

博士論文

**Specific Coordination Phenomena of Alkali Metal, Alkaline Earth Metal,
and the III Group Metal Ions with the Conjugate Anions
from Organic Acids in Non-Aqueous Solvents**

(非水溶媒中におけるアルカリ金属、アルカリ土類金属
および第III族金属イオンと有機酸の共役陰イオン間の配位現象)

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ABSTRACT

The coordination ability of alkali (Li^+ , Na^+), alkaline earth metal (Mg^{2+} , Ca^{2+} , or Ba^{2+}) and indium ions with sulfonates, phosphinate, phosphates and carboxylates has been examined by means of UV-visible spectroscopy, based on the specific interactions including precipitation of the non-charged species and the successive re-dissolution of the charged species, *i.e.*, “reverse-coordinated” species. The solubility products and “reverse” coordination constants have been successfully evaluated for all the systems.

The specific interactions between alkaline earth metal (M^{2+}) and *p*-toluenesulfonate (L^-), 1,5-naphthalenedisulfonate (L^{2-}), or 1,3,6-naphthalenetrisulfonate (L^{3-}) ions have been examined in primary alcohols as well as in the binary acetonitrile-alcohols (MeCN-MeOH, MeCN-EtOH), ethanol-methanol (EtOH-MeOH) and methanol-water (MeOH- H_2O) solvents. The precipitation of non-charged species (*e.g.* ML^0) and the successive re-dissolution of the precipitates, with increasing concentration of $\text{M}(\text{ClO}_4)_2$, have revealed the formation of cationic charged species or “reverse-coordinated” species, M_2L^{2+} , even in the protic media as well as the aprotic solvent MeCN. (Chapter 2)

In MeCN, the precipitation completely takes place between (M^+) or M^{2+} and 1,3,6-naphthalenetrisulfonate (L^{3-}). The precipitation of Li_3L and Mg_2L_3 re-dissolves partially to form the “reverse-coordinated” species of Li_4L^+ and Mg_2L^+ by the addition of excess amounts of the metal ions. Both precipitation and re-dissolution can occur between In^{3+} and L^{3-} in all the primary alcohols. The influences of H_2O or methanol on precipitation and re-dissolution reactions in MeCN have been investigated. (Chapter 3)

In MeCN and binary solvents of MeCN- H_2O and MeCN-MeOH, the specific interactions of M^+ and M^{2+} with various phosphorus anions, L^- , *i.e.*, diphenylphosphinate, diphenylphosphate, and bis(4-nitrophenyl)phosphate, have been examined. The formation of “reverse-coordinated”

species, M_2L^+ or ML^+ , has been observed in the presence of excess amounts of the metal ions to the anions. (Chapter 4)

In binary solvents of MeCN-MeOH and MeCN-H₂O, the coordination ability of M^+ or M^{2+} with and 1,4- or 2,3-naphthalenedicarboxylate has been examined by UV-visible spectroscopy. As for 1,4-naphthalenedicarboxylate (1.0×10^{-4} mol dm⁻³), an excess amounts of Na⁺ and Li⁺ causes formation of “reverse-coordinated” species of M_3L^+ in 10% MeOH-MeCN. The precipitation extent increases in the order of $Ca^{2+} > Ba^{2+} > Mg^{2+}$. The solubility products (pK_{sp}) and the “reverse” coordination constants ($\log K_3$ and $\log K_2$) have been evaluated in MeCN containing various content of MeOH or H₂O. (Chapter 5)

Keywords: “reverse” coordination; triple ion formation; UV spectroscopy; alkali or alkaline earth metal ions; acetonitrile; primary alcohols; protic-aprotic binary solvent mixtures.

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Chapter 1 Introduction

1.1. Ion Association

In aqueous solution, many salts (those consisting of anion of a strong acid and/or cation of a strong base) would dissociate almost completely. Dissociation is a process in which ionic compound (*i.e.* salt, complex, *etc.*) separates into smaller parts, like ions (anions, cations) and/or molecules: $AB \rightarrow A^+ + B^-$. In dilute solution, the ion association behavior of strong electrolytes have been successfully explained by Debye-Hückel theory [1] in 1920s, which modeled the dilute electrolyte solutions as consisting of completely dissociated ions perturbed by long-range Coulombic interactions.

However, in solvents having lower dielectric constants (permittivity), the differences are too large to be accounted for by any extension of the Debye-Hückel theory. In 1926, Bjerrum [2] introduced the concept of association of oppositely charged ions into dipolar pairs to explain the deviation of the experimental results from Debye-Hückel theory. Bjerrum theory deals explicitly with the formation of ion pairs, and can be used to calculate an expected value of the association constant for an equilibrium between two ions and an ion-pair. Based on the specific models of the ion-pair, many other theories of ion association have been proposed by Denison and Ramsey [3], Gilkerson [4], Fuoss [5-8] and other researchers [9-10].

The initial proposed concerning ion pair formation has had an enormous impact in many branches of chemistry including mechanistic organic chemistry [11, 12]. Ion association have attracted researcher's attention near a century due to its fundamental importance in solution, having been widespread investigating not only in electrolyte behavior [13-15], solvent properties [16-18] or thermodynamic studies [19-21] but also in application in widely different fields. Early in 1953, Schellm [22] applied Bjerrum theory to the binding of chloride by serum albumin with the assumption of shielding by the protein. Walser [23] examined the ion association between calcium, magnesium and inorganic phosphate, citrate and protein in normal human plasma. The formation of okadaic acid- K^+ complex was carried out in $CDCl_3$ by self-association of okadaic acid upon complexation with potassium ion [24]. Z. Shu *et al.* [25] determined that anion exchange

follows a dissociative mechanism for Mg^{2+} and an associative mechanism for Ca^{2+} , in order to discriminate between calcium and magnesium for these ions to perform their distinct biological functions. Schmuck [26] have synthesized a new class of flexible zwitterions, in which a carboxylate is linked *via* an alkyl chain with variable length (one to five methylene groups) to a guanidiniocarbonylpyrrole cation attribute to the self-association properties of zwitterions.

1.2. Triple-ion study

Besides ion-pair species, Fuoss and Kraus [27] considered that the triple-ion species would be formed in solvent of lower dielectric constants. They rationalized the appearance of a minimum in the relation between the molar conductivity and the concentration of electrolytes dissolved in media of low permittivity ($\epsilon_r < 12$ or 23.2) by postulating the existence of triple ions. Also, they introduced the idea of triple ion formation from an ion A^+ or B^- with an ion pair: $\text{A}^+ + \text{B}^- \rightleftharpoons \text{A}_2\text{B}^+$ and $\text{B}^- + \text{AB} \rightleftharpoons \text{AB}_2^-$ by the electrostatic forces.

The formation of a normal coordination-type species (A_2B^+) can be easily accepted by many chemists because of the possible stability on chelating in solution. Raban *et al.* [28, 29] reported experimental evidence for a chelated lithium bisacetylacetonate ($\text{Li}(\text{acac})_2^-$) complex in methanol solution. However, the “dilithium complex” of a ligand (L^-) [30] has still been regarded as an uncertain matter. Murray and Hiller [31] first suggested involvement of two lithium ions in a ligand loss during one-electron reduction of $\text{Fe}(\text{acac})_3$ in acetonitrile (MeCN) containing LiClO_4 as the supporting electrolyte:



Similarly, the formation of $[\text{CH}_3\text{COOLi}_2]^+$ species was suggested for the effect of LiClO_4 on the polarographic reduction of dimeric copper(II) acetate in MeCN [32]. The idea of both normal coordination and “reverse coordination” between a carboxylate ion and monovalent metal ions is illustrated in equation 1.1.

So far, the triple ion formation in various solvents have been investigated by means of electron spin resonance spectroscopy (ERS), conductometry, polarography, UV-visible, ^1H and ^{13}C NMR spectroscopy. Also, the formation constant have been calculated by different methods.

1.2.1. Electron spin resonance (ERS) or electron paramagnetic resonance (EPR) spectroscopy

T. E. Gough and P. R. Hindle [33] found the direct evidence for the existence of triple-ions by ESR studies. With the addition of sodium tetraphenylboride to solutions of sodium-semiquinone ion-pairs (NaD) in tetrahydrofuran (THF), the hyperfine lines of the protons in the semiquinone anions were split into seven lines (Fig. 1.1), an indication that two equivalent sodium nuclei interact with each anion (Na_2D^+). Meanwhile, they added NaX ($\text{X}^- = \text{Ph}_4\text{B}^-$, ClO_4^- , I^-) to sodium-semiquinone ion pair and found that triple ion formation was observed when $\text{X}^- = \text{Ph}_4\text{B}^-$, however, when $\text{X}^- = \text{ClO}_4^-$ or I^- intermolecular cation scrambling occurred, which results postulated that such scrambling reactions proceed *via* the triple ion [34]. Barzaghi [35] investigated the rate and the mechanism of sodium exchange between the 3,5-dinitrobenzonitrile-sodium ion pair and sodium tetraphenylborate (NaBPh) in THF by ESR spectroscopy.

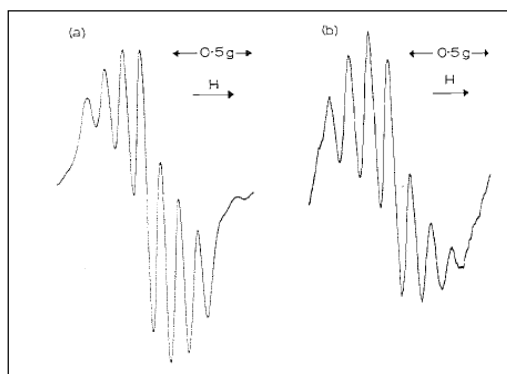


Fig. 1.1. ^{23}Na hyperfine multiplets of the triple ions (a) durosemiquinone- Na_2^+ and (b) 2,3-dimethyl-p-benzosemiquinone- Na_2^+ , showing the asymmetric broadening of the alkali metal splitting [33].

EPR spectroscopy can be utilized in the evaluation of certain kinetic and thermodynamic parameters that control processes and equilibria involving anion radicals [36]. The kinetics and the thermodynamics of triple-ion formation involving the anion radical of 1,3,5-trinitrobenzene associated with sodium cation in THF containing sodium tetraphenylborate were studied by EPR spectroscopy [36]. All hfs-constant and line-width data and their dependence on temperature and salt concentration have been interpreted in the frame of an adequate model for ionic association. The influence of the transport properties of the solution have also been discussed.

K. S. Chen and N. Hirota [37] examined the process of the formation of Li, Na and K triple

ions and kinetics of the formation and dissociation of triple ions ($M^+A^-M^+$) by comprehensive EPR studies. The authors demonstrated that intermediate triple ions or ion quadruplets are formed in the course of cation-transfer reactions. The equilibrium constants were estimated to be approximately $10^3 \sim 10^4 M^{-1}$ for the Na triple ion in THF at 25 °C. In order to obtain these species, higher concentrations of salts are needed. They also considered that the formation of triple ion strongly depends on the dissociation constant (K_D) of the added salts as well as the equilibrium constant (K_T) for the formation of triplet ion, because of the examined alkali metal salts generally form ion pairs in ethereal solutions.

1.2.2. Conductometry

By conductometry, the conditions and concentrations of chemical species can be examined based on the transformation phenomena of ionic species. As early as 1933, Fuoss and Kraus [27, 38, 39] reported and discussed conductivity data of the thiocyanate and tetraisopentylammonium nitrate, among other salts, in dioxane ($\epsilon_r = 2.21$), benzene ($\epsilon_r = 2.27$), and in dilute mixtures of benzene with 1,2-dichloroethane ($\epsilon_r = 2.8$) and of dioxane with water. The minima observed in conductometric curves ($\epsilon_r \leq 9.0$) were interpreted by the formation of the “symmetrical” triple ions.

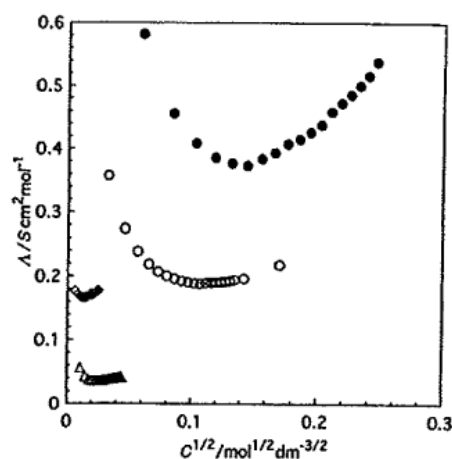


Fig. 1.2. Observed molar conductivities (Λ) in THF at 25 °C: (●) LiClO_4 ; (○) LiPic (lithium picrate); (◇) 2,4- $(\text{NO}_2)_2\text{C}_{10}\text{H}_5\text{OLi}$; (△) LiNO_3 [40].

In low permittivity solvents such as THF ($\epsilon_r = 7.58$, Fig. 1.2), 1,2-dimethoxyethane ($\epsilon_r = 7.2$), chloroform ($\epsilon_r = 4.8$), and ethyl acetate ($\epsilon_r = 6.0$), conductivities of a number of uni-univalent salts,

including tetrabutylammonium and lithium nitrophenolates were measured [40]. Minima in the conductometric curves ($\Lambda - C^{1/2}$) were observed for concentrations which were dependent upon both the salt and the solvent. The observed molar conductivities including C_{\min} could be completely explained by the formation of ion pairs, “symmetrical” triple ions, and (in some cases) additional formation of quadrupoles. A linear relationship (the slope of -1) between the triple ion formation constants and the salt concentrations at the minimum ($\log C_{\min}$) was given for all the salts in the various solvents.

Even with higher permittivities ($20 < \epsilon_r < 65$), in solvents of low solvating abilities, especially in protophobic aprotic solvents. The conductivity data of conductivity data of $n\text{-Bu}_3\text{NHCF}_3\text{CO}_2$ in MeCN ($\epsilon_r = 35.94$) were interpreted by triple-ion and quadrupole formation in addition to ion-pair formation [41]. The triple-ion and quadrupole formation from trialkylammonium halides, $\text{R}_3\text{NH}^+\text{X}^-$ [42], and lithium trifluoroacetate [43] can occur through hydrogen bonding and coordination bond forces, respectively, between or among the cation and the anion. Fig. 1.3 shows the Shedlovsky plots of lithium pentafluoropropionate ($\text{LiC}_2\text{H}_5\text{CO}_2$) in propylene carbonate (PC, $\epsilon_r \sim 65$): the relation between $1/\Lambda S$ and $C\Lambda S^2$ gave not a linear but a concave curve. Barthel *et al.* [44] have concluded from conductivity measurements that triple ions are formed by lithium fluoroacetates in PC at $C \leq 0.009$ M.

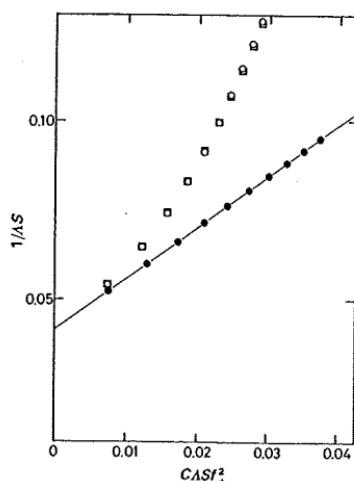
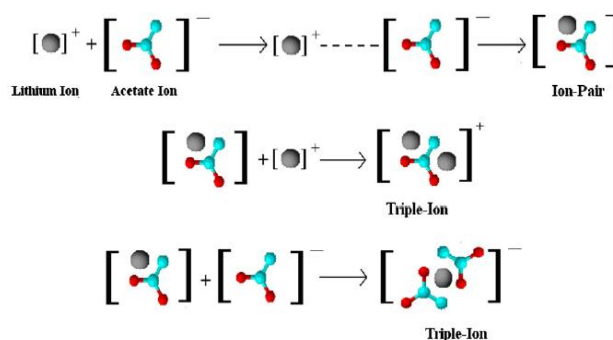


Fig. 1.3. Shedlovsky plots for $\text{LiC}_2\text{F}_5\text{CO}_2$ in PC: (○) experimentally observed points; (□) simulated points with ion pair, triple-ion, and quadrupole formation; (●) simulated points with ion-pair formation [42].

M. N. Roy and co-workers [45-50] have studied molecular interaction of ion-ion, ion-dipole

for some ethanoates and tetraalkylammonium iodides in THF, dimethyl sulfoxide (DMSO), *n*-hexanol and binary mixture by electrical conductance. By the Fuoss-Kraus theory of triple ions, the values of the ion-pair and triple-ion formation constants (K_P and K_T) were evaluated and the results have been discussed in terms of molecular scale model. Meanwhile, they explored the structure of ion-pair and triple-ion, Scheme 1.1 depicted the triple-ion formation for lithium acetate in pure THF.



Scheme 1.1. The triple-ion formation for lithium acetate in pure THF [45].

1.2.3. Polarography

Polarography has been a powerful means to determine the stability constants of metal complexes. By means of polarographic studies, the ion-pair formation of acetate ion and lithium ion in MeCN was examined [51]. When the concentration of LiClO_4 was low (1 – 20 mM) for the 0.35 mM acetate ion, the wave-height of the acetate ion was extremely depressed. The decrease in the anodic wave-height would be caused by the precipitation of CH_3COOLi . The anodic wave (–0.45 V) of the acetate disappears at 1:1 equivalent point. Again, an anodic wave from the acetate ion appeared at –0.05 – +0.06 V for the addition of a large excess of Li^+ , owing to the acetate ion exists in the form of electrochemically active species, $\text{CH}_3\text{COO}^-(\text{Li}^+)_2$ (Fig. 1.4). Also, the formation constant was evaluated as $K_f = 1 \times 10^{11} \text{ M}^{-2}$ for the reaction as equation 1.2.



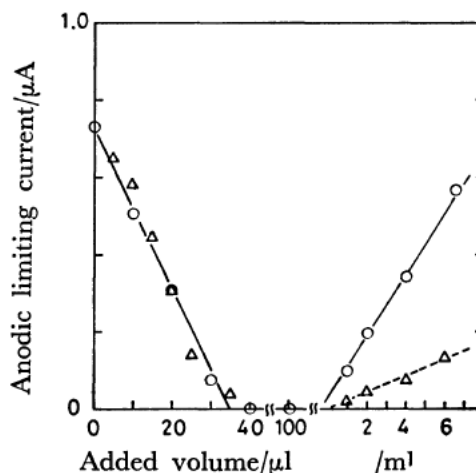


Fig. 1.4. Amperometric titration curves for 0.35 mM acetate ion of 20 ml by 0.2 M LiClO₄ and NaClO₄: (○) LiClO₄; (Δ) NaClO₄. The changes of total volume were corrected [51].

The interaction between the trialkylammonium ions (T^+) and the halide ions (X^-) is symmetrical in MeCN was observed by polarographic study [52, 53]. Both $(T^+)_2X^-$ and $T^+(X^-)_2$ type species are formed with the formation constants similar to each other.

1.2.4. NMR spectroscopy

^1H and ^{13}C NMR data can supply us with information of the electron density on a specific proton or carbon atom in molecules. Hiller *et al.* [30] have reported that the ^1H NMR spectrum of the $\text{Li}_2(\text{acac})^+$ exhibits signals at $\delta = 1.85$ and 5.28 ppm versus TMS, signals which were assigned to the methyl and methine protons in acetylacetone, respectively. Plewa *et al.* [54, 55] confirmed that the signals of the LiBF_4 and the MCF_3SO_3 ($M = \text{Li}^+, \text{Na}^+, \text{K}^+, (n\text{-Bu})_4\text{N}^+$) solutions in glyme (1,2-dimethoxyethane, DME, $\epsilon_r = 7.2$) were originating from free anions, pairs and triplets by ^{19}F NMR spectroscopy.

The interaction between lithium ion and tetrabutylammonium tropolonate ($n\text{-Bu}_4\text{NC}_7\text{H}_5\text{O}_2$) have been examined by ^1H NMR [56] (*cf.* Fig. 1.5). The addition of an equivalent amount of LiClO_4 ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) leads to remarkably lower magnetic-field shifts, as compared to the δ values without salt. By further addition of LiClO_4 , the chemical shifts were observed at lower magnetic-fields. Definitely 5-H was affected to the most extent by the addition of Li^+ . Meanwhile, the ^{13}C NMR chemical shifts of $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ $n\text{-Bu}_4\text{NC}_7\text{H}_5\text{O}_2$ showed that the 1,2-C signal

shifted slightly toward higher magnetic-fields, despite that positive charged species are interacting with the tropolonate ion. The formed dilithium tropolonate is illustrated as scheme 1.2.

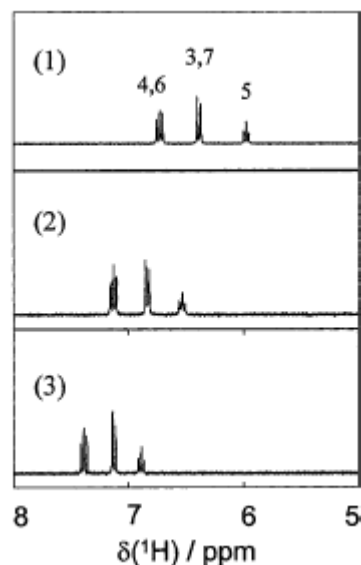
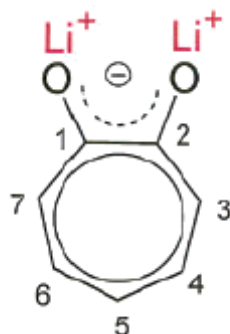
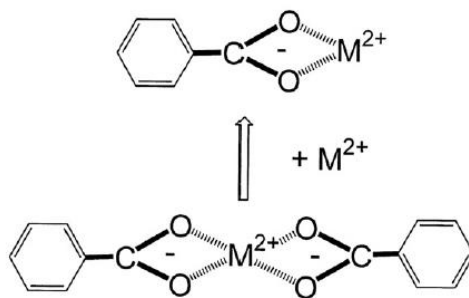


Fig. 1.5. ^1H NMR spectra of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ $n\text{-Bu}_4\text{NC}_7\text{H}_5\text{O}_2$ in the presence of LiClO_4 : (1) 0; (2) 1.0×10^{-3} ; (3) 0.50 mol dm^{-3} LiClO_4 [56].



Scheme 1.2. The structure of dilithium tropolonate [56].

The protonated 4-isopropyltropolone (H_2L^+) was produced by addition of methansulfonic or trifluoromethanesulfonic acid to 4-isopropyltropolone dissolve in MeCN [57]. The ^{13}C chemical shifts of all C-atoms in the seven-membered ring were assigned for H_2L^+ and HL as well as for the deprotonated species, L^- . The interaction between alkaline earth metal ions ($\text{M}^{2+} = \text{Mg}^{2+}, \text{Ba}^{2+}$) and benzoate ion (L^-) had been examined in MeCN by ^1H and ^{13}C NMR spectroscopy [58]. The results confirmed that the M^{2+} react with benzoate to form the precipitate (ML_2) and the triple cation or so-called “reverse-coordinated” species (ML^+) (scheme 1.3).



Scheme 1.3. Successive formation of ML_2 and ML^+ in MeCN [58].

1.2.5. Raman spectroscopy

York *et al.* [59] reported the Raman and IR studies on poly(ethylene imine) (LPEI) complexed with $LiCF_3SO_3$ and $NaCF_3SO_3$. As the salt concentration is increased in the LPEI– $LiCF_3SO_3$ system, in turn “free” ions, contact ion pairs and the triple cation $[Li_2CF_3SO_3]^+$ each become the dominant species present, whereas contact ion pairs appear to be the dominant ionic species over the same composition range in the LPEI– $NaCF_3SO_3$ system.

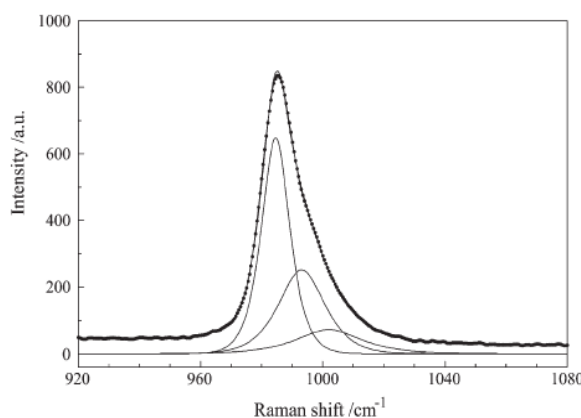


Fig. 1.6. Raman spectrum for a solution containing $4.098 \text{ mol kg}^{-1}$ (3.670 mol L^{-1}) $MgCl_2$ + $0.107 \text{ mol kg}^{-1}$ ($0.0956 \text{ mol L}^{-1}$) $MgSO_4$ at 23°C , showing the sum, component and (bottom trace) residual curves. Note the appearance of the new mode at 1005 cm^{-1} , which has been assigned to a triple ion, $Mg_2SO_4^{2+}(\text{aq})$ [60].

W. W. Rudolph [60] investigated the speciation of $MgSO_4$, because of the unusual sensitivity of the strong Raman band to minor perturbations in its environments. In $MgSO_4(\text{aq})$, the well-known asymmetry in the $\nu_1\text{-SO}_4^{2-}$ mode at $\sim 980 \text{ cm}^{-1}$ that develops with increasing concentration has been assigned to a mode at 993 cm^{-1} associated with the formation of an $MgOSO_3$ contact ion pair (CIP). In solutions with high Mg^{2+}/SO_4^{2-} concentration ratios, a further $\nu_1\text{-SO}_4^{2-}$ mode was

observed at 1005 cm^{-1} , which has been tentatively assigned to a $\text{Mg}_2\text{SO}_4^{2+}(\text{aq})$ triple ion (Fig. 1.6). Due to MgSO_4 is very common and plays important roles in many biological, geological, and chemical processes. Other papers [61-63] also examined the association behavior of MgSO_4 under different conditions using Raman spectroscopy. Analyses of the $\nu_1\text{-SO}_4^{2-}$ bands confirmed the presence of four-sulfate species of unassociated SO_4^{2-} , CIPs and triple ion.

Bacelon *et al.* [64] and Chabanel *et al.* [65] characterized the formation conditions for triple cations and triple anions of alkaline sulfocyanides (LiNCS , NaNCS) in nitromethane (CH_3NO_2), THF and 1,3-dioxolane through infrared and Raman spectroscopy.

