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Coordination phenomena of alkali metal, alkaline earth metal, and indium ions with the 1,3,6-naphthalenetrisulfonate ion in protic and aprotic solvents

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ABSTRACT

Not only in acetonitrile (MeCN) but also in primary alcohols (from methanol to 1-hexanol), the coordination ability of alkali metal (Li^+ , Na^+), alkaline earth metal (Mg^{2+} , Ca^{2+} , or Ba^{2+}), and indium (In^{3+}) ions with the 1,3,6-naphthalenetrisulfonate ion (L^{3-} , $1.0 \times 10^{-4} \text{ mol dm}^{-3}$) has been examined by means of UV-visible spectroscopy. In MeCN, the precipitation takes place completely between alkali metal or alkaline earth metal ions and L^{3-} . In the presence of excess amounts of the metal ions, the precipitates of Li_3L and Mg_2L_3 tend to re-dissolve partially to form the “reverse” coordinated species of Li_4L^+ and Mg_2L^+ . However, those precipitates of Na_3L , Ca_3L_2 , and Ba_3L_2

would not re-dissolve even in the presence of large excess amounts of the metal ions in MeCN. Between In^{3+} and L^{3-} , both precipitation and successive re-dissolution reactions can occur in all the primary alcohols. The solubility products ($\text{p}K_{\text{sp}}$) and “reverse” coordination constants with L^{3-} ($\log K_{4(1+)}$, $\log K_{2(2+)}$, and $\log K_{2(3+)}$ for alkali metal, alkaline earth metal, and indium ions, respectively) have been evaluated in MeCN, the primary alcohols, and binary solvents of MeCN- H_2O and MeCN-MeOH. Where, for instance, $K_{4(1+)} = [\text{M}_4\text{L}^+] / ([\text{M}^+]^4 [\text{L}^{3-}])$ for the reaction: $4 \text{M}^+ + \text{L}^{3-} \rightleftharpoons \text{M}_4\text{L}^+$. DFT calculations have been performed to predict the coordinating structures of the Li_4L^+ species in MeCN.

1. Introduction

The coordination chemistry of groups 1 and 2 metal compounds with organic ligands in the widest sense has been, until relatively recently, largely unknown compared to transition metal coordination networks [1], even though those metals play vital roles in biological system and pharmaceuticals [2]. Owing to lack of partly filled d- or f-shells, the complexing abilities of alkali metal and alkaline earth metal ions are much weaker than that of transition metal ions [3].

In aprotic solvents such as acetonitrile (MeCN), the specific coordination reactions between alkali metal or alkaline earth metal ions with some simple ions such as halides (Cl^- , Br^-) [4,5], tropolonate [6], sulfonates, and carboxylates [7] have been demonstrated by means of various analytical methods. With the increasing concentration of M^+ (an alkali metal ion), the specific reaction may proceed in three steps: at first, a half equivalence or less than that amount of M^+ interacts with an anion (L^-) to form the normal coordination species $[\text{ML}_2^-]$; then followed by the ion pair (ML) or precipitation formation by the addition of an equivalence of M^+ ; finally, a “triple

cation” $[M_2L^+]$, positively charged species, can be produced from the precipitates with an excess amount of M^+ , that is, the re-dissolution of precipitation. Chen and Hirota [8] have investigated the formation and dissociation of a triple ion ($M^+A^-M^+$, $M = Li, Na, K$, $A = \text{anthraquinone}$) through EPR studies and demonstrated that intermediate triple ions are formed in the course of cation-transfer reactions.

Fuoss and Kraus [9] have introduced the concept of triple ion between free ions and triple ions in the solvents of low permittivity ($\epsilon_r < 10$ or 23.2). According to their calculation, the triple ions based on the pure Coulombic interaction become unstable for $\epsilon_r > 23.2$ under certain conditions. The theory for triple ion has been developing for half a century [10]. Another view [11] have been given on these associations by coordination chemistry: the introduction of multiple hydrogen-bonding sites along with the resulting topological considerations in anion receptors leads to the concept of double valence for anions as well as for transition-metal ions. For anions, the primary valence is the negative charge on the anion and the secondary valence is provided by hydrogen bonds to the anion. In previous papers [12,13], we have regarded the “triple cation” as the “reverse” coordinated species. The coordination bonding forces as well as coulombic forces should contribute to the interaction between Li^+ and halide (Cl^- , Br^-) or thiocyanate (SCN^-) ions in iso-permittivity binary mixed solvents between THF and 2-ethyl-1-hexanol [14].

In low permittivity media ($\epsilon_r < 10$), triple ions may be produced by electrostatic interaction [9]. Indeed, we have verified that higher ion aggregation including triple ions could take place in higher permittivity media ($20 < \epsilon_r < 65$) of poor solvation abilities [15]. Furthermore, we have found that precipitation and re-dissolution reactions take place between Ba^{2+} and the 1,5-naphthalenedisulfonate ion even in the protic solvents, *e.g.* methanol or ethanol [16].

Murray and Hiller [17] first suggested the involvement of two lithium ions in a ligand loss

during one-electron reduction of $\text{Fe}(\text{acac})_3$ in MeCN containing LiClO_4 as the supporting electrolyte. The formation of triple ions from LiClO_4 with O-donors in non-aqueous solvents has been utilized for the electrochemical device [18] such as lithium battery [19]. A series of lithium based coordination phenomena, *e.g.* $\text{Li}_2\text{C}_6\text{H}_2\text{O}_4$ [20], $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$ [21], and $\text{Li}_2\text{C}_{14}\text{H}_6\text{O}_4$ [22], as the positive electrode material for the Li-ion battery have been reported in recent years. Oshovsky *et al.* [23] developed a novel method for constructing a supramolecular capsules based on triple ion (pyridinium-anion-pyridinium) interactions in methanol and water. The specific coordination reactions between alkali metal or alkaline earth metal ions and anions have been utilized for the color development or changes of indicators or dyes of sulfonic [24] and carboxylic [25-27] types.

Organosulfonates are widely used as surfactants and dyes, and are an important class of oxygen donor ligands toward alkali metal and alkaline earth metal ions [1]. Previously [7,16], the specific complexing behavior of alkali metal or alkaline earth metal ions with *p*-toluenesulfonate and 1,5-naphthalenedisulfonate ions has been thoroughly investigated in MeCN, alcohols, and binary solvents of MeCN- H_2O and MeCN-alcohols. Naphthalenetrisulfonate is commonly used as a chemical function of Suramin and Suradistas [28].

As an extension of the studies, in the present work, we examine the coordination behavior between alkali metal, alkaline earth metal, and indium ions with the 1,3,6-naphthalenetrisulfonate ion by means of UV spectroscopy. As the solvents, MeCN and primary alcohols (methanol, ethanol, 1-propanol, 1-butanol, and 1-hexanol) are used. Meanwhile, the effects of added water and methanol on the coordination behavior in MeCN are also examined.

2. Experimental section

2.1. Chemicals

The tetraethylammonium 1,3,6-naphthalenetrisulfonate $[(\text{Et}_4\text{N}^+)_3\text{L}^{3-}]$ was synthesized by following the method described previously [16]. A 1.0 g 1,3,6-naphthalenetrisulfonic acid and the equivalence of Et_4NOH (20 wt.% in H_2O , Aldrich) were mixed in methanol, followed by evaporation to dryness at $50\text{ }^\circ\text{C}$, and the salt was dried *in vacuo* at $80\text{ }^\circ\text{C}$. 1,3,6-Naphthalenetrisulfonic acid was prepared from the sodium salt [16].

