies in organic chemistry and supramolecular chemistry [2], and the prediction of drug solubility and chemical stability in pharmaceutical sciences [3]. Recently, the coordination reactions of the alkali metal and alkaline earth metal ions have been extensively investigated, due to their widespread application in the industry, their importance in maintaining the ionic equilibrium of the human body and especially their relevance in pharmaceutics [4]. The mixtures of aqueous–organic or organic–organic mixed solvents find a broad application in industries such as the manufacture of paints to detergents and deodorants [5] and enable the variation of properties for studying the ion–ion and ion–solvent interactions [6].

It is a common idea that the alkali metal or alkaline earth metal salts in low concentrations as electrolytes totally disassociate in aqueous solution. Through the series of studies, however, we have demonstrated that the specific interaction between alkali metal or alkaline earth metal ions and simple anions can operate in non-aqueous solvents by means of conductometry [7], polarography [8], UV–visible [9], <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic methods [10]. The formation of both the coordinated and the "reverse-coordinated" species in aprotic solvents has been proposed [11]: with half-equivalent amount of LiClO<sub>4</sub> or NaClO<sub>4</sub> added to carboxylate ions (L<sup>-</sup>) [12], the direct coordinated species (ML<sub>2</sub><sup>-</sup>) may form; however, precipitation (ML<sup>0</sup>) takes place in the presence of an equivalence of the metal ion, which is followed by the re-dissolution of the precipitates, due to the formation of the "reversecoordinated" species (M<sub>2</sub>L<sup>+</sup>), with increasing metal concentration.

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Although it is generally acknowledged that alkali metal or alkaline earth metal ions exhibit no coordination ability in dilute aqueous solution, aside from the chelate formation of alkaline earth metal ions with a powerful chelate reagent, such as EDTA (ethylenediamine-N, N', N'-tetraacetic acid), these metal ions may exhibit a more covalent character similar to transition metal compounds when polar organic solvents are used [13].

Acetonitrile (MeCN) is an archetype for dipolar aprotic solvents with simple molecular structure, which has attracted considerable interest in the study of the interplay between ion solvation and association of electrolyte solutions [14]. Acetonitrile of a relatively high permittivity ( $\varepsilon_r = ca. 36$ ) [15] is not only an aprotic solvent but also a protophobic solvent [16], having poor solvation ability (DN = 14.1, AN = 19.3 [17], cf. Table 1) toward both metal cations and anions. In many aprotic solvents, including MeCN, of higher permittivities, it has been reported [11] that the higher ion-aggregates, triple ions and quadrupoles, can be produced from trialkylammonium halides,  $R_3NH^+X^-$ , lithium trifluoroacetate, etc., basically through hydrogen bonding and coordination forces, respectively. The higher ion-aggregation from lithium fluoroalkanoates has been conclusively evidenced in another protophobic aprotic solvent, propylene carbonate [19] with the high permittivity of ca. 65 [15].

Contrastingly, protic solvents, such as water and primary alcohols with relatively higher donicity and acceptivity (Table 1), can strongly solvate both cations and anions. Even very small amounts of water (~0.5%) added to acetonitrile can significantly influence the coordination reaction between magnesium and *p*-toluenesulfonate ions [9b]. Although the permittivities of many primary alcohols (EtOH, 1-PrOH, 1-BuOH, 1-HexOH) are lower than that of MeCN, the donor (DN) and acceptor (AN) numbers of the alcohols under bulk conditions are much larger than those of MeCN (Table 1). Only ion pair formation has been found between Li<sup>+</sup> and the tropolonate ion (C<sub>7</sub>H<sub>5</sub>O<sub>2</sub><sup>-</sup>) in methanol [9a]. The actual donicity of bulk methanol (DN = 31.3 [18]) is much higher than the original value (DN = 20) reported by Gutmann [17].

Some sulfonic acids, such as methanesulfonic and *p*-toluenesulfonic acids, have been observed to be weak acids in benzonitrile (DN = 11.9, AN = 15.5) to form the 1:2-type homoconjugated species by means of conductometry [20]. Meanwhile, conductometric titrations with Et<sub>3</sub>N of di- and trisulfonic acids in MeCN have revealed the strong homoconjugation for the di- and trisulfonic acids [21]. In the previous study [9b], the precipitation and re-dissolution reactions of alkali metal ( $Li^+$ ,  $Na^+$ ) or alkaline earth metal ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ) ions with *p*-toluensulfonate and 1,5-, 2,6-, and 2,7-naphthalenedisulfonate ions in MeCN have been examined by means of UV spectroscopy. The addition of small amounts of water has influenced the specific reactions so strongly.

In the present work, the chemical interaction of alkaline earth metal ions  $(Mg^{2+}, Ca^{2+}, Ba^{2+})$  with *p*-toluensulfonate  $(L^{-})$ , 1,5-

Table 1	
Properties of the solvents concer	rned to the present study

-1	1	5	
Solvents	DN <sup>a</sup>	AN <sup>a</sup>	$\varepsilon_r^{b}$
Acetonitrile (MeCN)	14.1	19.3	35.94
Water (H <sub>2</sub> O)	40.3 <sup>c</sup> , 18.0 <sup>d</sup>	54.8	78.36
Methanol (MeOH)	31.3 <sup>c</sup> , 19 <sup>d</sup>	41.3	32.66
Ethanol (EtOH)	27.8 <sup>c</sup> , 20 <sup>d</sup>	37.1	24.55
Propanol (1-PrOH)	(27) <sup>e</sup>	-	20.45
Butanol (1-BuOH)	26.2 <sup>c</sup>	-	17.51
Hexanol (1-HexOH)	-	-	13.3

<sup>a</sup> Gutmann's donor and accepter number, Ref. [17].

<sup>b</sup> The permittivity values cited from Ref. [15].

<sup>c</sup> For bulk water, methanol and ethanol, Ref. [18].

<sup>d</sup> Isolated H<sub>2</sub>O and ROH molecules (not as the bulk solvents) in 1,2-dichloroethane, Ref. [17].

<sup>e</sup> Estimated from the donor numbers of MeOH and EtOH.

naphthalenedisulfonate (L<sup>2-</sup>), and 1,3,6-naphthalenetrisulfonate (L<sup>3-</sup>) ions (cf. Chart 1) in primary alcohols as well as MeCN is investigated by means of UV spectroscopy. The interactions between the alkaline earth metal and 1,5-naphthalenedisulfonate ions are carefully examined in binary mixed solvents of MeCN–MeOH, MeCN–EtOH, and even EtOH–MeOH and MeOH–H<sub>2</sub>O. The solubility products and "reverse coordination" constants have been successfully evaluated for the systems.

#### 2. Experimental section

#### 2.1. Chemicals

Tetraethylammonium *p*-toluenesulfonate was purchased from Aldrich. Tetraethylammonium 1,5-naphthalenedisulfonate was prepared as the previous method [9b]: A 1.0 g of 1,5-naphthalenedisulfonic acid tetrahydrate (Aldrich) was dissolved in methanol and was titrated with Et<sub>4</sub>NOH (20 wt.% in H<sub>2</sub>O, Aldrich) in methanol up to the equivalence point. The solution was evaporated to dryness at 50 °C, and the salt was dried in vacuo at 150 °C. Tetraethylammonium 1,3,6-naphthalenetrisulfonate was prepared from 1,3,6-naphthalenetrisulfonic acid in a similar method. However, the 1,3,6-naphthalenetrisulfonate was dried at 120 °C in vacuo, and the conductometric titration with trifluoromethanesulfonic acid suggested that the hydrated waters in the salts can be negligible.