1.2.6 UV-visible spectroscopy

Hojo *et al.* [66] observed the triple cation formation from substituted-benzoate ions in MeCN. The addition of LiClO_4 up to the equivalent amount of the benzoate ion (A^-) caused the decrease in the absorbance around 300 nm and, at the same time, the increase around 250 nm without precipitation; the appearance of an isosbestic point at 297 nm indicates the presence of A^- and Li^+A^- . The isosbestic point was shifted from 297 to 291 nm by the addition of an excess of Li^+ , which may suggest the coexistence of Li^+A^- and $(\text{Li}^+)_2\text{A}^-$. Meanwhile, a method for obtaining the formation constants of triple ion have been developed using the spectroscopic data.

In low permittivity media, the formation of triple ions is based on electrostatic interaction between ions in electric fields of low permittivity. However, in the solvent of higher permittivity ($20 < \epsilon_r < 65$) [67-72], chemical force (*i.e.*, covalent bonding or coordinating) as well as Coulombic interactions have been proved to play role on the formation of triple ion.

By a series of studies through UV-visible spectroscopy, it have been found that the interaction between alkali (M^+) or alkaline earth metal ions (M^{2+}) and anions (L^-) goes through a specific process: (1) the formation of a triple anion or normal coordination species (ML_2^-) by addition of half an equivalent amount of M^+ to L^- ; (2) precipitations takes place (ML) in the presence of an equivalence of the metal ion; (3) the precipitates successively re-dissolved to a triple cation or “reverse-coordinated” species (M_2L^+) by a large excess of metal ion. Murray [31] and Itabashi [32] have suggested the formation of “reverse-coordinated” species for acetylacetonate and acetate ions, respectively. The process as precipitation and re-dissolution shows as the first decrease and the

followed increase of UV absorbance of anion with increasing concentration of metal ions.

As so far, the triple formation or specific interaction between alkali metal or alkaline metal ions and a variety of benzoate [66], tropolonate [56], phosphate [73], sulfonate [73,74], and carboxylate [74] has been investigated in various solvents by UV-visible spectroscopy in our laboratory. As for the benzenesulfonate ion in MeCN, an excess amount of Li^+ caused the increase in the absorbance as the second Li^+ ion can attack the ion pair to form the “reverse-coordinated” species, whereas the addition of Na^+ caused a monotonous decrease of the absorbance (Fig. 1.7) [73]. In acetone, the “reverse” coordination formation constant was evaluated for $(\text{PhO})_2\text{PO}_2^-$ with Li^+ [73].

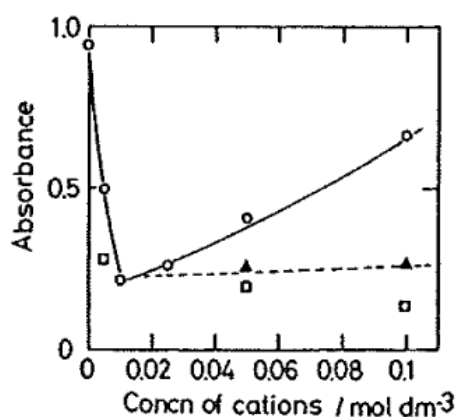


Fig. 1.7. Changes of absorbance of $\text{Et}_4\text{N}^+\text{C}_6\text{H}_5\text{SO}_3$ ($5.3 \times 10^{-3} \text{ mol dm}^{-3}$) with increasing concentration of alkali metal perchlorates in MeCN: (\circ) LiClO_4 ; (\square) NaClO_4 ; (\blacktriangle) Et_4NClO_4 in addition to 0.01 M LiClO_4 [73].

1.2.7. The other methods

Perelygin and Klimchuk [75] studied the interionic and ion-molecular interactions in solutions of LiNCS , NaNCS , KNCS , and $\text{Ca}(\text{NCS})_2$ in MeCN, acetone, pyridine, and tetrahydrofuran by vibrational spectroscopy. The spectra have characterized the ionic triplets ($\text{M}^+\text{NCS}^-\text{M}^+$ and $\text{SCN}^-\text{M}^+\text{NCS}^-$). Zalewska *et al.* [76] examined the effect of the type of alkali metal cation and salt concentration on ion-ion and ion-polyether interactions for poly(ethylene glycol) (PEG)-MSCN ($\text{M} = \text{Li}, \text{Na}, \text{K}$) electrolytes by means of impedance spectroscopy, DSC, rheological, and FT-IR techniques. The FT-IR spectrum showed that two regions are of interest for studies of ion-ion and ion-polymer interactions. These are $\sim 2050 \text{ cm}^{-1}$ and 1100 cm^{-1} , respectively, which characterizes the C-N stretching vibrations of the SCN^- anion and stretching

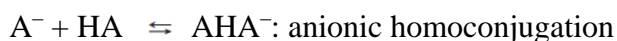
vibrations of C–O–C bonds of the polyether chains, respectively. The positions of the latter change with the formation of transient cross-links due to the interactions of alkali metal cations or positively charged triplets with base centers on polyether oxygen atoms. A detailed investigation of aqueous solutions of MgSO_4 has been made by dielectric relaxation spectroscopy [77]. Evidence has been obtained for the existence of a triple ion, $\text{Mg}_2\text{SO}_4^{2+}(\text{aq})$, or possibly a more aggregated species, at high electrolyte concentrations ($c > 1 \text{ M}$).

1.3. The relevant studies in our laboratory

The relative researches about the ion association behavior of electrolytes or the coordination behavior of alkali or alkaline earth metal ions have been studying in our laboratory over thirty years [78], which mainly including as (1) the homo- and heteroconjugation reaction; (2) salt effects in non-aqueous solution environment; (3) coordination and “reverse” coordination ability of alkali or alkaline earth metal ions.

1.3.1. Homo- and heteroconjugation

In amphiprotic solvent, such as water and ethanol, strong hydrogen-bonding between solvent s and solute would prevent the solutes interact together. However, in aprotic solvents, the conjugate anions (A^-) from weak acids (HA) may interact with the mother acid or a related acid (HA') molecular to form anionic homo- or heteroconjugated species as follows:



Similarly, cationic homo-or hetero-conjugated species are derived from the interaction between a weak base (B) and the conjugate acid (BH^+):



By means of conductometry, we [79] have observed that the sulfonic acids, such as methanesulfonic and *p*-toluenesulfonic acids, behave indeed as weak acids in benzonitrile ($\epsilon_r = 25.2$) to form 1:2-type homoconjugated species, $\text{A}^-(\text{HA})_2$. Benzonitrile has rather small values of Gutmann's donor and acceptor number [80], $\text{DN} = 11.9$ and $\text{AN} = 15.5$. The phosphoric acids,

including ortho-phosphoric acid $(\text{HO})_3\text{PO}$, can cause homoconjugation strong enough to give the maxima in conductometric titration curves even in DMF possessing a larger donicity ($\text{DN} = 26.6$, [80]). It has been demonstrated that the stability of OH groups in a phosphoric acid molecule of non-, mono- and diphenylphosphate $[(\text{PhO})_2(\text{HO})\text{PO}]$ derivatives. Conductometric titrations with triethylamine (Et_3N) of mono-, di-, and trisulfonic acids have been performed in MeCN, and strong homoconjugation for di- and trisulfonic acids have been revealed [81].

By means of polarography [51], it have been observed that an acetate or benzoate ion (A^-) forms a homoconjugation species, $\text{A}^-(\text{HA})_2$, with two molecules of the mother acid (HA) in the presence of a large excess of HA in MeCN solution. Our voltammetric experiments have evidenced also that the chloride or bromide ion can interact with two ammonium ions, such as Et_3NH^+ or $n\text{-Bu}_3\text{NH}^+$ [53], and inversely, the ammonium ions NH_4^+ , Et_3NH^+ , *etc.* can be coordinated by multiple numbers of Cl^- or Br^- in MeCN [52]. Thus, triple ion formation reactions, based on mainly the hydrogen-bonding force, have been vigorously examined by means of conductometry for various ammonium halides in protophobic aprotic solvents, acetone, MeCN, PC, PhCN, and PhNO_2 [52, 82].

Nevertheless, some investigators have insisted that the technical term “triple ions” should be restricted to those based on merely the electrostatic interaction, otherwise obscuring the electrostatic interactions leading ion pairs and triple ions [83]. At any rate, we have demonstrated that even sulfonate anions are apt to accept hydrogen bonding in protophobic aprotic solvents in the order of $\text{MeCN} < \text{PhCN} < \text{PhNO}_2$ [56], while sulfonic acids behave as almost strong acids in aqueous solution.

1.3.2. Salt effect in non-aqueous solution

The “non-aqueous environments” are realized in such conditions as (1) non-aqueous solvents with low solvation abilities, (2) aqueous solution containing large amounts of organic solvents or highly concentrated salts, (3) nano-scale water droplets in reverse micelle systems, (4) aqueous solution on the surface of ion-exchange resins, proteins, or at the interface with organic solvents and (5) water in supercritical conditions or at very high temperatures. We [78, 84] have proposed that properties of bulk water in aqueous solution should be altered into those of non-aqueous

solvents when the water structure is modified by some causes. Such water can be “reduced” to authentic singular H₂O molecules (also called “dihydrogen ether,” (H)–O–(H)) [85-87]. Reichardt *et al.* [88] have concisely interpreted “dihydrogen ether” that, at high salt concentrations [$c(\text{salt}) > 5 \text{ mol dm}^{-3}$], region C, according to the solvation model of Frank and Wen [89], can be abolished and only regions A and B survive, resulting in an aqueous solvent called “dihydrogen ether.”

Through a series of studies, we have demonstrated the specific interaction or “reverse” coordination could take place between alkali metal or alkaline earth metal ions and simple anions, such as halide, sulfonate, and carboxylate ions [78]. Such interactions may be observed only in “non-aqueous environments”. Furthermore, we confirmed that the existence of salt would affect the acid-base indicator [67, 69, 70, 90-92] and solvolysis (hydrolysis) reaction [68, 85, 94, 95].

By the addition of MClO₄ and M(ClO₄)₂ to rhodamine B base, the intramolecular γ -lactone ring (C–O) was found to be cleaved within the MeCN solution. Only Mg²⁺ was effective for crystal violet lactone; the magnesium ion has strong interaction with the carboxylate ion from the lactone [67]. It has been concluded that the changes or developments in colors of acid–base sulfonephthalein indicators, such as phenol red and bromothymol blue, are caused by the γ -sultone-ring opening through the chemical interaction between the metal cations of added salts and the sulfonate ions from the sulfonephthalein indicators [90]. A practical fluoran-based black color former reacts with alkali metal and alkaline earth metal ions to develop the black color in MeCN [69, 92].

The stabilization of carbocations in solution is a matter of great interest in considering the mechanisms of organic reactions, especially S_N1 and S_N2 reactions in solvolysis. By the addition of metal chlorides, such as HgCl₂, AlCl₃, and SnCl₄ to Ph₃CCl solutions (MeCN and MeNO₂ solvents), the trityl cation (Ph₃C⁺) can be formed even quantitatively through the following reaction [93]: $\text{Ph}_3\text{CCl} + \text{MCl}_m \rightleftharpoons \text{Ph}_3\text{C}^+ + [\text{MCl}_{m+1}]^-$. By means of UV-visible absorption spectroscopy, we have found that the Ph₃C⁺ ion is produced from Ph₃CX (X = Cl, Br) by the addition of MClO₄ (M = Li, Na) or M(ClO₄)₂ (M = Mg, Ca, Sr, Ba) in MeCN. The addition of the metal perchlorates to 4-MeO-substituted trityl chloride, (4-MeOC₆H₄)_nPh_{3–n}CCl ($n = 1\sim 3$), caused the production of the corresponding trityl cations [67]. These reactions could be utilized for the preparation of trityl perchlorate compounds [68].

In MeOH-H₂O mixed solvent, the “pseudo” first-order reaction rates (k/s^{-1}) for typical S_N1 substrates, such as 1-adamantyl bromide and *t*-butyl chloride, were found to increase exponentially with increasing concentration of alkali metal or alkaline earth metal perchlorates, whereas with a nonmetallic salt (Et₄NBr), the reaction rates decreased [85]. The positive effects of Na⁺ were smaller than those of Li⁺ while the effects of Mg²⁺ or Ba²⁺ were much larger. We have concluded that the observed positive effects of the metal perchlorates are due to the formation of “stable” carbocations (R⁺) through “chemical” interaction between the halides (X⁻) and the metal cations (M⁺, M²⁺) in the “modified” solvent.

1.3.3. Complexing ability of alkali metal and alkaline earth metal ions

Compared with transition metal ions, the coordination ability of alkali metal or alkaline earth metal should be much weaker owing to their lack of partly filled d- or f-shells. Fromm [96] stated that “the coordination chemistry of groups 1 and 2 metal compounds with organic ligands in the widest sense has been, until relatively, largely unknown compared to transition metal coordination network”. In aqueous solution, the weak complexes with alkali metal ions are often neglected, and a strong dependence of protonation constants for ligands on the concentration of background is generally ascribed to activity factors. However, Daniele *et al.* [97] stressed that a rigorous treatment of acid–base equilibria must also take into account the weak interaction between the ligand under study and the cation background. The complex formations of alkali metal ions with macrocyclic compounds, such as crown ethers, have been investigated widely by means of various techniques [98].

On basis of triple ion theory, we found a specific interaction would occur between higher concentration of alkali (M⁺) or alkaline earth metal (M²⁺) ions and simple anions not only by the Coulomb force but also coordination as well as hydrogen bonding force. The “triple cation” formed through the specific interaction of ion pair with metal ions is regarded as the “reverse-coordinated” species [78], which presents as one anion (univalence) toward two alkali metal ion or one to one complexes for alkaline earth metal ions.

As so far, by various methods, we examined the coordination ability of M⁺ or M²⁺ with different anion, *e.g.* halides (Cl⁻, Br⁻ [53, 67, 68]), sulfonates (mono- [73, 90], di-sulfonate [74]),

(PhO)₂PO₂⁻ [73], carboxylates (RCO₂⁻ [51, 66, 69], nitrophthalate [74]) and nitrophenolate [72] ions. The formation of “reverse-coordinated” specie, such as Cl⁻(Li⁺)₂ [53], PhSO₃(Li⁺)₂ [73], (PhO)₂PO₂⁻(Li⁺)₂ [73], RCO₂(M⁺)₂ (M = Li or Na) [51, 66], NO₂C₆H₃(COO⁻)₂(M²⁺)₂ (M = Mg, Ca, Ba) [74], R(SO₃⁻)₂(M²⁺)₂ (M = Mg) has been reported in acetonitrile, acetone or the mixed solvents of MeCN-H₂O. However, the formation of the (Li)₂L⁻ (L⁻ = tropolonate) was not observed in solvents of higher solvating abilities such as MeOH and N,N-dimethylformamide.

1.4. Objectives and the content of the thesis

Despite under controversy [83], the triple ion mechanism or theory [99] has been applied in studying on lithium batteries [100, 101], ion-aggregation [81] and supramolecular construction [102]. Also, we developed a method for color development or changes of indicators or dyes of sulfonic [90] and carboxylic [69, 92] types which dependent on the specific coordination reactions between alkali metal or alkaline earth metal ions.

Meanwhile, the results from the studies of specific interaction could give an important clue to recognize the kinetic mechanism in hydrolysis reactions under “non-aqueous solvent condition” or in biologic systems, supporting our proposal [85-87, 102-104] that the salt effects on the solvolysis of S_N 1 to S_N 2 haloalkane substrates can be accounted for without on conventional reaction schemes [105-108] or the arbitrary functions of various ion pairs.

The major purpose of this study is to further confirm that alkali metal, alkaline earth metal, and III Group metal ions actually have strong coordination ability, the specific association behaviors of those metal ions with different anions are investigated not only in aprotic solvent of poor solvation but also in protic solvent or aprotic–protic mixed solvents. The present works are as follows:

1. In primary alcohols as well as in the binary MeCN-alcohols, ethanol-methanol and methanol-water, the specific interactions between alkaline earth metal and *p*-toluenesulfonate, 1,5-naphthalenedisulfonate, or 1,3,6-naphthalenetrisulfonate ions are examined by means of UV-visible spectroscopy. (**Chapter 2**)
2. The coordination ability of alkali metal (Li⁺, Na⁺), alkaline earth metal (Mg²⁺, Ca²⁺, or Ba²⁺), and indium (In³⁺) ions with the 1,3,6-naphthalenetrisulfonate ion are examined not only in

MeCN but also in primary alcohols (from methanol to 1-hexanol). (**Chapter 3**)

3. In MeCN, the specific interactions of alkali metal and alkaline earth metal ions with various phosphorus anions, *i.e.*, diphenylphosphinate, diphenylphosphate, and bis(4-nitrophenyl)phosphate, are examined by means of UV-visible spectroscopy. Also, the influences of additional protic solvents, such as water, MeOH, or EtOH, on the chemical interaction between the metal ions and the anions are investigated. (**Chapter 4**)
4. In binary acetonitrile-water (MeCN-H₂O) and acetonitrile-methanol (MeCN-MeOH) solvents, the specific interactions between alkali metal or alkaline earth metal ions and 1,4- or 2,3-naphthalenedicarboxylate ions had been examined by UV-visible spectroscopy. (**Chapter 5**)

References

- [1] P. Debye, E. Hückel, Phys. Z. 24 (1923) 305.
- [2] N. Bjerrum, K. Dan, Vidensk. Selsk. 28 (1926) 288.
- [3] J.T. Denison, D.L. Ramsey, J. Am. Chem. Soc. 77 (1955) 2615.
- [4] W.R. Gilkerson, J. Chem. Phys. 26 (1956) 1199.
- [5] R.M. Fuoss, Trans. Faraday Soc. 30 (1934) 967.
- [6] R.M. Fuoss, J. Am. Chem. Soc. 57 (1935) 488.
- [7] R.M. Fuoss, J. Am. Chem. Soc. 80 (1958) 5059.
- [8] R.M. Fuoss, J. Chim. Phys. 66 (1969) 1191.
- [9] L.D. Pettit, S. Bruckenstein, J. Am. Chem. Soc. 78 (1966) 4783.
- [10] L.P. Hammett, Physical Organic Chemistry, 2nd. ed., McGraw-Hill, New York, 1970.
- [11] S. Winstein, P.E. Klinedinst, E. Clippinger, J. Am. Chem. Soc. 83 (1961) 4986.
- [12] E.A. Moelwyn-Hughes, Chemical Statics and Kinetics of Solutions, Academic Press, London, 1971.
- [13] G. Atkinson, S. Petrncci, J. Phys. Chem. 70 (1966) 3122.
- [14] A.G. Bishop, D.R. MacFarlane, D. McNaughton, M. Forsyth, J. Phys. Chem. 100 (1996) 2237.
- [15] A. Eiberweiser, A. Nazet, G. Hefter, R. Buchner, J. Phys. Chem. B 119 (2015) 5270.
- [16] F. Conti, P. Delogu, G. Pistoia, J. Phys. Chem. 72 (1968) 1396.

- [17] C.D. Stevenson, R.M. Fico Jr., E. C. Brown, *J. Phys. Chem. B* 102 (1998) 2841.
- [18] A. Pan, B. Naskar, G.K.S. Prameela, B.V.N.P. Kumar, A.B. Mandal, S.C. Bhattacharya, S.P. Moulik, *Langmuir* 28 (2012) 13830.
- [19] Y. Marcus, *J. Phys. Chem. B* 111 (2007) 572.
- [20] S. Bruckenstein, L.D. Pettit, *J. Am. Chem. Soc.* 88 (1966) 4790.
- [21] J.S. Chang, D.M. Golden. *J. Am. Chem. Soc.* 103 (1981) 496.
- [22] J. Schellman, *J. Phys. Chem.* 4 (1953) 472.
- [23] M. Walser, *J. Clin. Invest.* 40 (1961) 723.
- [24] A.H. Daranas, J.J. Fernández, E.Q. Morales, M. Norte, J.A. Gavín, *J. Med. Chem.* 47 (2004) 10.
- [25] Z. Sun, W. Zhang, M. Ji, R. Hartsock, K.J. Gaffney, *J. Phys. Chem. B* 117 (2013) 12268.
- [26] C. Schmuck, T. Rehm, L. Geiger, M. Schäfer, *J. Org. Chem.* 72 (2007) 6162.
- [27] R.M. Fuoss, C.A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 2387.
- [28] M. Raban, G. Yamamoto, *Inorg. Nucl. Chem. Lett.* 12 (1976) 946.
- [29] M. Raban, E.A. Noe, G. Yamamoto, *J. Am. Chem. Soc.* 99 (1977) 6527.
- [30] L.K. Hiller Jr., Cockrell, J.R. Jr., R.W.J. Murray, *Inorg. Nucl. Chem.* 31 (1969) 765.
- [31] R.W. Murray, L.K. Hiller Jr., *Anal. Chem.* 39 (1967) 1221.
- [32] E.J. Itabashi, *Electroanal. Chem.* 36 (1972) 179.
- [33] T.E. Gough, P.R. Hindle, *Can. J. Chem.* 47 (1969) 1698.
- [34] T.E. Gough, P.R. Hindle, *Can. J. Chem.* 48 (1970) 3959.
- [35] M. Barzaghi, P. Cremaschi, A. Gamba, G. Morosi, C. Oliva, M. Simonetta, *J. Am. Chem. Soc.* 100 (1978) 3132.
- [36] M. Barzaghi, C. Oliva, M. Simonetta, *J. Phys. Chem.* 85 (1981) 1799.
- [37] K.S. Chen, N. Hirota, *J. Am. Chem. Soc.* 94 (1972) 5550.
- [38] C.A. Kraus, R.M. Fuoss, *J. Am. Chem. Soc.* 55 (1933) 21.
- [39] R.M. Fuoss, C.A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 3614.
- [40] Z. Chen, M. Hojo, *J. Phys. Chem. B* 101 (1997) 10896.
- [41] M. Hojo, Y. Miyauchi, I. Nakatani, T. Mizobuchi, Y. Imai, *Chem. Lett.* 19 (1990) 1035.
- [42] Y. Miyauchi, M. Hojo, N. Ide, Y. Imai, *J. Chem. Soc., Faraday Trans.* 88 (1992) 1425.

- [43] Y. Miyauchi, M. Hojo, H. Moriyama, Y. Imai, *J. Chem. Soc., Faraday Trans.* 88 (1992) 3175.
- [44] J. Barthel, R. Neueder, H. Poepke, H. Wittmann, *J. Solution Chem.* 27 (1998) 1055.
- [45] M.N. Roy, R. Chanda, P. Chakraborti, A. Das, *Fluid Phase Equilib.* 322–323 (2012) 159.
- [46] M.N. Roy, P.K. Roy, R.S. Sah, P. Pradhan, B. Sinha, *J. Chem. Eng. Data* 54 (2009) 2429.
- [47] M.N. Roy, P. Pradhan, R.K. Das, B. Sinha, P. K. Guha, *J. Chem. Eng. Data* 53 (2008) 1417.
- [48] M.N. Roy, L. Sarkar, R. Dewan, *J. Chem. Thermodynamics* 43 (2011) 371.
- [49] A. Sinha, M.N. Roy, *J. Mol. Liquids* 140 (2008) 39.
- [50] I. Banik, M.N. Roy, *J. Chem. Thermodynamics* 63 (2013) 52.
- [51] M. Hojo, Y. Imai, *Bull. Chem. Soc. Jpn.* 56 (1983) 1963.
- [52] M. Hojo, T. Takiguchi, M. Hagiwara, H. Nagai, Y. Imai, *J. Phys. Chem.* 93 (1989) 955.
- [53] M. Hojo, H. Nagai, M. Hagiwara, Y. Imai, *Anal. Chem.* 59 (1987) 1770.
- [54] A. Plewa, M. Kalita, M. Siekierski, *Electrochimi. Acta* 53 (2007) 1527.
- [55] A. Plewa, M. Kalita, M. Marczewski, M. Siekierski, *Electrochimi. Acta* 55 (2010) 1389.
- [56] M. Hojo, T. Ueda, T. Inoue, M. Ike, *J. Phys. Chem. B* 111 (2007) 1759.
- [57] M. Hojo, T. Ueda, M. Ike, K. Okamura, T. Sugiyama, M. Kobayashi, H. Nakai, *J. Chem. Eng. Data* 55 (2010) 1986.
- [58] M. Hojo, T. Ueda, M. Ike, M. Kobayashi, H. Nakai, *J. Mol. Liquids* 145 (2009) 152.
- [59] S. York, R. Frech, A. Snow, D. Glatzhofer, *Electrochimi. Acta* 46 (2001) 1533.
- [60] W.W. Rudolph, G. Irmerb, G.T. Hefter, *Phys. Chem. Chem. Phys.* 5 (2003) 5253.
- [61] Y. Wan, X. Wang, W. Hu, I. Chou, *J. Phys. Chem. A* 119 (2015) 9027.
- [62] Y.H. Zhang, C.K. Chan, *J. Phys. Chem. A* 104 (2000) 9191.
- [63] R. Buchner, T. Chen, G. Hefter, *J. Phys. Chem. B* 108 (2004) 2365.
- [64] P. Bacelon, J. Corset, C. deLoze, *J. Solution Chem.* 9 (1980) 129.
- [65] M. Chabanel, Z. Wang, *J. Phys. Chem.* 88 (1984) 1441.
- [66] M. Hojo, A. Tanio, Y. Miyauchi, Y. Imai, *Chem. Lett.* (1991) 1827.
- [67] M. Hojo, H. Hasegawa, H. Tsurui, K. Kawamura, S. Minami, A. Mizobe, *Bull. Chem. Soc. Jpn.* 71 (1998) 1619.
- [68] M. Hojo, T. Ueda, M. Yamasaki, *J. Org. Chem.* 64 (1999) 4939.
- [69] M. Hojo, T. Ueda, M. Yamasaki, A. Inoue, S. Tokita, M. Yanagita, *Bull. Chem. Soc. Jpn.* 75

- (2002) 1569.
- [70] M. Hojo, H. Hasegawa, H. Yoneda, *Bull. Chem. Soc. Jpn.* 69 (1996) 971.
- [71] M. Hojo, H. Hasegawa, H.J. Yoneda, *Chem. Soc., Perkin Trans. 2* (1994) 1855.
- [72] M. Hojo, H. Hasegawa, A. Mizobe, Y. Ohkawa, Y. Miimi, *J. Phys. Chem.* 99 (1995) 16609.
- [73] M. Hojo, H. Hasegawa, Y. Miyauchi, H. Moriyama, H. Yoneda, S. Arisawa, *Electrochim. Acta* 39 (1994) 629.
- [74] M. Hojo, S. Ohta, K. Ayabe, K. Okamura, K. Kobiro, Z. Chen, *J. Mol. Liquids* 177 (2013) 145.
- [75] I.S. Pereygin, M.A. Klimchuk, *J. Struct. Chem.* 5 (1983) 710.
- [76] A. Zalewska, J. Stygar, E. Ciszewska, M. Wiktorko, W. Wieczorek, *J. Phys. Chem. B* 105 (2001) 5847.
- [77] R. Buchner, T. Chen, G. Hefter, *J. Phys. Chem. B* 108 (2004) 2365.
- [78] M. Hojo, *Pure Appl. Chem.* 80 (2008) 1539.
- [79] M. Hojo, Z. Chen, *Anal. Sci.* 15 (1999) 303.
- [80] V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum, New York, 1978.
- [81] M. Hojo, Y. Kondo, K. Zei, K. Okamura, Z. Chen, M. Kobayashi, *Bull. Chem. Soc. Jpn.* 87 (2014) 98.
- [82] M. Hojo, A. Watanabe, T. Mizobuchi, Y. Imai, *J. Phys. Chem.* 94 (1990) 6073.
- [83] Y. Marcus, G. Hefter, *Chem. Rev.* 106 (2006) 4585.
- [84] M. Hojo, T. Ueda, C. Daike, F. Takezaki, Y. Furuya, K. Miyamoto, A. Narutaki, R. Kato, *Bull. Chem. Soc. Jpn.* 79 (2006) 1215.
- [85] L.C. Manege, T. Ueda, M. Hojo, *Bull. Chem. Soc. Jpn.* 71 (1998) 589.
- [86] L.C. Manege, T. Ueda, M. Hojo, M. Fujio, *J. Chem. Soc., Perkin Trans. 2* (1998) 1961.
- [87] M. Hojo, S. Aoki, *Bull. Chem. Soc. Jpn.* 85 (2012) 1023.
- [88] C. Reichardt, D. Che, G. Heckenkemper, G. Schaefer, *Eur. J. Org. Chem.* 12 (2001) 2343.
- [89] H.S. Frank, W. Y. Wen, *Discuss. Faraday Soc.* 24 (1957) 133.
- [90] M. Hojo, T. Ueda, K. Kawamura, M. Yamasaki, *Bull. Chem. Soc. Jpn.* 73 (2000) 347.
- [91] M. Hojo, T. Ueda, A. Inoue, *Bull. Chem. Soc. Jpn.* 75 (2002) 2629.