Metal perchlorates without water, LiClO_4 (Wako), NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, and $\text{Ba}(\text{ClO}_4)_2$ (all Aldrich), were used as received. Calcium perchlorate tetrahydrates from Aldrich was dried *in vacuo* at $150\text{ }^\circ\text{C}$ to obtain anhydrous $\text{Ca}(\text{ClO}_4)_2$. Both $\text{In}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$ ($x = 8-10$) and $\text{In}(\text{CF}_3\text{SO}_3)_3$ were purchased from Aldrich. Commercially obtained solvents of GR grade (Wako), acetonitrile, methanol (MeOH), ethanol (EtOH), propanol (1-PrOH), butanol (1-BuOH), and hexanol (1-HexOH) were used as received. The water contents in the solvents are guaranteed to be less than 0.1% for MeCN and MeOH; less than 0.2% for the other primary alcohols. Water was purified by means of a MilliQ system (Millipore Corp.). The water contents of binary solvent systems in the present paper are represented by the volume ratio, % (v/v).

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 with a Hitachi centrifuge (model CT4D). Sometimes, a long aging time was needed to complete the precipitation reaction.

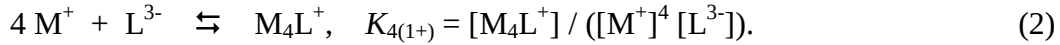
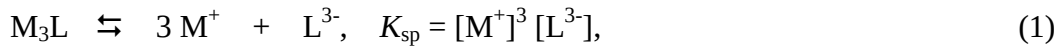
2.3. Evaluation of “reverse” coordination formation constants

The evaluation of “reverse” coordination formation constants between alkaline earth metal

(M²⁺) and 1,3,6-naphthalenetrisulfonate (L³⁻) ions has been already described in the previous paper [16]. The solubility products and “reverse” coordination constants between an alkali metal (M⁺) or the indium (M³⁺) ion and L³⁻ are evaluated as follows:

(a) Alkali metal ions [reaction between (1+) and (3-)]

The solubility product, K_{sp} , and the “reverse” coordination constant, $K_{4(1+)}$, at higher M⁺ concentrations, compared to L³⁻, are expressed by Eqs. 1 and 2, respectively.



The solubility s of M_3L or the total “ligand” concentration, c_t , in solution (not in precipitation) is expressed by Eq. 3.

$$s = c_t = [L^{3-}] + [M_4L^+] = K_{sp} [M^+]^{-3} (1 + K_{4(1+)} [M^+]^4) \quad (3)$$

The observed absorbance A_{bs} of L³⁻ (and M_4L^+) can be rationalized by Lambert-Beer’s law as Eq. 4.

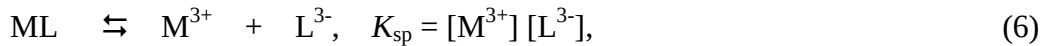
$$A_{bs} = \varepsilon c l \sim \varepsilon s l \quad (4)$$

Where ε , c , and l are the molar absorptivity (cm⁻¹ mol⁻¹ dm³) of L³⁻ (or M_4L^+), the concentration (mol dm⁻³), and the path-length (cm), respectively. Eq. 5 is given by introducing Eq. 3 into Eq. 4.

$$A_{bs} = \varepsilon l K_{sp} [M^+]^{-3} (1 + K_{4(1+)} [M^+]^4) \quad (5)$$

Eq. 5 can be arranged to be $A_{bs} = \varepsilon l K_{sp} K_{4(1+)} [M^+]$ with higher M⁺ concentrations and larger $K_{4(1+)}$ values,

(b) The indium ion [reaction between (3+) and (3-)]



The total “ligand” concentration, c_t , in solution is

$$c_t = [L^{3-}] + [M_2L^{3+}] = K_{sp} [M^{3+}]^{-1} (1 + K_{2(3+)} [M^{3+}]^2). \quad (8)$$

The observed absorbance A_{bs} is expressed as

$$A_{bs} = \varepsilon l c_t = \varepsilon l K_{sp} [M^{3+}]^{-1} (1 + K_{2(3+)} [M^{3+}]^2). \quad (9)$$

Eq. 9 can be arranged to be $A_{bs} = \varepsilon l K_{sp} K_{2(3+)} [M^{3+}]$ with higher M^{3+} concentrations and larger $K_{2(3+)}$ values.

3. Results and discussion

3.1. Coordination ability of alkali metal ions (Li^+ , Na^+) with the 1,3,6-naphthalenetrisulfonate ion (L^{3-}) in MeCN and alcohols

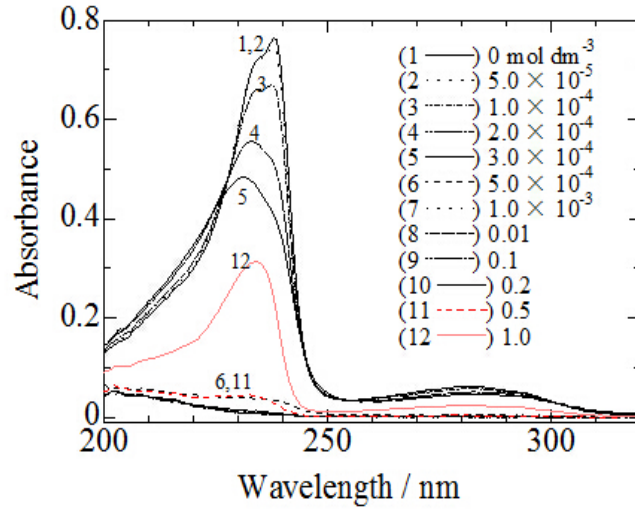
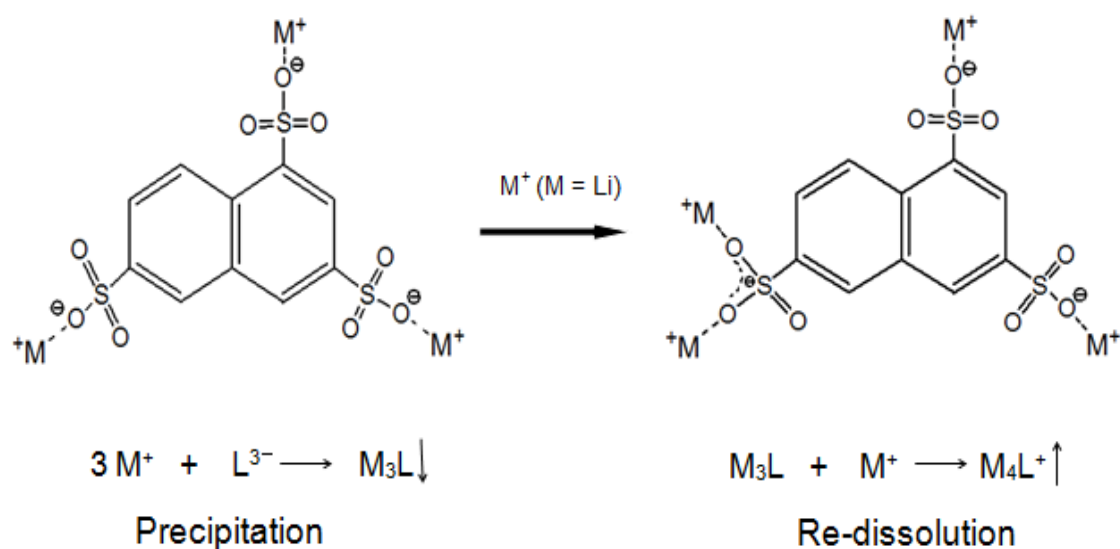


Fig. 1. The UV spectra of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion (0.1 cm path-length) with increasing concentration of $LiClO_4$ in MeCN.

Alkali metal ions have a great tendency to bond to $-SO_3^-$, with a majority of the coordination environment made up of sulfonate-oxygen atoms [29]. Acetonitrile, being an aprotic as well as protophobic solvent, possesses a rather higher permittivity ($\varepsilon_r = \text{ca. } 36$) [30] but poor solvation ability ($DN = 14.1$, $AN = 19.3$) [31a]. Fig. 1 shows the UV spectrum changes of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion $[(Et_4N^+)_3L^{3-}]$ with increasing concentration of $LiClO_4$ in MeCN.