1,3,6-Naphthalenetrisulfonic acid was prepared from the sodium salt as follows: 35 g of sodium 1,3,6-naphthalenetrisulfonate (purchased from TCI Shanghai, Chemical, China) was dissolved in pure water of 2 L, and the sodium ions were exchanged to protons with an ion-exchange column. The Na<sup>+</sup> concentration was determined by an atomic absorption spectrophotometer and was kept to be less than 0.1  $\mu$ g/mL. The elute solution was evaporated to dryness in a rotary evaporator at <35 °C, and the acid crystals were dried in vacuo at 35 °C.

Metal perchlorates without water,  $Mg(ClO_4)_2$  and  $Ba(ClO_4)_2$  (all Aldrich), were used as received. Calcium perchlorate tetrahydrate from Aldrich was dried in vacuo at 150 °C to obtain anhydrous  $Ca(ClO_4)_2$ . Commercially obtained acetonitrile (MeCN) solvents of GR and super dehydrated grades (Wako), containing <0.1 and <0.001% (v/v) H<sub>2</sub>O, respectively, were used as received. Alcohols (MeOH, EtOH, 1-PrOH, 1-BuOH, 1-HexOH) all from Wako were used. The water contents are certificated <0.1% (v/v) in MeOH and <0.2% (v/v) in all the other alcohols. Water was purified by means of a MilliQ system (Millipore Corp.). The percentage of a solvent in binary solvents is all expressed by the volume fraction [% (v/v)] in the present paper.

#### 2.2. Apparatus and procedure

UV-visible absorption spectra were measured at room temperature using a Shimadzu double-beam spectrophotometer (model UV-2550) in a 0.1 cm path-length quartz cuvette. When precipitation occurred, the solution was sonicated for a few minutes in a Branson ultrasonic bath (model Yamato 2510, 42 kHz and 125 W) and the supernatant solution was measured after centrifugation. Sometimes, a long aging time was needed to complete a precipitation reaction.

# 2.3. Evaluation of "reverse coordination" formation constants

The "reverse coordination" formation constants between the metal cations ( $M^{2+}$ ) and the "ligand" anions ( $L^-$ ,  $L^{2-}$ ) are evaluated by the UV–visible spectroscopic data as the method previously proposed [9b]. The formation constants of "reverse coordination" between the alkaline earth metal cations ( $M^{2+}$ ) and the 1,3,6-naphthalenetrisulfonate ion ( $L^{3-}$ ) are evaluated as follows.

The equilibrium constants for the precipitation reaction (the solubility products,  $K_{sp}$ ) and "reverse coordination" ( $K_{2(-3)}$ ) at higher M<sup>2+</sup> concentrations, compared to  $L^{3-}$ , are expressed by Eqs. (1) and (2), respectively.

$$M_{3}L_{2} = 3M^{2+} + 2L^{3-}, K_{sp} = \left[M^{2+}\right]^{3} \left[L^{3-}\right]^{2},$$
 (1)

$$2M^{2+} + L^{3-} \rightleftharpoons M_2 L^+, \quad K_{2(-3)} = \left[M_2 L^+\right] / \left(\left[M^{2+}\right]^2 \left[L^{3-}\right]\right).$$
(2)

The solubility *s* of  $M_3L_2$  or the total "ligand" concentration,  $c_t$ , in solution (and not in precipitation) is expressed by Eq. (3).

$$s = c_{t} = \left[L^{3-}\right] + \left[M_{2}L^{+}\right] = \sqrt{K_{sp}\left[M^{2+}\right]^{-3}} \left(1 + K_{2(-3)}\left[M^{2+}\right]^{2}\right).$$
(3)

The observed absorbance  $A_{bs}$  of  $L^{3-}$  (and  $M_2L^+$ ) can be rationalized by Lambert–Beer's law as,

$$A_{bs} = \varepsilon c l \sim \varepsilon s l \tag{4}$$

where  $\varepsilon$ , c, and l are the molar absorptivity (cm<sup>-1</sup> mol<sup>-1</sup> dm<sup>3</sup>) of L<sup>3-</sup> (or M<sub>2</sub>L<sup>+</sup>), the concentration (mol dm<sup>-3</sup>), and the path-length (cm), respectively. Eq. (5) is given by introducing Eq. (3) into Eq. (4).

$$A_{bs} = \varepsilon l \sqrt{K_{sp} [M^{2+}]}^{-3} \quad \left(1 + K_{2(-3)} [M^{2+}]^2\right)$$
(5)

Actually, with higher M<sup>2+</sup> concentrations and larger  $K_{2(-3)}$  values, Eq. (5) can be arranged to be  $A_{bs} = \varepsilon l \sqrt{K_{sp} \left[ M^{2+} \right] K_{2(-3)}}$ .

#### 3. Results and discussion

3.1. The specific interactions between alkaline earth metal and 1,5-naphthalenedisulfonate  $(L^{2-})$  ions in alcohols

We [9b] have already reported that Mg<sup>2+</sup> interacts with the 1,5naphthalenedisulfonate ion  $(L^{2-})$  to form the 1:1 precipitation (MgL), and the precipitation is successively re-dissolved (Mg<sub>2</sub> $L^{2+}$ ) by the addition of a large excess of  $Mg(ClO_4)_2$  in MeCN, whereas Ca<sup>2+</sup> and Ba<sup>2+</sup> ions can scarcely produce the soluble species of  $M_2L^{2+}$  from the precipitates in the same solvent. In protophobic aprotic solvents, such as MeCN (DN = 14.1, AN = 19.3[17]) [9b] and acetone (DN = 17.0, AN = 12.5 [17]) [9a,22], due to the lower donicity, the alkali metal cations (especially Li<sup>+</sup>) have a good opportunity to interact with simple anions (excluding  $ClO_4^-$ ,  $PF_6^-$ , etc.) to form not only the coordination-type species  $(LiL_2^-)$  and the ion pair  $(LiL^{0})$  but also the "reverse-coordinated" species  $(Li_{2}L^{+})$ . Conversely, such specific interactions between Li<sup>+</sup> and mono-charged anions have not been detected in the solvents of relatively high donicity, such as MeOH (DN = 31.3, AN = 41.3, cf. Table 1) [9a], DMF (DN = 26.6 [17]) and DMSO (DN = 29.8 [17]) [22]. Furthermore, the chemical interaction between metal cations and anions could be largely inhibited by addition of the protic solvents, such as H<sub>2</sub>O or MeOH, to MeCN [9].

However, even in ethanol of relatively high donicity, the precipitation and successive re-dissolution phenomena between Ba<sup>2+</sup> and L<sup>2-</sup> are observed (Fig. 1). Tetraethylammonium 1,5-naphthalenedisulfonate [(Et<sub>4</sub>N<sup>+</sup>)<sub>2</sub>L<sup>2-</sup>] has given a strong band at 228 nm ( $\varepsilon$ /cm<sup>-1</sup> mol<sup>-1</sup> dm<sup>3</sup> = 6.1 × 10<sup>4</sup>) and a smaller band at around 290 nm in MeCN [9b]. In EtOH, the wavelength of strong peak of L<sup>2-</sup> ( $\lambda_{max} = 227.5$  nm) is almost the same or just slightly shorter than that in MeCN. With increasing concentration of Ba(ClO<sub>4</sub>)<sub>2</sub>, the absorbance at around 227 nm decreases gradually, and the band suddenly disappears in the presence of an equivalence of Ba<sup>2+</sup>,  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>, which is accompanied by the complete precipitation. However, the successive re-dissolution of precipitates takes



**Fig. 1.** The UV spectra of  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> 1,5-naphthalenedisulfonate (0.1 cm pathlength) in EtOH with increasing concentration of Ba(ClO<sub>4</sub>)<sub>2</sub>.

place with further increasing  $Ba^{2+}$  concentration, which should be caused by the formation of the "reverse-coordinated" species of  $Ba_2L^{2+}$ . Whereas, those of BaL have never been re-dissolved by a large excess amount of  $Ba^{2+}$  in MeCN [9b], as mentioned above.