- [92] M. Hojo, T. Ueda, A. Inoue, S. Tokita, *J. Mol. Liquids* 148 (2009) 109.
- [93] M. Baaz, V. Gutmann, O. Kune, *Monatsh. Chem.* 93 (1962) 1142.
- [94] M. Hojo, T. Ueda, M. Yamasaki, A. Inoue, *Anal. Sci.* 16 (2000) 649.
- [95] L.D. Bayissa, Y. Ohmae, M. Hojo, *J. Mol. Liquids* 199 (2014) 294.
- [96] K.M. Fromm, *Coord. Chem. Rev.* 252 (2008) 856.
- [97] P.G. Daniele, C. Rigano, S. Sammartano, *Anal. Chem.* 57 (1985) 2956.
- [98] R.M. Izatt, K. Pawlak, J.S. Bradshaw, *Chem. Rev.* 91 (1991) 1721.
- [99] H.J. Gores, J.M.G. Barthel, *Pure Appl. Chem.* 67 (1995) 919.
- [100] R.L. Jarek, S.K. Shin, *J. Am. Chem. Soc.* 119 (1997) 10501.
- [101] G.V. Oshovsky, D.N. Reinhoudt, W. Verboom, *J. Am. Chem. Soc.* 128 (2006) 5270.
- [102] M. Hojo, T. Ueda, S. Inoue, Y. Kawahara, *J. Chem. Soc., Perkin Trans.2* (2000) 1735.
- [103] M. Hojo, T. Ueda, E. Ueno, T. Hamasaki, D. Fujimura, *Bull. Chem. Soc. Jpn.* 79 (2006) 751.
- [104] M. Hojo, T. Ueda, E. Ueno, T. Hamasaki, T. Nakano, *Bull. Chem. Soc. Jpn.* 83 (2010) 401.
- [105] S. Winstein, E. Clippinger, A. H. Fainberg, G. C. Robinson, *J. Am. Chem. Soc.* 76 (1954) 2597.
- [106] A.H. Fainberg, S. Winstein, *J. Am. Chem. Soc.* 78 (1956) 2767.
- [107] S. Winstein, P.E. Klinedinst Jr., G.C. Robinson, *J. Am. Chem. Soc.* 83 (1961) 885.
- [108] A. Loupy, B. Tchoubar, *Salt Effects in Organic and Organometallic Chemistry*, VCH, Weinheim, 1992, p 19.

Chapter 2 Specific coordination phenomena of alkaline earth metal ions with aromatic sulfonate ions in alcohols and binary solvents of acetonitrile-alcohols

ABSTRACT

The specific interactions between alkaline earth metal (Mg^{2+} , Ca^{2+} , or Ba^{2+}) and *p*-toluenesulfonate (L^-), 1,5-naphthalenedisulfonate (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_2O) solvents. The precipitation of non-charged species (*e.g.* ML^0) and the successive re-dissolution of the precipitates, with increasing concentration of $\text{M}(\text{ClO}_4)_2$, have revealed the formation of cationic charged species or “reverse-coordinated” species, M_2L^{2+} , even in the protic media as well as the aprotic solvent MeCN. The solubility products (K_{sp}) and the “reverse” coordination constants ($2\text{M}^{2+} + \text{L}^{2-} \rightleftharpoons \text{M}_2\text{L}^{2+}$, $K_{2(-2)} = [\text{M}_2\text{L}^{2+}] / [\text{M}^{2+}]^2 [\text{L}^{2-}]$) have been evaluated. In ethanol, both phenomena of the precipitation of ML^0 and the successive re-dissolution to produce M_2L^{2+} are observed for Ca^{2+} 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^0 ($\text{p}K_{\text{sp}} = 10.39$) and also the successive re-dissolution of Mg_2L^{2+} ($\log K_{2(-2)} = 8.08$). Even in methanol, the interaction between Ba^{2+} and L^{2-} results the precipitation ($\log K_{\text{sp}} = 8.28$) 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 the precipitation (BaL_2 or Ba_3L_2) 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 ($2\text{Ba}^{2+} + \text{L}^{3-} \rightleftharpoons \text{Ba}_2\text{L}^+$, $K_{2(-3)} = [\text{Ba}_2\text{L}^+] / ([\text{Ba}^{2+}]^2 [\text{L}^{3-}])$) are evaluated in ethanol and propanol as well as the binary EtOH-MeOH solvents, up to 70% (v/v) MeOH. The donicities towards M^{2+} of the media have been related to the $\text{p}K_{\text{sp}}$ and “reverse” coordination constants for L^- , L^{2-} and L^{3-} .

Keywords: “reverse” coordination in protic solvent; solvent donicity; solubility product; tripe ion formation through coordination; DFT calculation.

2.1. Introduction

The association modes of metal ions and anions in various solvents have acquired the great attention due to the extensive use in many areas of fundamental research, *e.g.* the evaluation of major physico-chemical 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 has been extensively investigated, due to its widespread application on industry, the importance in maintaining the ionic equilibrium of human's body and especially relevance in pharmaceuticals [4]. The mixtures of aqueous-organic or organic-organic mixed solvents find a broad application in industries 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], ^1H and ^{13}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_4 or NaClO_4 added to carboxylate ions (L^-) [12], the direct coordinated species (ML_2^-) may form, however, then the precipitation (ML^0) 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 "reverse-coordinated" species (M_2L^+), with increasing metal concentration.

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',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 interplay between ion solvation and association of electrolyte solutions [14]. Acetonitrile of a relatively high permittivity ($\epsilon_r = \text{ca. } 36$) [15] is not only an aprotic solvent but also a protophobic solvent [16], having poor solvation ability ($\text{DN} = 14.1$, $\text{AN} = 19.3$ [17], *cf.* Table 2.1) 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, $\text{R}_3\text{NH}^+\text{X}^-$, 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 2.1), can strongly solvate both cations and anions. Even very small amounts of water ($\sim 0.5\%$) 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 numbers (AN) of the alcohols under bulk conditions are much larger than those of MeCN (Table 2.1). Only ion pair formation has been found between Li^+ and the tropolonate ion ($\text{C}_7\text{H}_5\text{O}_2^-$) in methanol [9a]. The actual donicity of bulk methanol ($\text{DN} = 31.3$ [18]) is much higher than the original value ($\text{DN} = 20$) reported by Gutmann [17].

Table 2.1 Properties of the solvents concerned to the present study

Solvents	DN ^a	AN ^a	ϵ_r ^b
Acetonitrile (MeCN)	14.1	19.3	35.94
Water (H ₂ O)	40.3 ^c , 18.0 ^d	54.8	78.36
Methanol (MeOH)	31.3 ^c , 19 ^d	41.3	32.66
Ethanol (EtOH)	27.8 ^c , 20 ^d	37.1	24.55
Propanol (1-PrOH)	(27) ^c	34	20.45
Butanol (1-BuOH)	26.2 ^c	–	17.51
Hexanol (1-HexOH)	–	–	13.3

^a Gutmann's donor and acceptor number, Ref. [17]. ^b The permittivity values cited from Ref. [15].

^c For bulk water, methanol and ethanol, Ref. [18]. ^d Isolated H₂O and ROH molecules (not as the bulk solvents) in 1,2-dichloroethane, Ref. [17]. ^e Estimated from the donor numbers of EtOH and 1-BuOH.

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 Et₃N 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 (Mg²⁺, Ca²⁺, Ba²⁺) ions with *p*-toluenesulfonate 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 (Mg²⁺, Ca²⁺, Ba²⁺) with *p*-toluenesulfonate (L⁻), 1,5-naphthalenedisulfonate (L²⁻), and 1,3,6-naphthalenetrisulfonate (L³⁻) ions (*cf.* Chart 2.1) in primary alcohols as well as MeCN are 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-H₂O. The solubility products and “reverse” coordination constants have been successfully evaluated for the systems.

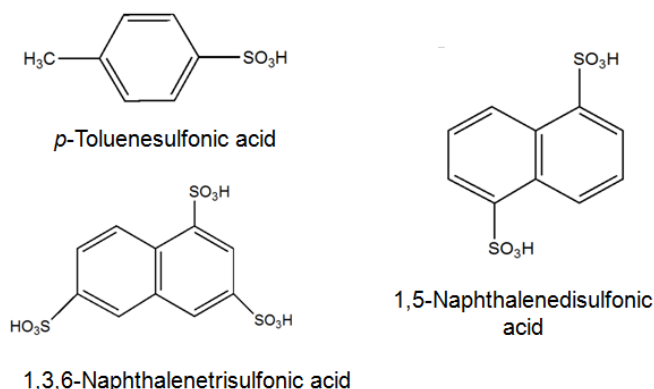


Chart 2.1. Aromatic sulfonic acids examined in the present study.

2.2. Experimental section

2.2.1. 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 tetrahydrates (Aldrich) was dissolved in methanol, and was titrated by Et₄NOH (20 wt. % in H₂O, 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: thirty-five grams of sodium 1,3,6-naphthalenetrisulfonate (purchased from TCI Shanghai, chemical, china) was dissolved in pure water of 2 liters, and the sodium ions were exchanged to protons with an ion-exchange column. The Na⁺ concentration was determined by an atomic absorption spectrophotometer, and was kept to be less than 0.1 µg/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(ClO₄)₂ and Ba(ClO₄)₂ (all Aldrich), were used as received. Calcium perchlorate tetrahydrates from Aldrich was dried in vacuo at 150 °C to obtain anhydrous Ca(ClO₄)₂. Commercially obtained acetonitrile (MeCN) solvents of GR and super dehydrated grades (Wako), containing < 0.1 and < 0.001% (v/v) H₂O, 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.

2.2.2. 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 a precipitation reaction.

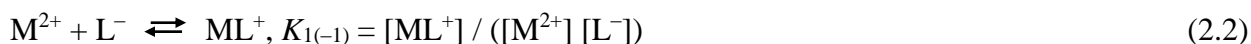
The energies calculations were performed using the computer facilities at Research Center for Computational Science, Okazaki, Japan and Research Institute for Information Technology, Kyushu University, Japan.

2.2.3. Evaluation of “reverse” coordination formation constants

The “reverse” coordination formation constants between the alkaline earth 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] as follows:

(a) In the case of ion charges of 2:1 (M^{2+} and L^-)

The reactions and equilibrium constants for precipitation dissolution (solubility products, K_{sp}) and “reverse” coordination ($K_{1(-1)}$) at higher M^{2+} concentrations, compared to L^- , are expressed by Eqs. 2.1 and 2.2, respectively.



The solubility s of ML_2 or the total “ligand” concentration, c_t , in solution (and not in precipitation) is expressed by Eq. 2.3.

$$s = c_t = [L^-] + [ML^+] = \sqrt{K_{sp} [M^{2+}]^{-1}} (1 + K_{1(-1)} [M^{2+}]). \quad (2.3)$$

The observed absorbance A_{bs} of L^- (and ML^+) can be rationalized by Lambert-Beer’s law as,

$$A_{bs} = \varepsilon c l \sim \varepsilon s l \quad (2.4)$$

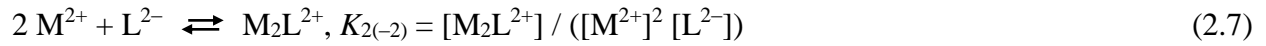
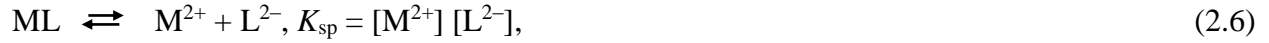
Where ε , c , and l are the molar absorptivity ($\text{cm}^{-1} \text{mol}^{-1} \text{dm}^3$) of L^- (or ML^+), the concentration (mol dm^{-3}), and the path-length (cm), respectively. Eq. 2.5 is given by introducing Eq. 2.3 into Eq. 2.4.

$$A_{bs} = \varepsilon l c_t = \varepsilon l \sqrt{K_{sp} [M^{2+}]^{-1}} (1 + K_{1(-1)} [M^{2+}]). \quad (2.5)$$

With higher M^{2+} concentrations and larger $K_{1(-1)}$ values, equation 2.5 can be arranged to be

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

(b) In the case of ion charges of 2:2 (M^{2+} and L^{2-})



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

$$c_t = [L^{2-}] + [M_2L^{2+}] = K_{sp} [M^{2+}]^{-1} (1 + K_{2(-2)} [M^{2+}]^2) \quad (2.8)$$

The observed absorbance A_{bs} is expressed as

$$A_{bs} = \varepsilon l K_{sp} [M^{2+}]^{-1} (1 + K_{2(-2)} [M^{2+}]^2) \quad (2.9)$$

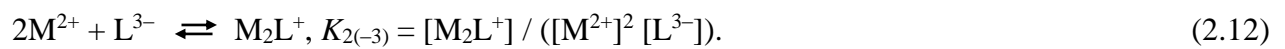
Eq. 2.9 (between 2:2 charged species) can be easily arranged for 1:1 species, *i.e.*, between M^+ and L^- as Eq. 2.10.

$$A_{bs} = \varepsilon l K_{sp} [M^+]^{-1} (1 + K_{2(-2)} [M^+]^2) \quad (2.10)$$

Actually, with higher M^{2+} concentrations and larger $K_{2(-2)}$ values, Eq. 2.10 can be arranged to be $A_{bs} = \varepsilon l K_{sp} K_{2(-2)} [M^{2+}]$.

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:

(c) In the case of ion charges of 2:3 (M^{2+} and L^{3-})



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

$$c_t = [L^{3-}] + [M_2L^+] = \sqrt{K_{sp} [M^{2+}]^{-3}} (1 + K_{2(-3)} [M^{2+}]^2) \quad (2.13)$$

The observed absorbance A_{bs} is expressed as

$$A_{bs} = \varepsilon l \sqrt{K_{sp} [M^{2+}]^{-3}} (1 + K_{2(-3)} [M^{2+}]^2) \quad (2.14)$$

With higher M^{2+} concentrations and larger $K_{2(-3)}$ values, Eq. (2.14) can be arranged to be $A_{bs} = \varepsilon l \sqrt{K_{sp} [M^{2+}]} K_{2(-3)}$.

2.3. Results and discussion

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

We [9b] have already reported that Mg^{2+} interacts with the 1,5-naphthalenedisulfonate ion (L^{2-}) to form the 1:1 precipitation (MgL), and the precipitation is successively re-dissolved (Mg_2L^{2+}) by the addition of a large excess of $Mg(ClO_4)_2$ in MeCN, whereas Ca^{2+} and Ba^{2+} 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^+) 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_2L^+). Conversely, such specific interactions between Li^+ 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 2.1) [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_2O or MeOH, to MeCN [9].

However, even in ethanol of relatively high donicity, the precipitation and successive re-dissolution phenomena between Ba^{2+} and L^{2-} are observed (Fig. 2.1). Tetraethylammonium 1,5-naphthalenedisulfonate $[(Et_4N^+)_2L^{2-}]$ has given a strong band at 228 nm ($\varepsilon/cm^{-1} \text{ mol}^{-1} \text{ dm}^3 = 6.1 \times 10^4$) and a smaller band at around 290 nm in MeCN [9b]. In EtOH, the wavelength of strong peak of L^{2-} ($\lambda_{max} = 227.5 \text{ nm}$) is almost the same or just slightly shorter than that in MeCN. With increasing concentration of $Ba(ClO_4)_2$, the absorbance at around 227 nm decreases gradually, and

the band suddenly disappears in the presence of an equivalence of Ba^{2+} , $1.0 \times 10^{-4} \text{ mol dm}^{-3}$, which is accompanied by the complete precipitation. However, the successive re-dissolution of precipitates takes 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.

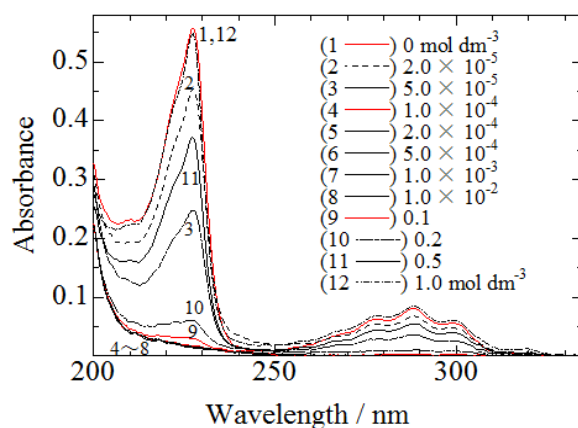


Fig. 2.1. The UV spectra of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate (0.1 cm path-length) in EtOH with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$.

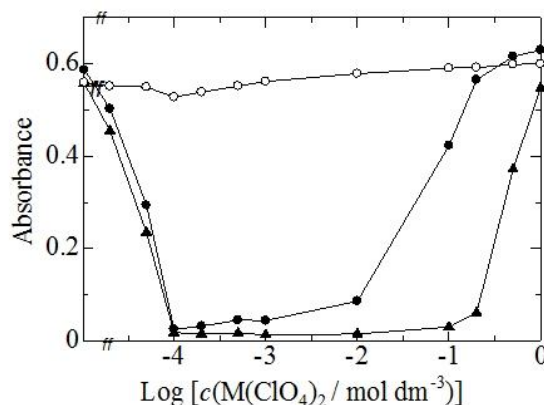
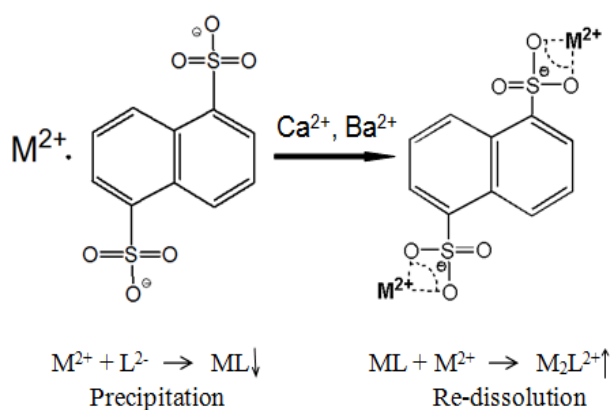


Fig. 2.2. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 227 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate ion with increasing concentration of alkaline earth metal ions in EtOH: (○) $\text{Mg}(\text{ClO}_4)_2$; (●) $\text{Ca}(\text{ClO}_4)_2$; (▲) $\text{Ba}(\text{ClO}_4)_2$.

Fig. 2.2 shows the changes in absorbance (at λ_{max}) of L^{2-} with increasing concentration of alkaline earth metal ions (Mg^{2+} , Ca^{2+} , Ba^{2+}) in ethanol. Neither the precipitation (nor the re-dissolution) occurs between Mg^{2+} and L^{2-} in EtOH, whereas Mg^{2+} can interact with L^{2-} to form precipitates of MgL and the “reverse-coordinated” species of Mg_2L^{2+} in MeCN [9b]. The precipitation between Ca^{2+} and L^{2-} takes place at the equivalence point, however, the precipitates

begin to re-dissolve after $0.01 \text{ mol dm}^{-3} \text{ Ca}^{2+}$ and completely re-dissolve at $1.0 \text{ mol dm}^{-3} \text{ Ca}(\text{ClO}_4)_2$. The precipitates of CaL are apt to re-dissolve successively to form Ca_2L^{2+} more easily than those of BaL , therefore, the values of “reverse” coordination constant (Table 2.2), $\log K_2$, for Ca_2L^{2+} and Ba_2L^{2+} are given to be 7.49 and 7.11, respectively. In the present paper, for simplicity, we may describe $\log K_2$ and not $\log K_{2(-2)}$ for the “reverse” coordination constants between M^{2+} and L^{2-} unless some confusion is anxious.

The interaction of the alkaline earth metal ions with the 1,5-naphthalenedisulfonate 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 2.1 shows the reaction scheme for the precipitation of ML ($\text{M} = \text{Ca}$ and Ba) and the successive re-dissolution of the precipitates in EtOH.



Scheme 2.1. Successive formation of ML and M_2L^{2+} ($\text{M} = \text{Ca}$ and Ba) for the 1,5-naphthalenedisulfonate ion 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. 2.3 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 $1.0 \text{ mol dm}^{-3} \text{ Mg}(\text{ClO}_4)_2$. In EtOH, however, the absorbance (at λ_{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 $1.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ L}^{2-}$ solution.

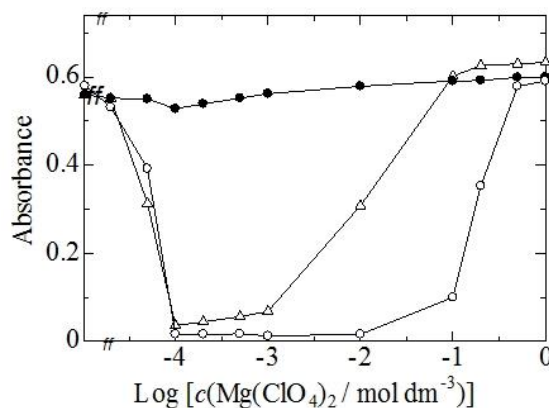


Fig. 2.3. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 227 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate ion with increasing concentration of $\text{Mg}(\text{ClO}_4)_2$ in different solvents: (●) EtOH; (Δ) 1-BuOH; (\circ) MeCN.

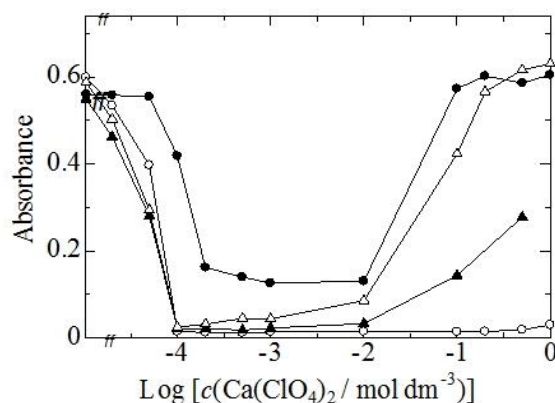


Fig. 2.4. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 227 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate ion with increasing concentration of $\text{Ca}(\text{ClO}_4)_2$ in different solvents: (●) MeOH; (Δ) EtOH; (\blacktriangle) 1-BuOH; (\circ) MeCN.

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 $\text{Ca}(\text{ClO}_4)_2$, *cf.* Ref. [9]. Fig. 2.4 shows that, in a protic solvent, MeOH, Ca^{2+} can react with L^{2-} to cause partial precipitation of CaL . The absorbance (at λ_{max}) of L^{2-} begins to decrease at $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ of Ca^{2+} , and the absorbance minimum of 0.126 is given in the presence of $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Ca}^{2+}$. Apparently, the excess amounts of Ca^{2+} to L^{2-} assist the precipitation reaction.

In EtOH, an equivalent amount of Ca^{2+} actually has caused the complete precipitation. At any rate, the precipitates would re-dissolve completely by an excess amount of $\text{Ca}(\text{ClO}_4)_2$ in both MeOH and EtOH. The precipitation of CaL in 1-BuOH takes place to a larger extent than in MeOH or EtOH. The $\text{p}K_{\text{sp}}$ values of CaL increased in the order of $\text{MeOH} < \text{EtOH} < 1\text{-BuOH}$ (*cf.* Table 2.2). Unfortunately, the solubility of $\text{Ca}(\text{ClO}_4)_2$ in 1-BuOH ($\epsilon_r = \text{ca. } 17.5$) is not enough to examine at $1.0 \text{ mol dm}^{-3} \text{ Ca}(\text{ClO}_4)_2$.