The L^{3-} ion gives a strong band at $\lambda_{\max} = 238$ nm ($\epsilon / \text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3 = \text{ca. } 7.8 \times 10^4$) and a weak broad band around 285 nm. With increasing concentration of LiClO_4 , the band at 238 nm decreases gradually, however, the absorbance of *ca.* 0.5 (at $\lambda_{\max}$) remains even in the presence of the equivalence of Li^+ ($3.0 \times 10^{-4} \text{ mol dm}^{-3}$). At the same time, the band peak shows a blue shift to 231 nm, which may suggest some strong interaction is operating between L^{3-} and Li^+ . Finally the band disappears completely in the presence of $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Li}^+$. However, we may mention that the absorbance from L^{3-} recovers partially when $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$ is added to L^{3-} , suggesting the formation of the “reverse” coordinated species of Li_4L^+ in the presence of the large excess amount of Li^+ .

The precipitation and successive re-dissolution reactions between Li^+ and L^{3-} in MeCN can be illustrated by Scheme 1. The precipitates of a lithium mono-sulfonate salt (benzenesulfonate [32] or *p*-toluenesulfonate [7]) have been re-dissolved completely by the addition of more than $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$ in MeCN. However, the precipitates of dilithium 1,5-naphthalenedisulfonate have never been re-dissolved in the presence of even $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$ [7]. DFT calculations have been performed to predict the coordinating structures of Li_4L^+ in MeCN (*cf.* the final section 3.6). The 1,3,6,6-derivative is shown tentatively in Scheme 1.



Scheme 1. Successive formation of M_3L and M_4L^+ ($M = Li$) for the 1,3,6-naphthalenetrisulfonate ion in MeCN.

The addition of $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ NaClO}_4$ to a $1.0 \times 10^{-4} \text{ mol dm}^{-3} L^{3-}$ solution causes complete precipitation. However, the precipitates of Na_3L would not be re-dissolved by the addition of a large excess concentrations of Na^+ (Fig. 2). Smaller ions are apt to coordinate more strongly due to stronger electrostatic interactions, according to the concept of hard and soft acids and bases (HSAB) [33].

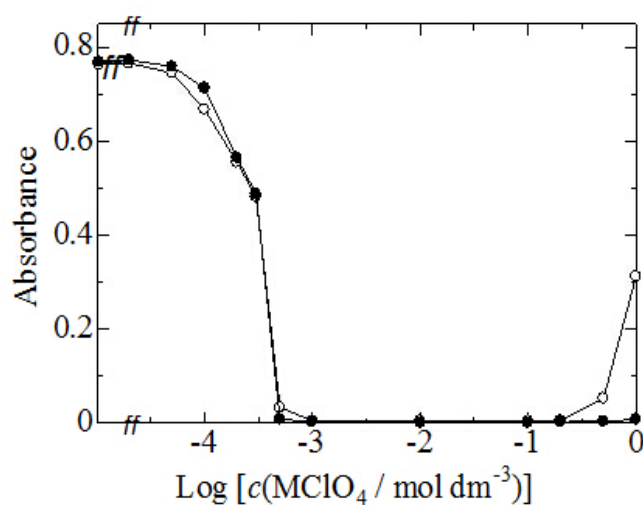


Fig. 2. Changes in absorbance ($\lambda = ca. 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthelenetrisulfonate ion with increasing concentration of alkali metal ions: (○) LiClO_4 ; (●) NaClO_4 .

In the primary alcohols of relatively high donicity and acceptivity, the specific interactions between Li^+ or Na^+ and L^{3-} are also examined, and the solubility products ($\text{p}K_{\text{sp}}$) and “reverse” coordination constants ($\log K_{4(1+)}$) in MeCN and primary alcohols are listed in Table 1. Neither precipitation nor re-dissolution between Li^+ and L^{3-} is found in all the primary alcohols (from MeOH to 1-HexOH). Between Na^+ and L^{3-} , however, the precipitation reaction can take place in 1-PrOH, 1-BuOH, and 1-HexOH (Fig. 3), while no apparent reaction in MeOH and EtOH. In 1-PrOH, incomplete precipitation occurs in the presence of more than $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Na}^+$. Considering that the donor number of 1-PrOH ($\text{DN} = 27$) [16] is close to that of EtOH ($\text{DN} = 27.8$) [31b], and that the permittivity of 1-PrOH ($\epsilon_r = 20.45$) [30] is smaller than EtOH ($\epsilon_r = 24.55$) [30], the stronger Coulombic interaction in 1-PrOH than EtOH may result in the precipitation between the ions. The precipitation of Na_3L takes place to a larger extent in 1-BuOH and 1-HexOH than in 1-PrOH, and the values of solubility products, $\text{p}K_{\text{sp}}$, are 10.4, 13.9, and 14.0 in 1-PrOH, 1-BuOH, and 1-HexOH, respectively (*cf.* Table 1).

All the alcohols are amphiprotic solvents and have rather strong solvation ability toward anions and cations. However, the permittivities of 1-BuOH and 1-HexOH are relatively small, *i.e.*, 17.51 and 13.3, respectively [30]. Therefore, we have to consider the incompleteness of the dissociation of NaClO_4 .

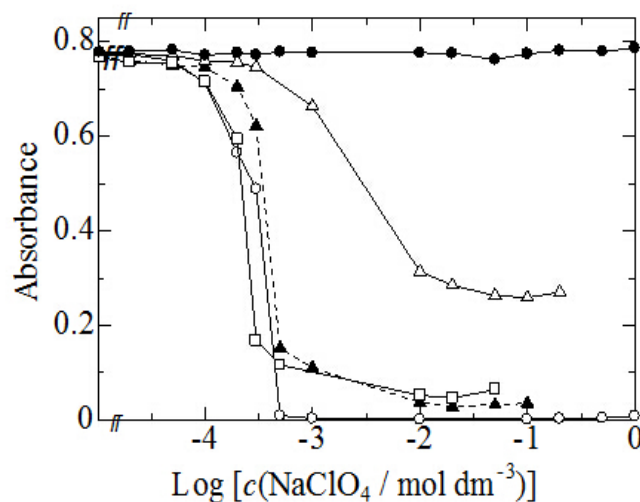


Fig. 3. Changes in absorbance ($\lambda = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion with increasing concentration of NaClO_4 in different solvents: (●) EtOH; (Δ) 1-PrOH; ($\blacktriangle$) 1-BuOH; ($\square$) 1-HexOH; ($\circ$) MeCN.

3.2. The influences of H_2O or MeOH on the precipitation and re-dissolution reactions between alkali metal ions and L^{3-} in MeCN

Ion association and solvation behavior of different electrolytes have been studied extensively in mixed solvents [34]. The studies of excess functions of binary mixtures are of considerable importance in understanding organic reaction mechanism [35] and the nature of molecular interaction [36].

Fig. 4 shows the influences of added water on the precipitation and the successive re-dissolution of lithium 1,3,6-naphthalenetrisulfonate (Li_3L) in MeCN. Without the additional water, the precipitation for $1.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ L}^{3-}$ occurs completely in a very wide concentration range of $1.0 \times 10^{-3} - 0.20 \text{ mol dm}^{-3} \text{ LiClO}_4$. In 1.0% H_2O -MeCN, however, the complete precipitation occurs in the presence of higher Li^+ concentrations, 0.10 and 0.20 mol dm^{-3} . With the addition of 2.0% H_2O , the precipitation becomes incomplete, that is, the interaction between ions is

inhibited by the added water. The further amount of Li^+ is needed to give some precipitates with increasing contents of H_2O in MeCN. The increase of the LiL_3 solubility with added water is reflected in the solubility products ($\text{p}K_{\text{sp}}$, *cf.* Table 2): the $\text{p}K_{\text{sp}}$ values are 16.1 and 6.4 in 2.0 and 5.0% H_2O , respectively. Finally, the precipitation reaction is totally inhibited by 10% H_2O .