Fig. 2 shows the changes in absorbance (at  $\lambda_{max}$ ) of  $L^{2-}$  with increasing concentration of alkaline earth metal ions (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>) in ethanol. Neither the precipitation (nor the re-dissolution) occurs between Mg<sup>2+</sup> and L<sup>2-</sup> in EtOH, whereas Mg<sup>2+</sup> can interact with L<sup>2-</sup> to form precipitates of MgL and the "reverse coordinated" species of Mg<sub>2</sub>L<sup>2+</sup> in MeCN [9b]. The precipitation between Ca<sup>2+</sup> and L<sup>2-</sup> takes place at the equivalence point, however, the precipitates begin to redissolve after 0.01 mol dm<sup>-3</sup> Ca<sup>2+</sup> and completely re-dissolve at 1.0 mol dm<sup>-3</sup> Ca(ClO<sub>4</sub>)<sub>2</sub>. The precipitates of CaL are apt to re-dissolve successively to form Ca<sub>2</sub>L<sup>2+</sup> more easily than those of BaL, therefore, the values of "reverse coordination" constant (Table 2), log K<sub>2</sub>, for Ca<sub>2</sub>L<sup>2+</sup> and Ba<sub>2</sub>L<sup>2+</sup> are given to be 7.49 and 7.11, respectively. In the present paper, for simplicity, we may describe log K<sub>2</sub> and not log K<sub>2(-2)</sub> for the "reverse coordination" constants between M<sup>2+</sup> and L<sup>2-</sup> unless some confusion is anxious.

The interaction of the alkaline earth metal ions with the 1,5naphthalenedisulfonate ion ( $L^{2-}$ ) in EtOH seems to be apparently different from that in MeCN, cf. Ref. [9b]. For the first time, however, we have discovered the specific interaction ( $M_2L^{2+}$ ) between the alkaline earth metal ions ( $M^{2+}$ ) and a divalent anion ( $L^{2-}$ ) in a protic solvent. Scheme 1 shows the reaction scheme for the precipitation of ML (M = Ca and Ba) and the successive re-dissolution of the precipitates in EtOH.

The interactions between alkaline earth metal ions and  $L^{2-}$  in other primary alcohols (MeOH, 1-PrOH, 1-BuOH) were also examined. Fig. 3



**Fig. 2.** Changes in absorbance ( $\lambda_{max}$  = ca. 227 nm) of  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> 1,5naphthalenedisulfonate ion with increasing concentration of alkaline earth metal ions in EtOH: ( $\bigcirc$ ) Mg(ClO<sub>4</sub>)<sub>2</sub>; ( $\bullet$ ) Ca(ClO<sub>4</sub>)<sub>2</sub>; ( $\blacktriangle$ ) Ba(ClO<sub>4</sub>)<sub>2</sub>.

# Table 2

Precipitation and re-dissolution reactions of alkaline earth metal and 1,5-naphthalenedisulfonate  $(L^{2-})$  ions in acetonitrile and alcohols.

Metal ions <sup>a</sup>	Equilibrium constants <sup>b</sup>	MeCN	MeOH	EtOH	1-PrOH	1-BuOH
Mg <sup>2+</sup>		•	No	No		•
	$(pK_{sp})$	10.92	-	-		10.39
	$(\mathbf{p}\mathbf{K}_{sp})^{c}$	11.11	-	-		10.93
		0	No	No		0
	$\log K_2$	7.15	-	-		8.08
Ca <sup>2+</sup>		•	<b>A</b>	•		•
	$(pK_{sp})$	> 9.82	8.26	10.74		10.80
	$(\mathbf{p}\mathbf{K}_{sp})^{c}$	>10.01	8.47	11.07		11.34
		No	0	0		$\triangle$
	log K <sub>2</sub>	-	5.60	7.49		7.04
Ba <sup>2+</sup>		•	<b>A</b>	•	•	•
	$(pK_{sp})$	> 9.82	8.28	11.00	10.62	10.89
	$(\mathbf{p}\mathbf{K}_{sp})^{c}$	>10.01	8.49	11.33	11.06	11.43
	*	No	0	0	$\triangle$	No
	log K <sub>2</sub>	-	5.58	7.11	-	-

*Explanatory notes*: Solid circles and triangles represent apparent complete and partial precipitation, respectively. The complete precipitation means here that the absorbance of the "ligand" anion  $(L^{2-})$  reaches <1/10 of the initial value at the equivalent or any amount of a metal ion. Open circles and triangles represent complete and partial redissolution of precipitation, respectively. The mark "No" indicates no precipitation or no re-dissolution.

<sup>b</sup> Solubility products ( $K_{sp}$ ) and "reverse coordination" constants ( $K_2$ ), cf. the Experimental section in Ref. [9b]. The uncertainties (errors) in  $K_{sp}$  values and "reverse coordination" constants may be less than  $\pm 0.01$  and  $\pm 0.05$ , respectively, in this table and Tables 3–4.

<sup>c</sup> Thermodynamic solubility products ( $K_{sp}$ ) corrected with the activity coefficients of ions. The mean activity coefficients of ions are evaluated from the limiting Debye–Hückel equation, log  $\gamma_{\pm} = -A|Z_{+}Z_{-}|\mu^{1/2}$ , cf. Ref. [28].

shows the differences in the interaction between  $Mg^{2+}$  and  $L^{2-}$  in EtOH and 1-BuOH, and in MeCN as the reference solvent. In MeCN, the precipitation completes at an equivalence of  $Mg^{2+}$ , and then re-dissolves completely in the presence of 1.0 mol dm $^{-3}$  Mg(ClO<sub>4</sub>)<sub>2</sub>. In EtOH, however, the absorbance (at  $\lambda_{max}$ ) of  $L^{2-}$  is almost unchanged with the increasing Mg $^{2+}$  concentration (vide supra), indicating that no apparent interaction takes place between Mg $^{2+}$  and  $L^{2-}$ . In 1-BuOH, the complete precipitation occurs at an equivalence of Mg $^{2+}$ , and the precipitates begin to re-dissolve at a 10-fold concentration of Mg $^{2+}$  added to the  $1.0 \times 10^{-4}$  mol dm $^{-3}$   $L^{2-}$  solution.

In the aprotic solvent, MeCN, the calcium ion has been found to cause the complete precipitation at an equivalence to  $L^{2-}$ ; however, CaL precipitates have never re-dissolved by a large excess amount of Ca(ClO<sub>4</sub>)<sub>2</sub>, cf. Ref. [9]. Fig. 4 shows that, in a protic solvent, MeOH, Ca<sup>2+</sup> can react with  $L^{2-}$  to cause partial precipitation of CaL. The absorbance (at  $\lambda_{max}$ ) of  $L^{2-}$  begins to decrease at 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup> of



Scheme 1. Successive formation of ML and  $M_2L^{2+}$  (M = Ca and Ba) for the 1,5-naphthalenedisulfonate ion in EtOH.



**Fig. 3.** Changes in absorbance ( $\lambda_{max} = ca. 227 \text{ nm}$ ) of  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  1,5naphthalenedisulfonate ion with increasing concentration of Mg(ClO<sub>4</sub>)<sub>2</sub> in different solvents: ( $\bullet$ ) EtOH; ( $\triangle$ ) 1-BuOH; ( $\bigcirc$ ) MeCN.

 $Ca^{2+}$ , and the absorbance minimum of 0.126 is given in the presence of  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> Ca<sup>2+</sup>. Apparently, the excess amounts of Ca<sup>2+</sup> to L<sup>2-</sup> assist the precipitation reaction.

