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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 ( $\text{Li}^+$ ,  $\text{Na}^+$ ), alkaline earth metal ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , or  $\text{Ba}^{2+}$ ), and indium ( $\text{In}^{3+}$ ) ions with the 1,3,6-naphthalenetrisulfonate ion ( $\text{L}^{3-}$ ,  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) 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  $\text{L}^{3-}$ . In the presence of excess amounts of the metal ions, the precipitates of  $\text{Li}_3\text{L}$  and  $\text{Mg}_2\text{L}_3$  tend to re-dissolve partially to form the “reverse” coordinated species of  $\text{Li}_4\text{L}^+$  and  $\text{Mg}_2\text{L}^+$ . However, those precipitates of  $\text{Na}_3\text{L}$ ,  $\text{Ca}_3\text{L}_2$ , and  $\text{Ba}_3\text{L}_2$  would not re-dissolve even in the presence of large excess amounts of the metal ions in MeCN. Between  $\text{In}^{3+}$  and  $\text{L}^{3-}$ , 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  $\text{L}^{3-}$  ( $\log K_{4(1+)}$ ,  $\log K_{2(2+)}$ , 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– $\text{H}_2\text{O}$  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  $\text{Li}_4\text{L}^+$  species in MeCN.

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## 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 ( $\text{Cl}^-$ ,  $\text{Br}^-$ ) [4,5], tropolonate [6], sulfonates, and carboxylates [7] have been demonstrated by means of various analytical methods. With the increasing concentration of  $\text{M}^+$  (an alkali metal ion), the specific reaction may proceed in three steps: at first, a half equivalence or less than that amount of  $\text{M}^+$  interacts with an anion ( $\text{L}^-$ ) 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  $\text{M}^+$ ; finally, a “triple cation”  $[\text{M}_2\text{L}^+]$ ,

positively charged species, can be produced from the precipitates with an excess amount of  $\text{M}^+$ , that is, the re-dissolution of precipitation. Chen and Hirota [8] have investigated the formation and dissociation of a triple ion ( $\text{M}^+\text{A}^-\text{M}^+$ ,  $\text{M} = \text{Li}, \text{Na}, \text{K}$ ,  $\text{A} = \text{anthraquinone}$ ) 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] has 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  $\text{Li}^+$  and halide ( $\text{Cl}^-$ ,  $\text{Br}^-$ ) or thiocyanate ( $\text{SCN}^-$ ) ions in iso-permittivity binary mixed solvents between THF and 2-ethyl-1-hexanol [14].

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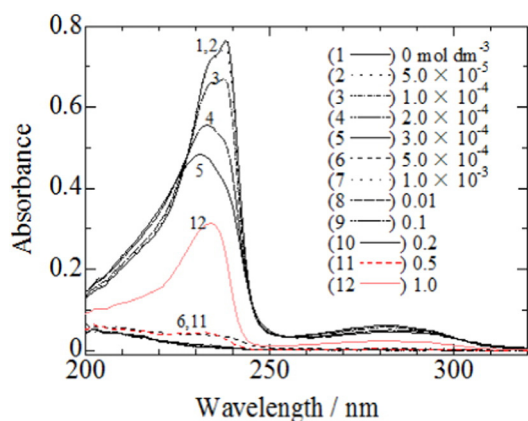
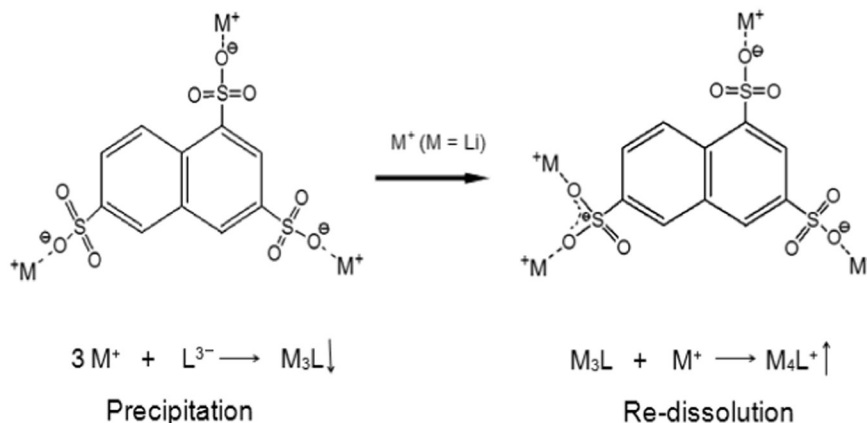


Fig. 1. The UV spectra of  $1.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$  1,3,6-naphthalenetrisulfonate ion (0.1 cm path-length) with increasing concentration of  $\text{LiClO}_4$  in MeCN.

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  $\text{Ba}^{2+}$  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  $\text{LiClO}_4$  as the supporting electrolyte. The formation of triple ions from  $\text{LiClO}_4$  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 capsule 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– $\text{H}_2\text{O}$  and MeCN–alcohols. Naphthalenetrisulfonate is commonly used as a chemical function of Suramin and Suradistas [28].



Scheme 1. Successive formation of  $\text{M}_3\text{L}$  and  $\text{M}_4\text{L}^+$  ( $\text{M} = \text{Li}$ ) for the 1,3,6-naphthalenetrisulfonate ion in MeCN.

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  $\text{Et}_4\text{NOH}$  (20 wt.% in  $\text{H}_2\text{O}$ , Aldrich) were mixed in methanol, followed by evaporation to dryness at  $50^\circ\text{C}$ , and the salt was dried in vacuo at  $80^\circ\text{C}$ . 1,3,6-Naphthalenetrisulfonic acid was prepared from the sodium salt [16].

Metal perchlorates without water,  $\text{LiClO}_4$  (Wako),  $\text{NaClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ , and  $\text{Ba}(\text{ClO}_4)_2$  (all Aldrich), were used as received. Calcium perchlorate tetrahydrates from Aldrich was dried in vacuo at  $150^\circ\text{C}$  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 ( $\text{M}^{2+}$ ) and 1,3,6-naphthalenetrisulfonate

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