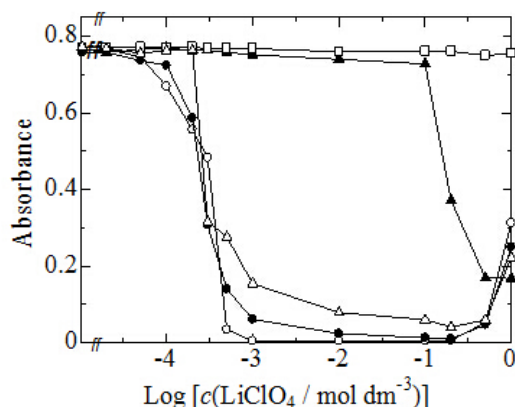


Fig. 4. Absorbance ($\lambda = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate in the presence of LiClO_4 in MeCN- H_2O mixtures: ($\circ$) 0; ($\bullet$) 1.0; (Δ) 2.0; ($\blacktriangle$) 5.0; ($\square$) 10% (v/v) of H_2O .

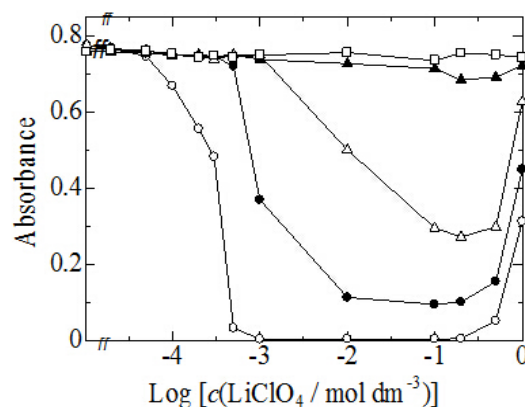


Fig. 5. Absorbance ($\lambda = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate in the presence of LiClO_4 in MeCN-MeOH mixtures: ($\circ$) 0; ($\bullet$) 5.0; (Δ) 7.0; ($\blacktriangle$) 10; ($\square$) 20% (v/v) of MeOH.

Compared with H_2O , the influences of MeOH (DN = 31.3) [31b] on the interaction between Li^+ and L^{3-} in MeCN are smaller (Fig. 5). With increasing content of MeOH, the precipitation become incomplete. The re-dissolution of the Li_4L^+ species is promoted apparently as the MeOH content increases in the solvent mixtures. However, the “reverse” coordination constant is not raised but reduced with increasing contents of MeOH: $\log K_{4(1+)} = 9.3$ and 6.1 in 5.0 and 7.0% MeOH, respectively (*cf.* Table 2). The 10% MeOH causes no precipitation nor re-dissolution reactions between Li^+ and L^{3-} .

The precipitation reaction Na_3L of is not influenced so much by small amounts of the added water (1.0 – 2.0%). However, 5.0% H_2O causes incomplete precipitation (*cf.* Table 2). When the H_2O content increases up to 10%, the absorbance remains almost unchanged. Even by the addition of 5.0% MeOH, the precipitation occurs almost completely, however, the precipitation becomes incomplete at 10% MeOH. The additional MeOH causes an increase of the Na_3L solubility, and the solubility products ($\text{p}K_{\text{sp}}$) are given to be 13.8, 10.3, and 5.1 for 5.0, 10, and 15% MeOH-MeCN, respectively (*cf.* Table 2), while $\text{p}K_{\text{sp}}$ is 15.4 in sole MeCN. Finally, the interaction between Na^+ and L^{3-} has not been observed in 20% MeOH. The absorbance minimum of L^{3-} appears at higher alkali metal concentrations with increasing H_2O or MeOH content in MeCN.

The properties of residual (or small amount of) water in organic solvents have been discussed previously [7,16]. Now that the “residual” water molecules in an organic solvent are isolated each other and cannot form the huge network through hydrogen bonding, its role in the non-aqueous solvent must be similar to diethyl ether [37,38]. Alcohols, such as MeOH and EtOH, possessing hydrogen bonding structure, have shown a behavior similar to H_2O in their chemical shifts (^1H NMR) with changing their contents in MeCN [12]. In the present section, we can conclude briefly that added H_2O or alcohols of the very small amounts ($< 1.0\%$) in MeCN does not influence so much on the interaction between M^+ and L^{3-} in MeCN.

3.3. The coordination reactions of alkaline earth metal ions (Mg^{2+} , Ba^{2+}) with L^{3-} in MeCN and alcohols

Fig. 6 shows the UV spectral changes of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion with increasing concentration of $\text{Mg}(\text{ClO}_4)_2$ in MeCN. The absorption band of L^{3-} around 238nm decreases obviously in the presence of $1.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Mg}^{2+}$ and suddenly disappears at an

equivalence of Mg^{2+} ($1.5 \times 10^{-4} \text{ mol dm}^{-3}$). The precipitates of Mg_3L_2 give no signal for the re-dissolution under the wide concentration range from $1.5 \times 10^{-4} \text{ mol dm}^{-3}$ to $0.20 \text{ mol dm}^{-3} \text{ Mg}^{2+}$. The peak absorbance shows a small rise at $0.50 \text{ mol dm}^{-3} \text{ Mg}^{2+}$, and increases significantly (to 0.548) in the presence of $1.0 \text{ mol dm}^{-3} \text{ Mg}(\text{ClO}_4)_2$, due to the formation of the “reverse” coordinated species of Mg_2L^+ , *cf.* Eq. 10.

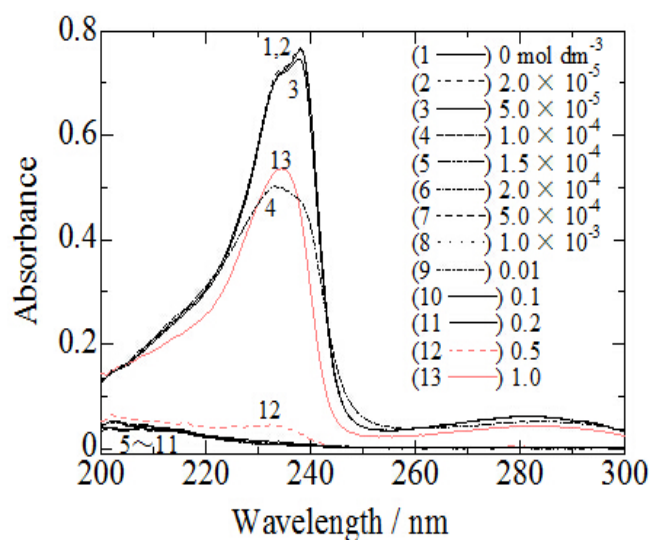


Fig. 6. UV spectra of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion (0.1 cm path-length) with increasing concentration of $\text{Mg}(\text{ClO}_4)_2$ in MeCN.

The complete precipitation occurs also between Ca^{2+} or Ba^{2+} and L^{3-} (Fig. 7), and the solubility product ($\text{p}K_{\text{sp}}$) values of Mg_3L_2 , Ca_3L_2 , and Ba_3L_2 are evaluated to be very close to one another, *i.e.*, 29.6, 32.4, and 31.5, respectively (*cf.* Table 1). Whereas, those of Ca_3L_2 or Ba_3L_2 would not be re-dissolved by a large excess amount of $\text{Ca}(\text{ClO}_4)_2$ or $\text{Ba}(\text{ClO}_4)_2$. In EtOH and 1-PrOH [16], two Ba^{2+} ions might be coordinated to O-atoms of sulfonates at 3- and 6-positions of 1,3,6-naphthalenetrisulfonate.