In EtOH, an equivalent amount of Ca<sup>2+</sup> actually has caused the complete precipitation. At any rate, the precipitates would re-dissolve completely by an excess amount of Ca(ClO<sub>4</sub>)<sub>2</sub> in both MeOH and EtOH. The precipitation of CaL in 1-BuOH takes place to a larger extent than in MeOH or EtOH. The pK<sub>sp</sub> values of CaL increased in the order of MeOH < EtOH < 1-BuOH (cf. Table 2). Unfortunately, the solubility of Ca(ClO<sub>4</sub>)<sub>2</sub> in 1-BuOH ( $\varepsilon_r$  = ca. 17.5) is not enough to examine at 1.0 mol dm<sup>-3</sup> Ca(ClO<sub>4</sub>)<sub>2</sub>.

Fig. 5 shows that the interaction of  $Ba^{2+}$  with  $L^{2-}$  is similar to that of  $Ca^{2+}$  in MeOH, apart from that the precipitation of BaL takes place to a larger extent than CaL. The absorbance minimum (at  $\lambda_{max}$ ) of 0.076 is given by the addition of  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup> Ba<sup>2+</sup>. As the permittivities and donor numbers of primary alcohols decrease, the precipitation proceeds more completely but the formation of the "reverse-coordinated" species seems to become more difficult: the absorbance (at  $\lambda_{max}$ ) are 0.372, 0.069, 0.061 in EtOH, 1-PrOH and 1-BuOH, respectively, in the presence of 0.5 mol dm<sup>-3</sup> Ba(ClO<sub>4</sub>)<sub>2</sub>.

# 3.2. In the binary solvents of MeCN–MeOH and MeOH–H<sub>2</sub>O

Fig. 6 shows the precipitation and the successive re-dissolution of MgL in the binary MeCN–MeOH solvents. In the 10% (v/v) MeOH mixed solvent, the precipitation takes place incompletely, compared to that in sole MeCN, and the successive re-dissolution of MgL is much promoted: the re-dissolution of MgL precipitates begins as low



**Fig. 4.** Changes in absorbance ( $\lambda_{max} = ca. 227 \text{ nm}$ ) of  $1.0 \times 10^{-4} \text{ mol dm}^{-3} 1,5-$  naphthalenedisulfonate ion with increasing concentration of Ca(ClO<sub>4</sub>)<sub>2</sub> in different solvents: ( $\bullet$ ) MeOH; ( $\Delta$ ) EtOH; ( $\Delta$ ) 1-BuOH; ( $\bigcirc$ ) MeCN.



**Fig. 5.** Changes in absorbance  $(\lambda_{max} = ca. 227 \text{ nm})$  of  $1.0 \times 10^{-4} \text{ mol dm}^{-3} 1,5-$  naphthalenedisulfonate ion with increasing concentration of Ba(ClO<sub>4</sub>)<sub>2</sub> in different solvents: ( $\bullet$ ) MeOH; ( $\triangle$ ) EtOH; ( $\blacktriangle$ ) 1-PrOH; ( $\square$ ) 1-BuOH; ( $\bigcirc$ ) MeCN.

as  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> Mg<sup>2+</sup>. The pK<sub>sp</sub> value and the "reverse coordination" constants are listed in Table 3. The interaction between the divalent cation and the divalent anion is almost inhibited in the 20% MeOH. In the previous paper [9b], we have reported that the addition of small amounts of water (1.0–5.0%) to MeCN tend to inhibit the Mg<sub>2</sub>L<sup>2+</sup> species to form from the MgL<sup>0</sup> precipitates, although the precipitation of the non-charged species itself was not so much influenced by these additional waters and that the addition of 10% water or more than that causes an increase of solubility of the MgL salt without assisting the formation of the Mg<sub>2</sub>L<sup>2+</sup> species. We have also reported that the effect of water upon the specific interaction between Li<sup>+</sup> and the tropolonate ion in MeCN is similar to but much more distinct than that of MeOH [9a].

Fig. 7 shows the precipitation and the successive re-dissolution of CaL in MeCN–MeOH and MeOH–H<sub>2</sub>O mixtures. In sole MeCN, the precipitates of CaL have formed completely at an equivalent amount of Ca<sup>2+</sup>, and CaL precipitates have been found not to be re-dissolved even by the large excess amount of Ca(ClO<sub>4</sub>)<sub>2</sub> [9b]. When 20% MeOH are added to MeCN, the precipitation and re-dissolution phenomena are not influenced so much: the precipitates form completely at an equivalence of Ca<sup>2+</sup> and are just partly re-dissolved by the addition of 1.0 mol dm<sup>-3</sup> Ca(ClO<sub>4</sub>)<sub>2</sub>. With increasing contents of MeOH, the precipitation reaction becomes incomplete and at the same time the re-dissolution is promoted. Calcium perchlorate of 1.0 mol dm<sup>-3</sup> causes the complete recovery in absorbance as the MeOH content in the solvent reaches 70% (cf. also Table 3).



**Fig. 6.** Changes in absorbance ( $\lambda_{max} = ca. 227 \text{ nm}$ ) of  $1.0 \times 10^{-4} \text{ mol dm}^{-3} 1,5-$  naphthalenedisulfonate ion with increasing concentration of Mg(ClO<sub>4</sub>)<sub>2</sub> in MeCN–MeOH mixtures: ( $\bigcirc$ ) 0; ( $\bigcirc$ ) 10; ( $\triangle$ ) 20; ( $\blacktriangle$ ) 50% (v/v) of MeOH.

#### Table 3

Precipitation	and	re-dissolution	reactions	between	alkaline	earth	metal	and	1,5-
naphthalened	isulfo	onate (L <sup>2-</sup> ) ions	in binary N	MeCN-Me	OH and N	leOH-l	H <sub>2</sub> O sol	vents	

Metal ion <sup>a</sup>	Equilibrium constants <sup>b</sup>						
MeCN-MeOI	H [MeOH contents/% (v/v)]	10	50	70	75	80	100
Mg <sup>2+</sup>		•	No	No	No	No	No
	$(pK_{sp})$	10.18	-	-	-	-	-
	(p <b>K</b> <sub>sp</sub> ) <sup>c</sup>	10.38	-	-	-	-	-
		0	No	No	No	No	No
	log K <sub>2</sub>	8.15	-	-	-	-	-
Ca <sup>2+</sup>		•	•	<b>A</b>	-	<b>A</b>	<b>A</b>
	$(pK_{sp})$	-	10.19	9.17	-	8.55	8.26
	$(\mathbf{p}\mathbf{K}_{sp})^{c}$	-	10.39	9.37	-	8.76	8.47
		No	$\bigtriangleup$	0	-	0	0
	$\log K_2$	-	-	5.45	-	5.52	5.60
Ba <sup>2+</sup>		•	•	•	•	•	<b>A</b>
	$(pK_{sp})$	-	9.20	8.74	8.47	-	8.28
	$(\mathbf{p}\mathbf{K}_{sp})^{c}$	-	9.40	8.95	8.68	-	8.49
		No	No	$\bigtriangleup$	0	0	0
	log K <sub>2</sub>	-	-	-	5.20	-	5.58
MeOH-H <sub>2</sub> O [	$H_2O$ contents/% (v/v)]	1.0	2.0	5.0	20	30	50
Ba <sup>2+</sup>		•	•	•	•		No
	$(pK_{sp})$	9.22	9.39	9.48	7.82	6.51	-
	$(\mathbf{p}\mathbf{K}_{sp})^{c}$	9.43	9.56	9.68	7.97	6.64	-
	* *	0	$\triangle$	No	No	No	No
	log K <sub>2</sub>	5.46	5.25	-	-	-	-

For the Explanatory notes, cf. Table 2.

<sup>a</sup>  $M(ClO_4)_2$ .

<sup>b</sup> Solubility products ( $K_{sp}$ ) and "reverse coordination" constants ( $K_2$ ), cf. the Experimental section in Ref. [9b].