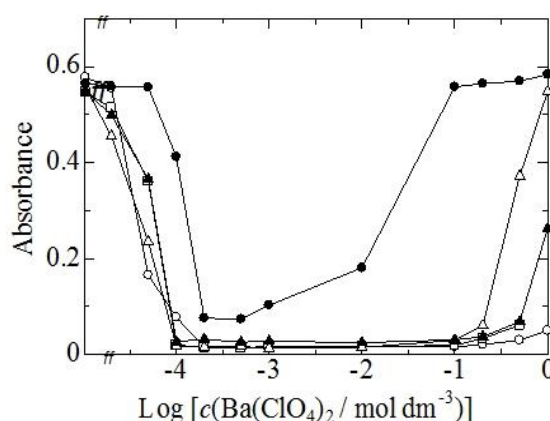


Fig. 2.5. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 227 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate ion with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$ in different solvents: (●) MeOH; (Δ) EtOH; (▲) 1-PrOH; (□) 1-BuOH; (○) MeCN.

Fig. 2.5 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 larger extent than CaL. The absorbance minimum (at λ_{max}) of 0.076 is given by the addition of $2.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ba}^{2+}$. 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 λ_{max}) are 0.372, 0.069, 0.061 in EtOH, 1-PrOH and 1-BuOH, respectively, in the presence of $0.5 \text{ mol dm}^{-3} \text{ Ba}(\text{ClO}_4)_2$.

2.3.2. In the binary solvents of MeCN-MeOH and MeOH- H_2O

Fig. 2.6 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 as $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Mg}^{2+}$. The pK_{sp} value and the “reverse” coordination constants are list in Table 2.3. 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_2L^{2+} species to form from the MgL^0 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_2L^{2+} species. We have also reported the effect of water upon the specific interaction between Li^+ and the tropolonate ion in MeCN is similar to but much more distinct than that of MeOH [9a].

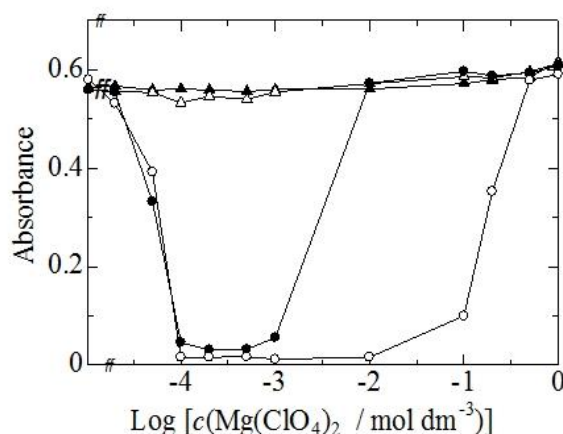


Fig. 2.6. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 227 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate ion with increasing concentration of $\text{Mg}(\text{ClO}_4)_2$ in MeCN-MeOH mixtures: (○) 0; (●) 10; (△) 20; (▲) 50% (v/v) of MeOH.

Fig. 2.7 shows the precipitation and the successive re-dissolution of CaL in MeCN-MeOH and MeOH- H_2O mixtures. In sole MeCN, the precipitates of CaL have formed completely at an equivalent amount of Ca^{2+} , and CaL precipitates have been found not be re-dissolved even by the large excess amount of $\text{Ca}(\text{ClO}_4)_2$ [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^{2+} , and are just partly re-dissolved by the addition of $1.0 \text{ mol dm}^{-3} \text{ Ca}(\text{ClO}_4)_2$. 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^{-3} causes the complete recovery in absorbance as the MeOH content in the solvent reaches 70% (*cf.* also Table 2.3).

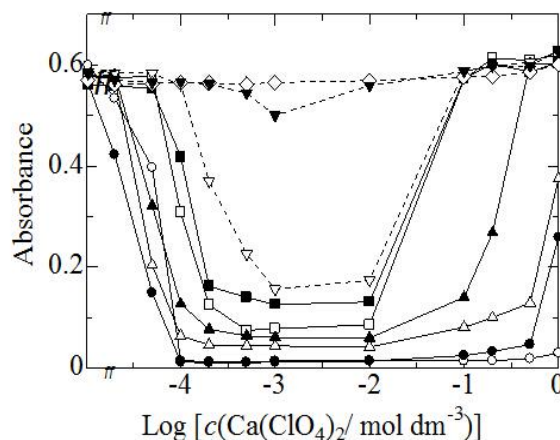


Fig. 2.7. Changes in absorbance ($\lambda_{\max} = \text{ca. } 227 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate ion with increasing concentration of $\text{Ca}(\text{ClO}_4)_2$ in MeCN-MeOH mixtures: (\circ) 0; (\bullet) 20; (Δ) 50; (\blacktriangle) 70; (\square) 80; (\blacksquare) 100% (v/v) of MeOH; and in MeOH- H_2O mixtures: (∇) 1.0; (\blacktriangledown) 2.0; (\diamond) 5.0% (v/v) of H_2O .

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^{2+} and L^{2-} in MeOH, the change in absorbance (at λ_{\max}) of $1.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ L}^{2-}$ are examined in MeOH- H_2O mixtures. With the addition of 1.0% water to MeOH, some small changes occurred in both the precipitation and re-dissolution reactions (*cf.* Fig. 2.7). The values of $\text{p}K_{\text{sp}}$ and $\log K_2$ are evaluated to be 6.57 and 4.01 in 1.0% H_2O -MeOH, while those values are 8.26 and 5.60 in the sole MeOH. The addition of 2.0% H_2O to MeOH, however, alters the interaction suddenly: the absorbance of L^{2-} decreases just slightly at $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Ca}^{2+}$. Finally, no decrease of the absorbance is observed in 5.0% H_2O . 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. 2.8 shows the absorbance changes of 1,5-naphthalenedisulfonate ion with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$ in the MeCN-MeOH mixtures. In sole MeCN, an equivalence Ba^{2+} has caused the complete precipitation of L^{2-} , and those precipitates have never been re-dissolved [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 re-dissolved even in the presence of $1.0 \text{ mol dm}^{-3} \text{ Ba}(\text{ClO}_4)_2$. A great difference is given at 75% MeOH and the absorbance (at λ_{max}) of $1.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ L}^{2-}$ are completely recovered at $0.2 \text{ mol dm}^{-3} \text{ Ba}^{2+}$ (*cf.* also Table 2.3). Among the three alkaline earth metal ions, we may notice that Ba^{2+} is the least influenced by the additional MeOH for the reactions between M^{2+} and L^{2-} in the binary MeCN-MeOH media.

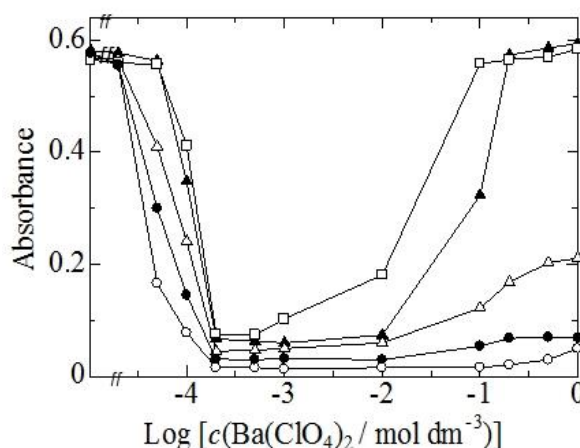


Fig. 2.8. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 227 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate ion with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$ in MeCN-MeOH mixtures: (\circ) 0; (\bullet) 50; (Δ) 70; (\blacktriangle) 75; (\square) 100 % (v/v) of MeOH.

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 ($\text{p}K_{\text{sp}}$) and “reverse” coordination constants ($\log K_2$) displayed in Fig. 2.9. The “reverse” coordination constants of Ca_2L^{2+} and Ba_2L^{2+} are close to each other, however, the precipitates of CaL are totally re-dissolved by an excess amount of Ca^{2+} in 70% MeOH, while that of BaL are totally re-dissolved not in 70% but 75% MeOH. In the binary MeCN-MeOH solvent system, the $\text{p}K_{\text{sp}}$ values of both CaL and BaL decrease, however, the $\log K_2$ values of CaL_2^+ and BaL_2^+ remains constant or slightly increase with increasing contents of $> 50\%$ MeOH (*cf.* also Table 2.3).

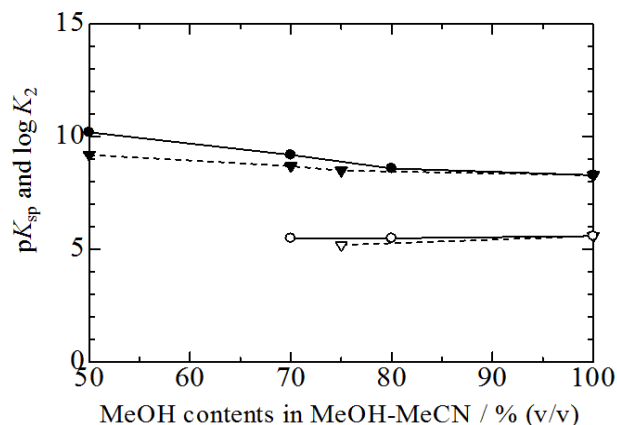


Fig. 2.9. The changes of solubility products (pK_{sp}) and “reverse” coordination constants ($\log K_2$) vs. MeOH contents in MeOH-MeCN for the interaction between Ca^{2+} (\bullet , \circ) or Ba^{2+} (\blacktriangledown , \triangledown) and 1,5-naphthalenedisulfonate ion. The solid and open symbols represent pK_{sp} and $\log K_2$, respectively.

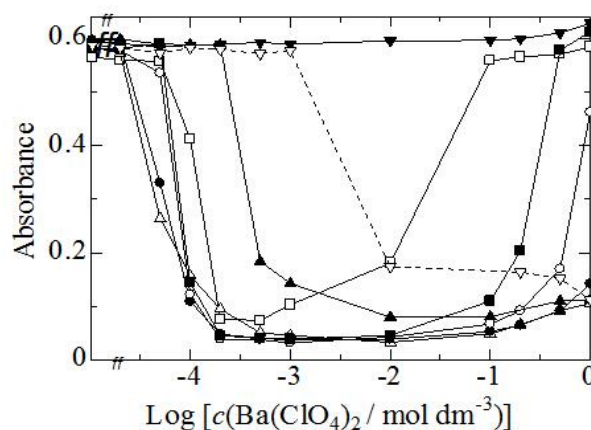


Fig. 2.10. Changes in absorbance ($\lambda_{\max} = \text{ca. } 227 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate ion with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$ in MeOH- H_2O mixtures: (\square) 0; (\blacksquare) 1.0; (\circ) 2.0; (\bullet) 5.0; (Δ) 10; (\blacktriangle) 20; (\triangledown) 30; (\blacktriangledown) 50% of H_2O .

Fig. 2.10 shows the influences of additional water (1.0 – 50%) on the successive reactions of precipitation and re-dissolution (the BaL^0 and Ba_2L^{2+} formation) for the 1,5-naphthalenedisulfonate ion (L^{2-}) in MeOH- H_2O . It is curious to report that the solubility of BaL decreases with increasing H_2O contents, *i.e.*, the pK_{sp} value of BaL increase from 8.28 for no additional water to 9.22, 9.39 and 9.48 for 1.0, 2.0 and 5.0% H_2O , respectively. On the other hand, the re-dissolution of the precipitates are inhibited with increasing contents of H_2O . Firstly, the re-dissolution is gradually reduced with increasing water contents (1.0 – 10%). With the water content of 20%, the absorbance (λ_{\max}) minimum of L^{2-} is still observed at $0.10 \text{ mol dm}^{-3} \text{ Ba}^{2+}$. With 30%

H₂O, the absorbance of L²⁻ suddenly decreases at $1.0 \times 10^{-2} \text{ mol dm}^{-3} \text{ Ba}^{2+}$, and continue to decrease monotonously up to $1.0 \text{ mol dm}^{-3} \text{ Ba}(\text{ClO}_4)_2$. 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.

2.3.3. In the binary MeCN-EtOH mixed solvents

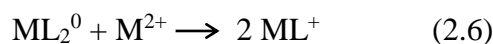
The coordination reactions between alkaline earth metal ions and L²⁻ were investigated also in MeCN-EtOH mixed solvents. The precipitation of MgL take place completely when an equivalence of Mg²⁺ are added to $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate (L²⁻) in the binary MeCN-EtOH 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 Mg₂L²⁺, logK₂, in the 10 and 30% EtOH solvents are evaluated to be 7.15 and 8.57, respectively. However, the interaction between Mg²⁺ and L²⁻ was totally inhibited in 50% EtOH (*cf.* Fig 2A.1).

Although the complete precipitation of CaL has taken place at an equivalence of Ca²⁺ 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(ClO₄)₂ in MeCN (*vide supra*), while the absorbance of L²⁻ (or Ca₂L²⁺) can be totally recovered by the addition of $0.02 \text{ mol dm}^{-3} \text{ Ca}^{2+}$ 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 $1.0 \text{ mol dm}^{-3} \text{ Ca}(\text{ClO}_4)_2$ (*cf.* Fig 2A.2). However, the precipitates of BaL are not re-dissolved by $1.0 \text{ mol dm}^{-3} \text{ Ba}(\text{ClO}_4)_2$ even in 50% EtOH-MeCN (*cf.* Fig 2A.3).

2.3.4. The specific interactions between Ba²⁺ and *p*-toluenesulfonate (L⁻) or 1,3,6-naphthalenetrisulfonate (L³⁻) in alcohols

The specific interactions of monosulfonate and trisulfonate ions with Ba²⁺ were also examined in the alcohols. The pK_a values of the sulfonic acids are shown in Table 2.4. 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 ($[\text{Et}_4\text{N}^+ \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-]$, L^-) in MeOH: the absorbance (at λ_{max}) of L^- remains almost unchanged with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$ (Fig. 2.11), 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 $[\text{Et}_4\text{N}^+ \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-]$ gives a strong band at 222 nm ($\epsilon/\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3 = 1.1 \times 10^4$), which shows a slight blue shift, compared with the band in MeCN ($\lambda_{\text{max}} = 223 \text{ nm}$). The interaction between Ba^{2+} and L^- causes some incomplete precipitation at the equivalence point ($5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ba}^{2+}$): the absorbance (at λ_{max}) minimum of 0.345 in EtOH, cf. 0.031 in MeCN. The absorbance is gradually recovered after the minimum, and totally recovered at $1 \times 10^{-2} \text{ mol dm}^{-3} \text{ Ba}^{2+}$, accompanied with the formation of “reverse-coordinated” species of ML^+ , cf. Eq. (2.6).



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

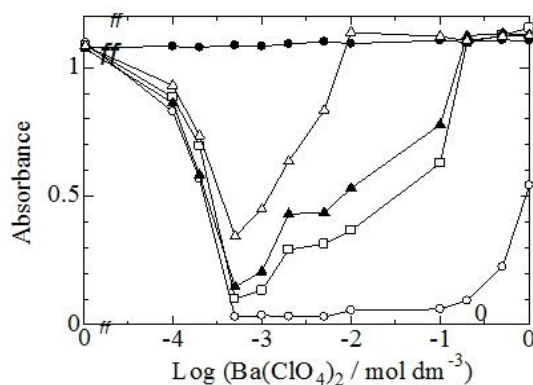
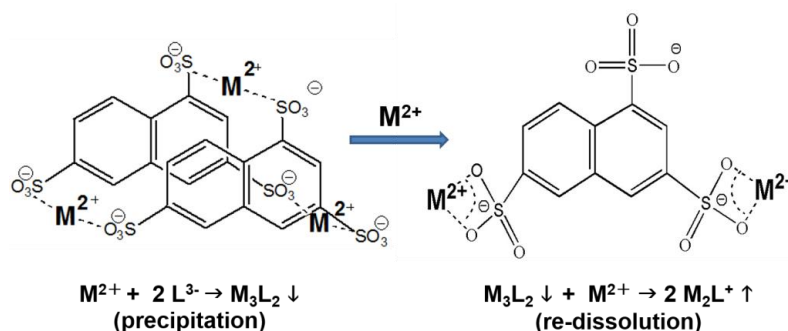


Fig. 2.11. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 222 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ p -toluenesulfonate ion with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$ in MeCN and alcohols: (○) MeCN; (●) MeOH; (Δ) EtOH; (▲) 1-PrOH; (□) 1-BuOH.

In MeCN, tetraethylammonium 1,3,6-naphthalenetrisulfonate (L^{3-}) gives a strong UV band at $\lambda_{\text{max}} = 238 \text{ nm}$ ($\epsilon/\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3 = \text{ca. } 7.7 \times 10^4$), apart from the broad band around 280 nm of the naphthalene body. The alkaline metal ions cause the complete precipitation at $1.5 \times 10^{-4} \text{ mol}$

dm^{-3} for $1.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ L}^{3-}$, but almost no re-dissolution of the precipitates at 1.0 mol dm^{-3} $\text{M}(\text{ClO}_4)_2$, except for $\text{Mg}(\text{ClO}_4)_2$. In MeOH, neither precipitation nor re-dissolution is caused for L^{3-} even by Ba^{2+} (Fig. 2.12). Regardless in MeOH, both precipitation and re-dissolution (between or among Ba^{2+} and L^{3-}) can take place in the other primary alcohols (from EtOH to 1-HexOH). The complete precipitation at the equivalence point ($[\text{Ba}^{2+}]:[\text{L}^{3-}] = 1.5:1.0$) should be based on the formation of Ba_3L_2 . The successive re-dissolution of the precipitates is supposed to the formation of the Ba_2L^+ species in EtOH and 1-PrOH, *cf.* Eq. (2.2) and Scheme 2.2. 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.



Scheme 2.2. Successive formation of M_3L_2 and M_2L^+ ($\text{M} = \text{Ba}$) for the 1,3,6-naphthalenetrisulfonate ion (L^{3-}) in EtOH and 1-PrOH.

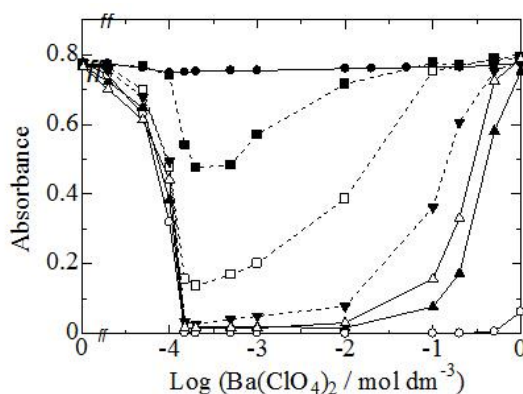


Fig. 2.12. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$ in MeCN and alcohols: (●) MeOH; (Δ) EtOH; (▲) 1-PrOH; (○) MeCN; and in EtOH-MeOH mixtures: (▼) 20; (□) 50; (■) 70% (v/v) of MeOH.

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 $2.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ba}^{2+}$, and the successive re-dissolution from Ba_3L_2 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. 2.12).

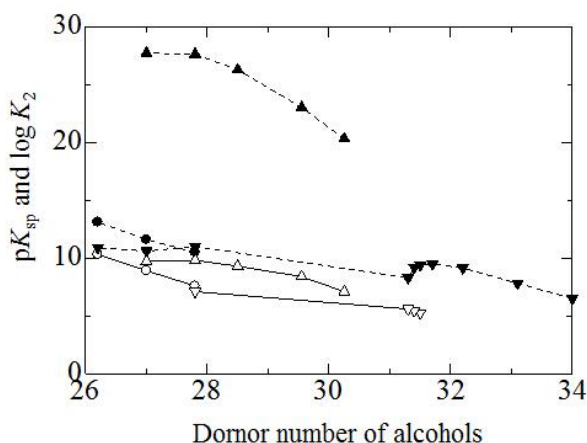


Fig. 2.13. The solubility products (pK_{sp}) and “reverse” coordination constants ($\log K_n$, $n = 1$ or 2) vs. donor numbers (DN) of alcohols for the interaction between Ba^{2+} and TsO^- , $1,5\text{-NDS}^{2-}$, and $1,3,6\text{-NTS}^{3-}$: (●, ○) *p*-toluenesulfonate (TsO^-); (▼, ▽) 1,5-naphthalenedisulfonate ($1,5\text{-NDS}^{2-}$); (Δ, ▲) 1,3,6-naphthalenetrisulfonate ($1,3,6\text{-NTS}^{3-}$). The solid and open symbols represent pK_{sp} and $\log K_n$, respectively. The binary mixed solvents of EtOH-MeOH and MeOH- H_2O are used for $28 < \text{DN} < 31$ and $31.5 < \text{DN} \leq 34$, respectively.

Fig. 2.13 shows the solubility products (pK_{sp}) and the “reverse” coordination constants ($\log K_{1(-1)}$, $\log K_{2(-2)}$, or $\log K_{2(-3)}$) for the interaction between Ba^{2+} and the sulfonate ions (L^- , L^{2-} , and L^{3-}) in different alcohols. In the primary alcohols of the lower donor numbers, such as 1-BuOH (DN = 26.2, *cf.* Table 2.1), the precipitation reaction is apt to take place to a larger extent than in methanol (DN = 31.3). In other words, 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^{2+} and L^{3-} 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, 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. 2.13. The donor numbers of the binary MeOH-H₂O system are estimated just assuming the linearity between 31.4 of MeOH and 40.3 of H₂O, up to 30% H₂O.

2.3.5. Computational prediction of the structures of Ba₂L⁺ in EtOH

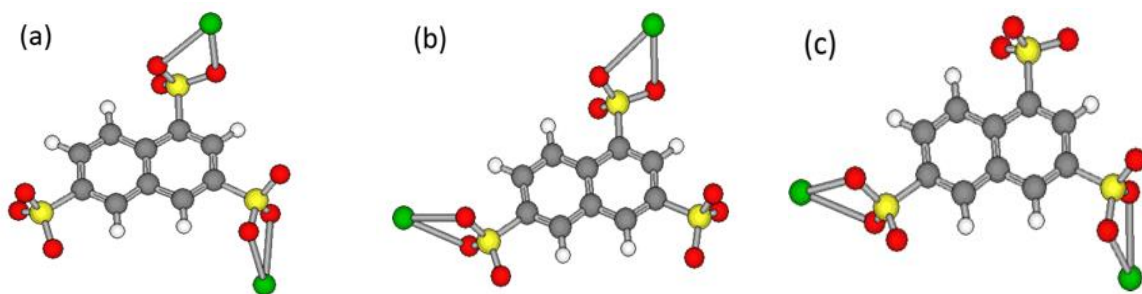


Fig. 2.14. The optimized structures of 1,3,6-naphthalenetrisulfonates to which two Ba²⁺ ions are coordinated at (a) 1,3-, (b) 1,6-, and (c) 3,6-positions.

For predicting the coordinating structures of Ba₂L⁺ shown in Scheme 2.2, 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. 2.14(a) – (c) show the projected views of optimized structures of 1,3,6-naphthalenetrisulfonates to which two Ba²⁺ ions are coordinated at (a) 1,3-, (b) 1,6-, and (c) 3,6-positions. For all three structures, Ba²⁺ ion coordinates to two O atoms of sulfonate. Accordingly, the S–O lengths coordinated by Ba²⁺ (1.49 – 1.50 Å) were slightly longer than those at free sulfonate (1.47 – 1.48 Å). Table 2.5 summarizes the relative energies for these Ba₂L⁺ 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.

2.4. 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-} , 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_2O). 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 influenced in protic 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.

Table 2.2 Precipitation and re-dissolution reactions of alkaline earth metal and 1,5-naphthalenedisulfonate (L^{2-}) ions in acetonitrile and alcohols.

Metal ions ^a	Equilibrium constants ^b	MeCN	MeOH	EtOH	1-PrOH	1-BuOH
Mg^{2+}		●	No	No		●
	(pK_{sp})	10.92	—	—		10.39
	(pK_{sp}) ^c	11.29	—	—		11.48
		○	No	No		○
	$\log K_2$	7.15	—	—		8.08

		●	▲	●		●
Ca ²⁺	(pK _{sp})	> 9.82	8.26	10.74		10.80
	(pK _{sp}) ^c	> 10.20	8.69	11.40		11.89
		No	○	○		△
	log K ₂	—	5.60	7.49		7.04
		●	▲	●	●	●
Ba ²⁺	(pK _{sp})	> 9.82	8.28	11.00	10.62	10.89
	(pK _{sp}) ^c	> 10.20	8.70	11.66	11.49	11.98
		No	○	○	△	No
	log K ₂	—	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 (L²⁻) 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(ClO₄)₂.

^b Solubility products (K_{sp}) and “reverse” coordination constants (K₂), *cf.* the Experimental section in Ref. [9b]. The uncertainties (errors) in K_{sp} values and “reverse” coordination constants may be less than ±0.01 and ±0.05, respectively, in this table and Tables 2.3 – 2.4.

^c 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].

Table 2.3 Precipitation and re-dissolution reactions between alkaline earth metal and 1,5-naphthalenedisulfonate (L²⁻) ions in binary MeCN-MeOH and MeOH-H₂O solvents.

Metal ions ^a	Equilibrium constants ^b	MeCN-MeOH [MeOH contents / % (v/v)]					
		10	50	70	75	80	100
Mg ²⁺		●	No	No	No	No	No
	(pK _{sp})	10.18	—	—	—	—	—
	(pK _{sp}) ^c	10.57	—	—	—	—	—
		○	No	No	No	No	No

	$\log K_2$	8.15	—	—	—	—	—
		●	●	▲	—	▲	▲
	(pK_{sp})	—	10.19	9.17	—	8.55	8.26
Ca^{2+}	$(pK_{sp})^c$	—	10.58	9.57	—	8.96	8.69
		No	△	○	—	○	○
	$\log K_2$	—	—	5.45	—	5.52	5.60
		●	●	●	●	●	▲
	(pK_{sp})	—	9.20	8.74	8.47	—	8.28
Ba^{2+}	$(pK_{sp})^c$	—	9.59	9.15	8.87	—	8.71
		No	No	△	○	○	○
	$\log K_2$	—	—	—	5.20	—	5.58
MeOH-H ₂ O [H ₂ O contents / % (v/v)]		1.0	2.0	5.0	20	30	50
		●	●	●	●	▲	No
	(pK_{sp})	9.22	9.39	9.48	7.82	6.51	—
Ba^{2+}	$(pK_{sp})^c$	9.64	9.77	9.87	8.11	6.76	—
		○	△	No	No	No	No
	$\log K_2$	5.46	5.25	—	—	—	—

For the *Explanatory notes*, cf. Table 2.2.