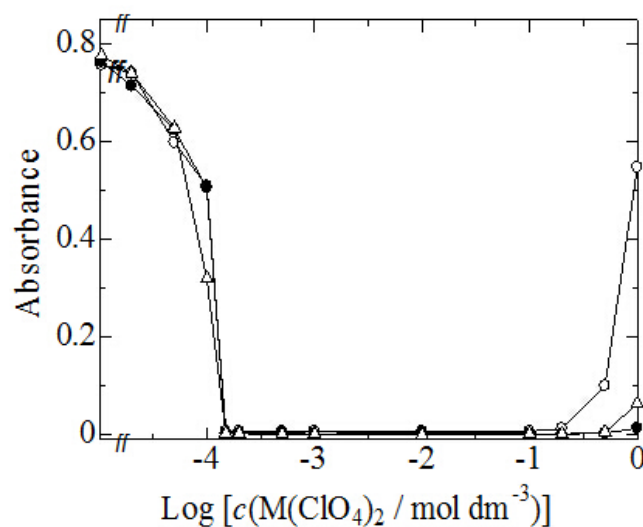


Fig. 7. Changes in absorbance ($\lambda = ca. 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion with increasing of alkaline earth metal ions in MeCN: ($\circ$) $\text{Mg}(\text{ClO}_4)_2$; ($\bullet$) $\text{Ca}(\text{ClO}_4)_2$; (Δ) $\text{Ba}(\text{ClO}_4)_2$.

In primary alcohols, as shown in Fig. 8, the interaction between Mg^{2+} and L^{3-} is much weaker than in MeCN. In MeOH, neither precipitation nor re-dissolution occurs between Mg^{2+} and L^{3-} . In EtOH, the absorbance shows a slight decrease to 0.669 at $2.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Mg}^{2+}$. Whereas, it have been reported that complete precipitation could take place between L^{3-} and Ba^{2+} in EtOH [16]. The precipitation occurs to a larger extent in 1-PrOH and 1-BuOH: the absorbance minimum values are 0.567 and 0.521, respectively, at $2.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Mg}^{2+}$.

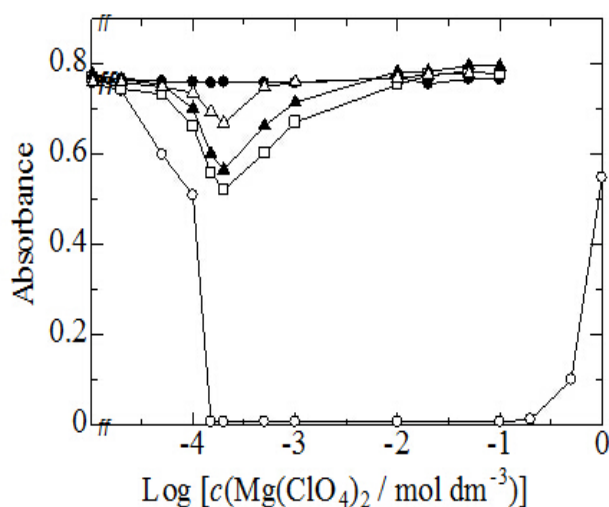


Fig. 8. The changes in absorbance ($\lambda = ca. 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion in the presence of $\text{Mg}(\text{ClO}_4)_2$ in alcohols and MeCN: (●) MeOH; (Δ) EtOH; ($\blacktriangle$) 1-PrOH; ($\square$) 1-BuOH; ($\circ$) MeCN.

3.4. The influences of H_2O or MeOH on the precipitation and re-dissolution between alkaline earth metal ions and L^{3-} in MeCN

Fig. 9 shows the influences of added water on the precipitation and the successive re-dissolution reactions of Mg_3L_2 in MeCN. Basically, the 1.0% H_2O in MeCN plays no significant role on the precipitation and re-dissolution. The precipitation occurs in a very wide concentration range from 1.5×10^{-4} to $0.20 \text{ mol dm}^{-3} \text{ Mg}^{2+}$ in sole MeCN and also 1.0% H_2O -MeCN. In 3.0% H_2O , however, the absorbance gradually increases in the presence of more than $2.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Mg}^{2+}$, while the precipitation occurs completely just after the equivalence of Mg^{2+} . In 5.0% H_2O , the precipitation becomes incomplete, meanwhile, the re-dissolution is promoted. Finally, the interaction is inhibited apparently with the 20% H_2O content. The $\text{p}K_{\text{sp}}$ value decreases with increasing contents of H_2O to be 26.0, 24.6, and 19.9 in 3.0, 5.0, and 10% H_2O -MeCN, respectively (*cf.* Table 3), while $\text{p}K_{\text{sp}}$ is 29.6 in sole MeCN (*cf.* Table 1).

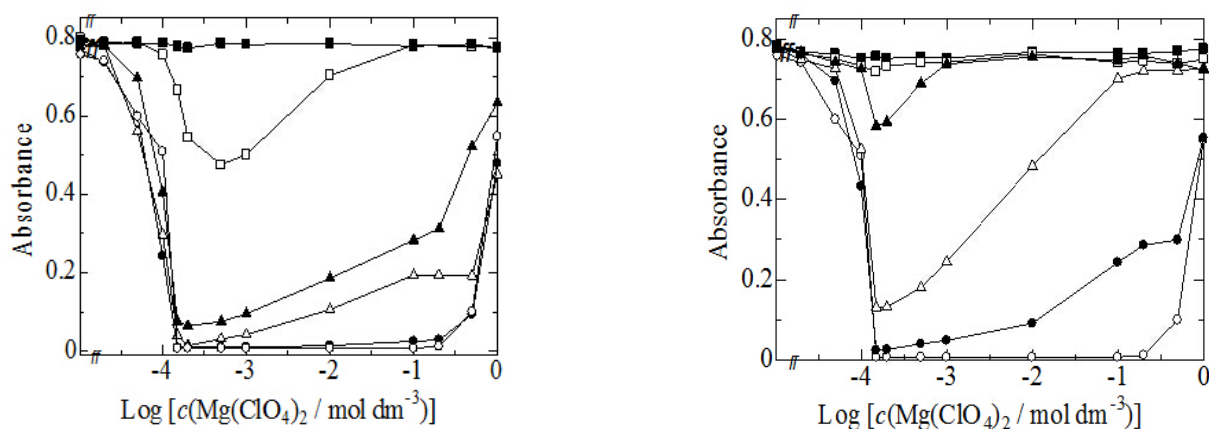


Fig. 9. Absorbance ($\lambda = ca. 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion in the presence of $\text{Mg}(\text{ClO}_4)_2$ in $\text{MeCN-H}_2\text{O}$ mixtures: ($\circ$) 0; ($\bullet$) 1.0; (Δ) 3.0 ($\blacktriangle$) 5.0; ($\square$) 10; ($\blacksquare$) 20% (v/v) of H_2O .

Fig. 10. Absorbance ($\lambda = ca. 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion in the presence of $\text{Mg}(\text{ClO}_4)_2$ in MeCN-MeOH mixtures: ($\circ$) 0; ($\bullet$) 5.0; (Δ) 10; ($\blacktriangle$) 15; ($\square$) 20; ($\blacksquare$) 50% (v/v) of MeOH .

The influences of MeOH on the coordination reaction between Mg^{2+} and L^{3-} are much smaller than those of H_2O (Fig. 10). Even with 5.0% MeOH , the precipitation occurs almost completely. When the amount of additional MeOH reaches 10% in MeCN , the precipitation becomes incomplete but the precipitates re-dissolve almost completely at more than $0.10 \text{ mol dm}^{-3} \text{ Mg}^{2+}$. Coincidentally, we have found the complete precipitation between Mg^{2+} and 1,5-naphthlenedisulfonate in MeCN containing 10% MeOH [16], which is probably ascribed to the stronger lattice energy between divalent metal cations and divalent anions. The solubility products (pK_{sp}) and “reverse” coordination constants ($\log K_{2(2+)}$) of the specific interaction between Mg^{2+} and L^{3-} in the binary solvents of $\text{MeCN-H}_2\text{O}$ and MeCN-MeOH are listed in Table 3.