<sup>c</sup> Cf. Table 2, note c) for the thermodynamic solubility products ( $K_{sp}$ ) corrected with the activity coefficients of ions.

We have proposed that the properties of the residual amount water in (aprotic) organic solvents should resemble to an ether [11,23], and we have termed it "dihydrogen ether" [24–26]. Through hydrogen bonding, however, the water molecules may interact with protic solvents, such as MeOH. In order to evaluate the effects of water on the specific interaction between Ca<sup>2+</sup> and L<sup>2-</sup> in MeOH, the change in absorbance (at  $\lambda_{max}$ ) of  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> L<sup>2-</sup> is examined in MeOH–H<sub>2</sub>O mixtures. With the addition of 1.0% water to MeOH, some small changes occurred in both the precipitation and re-dissolution reactions (cf. Fig. 7). The values of pK<sub>sp</sub> and log K<sub>2</sub> are evaluated to be 6.57 and 4.01 in 1.0% H<sub>2</sub>O–MeOH, while those values are 8.26 and 5.60 in the sole MeOH. The addition of 2.0% H<sub>2</sub>O to MeOH, however, alters the interaction suddenly: the absorbance of L<sup>2-</sup> decreases just



**Fig. 7.** Changes in absorbance ( $\lambda_{max} = ca. 227 \text{ nm}$ ) of  $1.0 \times 10^{-4} \text{ mol dm}^{-3} 1,5$ naphthalenedisulfonate ion with increasing concentration of  $Ca(ClO_4)_2$  in MeCN–MeOH mixtures: ( $\bigcirc$ ) 0; ( $\bullet$ ) 20; ( $\triangle$ ) 50; ( $\blacktriangle$ ) 70; ( $\square$ ) 80; ( $\blacksquare$ ) 100% (v/v) of MeOH; and in MeOH–H<sub>2</sub>O mixtures: ( $\bigtriangledown$ ) 1.0; ( $\blacktriangledown$ ) 2.0; ( $\diamondsuit$ ) 5.0% (v/v) of H<sub>2</sub>O.



**Fig. 8.** Changes in absorbance ( $\lambda_{max} = ca. 227 \text{ nm}$ ) of  $1.0 \times 10^{-4} \text{ mol dm}^{-3} 1,5$ -naphthalenedisulfonate ion with increasing concentration of  $Ba(ClO_4)_2$  in MeCN–MeOH mixtures: ( $\bigcirc$ ) 0; ( $\bigcirc$ ) 50; ( $\triangle$ ) 70; ( $\blacktriangle$ ) 75; ( $\square$ ) 100% (v/v) of MeOH.

slightly at  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> Ca<sup>2+</sup>. Finally, no decrease of the absorbance is observed in 5.0% H<sub>2</sub>O. As a short conclusion, the influence of water of a small amount (1.0–5.0%) in MeOH is large enough to alter the precipitation and successive re-dissolution reactions of CaL.

Fig. 8 shows the absorbance changes of 1,5-naphthalenedisulfonate ion with increasing concentration of Ba(ClO<sub>4</sub>)<sub>2</sub> in the MeCN–MeOH mixtures. In sole MeCN, an equivalence Ba<sup>2+</sup> has caused the complete precipitation of L<sup>2-</sup>, and those precipitates have never been redissolved [9b]. Even the MeOH content reaches 50%, both the precipitation and the successive re-dissolution of non-charged species (BaL) are not influenced so much, and the precipitation would not be redissolved even in the presence of 1.0 mol dm<sup>-3</sup> Ba(ClO<sub>4</sub>)<sub>2</sub>. A great difference is given at 75% MeOH and the absorbance (at  $\lambda_{max}$ ) of  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> L<sup>2-</sup> is completely recovered at 0.2 mol dm<sup>-3</sup> Ba<sup>2+</sup> (cf. also Table 3). Among the three alkaline earth metal ions, we may notice that Ba<sup>2+</sup> is the least influenced by the additional MeOH for the reactions between M<sup>2+</sup> and L<sup>2-</sup> in the binary MeCN–MeOH media.

the reactions between  $M^{2+}$  and  $L^{2-}$  in the binary MeCN–MeOH media. The interaction of  $Ba^{2+}$  with  $L^{2-}$  is rather similar to that of  $Ca^{2+}$  with  $L^{2-}$  in MeCN–MeOH. The similarity can be seen in the solubility products ( $pK_{sp}$ ) and "reverse coordination" constants ( $\log K_2$ ) displayed in Fig. 9. The "reverse coordination" constants of  $Ca_2L^{2+}$  and  $Ba_2L^{2+}$  are close to each other, however, the precipitates of CaL are totally redissolved by an excess amount of  $Ca^{2+}$  in 70% MeOH, while that of BaL are totally re-dissolved not in 70% but in 75% MeOH. In the binary MeCN–MeOH solvent system, the  $pK_{sp}$  values of both CaL and BaL



**Fig. 9.** The changes of solubility products  $(pK_{sp})$  and "reverse coordination" constants (log  $K_2$ ) vs. MeOH contents in MeOH–MeCN for the interaction between  $Ca^{2+}(\bullet, \bigcirc)$  or  $Ba^{2+}(\bullet, \bigtriangledown)$  and 1,5-naphthalenedisulfonate ion. The solid and open symbols represent  $pK_{sp}$  and log  $K_2$ , respectively.



**Fig. 10.** Changes in absorbance ( $\lambda_{max} = ca. 227 \text{ nm}$ ) of  $1.0 \times 10^{-4} \text{ mol dm}^{-3} 1,5-$  naphthalenedisulfonate ion with increasing concentration of Ba(ClO<sub>4</sub>)<sub>2</sub> in MeOH–H<sub>2</sub>O mixtures: ( $\Box$ ) 0; ( $\blacksquare$ ) 1.0; ( $\bigcirc$ ) 2.0; ( $\spadesuit$ ) 5.0; ( $\triangle$ ) 10; ( $\blacktriangle$ ) 20; ( $\bigtriangledown$ ) 30; ( $\blacktriangledown$ ) 50% of H<sub>2</sub>O.

decrease, however, the log  $K_2$  values of CaL<sup>2+</sup> and BaL<sup>2+</sup> remain constant or slightly increased with increasing contents of >50% MeOH (cf. also Table 3).

Fig. 10 shows the influences of additional water (1.0–50%) on the successive reactions of precipitation and re-dissolution (the BaL<sup>0</sup> and  $Ba_2L^{2+}$  formation) for the 1,5-naphthalenedisulfonate ion ( $L^{2-}$ ) in MeOH-H<sub>2</sub>O. It is curious to report that the solubility of BaL decreases with increasing  $H_2O$  contents, i.e., the  $pK_{sp}$  value of BaL increases from 8.28 for no additional water to 9.22, 9.39 and 9.48 for 1.0, 2.0 and 5.0% H<sub>2</sub>O, respectively. On the other hand, the re-dissolution of the precipitates is inhibited with increasing contents of H<sub>2</sub>O. Firstly, the redissolution is gradually reduced with increasing water contents (1.0-10%). With the water content of 20%, the absorbance ( $\lambda_{max}$ ) minimum of  $L^{2-}$  is still observed at 0.10 mol dm<sup>-3</sup> Ba<sup>2+</sup>. With 30% H<sub>2</sub>O, the absorbance of  $L^{2-}$  suddenly decreases at  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> Ba<sup>2+</sup> and continues to decrease monotonously up to 1.0 mol dm<sup>-3</sup> Ba(ClO<sub>4</sub>)<sub>2</sub>. The larger amounts of water cause an increase of solubility of the BaL salt. Neither precipitation nor re-dissolution is observed in the presence of 50% water.