^a M(ClO₄)₂.

^b Solubility products (K_{sp}) and “reverse” coordination constants (K_2), cf. the Experimental section in Ref. [9b].

^c Cf. Table 2.2, note c for the thermodynamic solubility products (K_{sp}) corrected with the activity coefficients of ions.

Table 2.4 Precipitation and re-dissolution reactions of Ba²⁺ with the mono-, di- and trivalent aromatic sulfonate ions in alcohols.

Et ₄ N ⁺ salts	pK_a^a	Equilibrium Constants ^b	MeOH	EtOH	1-PrOH	1-BuOH	1-HexOH
<i>p</i> -Toluenesulfonate	−0.43		No	▲	▲	▲	▲
(1.0 × 10 ^{−3} mol dm ^{−3})	8.01 ^c	(pK_{sp})	—	10.48	11.59	13.10	—
		(pK_{sp}) ^d		11.03	12.32	14.01	

			No	○	○	○	○
		$\log K_{1(-1)}$	—	7.58	8.9	10.32	—
1,5-Naphthalenedisulfonate	−0.60		▲	●	●	●	●
	$(1.0 \times 10^{-4} \text{ mol dm}^{-3})$	(pK_{sp})	(8.28)	(11.00)	(10.6)	(10.89)	—
		$(pK_{sp})^d$	(8.70)	(11.66)	(11.49)	(11.98)	
			○	○	△	△	No
		$\log K_{2(-2)}$	5.58	7.11	—	—	—
1,3,6-Naphthalenetrisulfonate	−0.76		No	●	●	●	●
	$(1.0 \times 10^{-4} \text{ mol dm}^{-3})$	(pK_{sp})	—	27.60	27.66	—	—
		$(pK_{sp})^d$		29.12	29.67		
			No	○	○	△	△
		$\log K_{2(-3)}$	—	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.

^a The first pK_a value of HA, H₂A, or H₃A in water, *cf.* SciFinder: Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2014 ACD/Labs).

^b Solubility products (K_{sp}) and “reverse” coordination constants (K_1 , K_2), *cf.* the Experimental section in the present paper and in Ref. [9b].

^c The pK_a values in acetonitrile, *cf.* Ref. [27]

^d *Cf.* Table 2.2, note c for the thermodynamic solubility products (K_{sp}) corrected with the activity coefficients of ions.

Table 2.5 Calculated relative energies for Ba₂L⁺ (L: 1,3,6-naphthalenetrisulfonate) in EtOH.

Positions of Ba ²⁺	Relative energy / kcal mol ^{−1}
1,3-	+1.19
1,6-	+0.71
3,6-	0.00

References

- [1] M. Aghaie, H. Aghaie, A. Ebrahimi, *J. Mol. Liquids* 135 (2007) 72.
- [2] G. Liu, M. Cons, T. Liu, *J. Mol. Liquids* 118 (2005) 27.
- [3] A. Jouyban, A. Shayanfar, T. Ghafourian, W.E. Acree, Jr, *J. Mol. Liquids* 195 (2014) 125.
- [4] C. Trujillo, A. M. Lamsabhi, O. Mó, M. Yáñez, 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 Tran.*, 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. Liquids* 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. Liquids* 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. Liquids* 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., *Treatise on Analytical Chemistry, Part 1, 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. Liquids* 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. Liquids* 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 and T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, London, 1973.
- [29] M.W. Schmidt, K.K. Baldrige, 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. Iikura, 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*, World Scientific, Singapore, 1999, vol. 3, ch. 2, pp. 49-74.
- [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.

Appendix

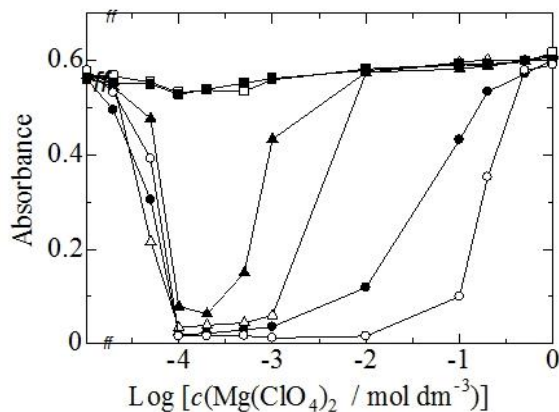


Fig. 2A.1. Changes in absorbance ($\lambda_{\max} = \text{ca. } 227 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate ion with increasing concentration of $\text{Mg}(\text{ClO}_4)_2$ in MeCN-EtOH mixtures: (\circ) 0; (\bullet) 10; (Δ) 20; (\blacktriangle) 30; (\square) 50; (\blacksquare) 100% (v/v) of EtOH.

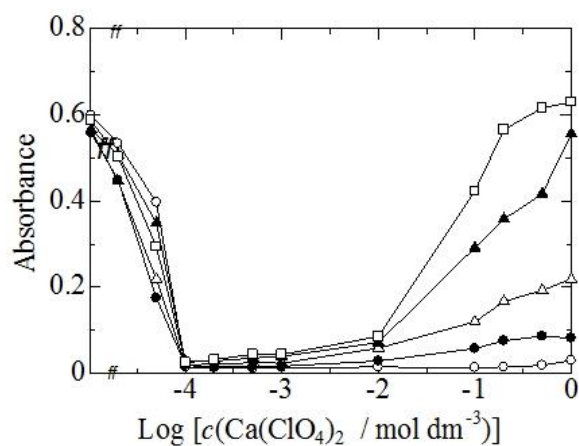


Fig. 2A.2. Changes in absorbance ($\lambda_{\max} = \text{ca. } 227 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate ion with increasing concentration of $\text{Ca}(\text{ClO}_4)_2$ in MeCN-EtOH mixtures: (\circ) 0; (\bullet) 20; (Δ) 30; (\blacktriangle) 50; (\square) 100% (v/v) of EtOH.

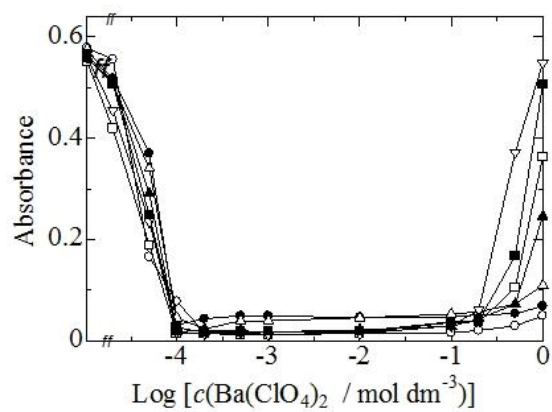


Fig. 2A.3. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 227 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,5-naphthalenedisulfonate ion with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$ in MeCN-EtOH mixtures: (○) 0; (●) 20; (△) 50; (▲) 70; (□) 80; (■) 90; (▽) 100 % (v/v) of EtOH.

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

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.

Keywords: coordination; stability constant; solubility product; ion pair; tripe ion formation; DFT calculation.

3.1. 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” $[\text{M}_2\text{L}^+]$, 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 ($\text{M}^+\text{A}^-\text{M}^+$, $\text{M} = \text{Li}, \text{Na}, \text{K}$, $\text{A} = \text{anthraquinone}$) 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 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.

3.2. Experimental section

3.2.1. 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 °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).

3.2.2. 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.

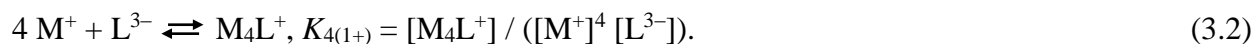
The energies calculations were performed using the computer facilities at Research Center for Computational Science, Okazaki, Japan and Research Institute for Information Technology, Kyushu University, Japan.

3.2.3. Evaluation of “reverse” coordination formation constants

The evaluation of “reverse” coordination formation constants between alkaline earth metal (M^{2+}) and 1,3,6-naphthalenetrisulfonate (L^{3-}) ions has been already described in the previous paper (*cf.* the experimental section of Chapter 2, [16]). The solubility products and “reverse” coordination constants between an alkali metal (M^+) or the indium (M^{3+}) ion and L^{3-} 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 L^{3-} , are expressed by Eqs. 3.1 and 3.2, respectively.



The solubility s of M_3L or the total “ligand” concentration, c_t , in solution (not in precipitation) is expressed by Eq. 3.3.

$$s = c_t = [\text{L}^{3-}] + [\text{M}_4\text{L}^+] = K_{\text{sp}} [\text{M}^+]^{-3} (1 + K_{4(1+)} [\text{M}^+]^4) \quad (3.3)$$

The observed absorbance A_{bs} of L^{3-} (and M_4L^+) can be rationalized by Lambert-Beer’s law as Eq. 3.4.

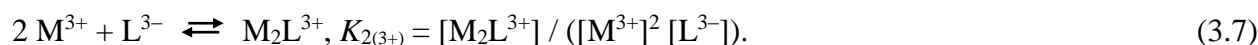
$$A_{bs} = \varepsilon c l \sim \varepsilon s l \quad (3.4)$$

Where ε , c , and l are the molar absorptivity ($\text{cm}^{-1} \text{mol}^{-1} \text{dm}^3$) of L^{3-} (or M_4L^+), the concentration (mol dm^{-3}), and the path-length (cm), respectively. Eq. 3.5 is given by introducing Eq. 3.3 into Eq. 3.4.

$$A_{bs} = \varepsilon l K_{\text{sp}} [\text{M}^+]^{-3} (1 + K_{4(1+)} [\text{M}^+]^4) \quad (3.5)$$

Eq. 3.5 can be arranged to be $A_{bs} = \varepsilon l K_{\text{sp}} K_{4(1+)} [\text{M}^+]$ 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

$$c_t = [\text{L}^{3-}] + [\text{M}_2\text{L}^{3+}] = K_{\text{sp}} [\text{M}^{3+}]^{-1} (1 + K_{2(3+)} [\text{M}^{3+}]^2). \quad (3.8)$$

The observed absorbance A_{bs} is expressed as

$$A_{bs} = \varepsilon l c_t = \varepsilon l K_{\text{sp}} [\text{M}^{3+}]^{-1} (1 + K_{2(3+)} [\text{M}^{3+}]^2). \quad (3.9)$$

Eq. 3.9 can be arranged to be $A_{bs} = \varepsilon l K_{\text{sp}} K_{2(3+)} [\text{M}^{3+}]$ with higher M^{3+} concentrations and larger $K_{2(3+)}$ values.

3.3. Results and discussion

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

Alkali metal ions have a great tendency to bond to $-\text{SO}_3^-$, 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 ($\epsilon_r = \text{ca. } 36$) [30] but poor solvation ability ($\text{DN} = 14.1$, $\text{AN} = 19.3$) [31a]. Fig. 3.1 shows the UV spectrum changes of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion $[(\text{Et}_4\text{N}^+)_3\text{L}^{3-}]$ with increasing concentration of LiClO_4 in MeCN. The L^{3-} ion gives a strong band at $\lambda_{\text{max}} = 238 \text{ nm}$ ($\epsilon/\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3 = \text{ca. } 7.8 \times 10^4$) 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 λ_{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 3.1. 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 3.3.6). The 1,3,6,6-derivative is shown tentatively in Scheme 3.1.

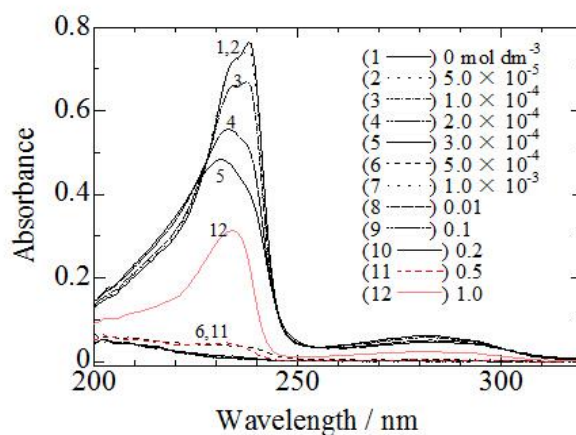
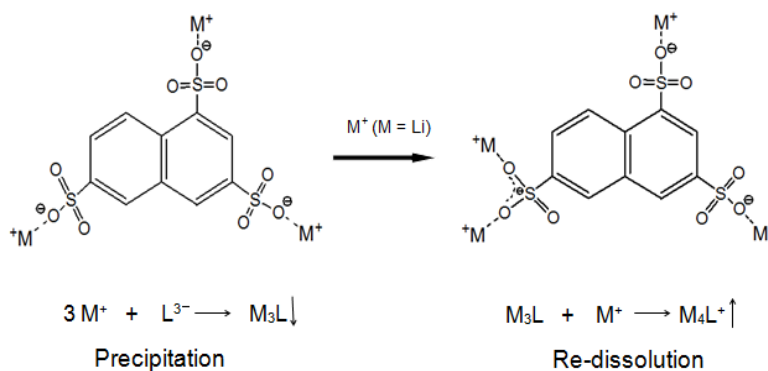


Fig. 3.1. The UV spectra of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion (0.1 cm path-length) with increasing concentration of LiClO_4 in MeCN.



Scheme 3.1. Successive formation of M_3L and M_4L^+ ($\text{M} = \text{Li}$) for the 1,3,6-naphthalenetrisulfonate ion in MeCN.

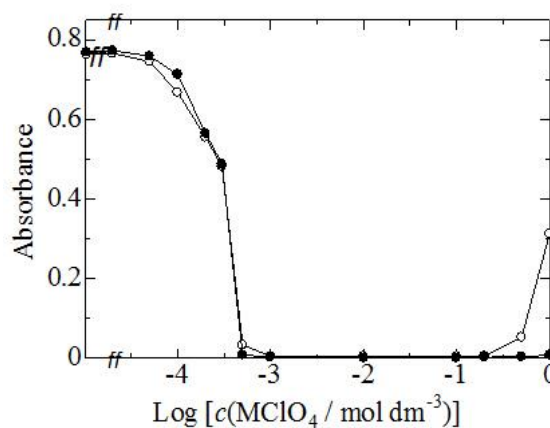


Fig. 3.2. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion with increasing concentration of alkali metal ions: (○) LiClO_4 ; (●) NaClO_4 .

The addition of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ 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 concentration of Na^+ (Fig. 3.2). 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].

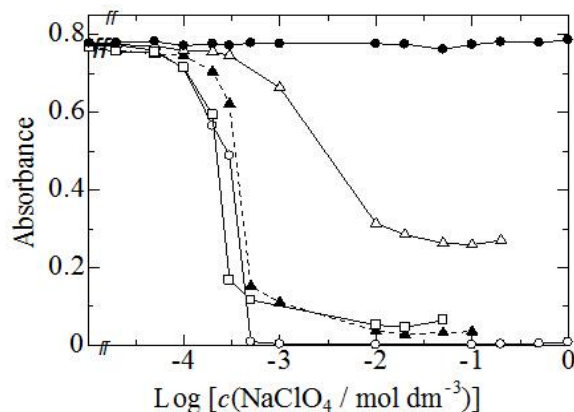


Fig. 3.3. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion with increasing concentration of NaClO_4 in different solvents: (●) EtOH; (Δ) 1-PrOH; (▲) 1-BuOH; (□) 1-HexOH; (○) MeCN.

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 3.1. 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. 3.3), 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 10.40, 13.90, and 14.00 in 1-PrOH, 1-BuOH, and 1-HexOH, respectively (*cf.* Table 3.1).

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 .

3.3.2. 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].

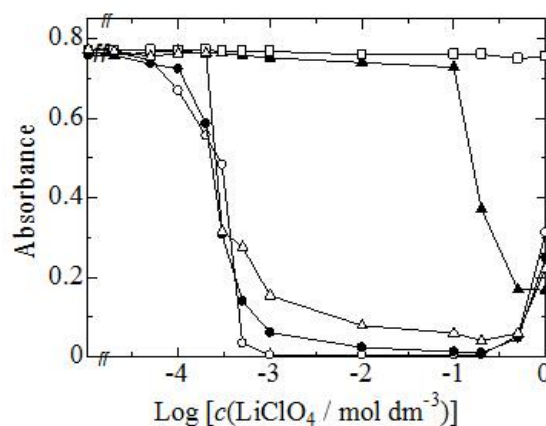


Fig. 3.4. Absorbance ($\lambda_{\text{max}} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate in the presence of LiClO_4 in $\text{MeCN-H}_2\text{O}$ mixtures: (○) 0; (●) 1.0; (△) 2.0; (▲) 5.0; (□) 10% (v/v) of H_2O .

Fig. 3.4 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% $\text{H}_2\text{O-MeCN}$, 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 3.2): the $\text{p}K_{\text{sp}}$ values are 16.12 and 6.42 in 2.0 and 5.0% H_2O , respectively. Finally, the precipitation reaction is totally inhibited by 10% H_2O .

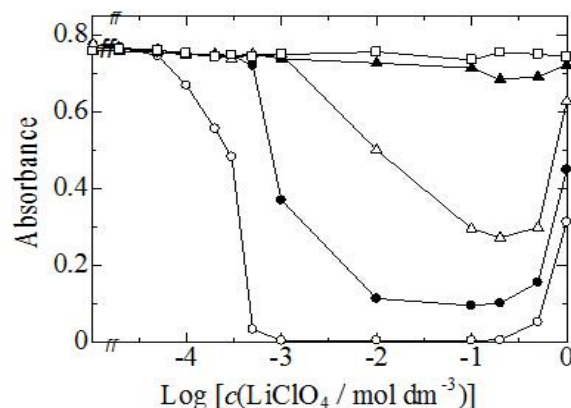


Fig. 3.5. Absorbance ($\lambda_{\text{max}} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate in the presence of LiClO_4 in MeCN-MeOH mixtures: (\circ) 0; (\bullet) 5.0; (Δ) 7.0; (\blacktriangle) 10; (\square) 20% (v/v) of MeOH.

Compared with H_2O , the influences of MeOH ($\text{DN} = 31.3$) [31b] on the interaction between Li^+ and L^{3-} in MeCN are smaller (Fig. 3.5). 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: $\log K_{4(1+)} = 9.30$ and 6.08 in 5.0 and 7.0% MeOH, respectively (*cf.* Table 3.2). The 10% MeOH causes no precipitation nor re-dissolution reactions between Li^+ and L^{3-} .

The precipitation reaction of Na_3L is not influenced so much by small amounts of the added water (1.0 – 2.0%), *cf.* Fig. 3A.1. However, 5.0% H_2O causes incomplete precipitation (*cf.* Table 3.2). 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 13.82, 10.26, and 5.14 for 5.0, 10, and 15% MeOH-MeCN, respectively (*cf.* Table 3.2), while $\text{p}K_{\text{sp}}$ is 15.37 in sole MeCN. Finally, the interaction between Na^+ and L^{3-} has not been observed in 20% MeOH (*cf.* Fig. 3A.2.). 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 H₂O in their chemical shifts (¹H NMR) with changing their contents in MeCN [12]. In the present section, we can conclude briefly that added H₂O or alcohols of the very small amounts (< 1.0%) in MeCN does not influence so much on the interaction between M⁺ and L³⁻ in MeCN.

3.3.3. The coordination reactions of alkaline earth metal ions (Mg²⁺, Ba²⁺) with L³⁻ in MeCN and alcohols

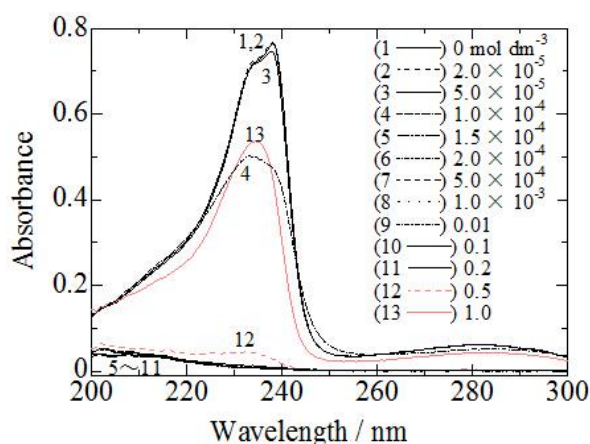


Fig. 3.6. UV spectra of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion (0.1 cm path-length) with increasing concentration of $\text{Mg}(\text{ClO}_4)_2$ in MeCN.

Fig. 3.6 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 L³⁻ 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. 3.10.



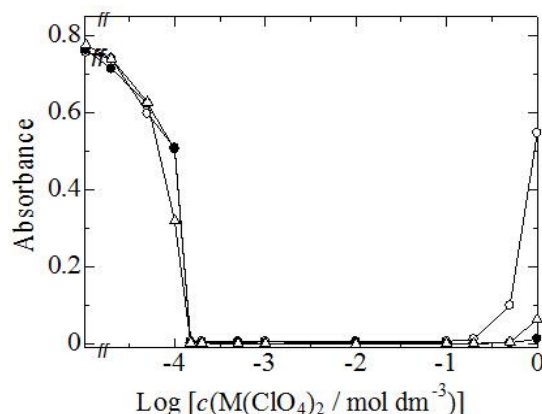


Fig. 3.7. Changes in absorbance ($\lambda_{\max} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion with increasing of alkaline earth metal ions in MeCN: (○) $\text{Mg}(\text{ClO}_4)_2$; (●) $\text{Ca}(\text{ClO}_4)_2$; (Δ) $\text{Ba}(\text{ClO}_4)_2$.

The complete precipitation occurs also between Ca^{2+} or Ba^{2+} and L^{3-} (Fig. 3.7), 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.*, 29.64, 32.39, and 31.54, respectively (*cf.* Table 3.1). 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.

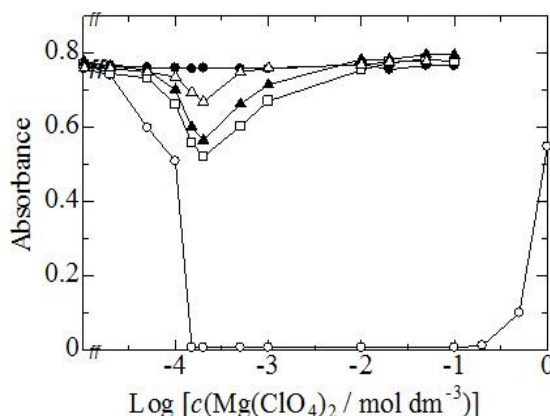


Fig. 3.8. The changes in absorbance ($\lambda_{\max} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion in the presence of $\text{Mg}(\text{ClO}_4)_2$ in alcohols and MeCN: (●) MeOH; (Δ) EtOH; (▲) 1-PrOH; (□) 1-BuOH; (○) MeCN.

In primary alcohols, as shown in Fig. 3.8, 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 $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ Mg^{2+} . Whereas, it has 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 $2.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Mg}^{2+}$.

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

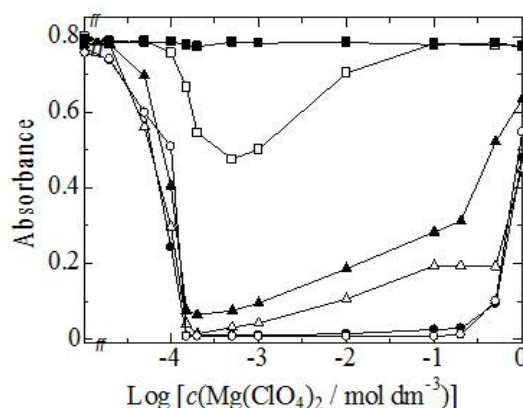


Fig. 3.9. Absorbance ($\lambda_{\text{max}} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion in the presence of $\text{Mg}(\text{ClO}_4)_2$ in MeCN- H_2O mixtures: (○) 0; (●) 1.0; (△) 3.0; (▲) 5.0; (□) 10; (■) 20% (v/v) of H_2O .

Fig. 3.9 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 26.00, 24.58, and 19.85 in 3.0, 5.0, and 10% H_2O -MeCN, respectively (*cf.* Table 3.3), while $\text{p}K_{\text{sp}}$ is 29.64 in sole MeCN (*cf.* Table 3.1).

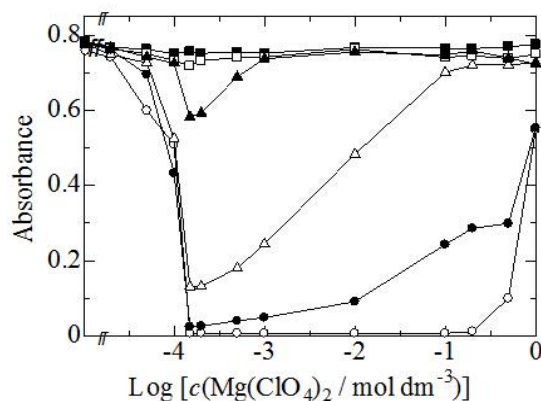


Fig. 3.10. Absorbance ($\lambda_{\max} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion in the presence of $\text{Mg}(\text{ClO}_4)_2$ in MeCN-MeOH mixtures: (\circ) 0; (\bullet) 5.0; (Δ) 10; (\blacktriangle) 15; (\square) 20; (\blacksquare) 50% (v/v) of MeOH.

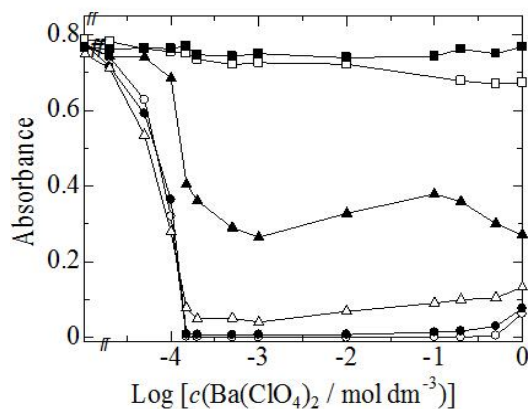


Fig. 3.11. Absorbance ($\lambda_{\max} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion in the presence of $\text{Ba}(\text{ClO}_4)_2$ in MeCN- H_2O mixtures: (\circ) 0; (\bullet) 5.0; (Δ) 10; (\blacktriangle) 15; (\square) 20; (\blacksquare) 30 % (v/v) of H_2O .