Fig. 11 shows the influences of the added water on the precipitation reaction of Ba_3L_2 in MeCN . The influences of additional 5.0% H_2O on the precipitation reaction of Ba^{2+} with L^{3-} are lesser than that of Mg^{2+} with L^{3-} . As the H_2O content reaches 10%, the precipitation occurs incompletely and it is inhibited at 20% H_2O .

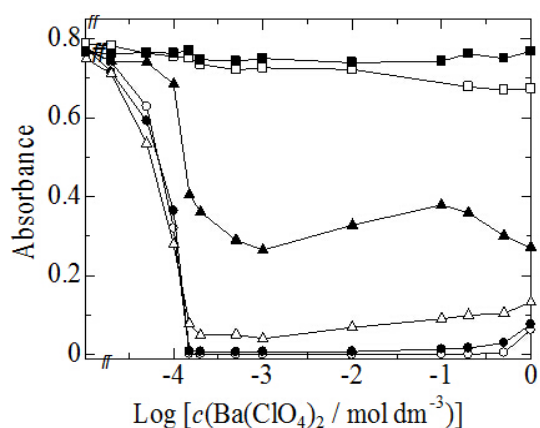


Fig. 11. Absorbance ($\lambda = ca. 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion in the presence of $\text{Ba}(\text{ClO}_4)_2$ in MeCN- H_2O mixtures: ($\circ$) 0; ($\bullet$) 5.0; (Δ) 10; ($\blacktriangle$) 15; ($\square$) 20; ($\blacksquare$) 30 % (v/v) of H_2O .

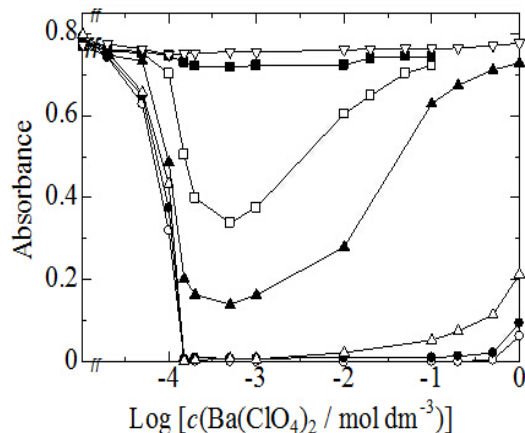


Fig. 12. Absorbance ($\lambda = ca. 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion in the presence of $\text{Ba}(\text{ClO}_4)_2$ in MeCN-MeOH mixtures: ($\circ$) 0; ($\bullet$) 10; (Δ) 20; ($\blacktriangle$) 40; ($\square$) 50; ($\blacksquare$) 70; (∇) 100 % (v/v) of MeOH

Fig. 12 shows the influences of the added MeOH on precipitation and the successive re-dissolution of Ba_3L_2 . The larger MeOH content of 10% gives almost no effect on the precipitation. Even with addition of 20% MeOH, the precipitate occurs completely and the re-dissolution of the precipitation is slightly promoted. With 40% MeOH, the precipitation reaction become weaker, and the re-dissolution is much promoted (*cf.* Table 3). In sole MeOH, neither precipitation nor re-dissolution takes place between Ba^{2+} with L^{3-} . Comparing between Figs. 11 and 12, we can notice clearly that the addition of MeOH to MeCN promotes largely the re-dissolution of the precipitates of Ba_3L_2 , whereas that of H_2O does scarcely.

3.5. The interaction between In^{3+} and L^{3-} in MeCN, MeCN- H_2O , and alcohols

As well as alkali metal and alkaline earth metal ions, group 13 metals are s-block elements.

The ionic radius of In^{3+} (0.80 Å [39]) is similar to that of Mg^{2+} (0.86 Å [40]), but In^{3+} possesses more electric field strength than Mg^{2+} . Compared to Al^{3+} , the lighter homologue, In^{3+} , has a pronounced tendency to expand its coordination sphere [41]. In order to discuss the effects of valence electron on association behavior of metal ions with anions, the reaction between In^{3+} and the 1,3,6-naphthalenetrisulfonate ion $[(\text{Et}_4\text{N}^+)_3\text{L}^{3-}]$ have been examined in MeCN and also primary alcohols.

In MeCN, the absorbance of L^{3-} at around 238 nm firstly decreases, then increases with the increasing concentration of In^{3+} [$\text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$ or $\text{In}(\text{CF}_3\text{SO}_3)_3$]. However, the precipitation and re-dissolution behavior was rather complicated.

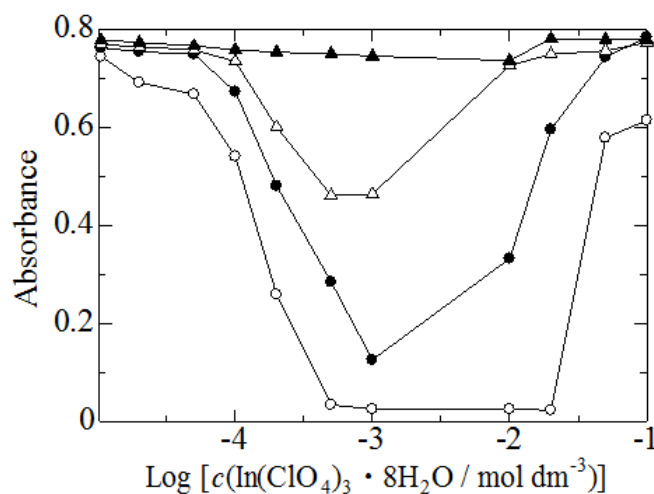


Fig. 13 Changes in absorbance ($\lambda = ca. 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion with increasing concentration of $\text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$ in MeCN- H_2O mixtures: (○) 10; (●) 30; (△) 50; (▲) 100% (v/v) of H_2O .

The addition of water on the reaction between In^{3+} [$(\text{ClO}_4^-)_3$] and L^{3-} causes more typical precipitation and the re-dissolution (Fig. 13). The absorbance minimum appears in a wide range

from 1.0×10^{-3} to 2.0×10^{-2} mol dm⁻³ in 10% H₂O. In 30% H₂O, the precipitation reaction becomes incomplete, but the absorbance of L³⁻ thoroughly recovers to the origin value (*ca.* 0.8) at 0.1 mol dm⁻³ In(ClO₄)₃. Even in 50% water, the precipitation can occur to a smaller extent, possibly owing to the strong interaction between the high electron density of In³⁺ and L³⁻. The solubility products (*pK_{sp}*) are evaluated to be 8.3, 7.8, and 7.2 in 10, 30, and 50% H₂O-MeCN, respectively (*cf.* Table 4). As for the In³⁺ ion in H₂O-MeCN binary solvents, we have to pay attention to the hydrolysis reactions of In³⁺ with H₂O. The large formation constant (*log K*) of In(OH)²⁺ between In³⁺ and OH⁻ has been reported to be 10.3 in aqueous solution [42].