### 3.3. In the binary MeCN-EtOH mixed solvents

The coordination reactions between alkaline earth metal ions and L<sup>2–</sup> were investigated also in MeCN–EtOH mixed solvents. The precipitation of MgL take place completely when an equivalence of Mg<sup>2+</sup> is added to  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> 1,5-naphthalenedisulfonate (L<sup>2–</sup>) in the binary MeCN–EtOH solvent of 10 or 20% EtOH. When the EtOH content reaches 30%, however, the precipitation becomes incomplete. The re-dissolution of the precipitates is promoted with increasing EtOH contents. The "reverse coordination" constant of Mg<sub>2</sub>L<sup>2+</sup>, log  $K_2$ , in the 10 and 30% EtOH solvents is evaluated to be 7.15 and 8.57, respectively. However, the interaction between Mg<sup>2+</sup> and L<sup>2–</sup> was totally inhibited in 50% EtOH.

Although the complete precipitation of CaL has taken place at an equivalence of Ca<sup>2+</sup> not only in MeCN but also in the sole EtOH, the re-dissolution of the precipitates happens differently in both sole solvents: the precipitates would never be re-dissolved by an excess amount of Ca(ClO<sub>4</sub>)<sub>2</sub> in MeCN (vide supra), while the absorbance of L<sup>2-</sup> (or Ca<sub>2</sub>L<sup>2+</sup>) can be totally recovered by the addition of 0.02 mol dm<sup>-3</sup> Ca<sup>2+</sup> in EtOH. The re-dissolution is gradually promoted as the EtOH contents increase in the binary solvent: the absorbance increased as 0.082, 0.219, and 0.558 for 20, 30, and 50% EtOH at 1.0 mol dm<sup>-3</sup> Ca(ClO<sub>4</sub>)<sub>2</sub>. However, the precipitates of BaL are not re-dissolved by 1.0 mol dm<sup>-3</sup> Ba(ClO<sub>4</sub>)<sub>2</sub> even in 50% EtOH–MeCN.

Table	4
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Precipitation and re-dissolution reactions of Ba<sup>2+</sup> with the mono-, di- and trivalent aromatic sulfonate ions in alcohols.

Et <sub>4</sub> N <sup>+</sup> salts	pKa <sup>a</sup>	Equilibrium constants <sup>b</sup>	MeOH	EtOH	1-PrOH	1-BuOH	1-HexOH HH
p-Toluenesulfonate	-0.43		No	<b>A</b>	<b>A</b>	<b>A</b>	<b>A</b>
$(1.0 \times 10^{-3} \text{ mol } \text{dm}^{-3})$	8.01 <sup>c</sup>	$(pK_{sp})$	-	10.48	11.59	13.10	-
		$(\mathbf{p}\mathbf{K}_{sp})^{d}$		10.85	12.07	13.71	
			No	0	0	0	0
		$\log K_{1(-1)}$	-	7.58	8.9	10.32	-
1,5-Naphthalenedisulfonate	-0.60		<b>A</b>	•	•	•	•
$(1.0 \times 10^{-4} \text{ mol } \text{dm}^{-3})$		$(pK_{sp})$	(8.28)	(11.00)	(10.6)	(10.89)	-
		$(\mathbf{p}\mathbf{K}_{sp})^{d}$	(8.49)	(11.33)	(11.06)	(11.43)	
			0	0	$\triangle$	$\triangle$	No
		$\log K_{2(-2)}$	5.58	7.11	-	-	-
1,3,6-Naphthalenetrisulfonate	-0.76		No	•	•	•	•
$(1.0 \times 10^{-4} \text{ mol } \text{dm}^{-3})$		$(pK_{sp})$	-	27.60	27.66	-	-
		$(\mathbf{p}\mathbf{K}_{sp})^{d}$		28.21	28.46		
			No	0	0	$\bigtriangleup$	$\triangle$
		$\log K_{2(-3)}$	-	9.76	9.86	-	-

*Explanatory notes*: Solid circles and triangles represent apparent complete and partial precipitation, respectively. The complete precipitation means here that the absorbance of a "ligand" anion  $(L^-, L^{2-}, and L^{3-})$  reaches <1/10 of the initial value at the equivalent or any amount of a metal ion. Open circles and triangles represent complete and partial re-dissolution of precipitation, respectively. The mark "No" indicates no precipitation or no re-dissolution.

<sup>a</sup> The first pK<sub>a</sub> value of HA, H<sub>2</sub>A, or H<sub>3</sub>A in water, cf. SciFinder: Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994–2014 ACD/Labs).

<sup>b</sup> Solubility products (*K*<sub>sp</sub>) and "reverse coordination" constants (*K*<sub>1</sub>, *K*<sub>2</sub>), cf. the Experimental section in the present paper and in Ref. [9b].

<sup>c</sup> The pK<sub>a</sub> values in acetonitrile, cf. Ref. [27].

<sup>d</sup> Cf. Table 2, note c) for the thermodynamic solubility products ( $K_{sp}$ ) corrected with the activity coefficients of ions.

# 3.4. The specific interactions between $Ba^{2+}$ and p-toluenesulfonate $(L^{-})$ or 1,3,6-naphthalenetrisulfonate $(L^{3-})$ in alcohols

The specific interactions of monosulfonate and trisulfonate ions with  $Ba^{2+}$  were also examined in the alcohols. The pK<sub>a</sub> values of the sulfonic acids are shown in Table 4. The permittivity of MeOH is close to that of MeCN; however, the donor number and acceptor number of MeOH are much larger than those of MeCN. Neither the normal coordination species nor the "reverse-coordinated" species is observed between  $Ba^{2+}$  and *p*-toluenesulfonate ([Et<sub>4</sub>N<sup>+</sup>  $CH_3C_6H_4SO_3^{-}$ ], L<sup>-</sup>) in MeOH: the absorbance (at  $\lambda_{max}$ ) of L<sup>-</sup> remains almost unchanged with increasing concentration of Ba(ClO<sub>4</sub>)<sub>2</sub> (Fig. 11), while the precipitation of BaL has taken place to a large extent between  $Ba^{2+}$  and 1,5-naphthalenedisulfonate ( $L^{2-}$ ) ions in MeOH (vide supra). In EtOH, the UV absorption spectrum of the *p*-toluenesulfonate ion [Et<sub>4</sub>N<sup>+</sup> CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>] gives a strong band at 222 nm ( $\varepsilon/cm^{-1}$  mol<sup>-1</sup> dm<sup>3</sup> = 1.1 × 10<sup>4</sup>), which shows a slight blue shift, compared with the band in MeCN ( $\lambda_{max} = 223$  nm). The interaction between Ba<sup>2+</sup> and L<sup>-</sup> causes some incomplete precipitation at the equivalence point  $(5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ba}^{2+})$ : the absorbance (at  $\lambda_{max}$ ) minimum of 0.345 in EtOH, cf. 0.031 in MeCN. The absorbance



$$ML_2^{0} + M^{2+} \rightarrow 2ML^+ \tag{6}$$

The precipitation of  $BaL_2$  takes place to a larger extent in 1-PrOH and 1-BuOH than in EtOH. Neither precipitation nor successive redissolution occurs between  $Ca^{2+}$  and  $L^-$  in all the alcohols even 1-HexOH.