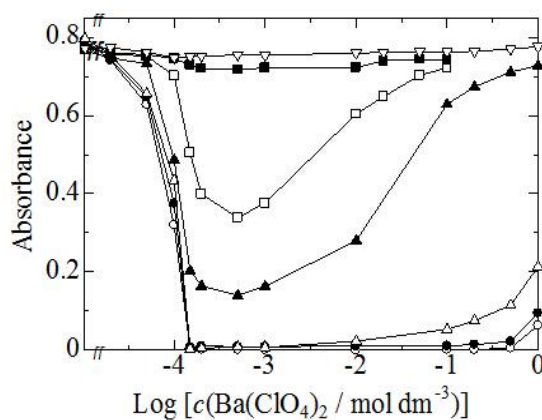


Fig. 3.12. Absorbance ($\lambda_{\max} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion in the presence of $\text{Ba}(\text{ClO}_4)_2$ in MeCN-MeOH mixtures: (\circ) 0; (\bullet) 10; (Δ) 20; (\blacktriangle) 40; (\square) 50; (\blacksquare) 70; (∇) 100 % (v/v) of MeOH.

MeOH.

The influences of MeOH on the coordination reaction between Mg^{2+} and L^{3-} are much smaller than those of H_2O (Fig. 3.10). 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-naphthalenedisulfonate 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 ($\text{p}K_{\text{sp}}$) and “reverse” coordination constants ($\log K_{2(2+)}$) of the specific interaction between Mg^{2+} and L^{3-} in the binary solvents of MeCN- H_2O and MeCN-MeOH are listed in Table 3.3. Fig. 3.11 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. 3.12 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 3.3). In sole MeOH, neither precipitation nor re-dissolution takes place between Ba^{2+} with L^{3-} . Comparing between Figs. 3.11 and 3.12, 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.

3.3.5. 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 \AA [39]) is similar to that of Mg^{2+} (0.86 \AA [40]), but In^{3+} possesses more electric field strength than Mg^{2+} . Compared to Al^{3+} , the lighter homolog, 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.

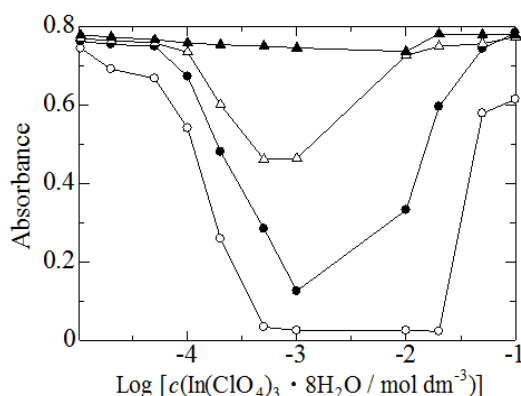


Fig. 3.13. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion with increasing concentration of $\text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$ in MeCN- H_2O mixtures: (○) 10; (●) 30; (△) 50; (▲) 100% (v/v) of H_2O .

The addition of water on the reaction between $\text{In}^{3+} [(\text{ClO}_4^-)_3]$ and L^{3-} causes more typical precipitation and the re-dissolution (Fig. 3.13). The absorbance minimum appears in a wide range from 1.0×10^{-3} to $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ in 10% H_2O . In 30% H_2O , the precipitation reaction becomes incomplete, but the absorbance of L^{3-} thoroughly recovers to the origin value (ca. 0.8) at $0.1 \text{ mol dm}^{-3} \text{ In}(\text{ClO}_4)_3$. Even in 50% water, the precipitation can occur to a smaller extent, possibly owing to the strong interaction between the high electron density of In^{3+} and L^{3-} . The solubility products ($\text{p}K_{\text{sp}}$) are evaluated to be 8.28, 7.80, and 7.24 in 10, 30, and 50% H_2O -MeCN, respectively (*cf.* Table 3.4). As for the In^{3+} ion in H_2O -MeCN binary solvents, we have to pay attention to the hydrolysis reactions of In^{3+} with H_2O . The large formation constant ($\log K$) of $\text{In}(\text{OH})^{2+}$ between In^{3+} and OH^- has been reported to be 10.3 in aqueous solution [42].

The specific interaction between In^{3+} and L^{3-} can take place in all the primary alcohols (Fig. 3.14). At first, the L^{3-} absorbance decreases with increasing concentration of $\text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$, and gradually increases after reaching its minimum at $2.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ In}^{3+}$, finally almost recovers its original value. The minimum absorbance of L^{3-} is 0.134, 0.031, and 0.023 in MeOH, EtOH,

and 1-HexOH at $2.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ In}^{3+}$. Scheme 3.2 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 3.1.

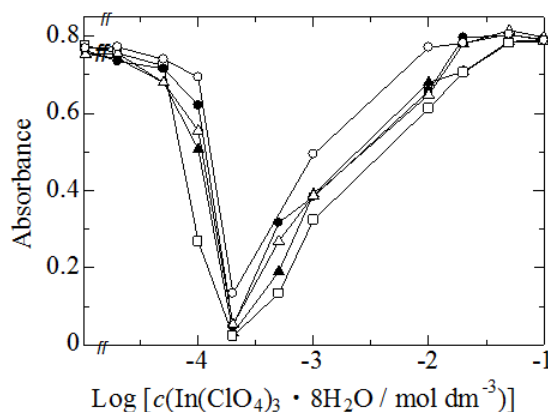
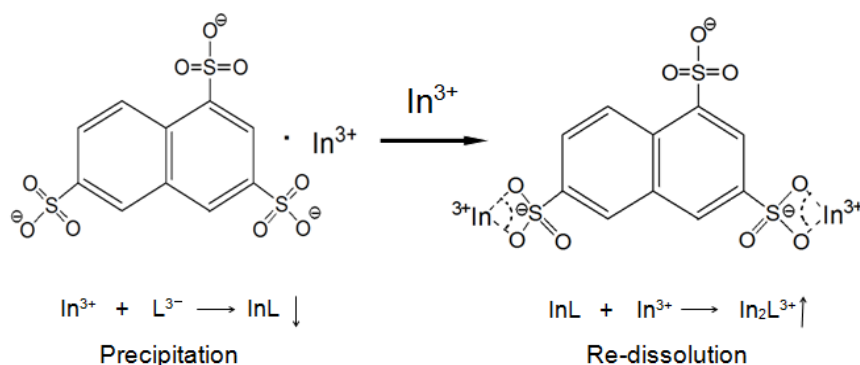


Fig. 3.14. Absorbance ($\lambda_{\text{max}} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate in the presence of $\text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$ in primary alcohols: (○) MeOH; (●) EtOH; (Δ) 1-PrOH; (▲) 1-BuOH; (□) 1-HexOH.



Scheme 3.2. Successive formation of InL and In_2L^{3+} for the 1,3,6-naphthalenetrisulfonate ion in MeCN- H_2O or sole alcohols.

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

For predicting the coordinating structures of Li_4L^+ in Scheme 3.1, 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. 3.15(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 3.5 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.

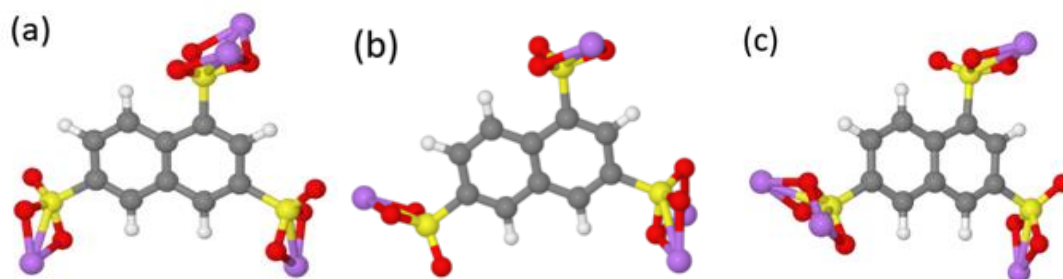


Fig. 3.15. The optimized structures of 1,3,6-naphthalenetrisulfonates to which four Li^+ ions are coordinated at (a) 1,1,3,6, (b) 1,3,3,6, and (c) 1,3,6,6 positions.

3.4. 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-}) has 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.

Table 3.1 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 [$(Et_4N^+)_3L^{3-}$] 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
	(pK_{sp})	15.37	–	–	–	–	–
	(pK_{sp}) ^c	15.71	–	–	–	–	–
		△	No	No	No	No	No
	$\log K_{4(1+)}$	10.98	–	–	–	–	–
Na^+		●	No	No	▲	▲	▲
	(pK_{sp})	15.37	–	–	10.40	13.90	14.00
	(pK_{sp}) ^c	15.71	–	–	11.20	14.91	15.52
		No	No	No	No	No	No
	$\log K_{4(1+)}$	–	–	–	–	–	–
Mg^{2+}		●	▲	▲	▲	▲	▲
	(pK_{sp})	29.64	–	19.67	20.04	20.21	–
	(pK_{sp}) ^c	30.49	–	21.19	22.05	22.70	–
		△	○	○	○	○	○
	$\log K_{2(2+)}$	10.68	–	–	–	–	–
Ca^{2+}		●	No	●	●		
	(pK_{sp})	32.39	–	25.18	25.55		
	(pK_{sp}) ^c	33.24	–	26.70	27.55		
		No	No	○	○		
	$\log K_{2(2+)}$	–	–	9.00	9.01		
Ba^{2+}		●	No	●	●	●	
	(pK_{sp})	31.54	–	27.60 ^d	27.66 ^d	26.41	
	(pK_{sp}) ^c	32.39	–	29.12	29.67	28.92	

	No	No	○	○	△	
$\log K_{2(2+)}$	—	—	9.76 ^d	9.86 ^d	9.20	
	▲	▲	●	●	●	●
(pK_{sp})	^e	8.17	8.28	8.34	8.36	8.92
In^{3+} $(pK_{sp})^c$		10.35	10.90	11.90	12.86	(15.75) ^f
	△	○	○	○	○	○
$\log K_{2(3+)}$	^e	6.52	6.00	6.08	6.18	7.45

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^{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.

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

^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] or Chapter 2.

^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 3.2 Precipitation and re-dissolution reactions of alkali metal ions with the 1,3,6-naphthalenetrisulfonate ion in binary solvents of MeCN- H_2O and MeCN-MeOH.

Metal ions ^a	Equilibrium constants ^b				
	MeCN- H_2O [H_2O contents / % (v/v)]	1.0	2.0	5.0	10
		●	▲	▲	No
Li^+	(pK_{sp})	16.14	16.12	6.42	—
	$(pK_{sp})^c$	16.48	16.45	6.73	—
		△	△	No	No

		MeCN-H ₂ O [H ₂ O contents / % (v/v)]				
		1.0	3.0	5.0	10	20
Na ⁺	log $K_{4(1+)}$	11.68	11.58	–	–	
		●	●	▲		No
	(p K_{sp})	16.16	15.55	10.52	–	
	(p K_{sp}) ^c	16.50	15.88	10.84	–	
		No	No	No	No	
		MeCN-MeOH				
		[MeOH contents / % (v/v)]				
		5.0	7.0	10	15	20
Li ⁺		▲	▲	No		No
	(p K_{sp})	13.54	10.19	–		–
	(p K_{sp}) ^c	13.88	10.53	–		–
		△	△	No		No
	log $K_{4(1+)}$	9.30	6.08	–		–
Na ⁺		▲		▲	▲	No
	(p K_{sp})	13.82		10.26	5.14	–
	(p K_{sp})	14.17		10.61	5.49	–
		△		△	△	No
	log $K_{4(1+)}$	–		–	–	–

For the *Explanatory notes*, cf. Table 3.1.

^a MClO₄.

^b Solubility products (K_{sp}) and “reverse” coordination constants ($K_{4(1+)}$), cf. the Experimental section.

^c Cf. Table 3.1, 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 3.3 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
Mg ²⁺		●	▲	▲	▲	No
	(p K_{sp})	29.70	26.00	24.58	19.85	–

	(pK _{sp}) ^c	30.54	26.81	25.37	20.58	–
		△	△	△	○	No
	log K ₂₍₂₊₎	10.59	8.76	7.79	5.88	–
		5.0	10	15	20	30
		●	▲	▲	No	No
Ba ²⁺	(pK _{sp})	29.15	24.40	20.85	–	–
	(pK _{sp}) ^c	29.93	25.12	21.52	–	–
		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})	26.01	23.33	–	–	–
	(pK _{sp})	26.87	24.19	–	–	–
		△	△	○	No	No
	log K ₂₍₂₊₎	9.36	7.62	–	–	–
		10	20	40	50	70
		●	●	▲	▲	No
Ba ²⁺	(pK _{sp})	26.01	23.33	22.09	20.41	–
	(pK _{sp}) ^c	26.88	24.21	23.03	21.36	–
		No	No	○	○	No
	log K ₂₍₂₊₎	–	–	7.53	6.67	–

For the *Explanatory notes*, cf. Table 3.1.

^a M(ClO₄)₂.

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

^c Cf. Table 3.1, 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 3.4 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

		●	▲	▲	No
In ³⁺	(pK _{sp})	8.28	7.80	7.24	–
	(pK _{sp}) ^c	9.58	8.78	8.01	–
		△	○	○	No
	log K ₂₍₃₊₎	5.36	5.38	5.20	–

For the *Explanatory notes*, cf. Table 3.1.

^a In(ClO₄)₃·8H₂O.

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

^c Cf. Table 3.1, 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-H₂O, have been interpolated from the data from Ref. [44].

Table 3.5 Calculated relative energies for Li₄L⁺ (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

References

- [1] K.M. Fromm, *Coord. Chem. Rev.* 252 (2008) 856.
- [2] H.Maeda, O. Mizutani, Y. Yamagata, E. Ichishima, T. Nakajima, *J. Biochem.* 129 (2001) 675.
- [3] N.S. Poonia, A. V. Bajaj, *Chem. Rev.* 79 (1979) 389.
- [4] M. Hojo, H. Nagai, M. Hagiwara, Y. Imai, *Anal. Chem.* 59 (1987) 1770.
- [5] M.N. Roy, L. Sarkar, R. Dewan, *J. Chem. Thermodynamics* 43 (2011) 371.
- [6] M. Hojo, T. Ueda, T. Inoue, M. Ike, *J. Phys. Chem. B* 111(2007) 1759.
- [7] M. Hojo, S. Ohta, K. Ayabe, K. Okamura, K. Kobiro, Z. Chen, *J. Mol. Liquids* 177 (2013) 145.
- [8] K.S. Chen, N. Hirota, *J. Am. Chem. Soc.* 94 (1997) 5550.
- [9] R.M. Fuoss, C.A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 2387.
- [10] S. Petrucci, E. M. Eyring, *J. Phys. Chem.* 95 (1991) 1731.

- [11] K. Bowman-James, *Acc. Chem. Res.* 38 (2005) 671.
- [12] M. Hojo, *Pure Appl. Chem.* 80 (2008) 1540.
- [13] M. Hojo, T. Ueda, M. Ike, M. Kobayashi, H. Nakai, *J. Mol. Liquids* 145 (2009) 152.
- [14] M. Hojo, T. Ueda, Z. Chen, M. Nishimura, *J. Electroanal. Chem.* 468 (1999) 110.
- [15] M. Hojo, T. Ueda, M. Nishimura, H. Hamada, *J. Phys. Chem. B* 103 (1999) 8965.
- [16] X. Chen, K. Ayabe, M. Hojo, Z. Chen, M. Kobayashi, *J. Mol. Liq. J. Mol. Liquids* 199 (2014) 445.
- [17] R.W. Murray, L.K. Hiller, Jr., *Anal. Chem.* 39 (1967) 1221.
- [18] H.J. Gores, J.M.G. Barthel, *Pure Appl. Chem.* 67 (1995) 919.
- [19] R.L. Jarek, S. K. Shin, *J. Am. Chem. Soc.* 119 (1997) 10501.
- [20] J. Xiang, C. Chang, M. Li, S. Wu, L. Yuan, J. Sun, *Cryst. Growth Des.* 8 (2008) 280.
- [21] H. Chen, M. Armand, M. Courty, M. Jiang, C. P. Grey, F. Dolhem, J. M. Tarascon, P. Poizot, *J. Am. Chem. Soc.* 131 (2009) 8984.
- [22] R.H. Zeng, X.P. Li, Y.C. Qiu, W.S. Li, J. Yi, D. S. Lu, C. L. Tan, M. Q. Xu, *Electrochem. Commum.* 12 (2010) 1253.
- [23] G.V. Oshovsky, D.N. Reinhoudt, W. Verboom, *J. Am. Chem. Soc.* 128 (2006), 5270.
- [24] M. Hojo, T. Ueda, K. Kawamura, M. Yamasaki, *Bull. Chem. Soc. Jpn.* 73 (2000) 347.
- [25] M. Hojo, H. Hasegawa, H. Tsurui, K. Kawamura, S. Minami, A. Mizobe, *Bull. Chem. Soc. Jpn.* 71 (1998) 1619.
- [26] M. Hojo, T. Ueda, M. Yamasaki, A. Inoue, S. Tokita, M. Yanagita, *Bull. Chem. Soc. Jpn.* 75 (2002) 1569.
- [27] M. Hojo, T. Ueda, A. Inoue, S. Tokita, *J. Mol. Liquids* 148 (2009) 109.
- [28] V.K. Ganesh, S.K. Muthuvel, S.A. Smith, G.J. Kotwal, K.H.M. Murthy, *Biochemistry*, 44 (2005) 10757.
- [29] B. J. Gunderman, I.D. Kabell, P. J. Squattrito, S.N. Dubey, *Inorg. Chim. Acta* 258 (1997) 237.
- [30] J.A. Riddick, W.B. Bunger, T.K. Sakano, *Organic Solvent, Physical Properties and Methods of Purification*, 4th ed. John Wiley & Sons, New York, 1986.
- [31] (a) V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum, New York, 1978. (b) Y. Marcus, *J. Solution Chem.* 13 (1984) 599.

- [32] M. Hojo, H. Hasegawa, Y. Miyauchi, H. Moriyama, H. Yoneda, S. Arisawa, *Electrochim. Acta* 39 (1994) 629.
- [33] I. Svaneda, S. Boija, A. Almesaker, G. Persson, F. Andersson, E. Hedenstrom, D. Bylund, M. Norgren, H. Edlund, *Langmuir* 30 (2014) 4605.
- [34] R.S. Sah, B. Sinha, M.N. Roy, *Fluid Phase Equilib.* 307 (2011) 216.
- [35] J.A. Krom, J.T. Petty, A. Streitwieser, *J. Am. Chem. Soc.* 115 (1993) 8024.
- [36] P.S. Nikam, M. C.Jadhav, M. Hasan, *J. Chem. Eng. Data* 41 (1996) 1028.
- [37] C. Reichardt, D. Che, G. Heckenkemper, G. Schäfer, *Eur. J. Org. Chem.* (2001) 2343.
- [38] M. Hojo, T. Ueda, S. Inoue, Y. Kawahara, *J. Chem. Soc. Perkin Trans. 2* (2000) 1735.
- [39] I. Peckermann, D. Robert, U. Englert, T. P. Spaniol, J. Okuda, *Organometallics* 27 (2008) 4817.
- [40] G. Wulfsberg, *Principles of Descriptive Inorganic Chemistry*; University Science Books: Sausalito, 1991.
- [41] D. A. Atwood, *Coord. Chem. Rev.* 176 (1998), 407.
- [42] (a) K.B. Yatsimirskii, V.P. Vasil'ev, *Instability Constants of Complex Compounds*, Pergamon, Oxford, 1960. (b) E.M. Hattox, T. De Vries, *J. Am. Chem. Soc.*, 58 (1936), 2126.
- [43] A.K. Covington and T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, London, 1973.
- [44] A.M. Nikitin, A.P. Lyubartsev, *J. Comput. Chem.* 28 (2007) 2020.
- [45] M.S. Bakshi, J. Singh, H. Kaur, S.T. Ahmad, G. Kaur, *J. Chem. Eng. Data* 41 (1996) 1459.
- [46] 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.
- [47] (a) H. Iikura, 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.
- [48] T.H. Dunning Jr., *J. Chem. Phys* 90 (1989) 1007.
- [49] M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* 24 (2003) 669.
- [50] A.V. Barenich, C.J. Cramer, D.G. Truhlar, *J. Phys. Chem. B* 113 (2009) 6378.

Appendix

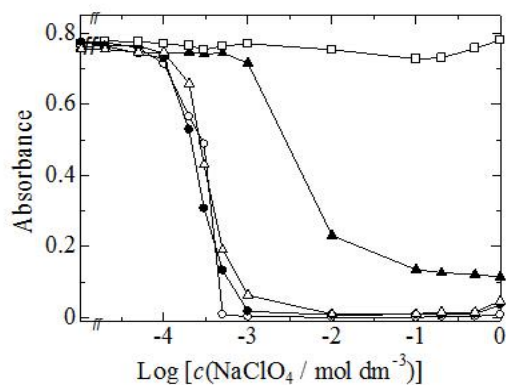


Fig. 3A.1. Absorbance ($\lambda_{\max} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion in the presence of NaClO_4 in MeCN- H_2O mixtures: (\circ) 0; (\bullet) 1.0; (Δ) 2.0; (\blacktriangle) 5.0; (\square) 10% (v/v) of H_2O .

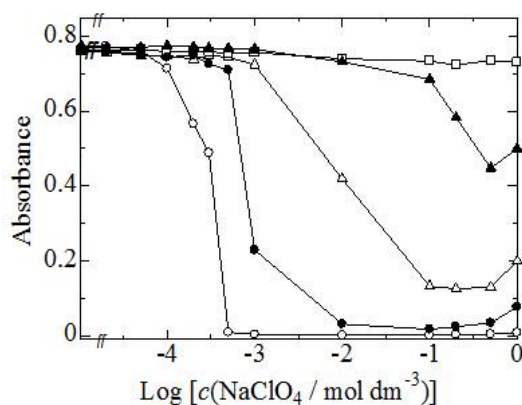


Fig. 3A.2. Absorbance ($\lambda_{\max} = \text{ca. } 238 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,3,6-naphthalenetrisulfonate ion in the presence of NaClO_4 in MeCN-MeOH mixtures: (\circ) 0; (\bullet) 5.0; (Δ) 10; (\blacktriangle) 15; (\square) 20% (v/v) of MeOH.

Chapter 4 Complexing ability of alkali metal and alkaline earth metal ions with organic phosphinate or phosphates in acetonitrile and binary solvents with protic solvents

ABSTRACT

In acetonitrile (MeCN), the specific interactions of alkali metal ($M^+ = Li^+$ or Na^+) and alkaline earth metal ions ($M^{2+} = Mg^{2+}$, Ca^{2+} , or Ba^{2+}) with various phosphorus anions, L^- , *i.e.*, diphenylphosphinate, diphenylphosphate, and bis(4-nitrophenyl)phosphate, have been examined by means of UV-visible spectroscopy. The formation of “reverse-coordinated” or coordinated species, M_2L^+ or ML^+ , has been observed in the presence of excess amounts of the metal ions to the anions. Between all the M^+ or M^{2+} ions and $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion ($n\text{-Bu}_4\text{N}^+\text{Ph}_2\text{PO}_2^-$), both the precipitation of the non-charged species (ML or ML_2) and the successive re-dissolution of the precipitates take place. The addition of the alkaline earth metal ions of just the equi-molar to L^- causes almost complete dissolution of the precipitates through the soluble ML^+ coordinated species. As for the diphenylphosphate ion [$n\text{-Bu}_4\text{N}^+(\text{PhO})_2\text{PO}_2^-$], no apparent interaction can be insisted between the alkali metal ions or Mg^{2+} and $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate ion, based on just no precipitation occurrence. Only Na^+ and Ba^{2+} can cause obvious precipitation with $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ bis(4-nitrophenyl)phosphate. A good evidence, however, has been provided by the conductometric titration of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ $n\text{-Bu}_4\text{N}^+(\text{PhO})_2\text{PO}_2^-$ with LiClO_4 or $\text{Mg}(\text{ClO}_4)_2$ in MeCN that the “strong” interaction still operate between L^- and Li^+ or Mg^{2+} regardless of no precipitation (nor the successive re-dissolution). The addition of protic solvents, such as water, MeOH, or EtOH, influences significantly the chemical interaction between the metal ions and the anions in MeCN. The solubility products (K_{sp}) and the “reverse coordination” or coordination constants ($K_2 = [M_2L^+] / ([M^+]^2[L^-]$, $K_1 = [ML^+] / ([M^{2+}][L^-])$) have been evaluated for the systems.

Keywords: “reverse” coordination; indifferent electrolyte; solubility product; solvation; UV-visible spectroscopy; hydrolysis in biochemical system.

4.1.Introduction

As one of the sixth most abundant elements in the human body, phosphorus plays an

important role in life process. Metal phosphates have been gathering great interest, widespread investigating in biochemical [1] and pharmaceutical fields [2]. Alkali metal and alkaline earth metal ions have very specific functions in biological systems, although alkali metal- or alkaline earth metal-phosphates [3] are less recognized than transition metal-phosphates [4-6] due to their weaker coordination ability. Many studies [7-9] have authenticated that the metal ions can play a structural role on catalyzing the hydrolysis of phosphate diester.

In recent decades, the effects of added salts on the hydrolysis rates of various compounds have been examined in our laboratory [10-16]. The exponential increases in hydrolysis rates of S_N1 substrates ($R-X$) in binary mixtures between H_2O and many organic solvents containing concentrated alkali metal or alkaline earth metal (M^+ or M^{2+}) perchlorates have been explained successfully by the concept of the specific chemical interaction between M^+ or M^{2+} and simple anions. That is, the direct chemical interaction between the metal cations and the leaving-group anions (X^-) can generate favorably the carbocation (R^+) as the reaction intermediate even in “aqueous” solution containing organic solvents.