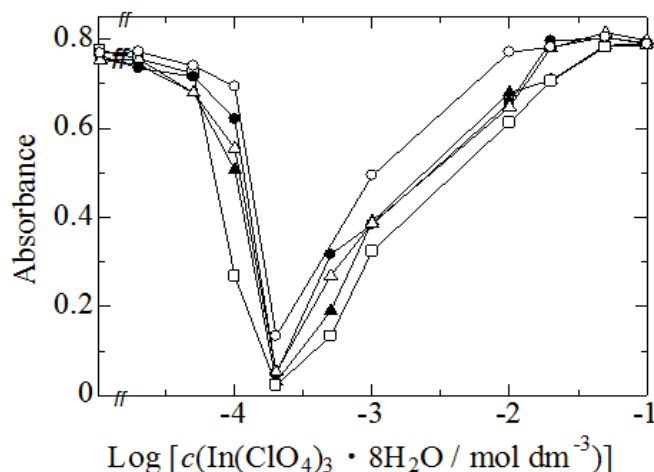
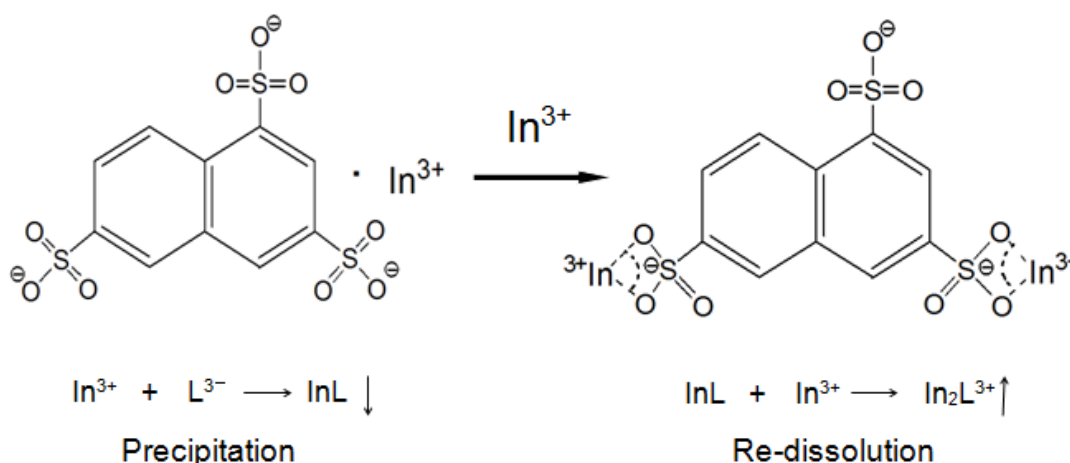


Fig. 14. Absorbance ($\lambda = ca. 238$ nm) of 1.0×10^{-4} mol dm⁻³ 1,3,6-naphthalenetrisulfonate in the presence of In(ClO₄)₃·8H₂O in primary alcohols: (○) MeOH; (●) EtOH; (Δ) 1-PrOH; (▲) 1-BuOH; (□) 1-HexOH.

The specific interaction between In³⁺ and L³⁻ can take place in all the primary alcohols (Fig. 14). At first, the L³⁻ absorbance decreases with increasing concentration of In(ClO₄)₃·8H₂O, and gradually increases after reaching its minimum at 2.0×10^{-4} mol dm⁻³ In³⁺, finally almost recovers its original value. The minimum absorbance of L³⁻ is 0.134, 0.031, and 0.023 in MeOH, EtOH, and 1-HexOH at 2.0×10^{-4} mol dm⁻³ In³⁺. Scheme 2 represents the precipitation of InL and the

successive re-dissolution of precipitates through interaction between InL and In^{3+} , causing the “reverse” coordinated species of In_2L^{3+} . The solubility products ($\text{p}K_{\text{sp}}$) and “reverse” coordination constants ($\log K_{2(3+)}$) in the sole alcohols are listed also in Table 1.



Scheme 2. Successive formation of InL and In_2L^{3+} for the 1,3,6-naphthalenetrisulfonate ion in MeCN- H_2O or sole alcohols.

3.6. Computational prediction of the structures of Li_4L^+ in MeCN

For predicting the coordinating structures of Li_4L^+ in Scheme 1, we performed geometry optimization using GAMESS program package [46]. All geometries were optimized with the density functional theory (DFT) employing the long-range corrected BOP (LC-BOP) exchange-correlation functional [47]. The aug-cc-pVDZ basis sets [48] was adopted for oxygen atoms, while the cc-pVDZ set [48] was used for the other atoms. In the present paper, the acetonitrile solvent was taken into consideration by the conductor-like polarizable continuum model (C-PCM) [49] with the solvation model density (SMD) [50].

Fig. 15(a)–(c) show the projected views of optimized structures of

1,3,6-naphthalenetrisulfonates to which four Li^+ ions are coordinated at (a) 1,1,3,6, (b) 1,3,3,6, and (c) 1,3,6,6 positions. Each Li^+ ion coordinates to two O atoms even at the sulfonate group coordinated by two Li^+ ions. Therefore, two Li^+ ions simultaneously coordinate to the same O atom of the sulfonate group. Accordingly, the S–O lengths coordinated by two Li^+ ions (1.54–1.55 Å) were slightly longer than those coordinated by one Li^+ ion (1.52–1.53 Å), though these S–O lengths were significantly elongated from those at free sulfonate (1.48 Å). Table 5 summarizes the relative energies for these Li_4L^+ structures obtained by the DFT calculations in MeCN. The 1,1,3,6-coordinated structure is the most stable among these three species, although the difference from the most unstable 1,3,3,6-coordinated structure is less than 0.4 kcal/mol. Therefore, all these structures are probable in MeCN, or the stability in the free energy may change by the condition of the solution.

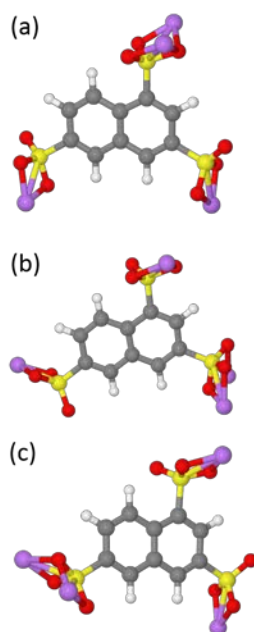


Fig. 15. The optimized structures of 1,3,6-naphthalenetrisulfonates to which four Li^+ ions are coordinated at (a) 1,1,3,6, (b) 1,3,3,6, and (c) 1,3,6,6 positions.

Conclusion

The coordination ability of alkali metal (Li^+ , Na^+), alkaline earth metal (Mg^{2+} , Ba^{2+}), and indium (In^{3+}) ions with 1,3,6-naphthalenetrisulfonate (L^{3-}) have been examined in primary alcohols as well as MeCN. In MeCN, all the alkali metal and alkaline earth metal ions can interact with L^{3-} to form complete precipitates, however, the re-dissolution behavior of the precipitates is quite different from one another: the “reverse” coordinated species of Li_4L^+ and Mg_2L^+ can be partially produced from the non-charged species, but the precipitates of Na_3L , Ca_3L_2 , and Ba_3L_2 are never re-dissolved even by large excess amounts of the corresponding metal ions in sole MeCN. The coordination reaction of In^{3+} in MeCN is much stronger than that of alkali metal or alkaline earth metal ion. We may conclude that the whole phenomena in the present work may not be accounted for comprehensively just by evaluating the proper activity coefficients of ions without considering the “reverse” coordination between (or among) the metal and L^{3-} ions under some protic as well as aprotic media conditions.

Acknowledgement

The present calculations were performed using the computer facilities at Research Center for Computational Science, Okazaki, Japan and Research Institute for Information Technology, Kyushu University, Japan.

Table 1 Precipitation and re-dissolution reactions of alkali metal (Li^+ , Na^+), alkaline earth metal ions (Mg^{2+} , Ba^{2+}), and indium (In^{3+}) ions and 1,3,6-naphthalenetrisulfonate $[(\text{Et}_4\text{N}^+)_3\text{L}^{3-}]$ in sole solvents of MeCN and primary alcohols.