In MeCN, tetraethylammonium 1,3,6-naphthalenetrisulfonate ( $L^{3-}$ ) gives a strong UV band at  $\lambda_{max} = 238$  nm ( $\varepsilon/cm^{-1}$  mol<sup>-1</sup> dm<sup>3</sup> = ca. 7.7 × 10<sup>4</sup>), apart from the broad band around 280 nm of the naphthalene body. The alkaline metal ions cause the complete precipitation at  $1.5 \times 10^{-4}$  mol dm<sup>-3</sup> for  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>  $L^{3-}$ , but almost no re-dissolution of the precipitates at 1.0 mol dm<sup>-3</sup> M(ClO<sub>4</sub>)<sub>2</sub>, except for Mg(ClO<sub>4</sub>)<sub>2</sub>. In MeOH, neither precipitation nor re-dissolution is caused for  $L^{3-}$  even by Ba<sup>2+</sup> (Fig. 12). Regardless in MeOH, both precipitation and re-dissolution (between or among Ba<sup>2+</sup> and  $L^{3-}$ ) can take place in the other primary alcohols (from EtOH to 1-HexOH). The complete precipitation at the equivalence point ( $[Ba^{2+}]:[L^{3-}] = 1.5:1.0$ )



**Fig. 11.** Changes in absorbance  $(\lambda_{max} = \text{ca. } 222 \text{ nm})$  of  $1.0 \times 10^{-3} \text{ mol } \text{dm}^{-3} \text{ } p$ -toluenesulfonate ion with increasing concentration of Ba(ClO<sub>4</sub>)<sub>2</sub> in MeCN and alcohols: ( $\bigcirc$ ) MeCN; ( $\bullet$ ) MeOH; ( $\triangle$ ) EtOH; ( $\blacktriangle$ ) 1-PrOH; ( $\square$ ) 1-BuOH.



**Fig. 12.** Changes in absorbance ( $\lambda_{max} = ca. 238 \text{ nm}$ ) of  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  1,3,6-naphthalenetrisulfonate ion with increasing concentration of Ba(ClO<sub>4</sub>)<sub>2</sub> in MeCN and alcohols: ( $\bullet$ ) MeOH; ( $\triangle$ ) EtOH; ( $\blacktriangle$ ) 1-PrOH; ( $\bigcirc$ ) MeCN; and in EtOH–MeOH mixtures: ( $\mathbf{V}$ ) 20; ( $\Box$ ) 50; ( $\mathbf{I}$ ) 70% (v/v) of MeOH.



Scheme 2. Successive formation of  $M_2L_3$  and  $M_2L^+$  (M = Ba) for the 1,3,6-naphthalenetrisulfonate ion ( $L^{3-}$ ) in EtOH and 1-PrOH.

should be based on the formation of  $Ba_3L_2$ . The successive re-dissolution of the precipitates is attributed to the formation of the  $Ba_2L^+$  species in EtOH and 1-PrOH, cf. Eq. (2) and Scheme 2. The most probable occupations by two barium ions in the 1-, 3-, and 6-positions are discussed in the final section of the present paper.

We are so interested in the large different influences with solvent alcohols, especially, the difference between MeOH and EtOH that we examine the specific phenomena in the binary MeOH–EtOH mixed system. In the 20% MeOH solvent, still occurs the almost complete precipitation at  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup> Ba<sup>2+</sup>, and the successive re-dissolution from Ba<sub>3</sub>L<sub>2</sub> is promoted. With the 50% MeOH content, the precipitation becomes incomplete, and the successive re-dissolution is promoted. Even at 70% MeOH–EtOH, precipitation formation and re-dissolution phenomena can be observed (Fig. 12).

Fig. 13 shows the solubility products  $(pK_{sp})$  and the "reverse coordination" constants  $(\log K_{1(-1)}, \log K_{2(-2)}, \text{ or } \log K_{2(-3)})$  for the interaction between Ba<sup>2+</sup> and the sulfonate ions  $(L^-, L^{2-}, \text{ and } L^{3-})$  in different alcohols. In the primary alcohols of the lower donor numbers, such as 1-BuOH (DN = 26.2, cf. Table 1), the precipitation reaction is apt to take place to a larger extent than in methanol (DN = 31.3). In other wards, with increasing donicity of the alcohols, the  $pK_{sp}$  values decrease. At the same time, the log  $K_n$  values would be depressed. For the interaction between Ba<sup>2+</sup> and L<sup>3-</sup> in the binary EtOH–MeOH solvent system, the  $pK_{sp}$  values decrease as 27.6, 26.3, 23.0, and 20.3 in a good accordance with the log  $K_{2(-3)}$  of 9.8, 9.3, 8.4, and 7.5 in 0, 20, 50, and 70% MeOH (the DN of 27.8, 28.5, 29.55, and 30.25), respectively. However,



**Fig. 13.** The solubility products  $(pK_{sp})$  and "reverse coordination" constants  $(\log K_n, n = 1 \text{ or } 2)$  vs. donor numbers (DN) of alcohols for the interaction between Ba<sup>2+</sup> and TSO<sup>-</sup>, 1,5-NDS<sup>2-</sup>, and 1,3,6-NTS<sup>3-</sup>: (•, ○) *p*-toluenesulfonate (TsO<sup>-</sup>); (•, ▽) 1,5-naphthalenedisulfonate (1,5-NDS<sup>2-</sup>); (•, △) 1,3,6-naphthalenetrisulfonate (1,3,6-NTS<sup>3-</sup>). The solid and open symbols represent  $pK_{sp}$  and  $\log K_n$ , respectively. The binary mixed solvents of EtOH–MeOH and MeOH–H<sub>2</sub>O are used for 28 < DN < 31 and 31.5 < DN ≤ 34, respectively.

we have to report an irregular fact that the solubility of BaL (barium 1,5-naphthalenedisulfonate) decreases with the addition of the smaller amount of water (1.0–10%), which is also displayed in Fig. 13. The donor numbers of the binary MeOH–H<sub>2</sub>O system are estimated just assuming the linearity between 31.4 of MeOH and 40.3 of H<sub>2</sub>O, up to 30% H<sub>2</sub>O.



**Fig. 14.** The optimized structures of 1,3,6-naphthalenetrisulfonates to which two  $Ba^{2+}$  ions are coordinated at (a) 1,3-, (b) 1,6-, and (c) 3,6-positions.

Table 5 Calculated relative energies for  $Ba_2L^+$  (L: 1,3,6-naphthalenetrisulfonate) in EtOH.

Positions of Ba <sup>2+</sup>	Relative energy/kcal mol <sup>-1</sup>
1,3-	+1.19
1,6-	+0.71
3,6-	0.00

### 3.5. Computational prediction of the structures of $Ba_2L^+$ in EtOH

For predicting the coordinating structures of  $Ba_2L^+$  shown in Scheme 2, we performed geometry optimization using GAMESS program package [29]. All geometries were optimized with the density functional theory (DFT) employing the long-range corrected BOP (LC-BOP) exchange-correlation functional [30]. Except for hydrogen atoms, all core electrons were treated by the model core potential (MCP) [31], and the valence electrons were described via MCP-dzp basis set [32], while the diffuse functions were augmented to oxygen atoms. For hydrogen atoms, the cc-pVDZ set [33] was adopted. In this paper, we only report the results for the lowest energy conformers. In the present calculations, the ethanol solvent was taken into consideration by the conductor-like polarizable continuum model (C-PCM) [34] with the solvation model density (SMD) [35].

Fig. 14(a)–(c) show the projected views of optimized structures of 1,3,6-naphthalenetrisulfonates to which two Ba<sup>2+</sup> ions are coordinated at (a) 1,3-, (b) 1,6-, and (c) 3,6-positions. For all three structures, Ba<sup>2+</sup> ion coordinates to two O atoms of sulfonate. Accordingly, the S–O lengths coordinated by Ba<sup>2+</sup> (1.49–1.50 Å) were slightly longer than those at free sulfonate (1.47–1.48 Å). Table 5 summarizes the relative energies for these Ba<sub>2</sub>L<sup>+</sup> structures obtained by the DFT calculations in ethanol. The 3,6-coordinated structure is the most stable among these three species, although the difference from the most unstable 1,3-coordinated structure is less than 1.2 kcal/mol.