In low solvating media of relatively high permittivities ($20 < \epsilon_r < 65$), the coordination or “reverse” coordination phenomena of alkali metal (M^+) or alkaline earth metal (M^{2+}) ions with various anions, such as Cl^- [17,18], SCN^- [19], tropolonates [20,21], sulfonates [22,23,24], and carboxylates [22,25,26], have been examined over past three decades in our group by means of voltammetry, conductometry, UV-visible, and NMR spectroscopy. Where the term of “reverse” coordination represents a species (such as M_2X^+) driven by a single-charged anion (X^-) with two or more of alkali metal ion (M^+) through the chemical interaction above the Coulombic force [27]. We have reported that higher ion-aggregation (over the ion pair formation between ions) takes place not only in low permittivity media ($\epsilon_r < 10$) [28] but also in the media of relatively high permittivity ($20 < \epsilon_r < 65$) [29]. We have attributed the higher ion-aggregation to the coordination (of M^+ or M^{2+}) as well as hydrogen bonding forces (of R_3NH^+) in addition to Coulombic forces [30]. Holmes [31] has examined the hydrogen-bonding between imidazole and diphenylphosphate by 1H NMR, IR, and X-ray technique.

The concept of triple ions in low permittivity media ($\epsilon_r < 12$ or 23.2) has been originated by Fuoss and Kraus [32]. The triple ion formation between an ion pair and a free ion due to the

Coulomb force [32, 33] should be discussed more. Nevertheless, the triple ion mechanism or theory [34] has been applied in studying on lithium batteries [35], ion-aggregation [36], the color developer of dyes [37, 38], and supramolecular construction [39].

In DMF, the higher aggregations of dihydrogenphosphate has been observed [40]. NMR relaxation studies have shown that the sodium ion interacts with the dibutyl phosphate to form ion-aggregates in concentrated aqueous solution of sodium dibutyl phosphate [41]. In the solubility study [23], the specific interaction has been observed between Li^+ and diphenylphosphate $[(\text{PhO})_2\text{PO}_2^-]$, in acetone, but somehow strangely not in acetonitrile.

Acetonitrile (MeCN) is a relatively high permittivity solvent ($\epsilon_r = 35.94$ [42]) of low donor and acceptor numbers ($\text{DN} = 14.1$, $\text{AN} = 19.3$ [43]), attracting considerable interest in the study of the interplay between ion solvation and association of electrolyte solution [44]. In MeCN, the formation of the precipitates and successive formation of “reverse-coordinated” species has been reported for M^+ and M^{2+} with nitrophthalates or sulfonates (*p*-toluenesulfonate, 1,5-naphthalenedisulfonate, and 1,3,6-naphethalenetrisulfonate) [22,24].

In the present work, the complexing ability of M^+ or M^{2+} with diphenylphosphinate, diphenylphosphate, and bis(4-nitrophenyl)phosphate is examined by means of UV spectroscopy in MeCN, a protophobic and aprotic solvent. The influences of protic solvents, such as water, methanol, or ethanol, are also investigated. The coordination or “reverse” coordination formation constants of anions have been evaluated using UV visible spectroscopic data. The aim of this paper is to try convincing one that alkali metal and alkaline earth metal ions in poor salvation media can exhibit unexpectedly strong coordination ability, not so well as 4d-shell metal ions (such as Ag^+ , Cd^{2+}) in aqueous solution. We would like to recognize that the interaction between phosphates and Mg^{2+} or Ca^{2+} in biochemical systems should be through the real chemical force and not just the electrostatic interaction.

4.2. Experimental

4.2.1. Chemicals

Diphenylphosphinic, diphenylphosphate, and bis(4-nitrophenyl)phosphate acids were purchased from Aldrich. Tetrabutylammonium diphenylphosphinate ($n\text{-Bu}_4\text{N}^+\text{Ph}_2\text{PO}_2^-$) was

prepared as follows: A 1.0 g of diphenylphosphinic acid was dissolved in methanol, and was titrated by *n*-Bu₄NOH (Wako) in methanol up to an equivalence point. The solution was evaporated to dryness at 50 °C, and the salt was dried in vacuo at 120 °C. Tetrabutylammonium diphenylphosphate [*n*-Bu₄N⁺(PhO)₂PO₂⁻] was prepared from diphenylphosphate acid in a similar way.

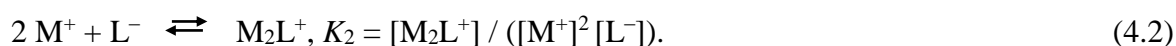
Metal perchlorates without hydrate water, LiClO₄, NaClO₄, Mg(ClO₄)₂, and Ba(ClO₄)₂ (all Aldrich), were used as received. Calcium perchlorate tetrahydrates from Aldrich was dried in vacuo at 150 °C to obtain anhydrous Ca(ClO₄)₂. Triethylamine (Et₃N), Et₄NClO₄, acetonitrile, acetone (the spectroscopic grade), methanol, and ethanol all from Wako were used as received. The water contents of acetonitrile, methanol, and ethanol are certificated to be less than 0.1, 0.1, and 0.2%, respectively. Water was purified by means of a MilliQ system (Millipore Corp.). The percentage of the solvent in binary solvents is all expressed by the volume fraction [% (v/v)] in the present paper.

4.2.2. Apparatus and procedure

UV-visible absorption spectra were measured at room temperature using a Shimadzu double-beam spectrophotometer (model UV-2550) in 0.01, 0.05, and 0.1 cm path-length quartz cuvettes. 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 a precipitation reaction. Electrical conductance was measured at 25 ± 0.02 °C with an Agilent LCR meter model HP4284 at 1 kHz in a conductivity cell with a cell constant of 0.4959 S cm⁻¹.

The evaluation method of solubility products (*pK_{sp}*) and “reverse” coordination formation constants (*K₂* and *K₁* for Eqs. 4.2 and 4.4, respectively) between metal cations (M⁺, M²⁺) and “ligand” anions (L⁻) have been proposed in the previous paper [22] and Chapter 2.

(a) Alkali Metal ions



(b) Alkaline earth metal ions



4.3. Results and discussion

4.3.1. The diphenylphosphinate ion (L^-)

4.3.1.1. Specific interaction between the diphenylphosphinate ion (L^-) and M^+ or M^{2+}

The diphenylphosphinate ion (Ph_2PO_2^- : L^-) of $n\text{-Bu}_4\text{N}^+ \text{L}^-$ ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) in acetonitrile (MeCN) gives a broad peak around 226 nm ($\epsilon/\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3 = \text{ca. } 1.35 \times 10^4$) but the aromatic band around 265 nm is very weak (Fig. 4.1). When LiClO_4 is added to the solution, the L^- absorbance gradually decreases with increasing concentration of LiClO_4 , and reaches its minimum value of 0.099 at an equivalence of Li^+ ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$), accompanying white precipitates. However, the further addition of LiClO_4 causes the precipitates to re-dissolve partially at $0.10 \text{ mol dm}^{-3} \text{ Li}^+$ and completely at $0.50 \text{ mol dm}^{-3} \text{ Li}^+$ or more. The peak absorbance of the solution recovers fully the initial value, showing a slight blue shift ($\lambda_{\text{max}} = 223.5 \text{ nm}$).

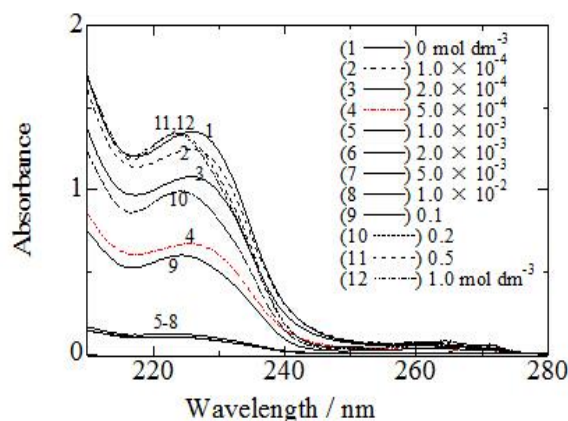


Fig. 4.1. UV spectra of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion (L^-) of $n\text{-Bu}_4\text{N}^+\text{L}^-$ (0.1 cm path-length) in MeCN with increasing concentration of LiClO_4 .

The addition of an equivalence of NaClO_4 to the L^- ion also causes precipitation similarly, but the re-dissolution of the precipitates of NaL is not completed even in the presence of an excess amount of Na^+ (cf. Fig. 4.2). Scheme 4.1 indicates the manner of the ML ($\text{M} = \text{Li}$ and Na) precipitation and the successive re-dissolution of ML through M_2L^+ .

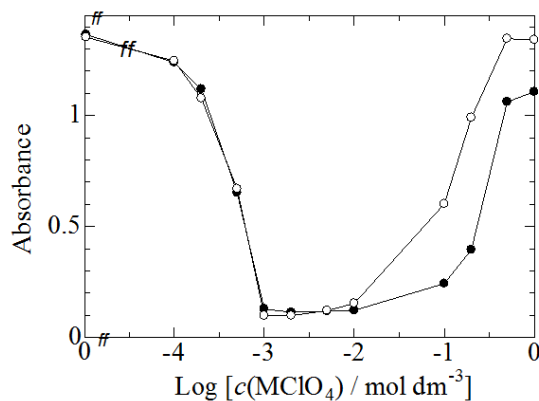
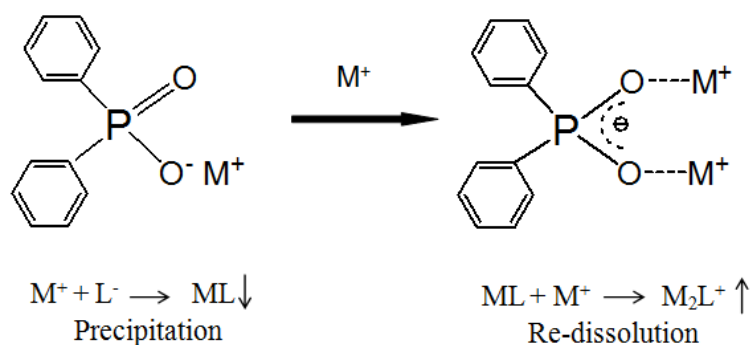


Fig. 4.2. Changes in absorbance ($\lambda_{\max} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of alkali metal ions in MeCN: (○) LiClO_4 ; (●) NaClO_4 .



Scheme 4.1. Successive formation of ML and M_2L^+ ($\text{M} = \text{Li}$ and Na) for the diphenylphosphinate ion in MeCN.

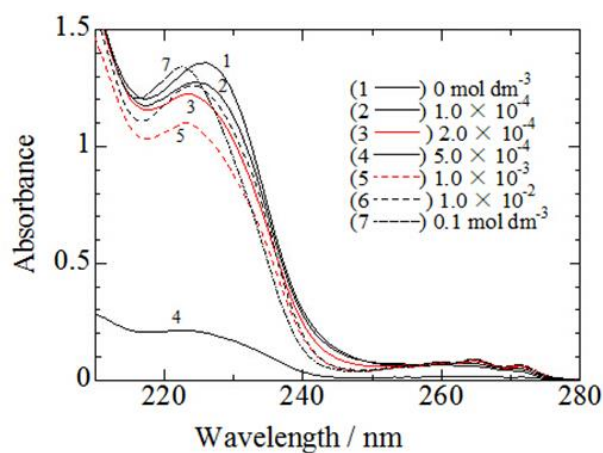


Fig. 4.3. UV spectra of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate (0.1 cm path-length) with increasing concentration of $\text{Mg}(\text{ClO}_4)_2$ in MeCN.

Fig. 4.3 shows the UV spectral changes of L^- ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) with increasing concentration of $\text{Mg}(\text{ClO}_4)_2$ in MeCN. The absorbance suddenly decreases to reach its minimum in the presence of an equivalence of $\text{Mg}(\text{ClO}_4)_2$ ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$). However, even 7.0×10^{-4}

or $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Mg}^{2+}$ causes the re-dissolution of the precipitates and also a drastic increase in the intensity of the absorption band around 226 nm. With the further addition of Mg^{2+} , the absorbance band recovers completely the initial value, (showing a blue shift to 223 nm), which should indicate the formation of the coordinated species, MgL^+ .

We would like to confirm concisely that the increase in the ionic strength is not the main factor for the recovering of the absorbance in the presence of higher $\text{Mg}(\text{ClO}_4)_2$ concentrations. The ionic strength of the MgL_2 -precipitated-solution (the supernatant contains $1.0 \times 10^{-3} \text{ mol dm}^{-3} n\text{-Bu}_4\text{NClO}_4$) has been increased up to 0.1 by Et_4NClO_4 . As is shown in Fig. 4.4, however, the absorbance value of L^- remains constant without the re-dissolution of precipitation.

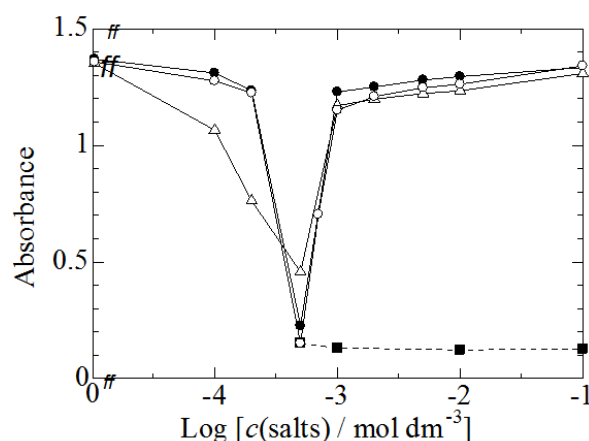
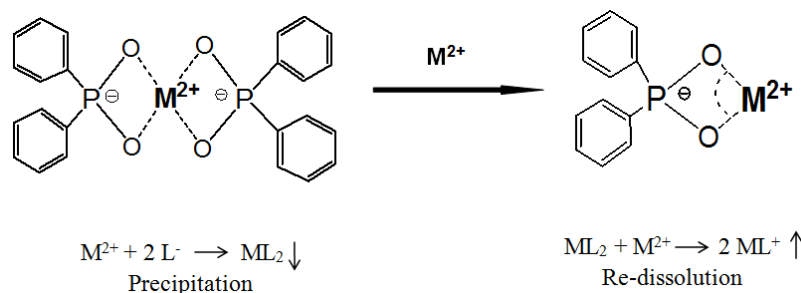


Fig. 4.4. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of alkaline earth metal ions in MeCN: (○) $\text{Mg}(\text{ClO}_4)_2$; (●) $\text{Ca}(\text{ClO}_4)_2$; (△) $\text{Ba}(\text{ClO}_4)_2$; (■) Et_4NClO_4 in addition to $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Mg}(\text{ClO}_4)_2$.

The coordination behavior of Ca^{2+} with L^- is very similar to that of Mg^{2+} (cf. Fig. 4.4). The precipitation takes place in the presence of $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ca}(\text{ClO}_4)_2$, then the re-dissolution occurs suddenly with $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Ca}^{2+}$. Strange to say, the precipitation of BaL_2 occurs only to a smaller extent than that of MgL_2 and CaL_2 . Scheme 4.2 shows the precipitation of ML_2 ($\text{M} = \text{Mg}, \text{Ca}, \text{and Ba}$) and the successive re-dissolution of ML_2 through ML^+ . The equilibrium constants of the reactions between M^+ or M^{2+} and the diphenylphosphinate ion (L^-) in MeCN are listed in Table 4.1. The “reverse coordination” or coordination constants indicate the interaction increases in the order of $\text{Na}^+ < \text{Li}^+$ and $\text{Ba}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+}$. In the previous paper [25], the sudden formation of ML^+ -type species has been observed from the precipitates of ML_2 for the benzoate

ion in MeCN, and furthermore the $\text{C}_6\text{H}_5\text{CO}_2\text{Ca}^+$ ion has been detected, indeed, by the electrospray ionization mass spectroscopy [24].



Scheme 4.2. Successive formation of ML_2 and ML^+ ($\text{M} = \text{Mg}, \text{Ca}, \text{and Ba}$) for the diphenylphosphinate ion in MeCN.

4.3.1.2. The influences of added water and methanol on the interaction between M^+ or M^{2+} and the diphenylphosphinate ion (L^-)

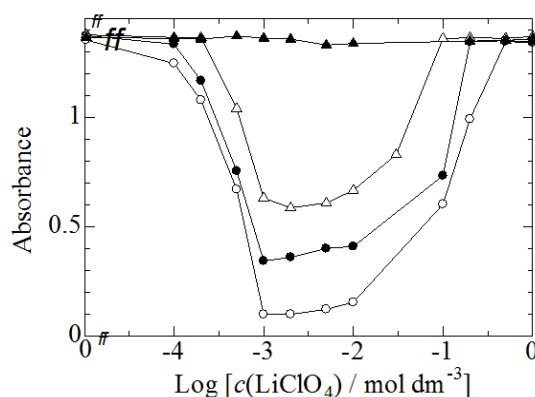


Fig. 4.5. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of LiClO_4 in MeCN- H_2O mixtures: (o) 0; (●) 1.0; (Δ) 2.0; (▲) 5.0% (v/v) of H_2O .

We have urged that the properties of “residual water” (the water remains after drying) in non-aqueous solvents are much different from those of the bulk water and that the presence of such “minor” water can be often ignored [27]. However, additional water or protic solvents in MeCN may cause strong influences on the reactions between alkali metal or alkaline earth metal ions and the diphenylphosphinate ion (L^-) because of the stronger salvation toward both the metal and L^- ions by the additional water.

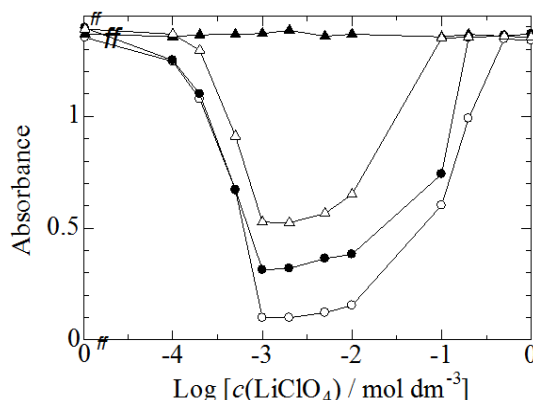


Fig. 4.6. Changes in absorbance ($\lambda_{\max} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of LiClO_4 in MeCN-MeOH mixtures: (○) 0; (●) 2.0; (Δ) 5.0; (▲) 10% (v/v) of MeOH.

Fig. 4.5 shows the influences of added water on the precipitation and the successive re-dissolution of lithium diphenylphosphinate (LiL) in MeCN. The added water of a small content disturbs the precipitation of LiL , and the absorbance minimum increases from 0.099 in 0.0% H_2O to 0.343 and 0.586 in 1.0 and 2.0% H_2O , respectively. The solubility products ($\text{p}K_{\text{sp}}$) are evaluated to be 8.28, 7.20, and 6.28 in 0.0, 1.0, and 2.0% H_2O , respectively (*cf.* Tables 4.1 and 4.2). The re-dissolution of precipitates seems to be promoted apparently by the additional H_2O . At 0.10 mol dm^{-3} LiClO_4 , the absorbance increases as 0.602, 0.733, and 1.36 for 0.0, 1.0, and 2.0% H_2O , respectively. The precipitation and re-dissolution reactions are completely inhibited in 5.0% H_2O .

The influences of MeOH on the interaction between Li^+ and L^- in MeCN are very similar but smaller than those of H_2O (Fig. 4.6). In 2.0% MeOH and 1.0% H_2O , solubility products ($\text{p}K_{\text{sp}}$) are observed to be 7.30 and 7.20, respectively, and “reverse” coordination constants ($\log K_2$) are 5.02 and 4.93 (*cf.* Table 4.2). In 10% MeOH, no apparent precipitation or re-dissolution reactions are observed between Li^+ and L^- . We can easily notice that the useful solvation parameters for the added protic solvents of $> 0.5 \%$ H_2O and MeOH in MeCN should be those ($\text{DN}_{\text{bulk}} = 40.3$ and 31.3) given by Marcus [45] and not the originally given by Gutmann ($\text{DN} = 18.0$ and 19) [43] for H_2O and MeOH, respectively.

The influences of added water (*cf.* Fig. 4A.1) and methanol (*cf.* Fig. 4A.2) have been also examined on the interaction between Na^+ and L^- . It is worth noticing that the added water or methanol gives larger influences on the interaction between Na^+ and L^- than that for Li^+ . In 5.0% MeOH, for instance, the precipitation of NaL occurs only slightly ($\text{p}K_{\text{sp}} = 4.09$), while that of LiL

still takes place to a relatively large extent ($pK_{sp} = 6.83$, *cf.* Table 4.2). In the reactions with sulfonate anions [22, 24], however, the metal ions of larger size or lower charge density have been less affected by the added H_2O and $MeOH$.

Fig. 4.7(a) shows the influences of added water (1.0 – 5.0%) on the precipitation and the successive re-dissolution of CaL_2 . Without H_2O , as shown Fig. 4.4, the distinct precipitation takes place at an equivalence of Ca^{2+} . In the presence of 1.0 and 2.0% H_2O , no remarkable influences are observed in the precipitation and re-dissolution reactions, that is, the pK_{sp} values for 0.0, 1.0, and 2.0% H_2O are given to be 11.35, 11.31, and 10.96 and $\log K_1 = 4.11$, 4.11, and 3.93, respectively (*cf.* Tables 4.1 and 4.3). The absorbance minimum increases to 0.611 in 4.0% H_2O , and finally it almost disappears in 5.0% H_2O . The influences of $MeOH$ on the coordination reaction between Ca^{2+} and L^- are smaller than H_2O [Fig. 4.7(b)]. With increasing contents of $MeOH$, the precipitation reaction takes place to lesser extent. Precipitation may take place in 10% $MeOH$, but it is almost inhibited in 15% $MeOH$. The higher solubility of CaL and the sudden increase of absorbance with increasing Ca^{2+} $[(0.5 - 1.0) \times 10^{-3} \text{ mol dm}^{-3}]$ in 5.0% $MeOH$ kept us from evaluating appropriate K_1 values [*cf.* Fig. 4.7(b)].

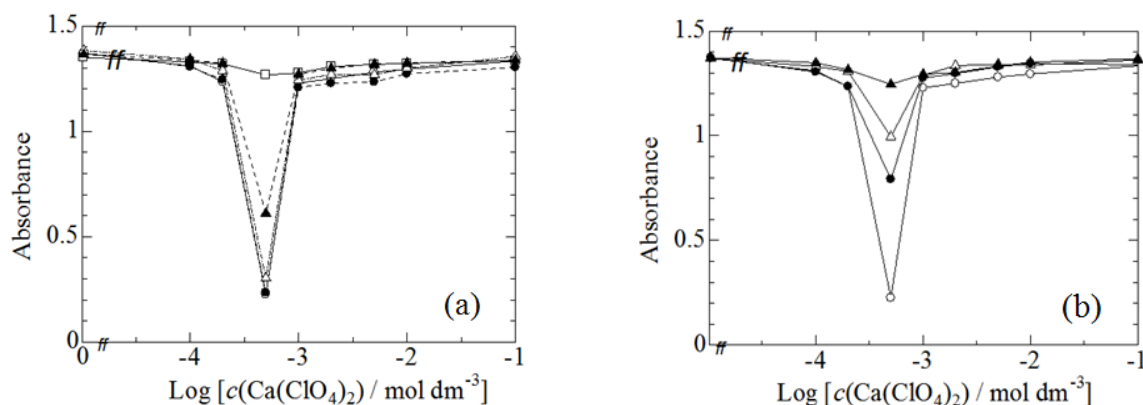


Fig. 4.7(a). Changes in absorbance ($\lambda_{max} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of $Ca(ClO_4)_2$ in $MeCN-H_2O$ mixtures: (\circ) 0; (\bullet) 1.0; (Δ) 2.0; (\blacktriangle) 4.0; (\square) 5.0% (v/v) of H_2O .

Fig. 4.7(b). Changes in absorbance ($\lambda_{max} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of $Ca(ClO_4)_2$ in $MeCN-MeOH$ mixtures: (\circ) 0; (\bullet) 5.0; (Δ) 10; (\blacktriangle) 15% (v/v) of $MeOH$.

The added water (0 – 10%) has influenced in a different way for Mg^{2+} with L^- . When 0.50% H_2O is added to MeCN, the dissolution of MgL at $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Mg}^{2+}$ (without added water, Fig. 4.4) is obstructed remarkably and the absorbance of L^- recovers its original value at as high as $1.0 \times 10^{-2} \text{ mol dm}^{-3} \text{ Mg}^{2+}$. The addition of 10% H_2O causes no precipitation between Mg^{2+} and L^- (cf. Fig. 4A.3). Compared with H_2O , methanol causes much smaller influences on the interaction between Mg^{2+} and L^- . The precipitation and re-dissolution reactions disappear in 30% MeOH (cf. Fig. 4A.4).

The influences of added water (1.0 – 5.0%) have been examined also for BaL_2 . With the addition of 1.0% H_2O , very interestingly, the absorbance minimum value (at an equivalence) decreases from 0.451 to 0.346. In 5.0% H_2O , the precipitation and re-dissolution reactions are not observed. In general, the water influences on the interaction of Ba^{2+} and L^- are similar to those on Ca^{2+} and L^- (cf. Fig. 4A.5).

The influences of added MeOH on the behavior of precipitation and the successive re-dissolution of BaL_2 are rather complicated (cf. Fig. 4A.6). When MeCN contains 10% MeOH, the $\text{p}K_{\text{sp}}$ is evaluated to be 10.73. This value is still very close to that in 5.0% MeOH ($\text{p}K_{\text{sp}} = 10.96$, cf. Table 4.3). The precipitation takes place in 20% MeOH, but finally, neither precipitation nor re-dissolution appears in 30% MeOH.

4.3.2. Diphenylphosphate (L^- and HL)

4.3.2.1. Specific interaction between M^+ or M^{2+} and the diphenylphosphate ion (L^-) or the mixture of diphenylphosphate (HL) with Et_3N

Diphenylphosphate [$(\text{PhO})_2\text{PO}_2\text{H}$, phosphoric acid diphenyl ester] in the group of weak acids is fairly strong in water ($\text{p}K_{\text{a}} = \text{ca. } 1.5$) [23]. The UV absorption spectrum of tetrabutylammonium diphenylphosphate [$n\text{-Bu}_4\text{N}^+(\text{PhO})_2\text{PO}_2^-$] exhibits a band at around 206 nm in MeCN.