Metal ions ^a	Equilibrium constants ^b	MeCN	MeOH	EtOH	1-PrOH	1-BuOH	1-HexOH
Li^+		●	No	No	No	No	No
	($\text{p}K_{\text{sp}}$)	15.4	—	—	—	—	—

	(pK _{sp}) ^c	15.7	—	—	—	—	—
		△	No	No	No	No	No
	log K ₄₍₁₊₎	11.0	—	—	—	—	—
		●	No	No	▲	▲	▲
Na ⁺	(pK _{sp})	15.4	—	—	10.4	13.9	14.0
	(pK _{sp}) ^c	15.7	—	—	11.2	14.9	15.5
		No	No	No	No	No	No
	log K ₄₍₁₊₎	—	—	—	—	—	—
		●	▲	▲	▲	▲	▲
Mg ²⁺	(pK _{sp})	29.6	—	19.7	20.0	20.2	—
	(pK _{sp}) ^c	30.5	—	21.2	22.1	22.7	—
		△	○	○	○	○	○
	log K ₂₍₂₊₎	10.7	—	—	—	—	—
		●	No	●	●		
Ca ²⁺	(pK _{sp})	32.4	—	25.2	25.6		
	(pK _{sp}) ^c	33.2	—	26.7	27.6		
		No	No	○	○		
	log K ₂₍₂₊₎	—	—	9.0	9.0		
		●	No	●	●	●	
Ba ²⁺	(pK _{sp})	31.5	—	27.6 ^d	27.7 ^d	26.4	
	(pK _{sp}) ^c	32.4	—	29.1	29.7	28.9	
		No	No	○	○	△	
	log K ₂₍₂₊₎	—	—	9.8 ^d	9.9 ^d	9.2	
		▲	▲	●	●	●	●
In ³⁺	(pK _{sp})	^e	8.2	8.3	8.3	8.4	8.9
	(pK _{sp}) ^c		10.4	10.9	11.9	12.9	(15.8) ^f
		△	○	○	○	○	○
	log K ₂₍₃₊₎	^e	6.5	6.0	6.1	6.2	7.5

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 (L³⁻) 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.

^a $M(\text{ClO}_4)_n$.

^b Solubility products (K_{sp}) and “reverse” coordination constants ($K_{4(1+)}$, $K_{2(2+)}$, $K_{2(3+)}$), *cf.* the experimental section in the present paper and in Ref. [16].

^c Thermodynamic solubility products (K_{sp}) corrected with the activity coefficients of ions. The mean activity coefficients of ions are roughly evaluated from the limiting Debye-Hückel equation, $\log \gamma_{\pm} = -A|Z_+ Z_-| \mu^{1/2}$, *cf.* Ref. [43].

^d The values have been proposed in Ref. [16].

^e They were not evaluated because of the complex interaction between (or among) In^{3+} and L^{3-} in sole MeCN.

^f The low permittivity of hexanol ($\epsilon_r = 13.3$) causes very low activity coefficients for triple charged ions, if evaluated by the limiting Debye-Hückel equation.

Table 2 Precipitation and re-dissolution reactions of alkali metal ions with the 1,3,6-naphthalenetrisulfonate ion in binary solvents of MeCN-H₂O and MeCN-MeOH.

Metal ions ^a	Equilibrium constants ^b					
	MeCN- H ₂ O [H ₂ O contents / % (v/v)]	1.0	2.0	5.0	10	
Li ⁺		●	▲	▲	No	
	(pK _{sp})	16.1	16.1	6.4	—	
	(pK _{sp}) ^c	16.5	16.5	6.7	—	
		△	△	No	No	
	log K ₄₍₁₊₎	11.7	11.6	—	—	
Na ⁺		●	●	▲	No	
	(pK _{sp})	16.2	15.6	10.5	—	
	(pK _{sp}) ^c	16.5	15.9	10.8	—	
		No	No	No	No	
	log K ₄₍₁₊₎	—	—	—	—	
	MeCN-MeOH [MeOH contents / % (v/v)]	5.0	7.0	10	15	20
Li ⁺		▲	▲	No		No

	(pK _{sp})	13.5	10.2	—	—
	(pK _{sp}) ^c	13.9	10.5	—	—
		△	△	No	No
	log K ₄₍₁₊₎	9.3	6.1	—	—
		▲		▲	▲
					No
	(pK _{sp})	13.8		10.3	5.1
	(pK _{sp})	14.2		10.6	5.5
		△		△	△
					No
	log K ₄₍₁₊₎	—		—	—

For the Explanatory notes, *cf.* Table 1.

^a MClO₄.

^b Solubility products (K_{sp}) and “reverse” coordination constants (K₄₍₁₊₎), *cf.* the Experimental section.

^c *Cf.* Table 1, note c for the thermodynamic solubility products (K_{sp}) corrected with the activity coefficients of ions. The permittivity values of the binary solvent systems, MeCN-H₂O and MeCN-MeOH, have been interpolated from the data from Ref. [44] and [45], respectively.

Table 3 Precipitation and re-dissolution reactions of alkaline earth metal ions with the 1,3,6-naphthalenetrisulfonate ion in binary solvents of MeCN-H₂O and MeCN-MeOH.

Metal ions ^a	Equilibrium constants ^b	MeCN- H ₂ O [H ₂ O contents / % (v/v)]				
		1.0	3.0	5.0	10	20
		●	▲	▲	▲	No
	(pK _{sp})	29.7	26.0	24.6	19.9	—
	(pK _{sp}) ^c	30.5	26.8	25.4	20.6	—
		△	△	△	○	No
	log K ₂₍₂₊₎	10.6	8.8	7.8	5.9	—
		5.0	10	15	20	30
Ba ²⁺		●	▲	▲	No	No

	(pK _{sp})	29.2	24.4	20.9	—	—
	(pK _{sp}) ^c	29.9	25.1	21.5	—	—
		No	No	No	No	No
	log K ₂₍₂₊₎	—	—	—	—	—
MeCN-MeOH [MeOH contents / % (v/v)]						
		5.0	10	15	20	50
		●	▲	▲	No	No
Mg ²⁺	(pK _{sp})	26.0	23.3	—	—	—
	(pK _{sp})	26.9	24.2	—	—	—
		△	△	○	No	No
	log K ₂₍₂₊₎	9.4	7.6	—	—	—
		10	20	40	50	70
		●	●	▲	▲	No
	(pK _{sp})	26.0	23.3	22.1	20.4	—
Ba ²⁺	(pK _{sp}) ^c	26.9	24.2	23.0	21.3	—
		No	No	○	○	No
	log K ₂₍₂₊₎	—	—	7.5	6.7	—

For the Explanatory notes, *cf.* Table 1.

^a M(ClO₄)₂.

^b Solubility products (K_{sp}) and “reverse” coordination constants (K₂₍₂₊₎), *cf.* the Experimental section in Ref. [16].

^c *Cf.* Table 1, note c for the thermodynamic solubility products (K_{sp}) corrected with the activity coefficients of ions. The permittivity values of the binary solvent systems, MeCN-H₂O and MeCN-MeOH, have been interpolated from the data from Ref. [44] and [45], respectively.

Table 4 Precipitation and re-dissolution reactions between In³⁺ and the 1,3,6-naphthalenetrisulfonate ion in binary MeCN-H₂O media.

Metal ions ^a	Equilibrium constants ^b	MeCN-H ₂ O [H ₂ O contents / % (v/v)]			
		10	30	50	100
In ³⁺		●	▲	▲	No
	(pK _{sp})	8.3	7.8	7.2	—

$(pK_{sp})^c$	9.6	8.8	8.0	—
	$\triangle$	$\circ$	$\circ$	No
$\log K_{2(3+)}$	5.4	5.4	5.2	—

For the Explanatory notes, *cf.* Table 1.

^a $\text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$.

^b Solubility products (K_{sp}) and “reverse” coordination constants ($K_{2(3+)}$), *cf.* the Experimental section.

^c *Cf.* Table 1, note c for the thermodynamic solubility products (K_{sp}) corrected with the activity coefficients of ions. The permittivity values of the binary solvent system, MeCN- H_2O , have been interpolated from the data from Ref. [44].

Table 5 Calculated relative energies for Li_4L^+ (L: 1,3,6-naphthalenetrisulfonate) in MeCN.

Positions of Li^+	Relative energy / kcal mol^{-1}
1,1,3,6	0.00
1,3,3,6	+0.32
1,3,6,6	+0.07

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