# 4. Conclusion

In the present study, the coordination phenomena of alkaline earth metal ions  $(M^{2+})$  with the mono-. di-. and trisulfonate ions  $(L^{-}, L^{2-}, L^{2-})$ and  $L^{3-}$ ) have been observed in sole alcohols as well as the binary solvent mixtures. We have demonstrated that the precipitation of the non-charged species, i.e.  $ML_2^0$ ,  $ML^0$ , and  $M_3L_2^0$  and the successive formation of the "reverse coordinated" species  $(ML^+, M_2L^{2+}, and M_2L^+)$  take place not only in an aprotic solvent, acetonitrile, but also in protic media, i.e. alcohols and their binary mixtures (including H<sub>2</sub>O). Even in methanol,  $Ca^{2+}$  and  $Ba^{2+}$  can interact with  $L^{2-}$  to form precipitates and also the "reverse coordinated" species. However, no apparent coordination phenomena have been observed between all the alkaline earth metal ions  $(Mg^{2+}, Ca^{2+}, and Ba^{2+})$  and  $L^-$  or  $L^{3-}$  in MeOH. In the other primary alcohols (from ethanol to hexanol), both the precipitation and successive re-dissolution reactions occur between  $Ba^{2+}$  and  $L^-$ ,  $L^{2-}$  or  $L^{3-}$  at different degrees. The reactivities of alkaline earth metal ions are apt to influence proic solvents in the order of  $Ba^{2+} < Ca^{2+} < Mg^{2+}$ . We have explained successfully the re-dissolution of precipitates in the protic media based on the coordination or "reverse coordination" ability of the alkaline earth metal ions with the sulfonate ions and not based on the changes in the activity coefficients of solutes.

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#### 1,3,6-Naphthalenetrisulfonic acid

Chart 1. Aromatic sulfonic acids examined in the present study.

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# References

- [1] M. Aghaie, H. Aghaie, A. Ebrahimi, J. Mol. Liq. 135 (2007) 72.
- [2] G. Liu, M. Cons, T. Liu, J. Mol. Liq. 118 (2005) 27.
- [3] A. Jouyban, A. Shayanfar, T. Ghafourian, W.E. Acree Jr., J. Mol. Liq. 195 (2014) 125.
- [4] C. Trujillo, A.M. Lamsabhi, O. Mó, M. Yánez, J. Salpin, Int. J. Mass Spectrom. 306 (2011) 27.
- [5] J. Mbuna, T. Takayanagi, M. Oshima, S. Motomizu, J. Chromatogr. A 1069 (2005) 261.
- [6] M.N. Roy, R. Chanda, P. Chakraborti, A. Das, Fluid Phase Equilib, 322–323 (2012) 159.
- [7] M. Hojo, Y. Miyauchi, A. Tanio, Y. Imai, J. Chem. Soc. Faraday Trans. 87 (1991) 3847.
- [8] M. Hojo, H. Nagai, M. Hagiwara, Y. Imai, Anal. Chem. 59 (1987) 1770.
- [9] (a) M. Hojo, T. Ueda, T. Inoue, M. Ike, M. Kobayashi, H. Nakai, J. Phys. Chem. B 111 (2007) 1759;
  - (b) M. Hojo, S. Ohta, K. Ayabe, K. Okamura, K. Kobiro, Z. Chen, J. Mol. Liq. 177 (2013) 145.
- [10] (a) M. Hojo, T. Ueda, M. Ike, K. Okamura, T. Sugiyama, M. Kobayashi, H. Nakai, J. Chem. Eng. Data 55 (2010) 1986;
- (b) M. Hojo, T. Ueda, M. Ike, M. Kobayashi, H. Nakai, J. Mol. Liq. 145 (2009) 152.
- [11] M. Hojo, Pure Appl. Chem. 80 (2008) 1539.
- [12] M. Hojo, A. Tanio, Y. Miyauchi, Y. Imai, Chem. Lett. (1991) 1827.
- [13] K.M. Fromm, Coord. Chem. Rev. 252 (2008) 856.
- [14] P. Eberspächer, E. Wismeth, R. Buchner, J. Barthel, J. Mol. Liq. 129 (2006) 3.
- [15] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents, Physical Properties and Methods of Purification, 4th ed. John Wiley & Sons, New York, 1986.
- [16] I.M. Kolthoff, M.K. Chantooni Jr., Theory and Practice, vol. 2, John Wiley & Sons, New York, 1979, p. 239, (Section D).
- [17] V. Gutmann, The Donor–Acceptor Approach to Molecular Interactions, Plenum, New York, 1978.
- [18] Y. Marcus, J. Solution Chem. 13 (1984) 599.
- [19] M. Hojo, T. Ueda, H. Hamada, Z. Chen, S. Umetani, J. Mol. Liq. 149 (2009) 24.
- [20] M. Hojo, Z. Chen, Anal. Sci. 151 (1999) 303.
- [21] M. Hojo, Y. Kondo, K. Zei, K. Okamura, Z. Chen, M. Kobayashi, Bull. Chem. Soc. Jpn. 87 (2014) 98.
- [22] M. Hojo, T. Ueda, M. Nishimura, H. Hamada, M. Matsui, S. Umetani, J. Phys. Chem. B 103 (1999) 8965.
  - [23] M. Hojo, R. Kato, A. Narutaki, T. Maeda, Y. Uji-yie, J. Mol. Liq. 163 (2011) 161.
  - [24] C. Reichardt, D. Che, G. Heckenkemper, G. Schäfer, Eur. J. Org. Chem. (2001) 2343.
  - [25] L.C. Manege, T. Ueda, M. Hojo, Bull. Chem. Soc. Jpn. 71 (1998) 589.
  - [26] M. Hojo, T. Ueda, S. Inoue, Y. Kawahara, J. Chem. Soc. Perkin Trans. 2 (2000) 1735.
  - [27] K. Izutsu, Acid–Base Dissociation Constants in Dipolar Aprotic Solvents, Blackwell,
  - Oxford, 1990. [28] A.K. Covington, T. Dickinson, Physical Chemistry of Organic Solvent Systems, Plenum, London, 1973.
  - [29] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery Jr., J. Comput. Chem. 14 (1993) 1347.
  - [30] (a) H. likura, T. Tsuneda, T. Yanai, K. Hirao, J. Chem. Phys. 115 (2001) 3540;
    (b) A.D. Becke, Phys. Rev. A 38 (1988) 3098;
  - (c) T. Tsuneda, T. Suzumura, K. hirao, J. Chem. Phys. 110 (1999) 10664.
  - [31] M. Klobukowski, S. Huzinaga, Y. Sakai, Computational Chemistry: Reviews of Current Trends, vol. 3, World Scientific, Singapore, 1999, pp. 49–74, (ch. 2).
  - [32] (a) Y. Sakai, E. Miyoshi, M. Klobukowski, S. Huzinaga, J. Chem. Phys. 106 (1997) 8084;
    (b) T. Noro, M. Sekiya, T. Koga, Theor. Chem. Acc. 98 (1997) 25;
    - (c) M. Sekiya, T. Noro, T. Koga, H. Matsuyama, J. Mol. Struct. Theochem 451 (1998) 51;
    - (d) M. Sekiya, T. Noro, Y. Osanai, T. Koga, Theor. Chem. Acc. 106 (2001) 297;
    - (e) T. Noro, M. Sekiya, Y. Osanai, E. Miyoshi, T. Koga, J. Chem. Phys. 119 (2003) 5142;
    - (f) H. Anjima, S. Tsukamoto, H. Mori, H. Mine, M. Klobukowski, E. Miyoshi, J.
    - Comput. Chem. 28 (2007) 2424.
  - [33] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
  - [34] M. Cossi, N. Rega, G. Scalmani, V. Barone, J. Comput. Chem. 24 (2003) 669.
  - [35] A.V. Barenich, C.J. Cramer, D.G. Truhlar, J. Phys. Chem. B 113 (2009) 6378.