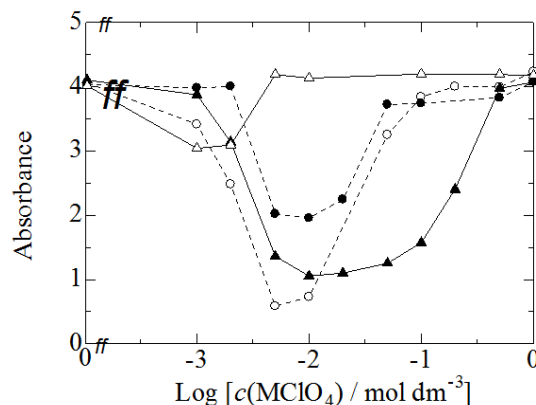


Fig. 4.8. Changes in absorbance ($\lambda_{\max} = \text{ca. } 206 \text{ nm}$) of $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphate ion (0.05 cm path-length) with increasing LiClO_4 and NaClO_4 concentrations in MeCN (triangles) and acetone (circles). The open and solid symbols represent LiClO_4 and NaClO_4 , respectively.

In MeCN, no apparent interaction could be detected between Li^+ or Na^+ and $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate (L^-). However, in a higher L^- concentration solution, $5.0 \times 10^{-3} \text{ mol dm}^{-3}$, the precipitation of LiL or NaL takes place (Fig. 4.8). The $\text{p}K_{\text{sp}}$ and $\log K_2$ values can be evaluated for Na^+ but not for Li^+ and L^- (*cf.* Table 4.4). Further details will be discussed for the interaction between Li^+ and L^- along with between Mg^{2+} and L^- (*vide infra*).

In acetone, the precipitation of LiL^- occurs to a larger extent than that of NaL . The Li^+ ion may have a stronger tendency than Na^+ to associate with L^- in acetone ($\epsilon_r = 20.56$) [23]. The $\text{p}K_{\text{sp}}$ and $\log K_2$ values have been evaluated from 5.0×10^{-3} diphenylphosphate ion (Fig. 4.8) to be 6.28 and 4.07, respectively, for Li^+ and also 5.20 and 4.29 for Na^+ . By means of polarography on DME, coincidentally, we [23] have reported (rather larger) overall formation constants of LiX_2^- and Li_2X^+ to be $10^{6.5}$ and $10^{7.1}$, respectively, in acetone, where $\text{X} = (\text{PhO})_2\text{PO}_2$. Fig. 4.9(a) shows the absorbance ($\lambda_{\max} = \text{ca. } 206 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate ion (L^-) with increasing concentration of alkaline earth metal ions in MeCN. Almost no absorbance changes appear by the addition of Mg^{2+} , *i.e.*, no apparent interaction between L^- and Mg^{2+} . With increasing concentration of $\text{Ca}(\text{ClO}_4)_2$, however, the absorbance firstly decreases and reaches its minimum at an equivalence of $\text{Ca}(\text{ClO}_4)_2$ ($2.5 \times 10^{-4} \text{ mol dm}^{-3}$), then the equi-molar $\text{Ca}(\text{ClO}_4)_2$ ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$) causes suddenly the re-dissolution of precipitates and also the drastic increase in absorbance, the $\text{p}K_{\text{sp}}$ and $\log K_1$ are listed as 13.07 and 4.72 in Table 4.4. Almost complete precipitation is caused by an equivalence of $\text{Ba}(\text{ClO}_4)_2$, and the precipitation continues up to $1.0 \times 10^{-2} \text{ mol dm}^{-3}$

Ba^{2+} . The precipitates of BaL_2 partially re-dissolve at $0.10 \text{ mol dm}^{-3} \text{ Ba}^{2+}$, and finally the absorbance recovers the original value at $0.20 - 1.0 \text{ mol dm}^{-3} \text{ Ba}^{2+}$. The UV spectral changes of $n\text{-Bu}_4\text{N}^+ \text{L}^-$ in the presence of increasing $\text{Ba}(\text{ClO}_4)_2$ concentrations are shown in Fig. 4.10. Scheme 4.3 shows the (reverse) coordinated species of ML^+ ($\text{M} = \text{Ca}, \text{Ba}$), *i.e.*, the 1:1 complex formation from the ML_2 precipitate.

Fig. 4.9(b) shows the changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 206 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate (HL) containing an equivalent amount of Et_3N with increasing of alkaline earth metal ions in MeCN. Comparing Fig. 4.9(a) with 4.9(b), it is obvious that the alkaline earth metal ions react with both $(n\text{-Bu}_4\text{N}^+) \text{L}^-$ and $\text{Et}_3\text{N}\text{-HL}$ (or $\text{Et}_3\text{NH}^+ \text{---} \text{L}^-$) in a very similar way. Strictly speaking, the proper interactions (without any obstruction) should be observed only with $(n\text{-Bu}_4\text{N}^+) \text{L}^-$ and not with $\text{Et}_3\text{N}\text{-HL}$ (or $\text{Et}_3\text{NH}^+ \text{---} \text{L}^-$). However, in the following sections, we examine the metal ion reaction with $\text{Et}_3\text{N}\text{-HL}$ for experimental simplicity. It may be worth mentioning that the hydrogen bonding interaction (in addition to the Coulombic interaction) between R_3NH^+ and $(\text{PhO})_2\text{PO}_2^-$ is much stronger than the mere Coulombic interaction between R_4N^+ and $(\text{PhO})_2\text{PO}_2^-$ in several protophobic aprotic solvents, such as MeCN, benzonitrile, nitrobenzene, and propylene carbonate, according to the conductometric data [23]. Nevertheless, $n\text{-Bu}_4\text{N}^+ \text{L}^-$ and $\text{Et}_3\text{N}\text{-HL}$ give similar $\text{p}K_{\text{sp}}$ and $\log K_1$ values for Ca^{2+} and Ba^{2+} in MeCN (*cf.* Table 4.4).

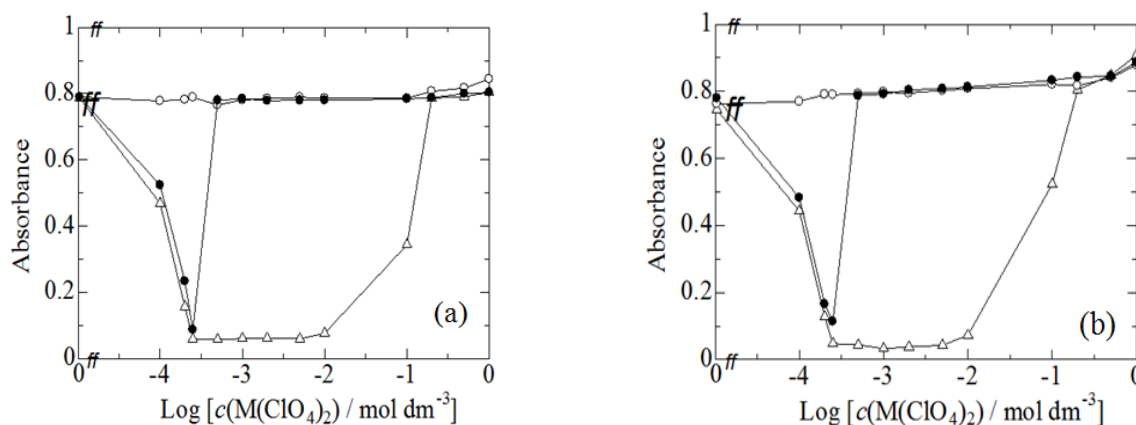


Fig. 4.9(a). Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 206 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate ion with increasing of alkaline earth metal ions in MeCN: (\circ) $\text{Mg}(\text{ClO}_4)_2$; (\bullet) $\text{Ca}(\text{ClO}_4)_2$; (Δ) $\text{Ba}(\text{ClO}_4)_2$.

Fig. 4.9(b). Changes in absorbance (λ_{\max} = ca. 206 nm) of 5.0×10^{-4} mol dm $^{-3}$ diphenylphosphate (HL) containing 5.0×10^{-4} mol dm $^{-3}$ Et $_3$ N with increasing of alkaline earth metal ions in MeCN: (○) Mg(ClO $_4$) $_2$; (●) Ca(ClO $_4$) $_2$; (Δ) Ba(ClO $_4$) $_2$.

By means of the present method utilizing the successive reactions of precipitation and re-dissolution, no interaction between a metal ion and L^- can be indicated unless the precipitation reaction occurs properly. Nevertheless, we may predict the log K_2 of ~ 4.2 for Li^+ and log K_1 of ~ 5.0 for Mg^{2+} with the L^- ion in MeCN, judging from the log K_2 and log K_1 values for the interaction between M^+ or M^{2+} and the analogous compound (diphenylphosphinate, $Ph_2PO_2^-$), given in Table 4.1.

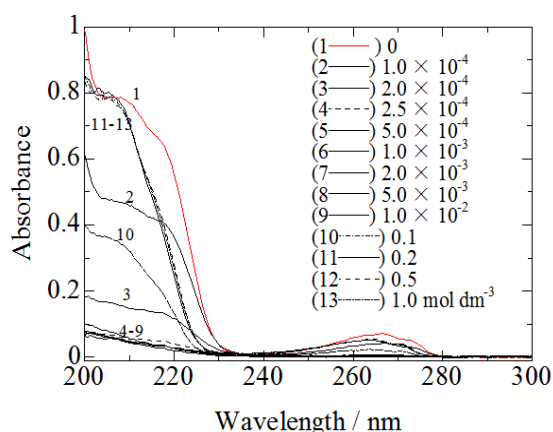
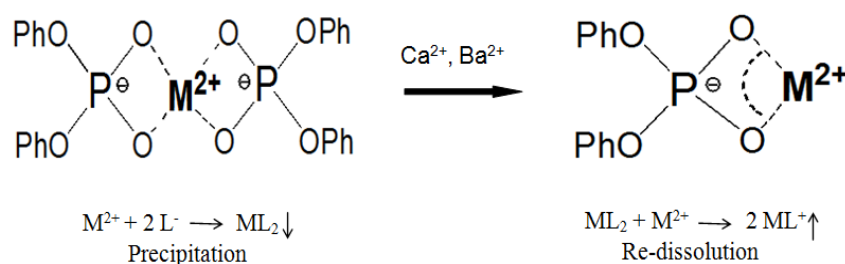


Fig. 4.10. UV spectra of 5.0×10^{-4} mol dm $^{-3}$ diphenylphosphate ion (0.1 cm path-length) with increasing concentration of Ba(ClO $_4$) $_2$ in MeCN.



Scheme 4.3. Successive formation of ML_2 ($M = Ca$ and Ba) and ML^+ for the diphenylphosphate ion (L^-) in MeCN.

The specific interaction between Li^+ or Mg^{2+} and 5.0×10^{-4} mol dm $^{-3}$ L^- in MeCN cannot be obviously detected from the UV spectral changes, as described above. Without observing distinct phenomena of precipitation and the successive re-dissolution, we cannot insist that Li^+ or Mg^{2+}

keeps still the strong interaction with L^- . However, conductometric titrations of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ tetrabutylammonium diphenylphosphate [$n\text{-Bu}_4\text{N}^+(\text{PhO})_2\text{PO}_2^-$] with LiClO_4 and $\text{Mg}(\text{ClO}_4)_2$ have supplied us with the good evidence for the interaction. The deviation point has been given at an equivalence point for LiClO_4 ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$) or for $\text{Mg}(\text{ClO}_4)_2$ ($2.5 \times 10^{-4} \text{ mol dm}^{-3}$), as shown in Fig. 4.11(a) or Fig. 4.11(b), respectively, indicating that the chemical interaction operates actually between Li^+ or Mg^{2+} and $5.0 \times 10^{-4} \text{ mol dm}^{-3} L^-$. It may be worth mentioning again that the both systems give no precipitation indeed. The solubility of non-charged species for Li^+ and Mg^{2+} with L^- must be too high to form precipitates under those conditions.

At an equivalence point ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$) in the titration curve with LiClO_4 , the observed specific conductance ($k/S \text{ cm}^{-1}$) of 0.1425×10^{-3} equals 285 of the molar conductivity ($\Lambda/S \text{ cm}^2 \text{ mol}^{-1}$). In the solution, we can expect the presence of two pairs of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ $\text{Li}^+(\text{PhO})_2\text{PO}_2^-$ and $n\text{-Bu}_4\text{N}^+\text{ClO}_4^-$.

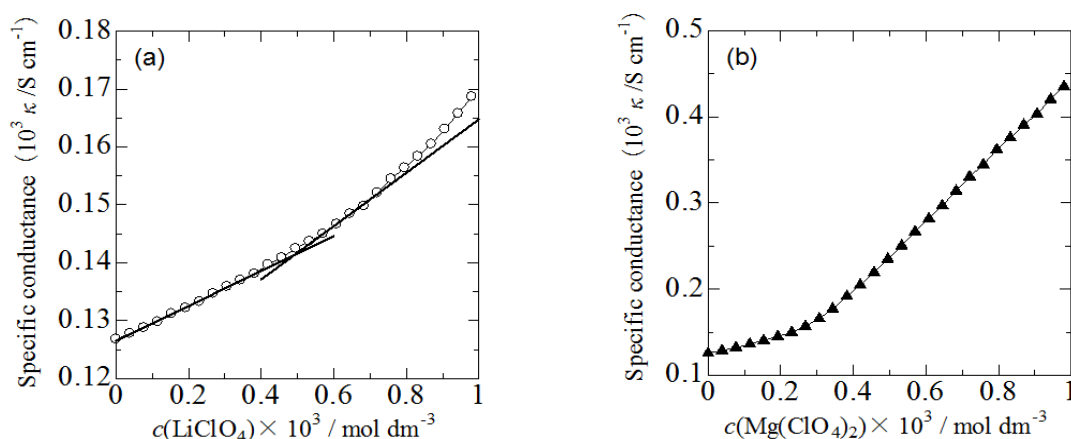


Fig. 4.11(a). Conductometric titration curve of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate ion [$n\text{-Bu}_4\text{N}^+(\text{PhO})_2\text{PO}_2^-$] with increasing concentration of LiClO_4 in MeCN.

Fig. 4.11(b). Conductometric titration curve of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate ion [$n\text{-Bu}_4\text{N}^+(\text{PhO})_2\text{PO}_2^-$] with increasing concentration of $\text{Mg}(\text{ClO}_4)_2$ in MeCN.

The observed Λ value (ca. 118) of $\text{Li}^+(\text{PhO})_2\text{PO}_2^-$ at the equivalence point has been found to be smaller than the calculated Λ one (130.6) for the independent Li^+ and $(\text{PhO})_2\text{PO}_2^-$. The $\Lambda_{\text{clcd}}[\text{Li}^+(\text{PhO})_2\text{PO}_2^-] = \Lambda_0[n\text{-Bu}_4\text{N}^+(\text{PhO})_2\text{PO}_2^-] (123.0) + \Lambda_0(\text{LiClO}_4) (174.8) [29] - \Lambda_0(n\text{-Bu}_4\text{N}^+\text{ClO}_4^-) (167.2) [29] = 130.6$. By the way, the Λ_0 value of $n\text{-Bu}_4\text{N}^+(\text{PhO})_2\text{PO}_2^-$ has not directly been measured yet, therefore, the values is estimated by the calculation from $\Lambda_0[\text{Et}_4\text{N}^+(\text{PhO})_2\text{PO}_2^-]$

(149.1) [23] and the difference (26.1) between Et_4N^+ and $n\text{-Bu}_4\text{N}^+$ [17]. We should note that any tetraalkylammonium and perchlorate ions have no chemical interaction except for the Coulombic force, that is, $\text{R}_4\text{N}^+\text{X}^-$ or $\text{Li}^+\text{ClO}_4^-$ is a strong electrolyte in higher permittivity media such as MeCN. For instance, the association constants of $n\text{-Bu}_4\text{NClO}_4$, LiClO_4 , and $\text{Et}_4\text{N}^+(\text{PhO})_2\text{PO}_2^-$ have been reported to be $K_a = 0$, 13.6 [29], and ca. 4.0 [23], respectively.

It is worth mentioning once more that the balance (ca. 118) between 285 and 167.2, attributed to the molar conductivity of $\text{Li}^+(\text{PhO})_2\text{PO}_2^-$, seems to be enough smaller than the sum value (130.6) of independent Λ_0 values of Li^+ and $(\text{PhO})_2\text{PO}_2^-$. Therefore, we can predict the “strong” interaction between $(\text{PhO})_2\text{PO}_2^-$ and Li^+ in MeCN, even without observing precipitates. The observed specific conductance of 0.129×10^{-3} from the titration with $\text{Mg}(\text{ClO}_4)_2$ may also support the “strong” interaction between Mg^{2+} and L^- under no precipitation conditions.

4.3.2.2. The influences of added H_2O , MeOH , and EtOH on the interaction between M^+ or M^{2+} and the mixture of HL with Et_3N

Fig. 4.12 shows the influences of added H_2O on precipitation and the successive re-dissolution reactions of BaL_2 in MeCN. The precipitation is obviously restrained but the re-dissolution is promoted apparently by the added H_2O . The (reverse) coordination constants ($\log K_1$) are given as “pseudo” values to be 4.25, 3.95, and 3.08 in 1.0, 2.0, and 3.0% H_2O (Table 4A.1), respectively. These values may be valid just relatively. In 5.0% H_2O , the absorbance decrease (*i.e.*, precipitation) occurs slightly at 2.5×10^{-4} and $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ba}^{2+}$. The 10% H_2O addition causes no apparent precipitation or re-dissolution reactions between Ba^{2+} and L^- .

Both MeOH ($\text{DN}_{\text{bulk}} = 31.3$ [45]) and EtOH ($\text{DN}_{\text{bulk}} = 27.8$ [45]) are protic solvents of higher donicities. Not only MeOH but also EtOH may inhibit the precipitation between Ba^{2+} and L^- , and the influences may increase in the order of $\text{EtOH} < \text{MeOH} < \text{H}_2\text{O}$ [*cf.* Fig. 4.13(a) and 4.13(b)]. With increasing contents of MeOH and EtOH , the precipitation reactions become incomplete. The slight precipitation occurs in 15% MeOH or 30% EtOH , and the interaction is totally hidden by 20% MeOH and 50% EtOH (Table 4A.1).

Table 4.5 lists the equilibrium constants of the reactions between Ba^{2+} and the (1:1) $\text{Et}_3\text{N}\text{-HL}$ (5.0×10^{-3} and $5.0 \times 10^{-3} \text{ mol dm}^{-3}$) mixture in MeCN-MeOH. Even in 15 – 30% MeOH , the

precipitation and “reverse” coordination can take place between $5.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Et}_3\text{N-HL}$ and Ba^{2+} to a relatively large extent. The (reverse) coordination constants of $5.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Et}_3\text{N-HL}$ have been given as “pseudo” values to be $\log K_1 = 3.35, 3.06$, and 2.68 in 15, 20, and 30% MeOH, respectively. The above results indicate clearly that, by performing experiments with higher concentrations (*e.g.*, a ten-fold) of L^- , we have still the chance to obtain equilibrium constants even though no precipitation takes place for a metal ion with a lower L^- concentration. Table 4.5 may convince us that the equilibrium values evaluated from different L^- ($\text{Et}_3\text{N-HL}$) concentrations are well consistent.

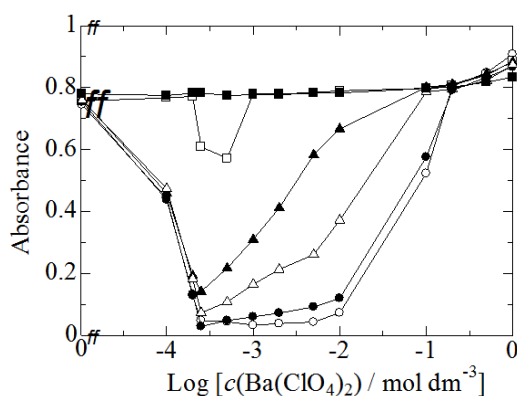


Fig. 4.12. Absorbance ($\lambda_{\text{max}} = \text{ca. } 206 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate containing $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Et}_3\text{N}$ in the presence of $\text{Ba}(\text{ClO}_4)_2$ in MeCN- H_2O mixtures: (○) 0; (●) 1.0; (Δ) 2.0; (▲) 3.0; (□) 5.0; (■) 10% (v/v) of H_2O .

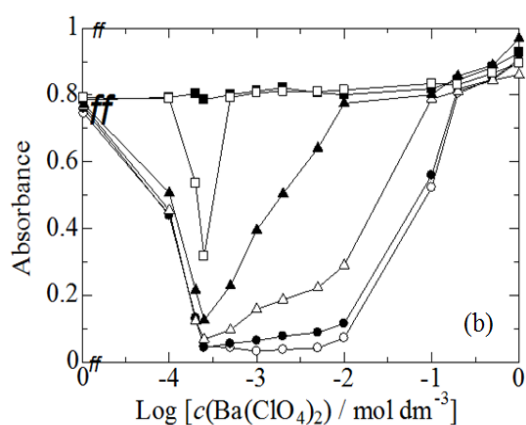
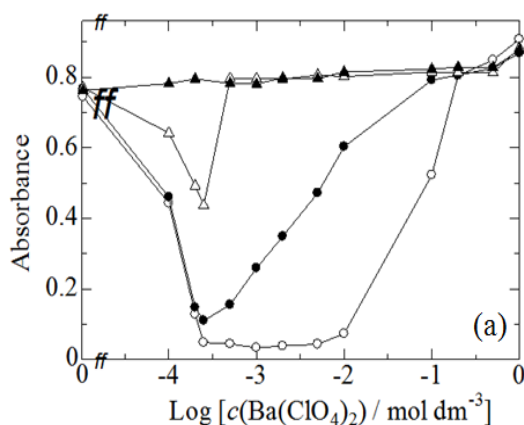


Fig. 4.13(a). Absorbance ($\lambda_{\text{max}} = \text{ca. } 206 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate containing $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Et}_3\text{N}$ in the presence of $\text{Ba}(\text{ClO}_4)_2$ in MeCN-MeOH mixtures: (○) 0; (●) 10; (Δ) 15; (▲) 20% (v/v) of MeOH.

Fig. 4.13(b). Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 206 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate containing $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Et}_3\text{N}$ in the presence of $\text{Ba}(\text{ClO}_4)_2$ in MeCN-EtOH mixtures: (\circ) 0; (\bullet) 5.0; (Δ) 10; (\blacktriangle) 20; (\square) 30; (\blacksquare) 50% (v/v) of EtOH.

4.3.3. Bis(4-nitrophenyl)phosphate (HL)

4.3.3.1. Specific interaction between M^+ or M^{2+} and the mixture of HL with Et_3N

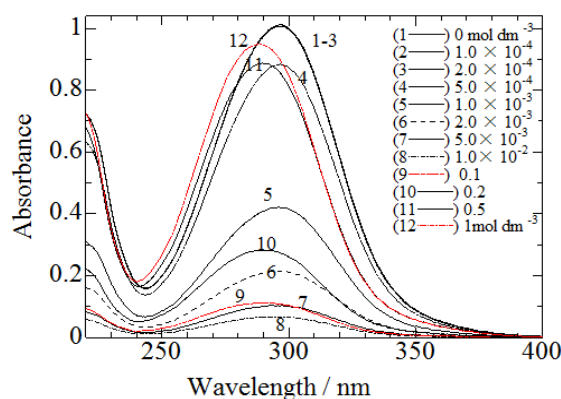
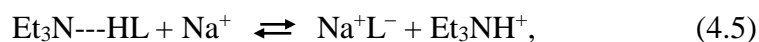


Fig. 4.14. UV spectra of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ bis(4-nitrophenyl)phosphate (0.1 cm path-length) containing $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Et}_3\text{N}$ with increasing concentration of NaClO_4 in MeCN.

Fig. 4.14 shows the UV spectral changes of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ bis(4-nitrophenyl)-phosphate (HL) containing an equivalent amount of Et_3N ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$), as the function of NaClO_4 concentration. The UV spectrum of Et_3N -HL shows two distinct absorption bands at around 218 nm and 295 nm ($\epsilon/\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3 = \text{ca. } 2.0 \times 10^4$). With increasing concentration of NaClO_4 , if we may pay attention to the band at around 295 nm, it decreases gradually and reaches its minimum of 0.067 at $1.0 \times 10^{-2} \text{ mol dm}^{-3} \text{ NaClO}_4$, accompanying white precipitates (*cf.* Eq. 4.5). Then, the band absorbance begins to increase with the addition of more than $1.0 \times 10^{-2} \text{ mol dm}^{-3} \text{ Na}^+$, and recovers almost the original value at $1.0 \text{ mol dm}^{-3} \text{ Na}^+$ (*cf.* Eq. 4.6). Meanwhile, the band shows a remarkable blue shift to 287 nm, suggesting the formation of a “reverse-coordinated” species of Na_2L^+ . The evaluated values of $\text{p}K_{\text{sp}}$ and $\log K_2$ between Na^+ and L^- in MeCN are 6.70 and 3.75, respectively. However, no apparent interaction is detected between Li^+ and L^- based on the almost constant absorbance values of the Et_3N -HL mixture (Fig. 4.15), except for the blue shifts with increasing Li^+ concentrations.



The UV spectral changes of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ $\text{Et}_3\text{N-HL}$, as the function of $\text{Ba}(\text{ClO}_4)_2$ concentration, are shown in Fig. 4.16. The absorption band at around 290 – 295 nm almost disappears on the addition of an equivalence of Ba^{2+} ($2.5 \times 10^{-4} \text{ mol dm}^{-3}$), accompanying white precipitates. The absorbance begins to increase with the further addition Ba^{2+} , forming the (reverse) coordinated species of BaL^+ . The “pseudo” values of $\text{p}K_{\text{sp}}$ and $\log K_1$ between Ba^+ and L^- in MeCN are obtained to be 13.68 and 4.81. The partial ionization of HL and the coordination reaction are illustrated by Schemes 4.4 and 4.5. According to Fig. 4.17, a slight precipitation reaction may take place between bis(4-nitrophenyl)phosphate and Mg^{2+} or Ca^{2+} . Only Na^+ and Ba^{2+} cause observable interactions with L^- through the remarkable precipitation and re-dissolution reactions. However, we never believe that the bis(4-nitrophenyl)phosphate ion cannot interacts with Li^+ , Mg^{2+} , or Ca^{2+} in MeCN. The solubilities of the non-charged species for Li^+ , Mg^{2+} , and Ca^{2+} should be just too high to form precipitates in the solvent. Needless to mention, the chemical interaction operates actually between Li^+ , Mg^{2+} , or Ca^{2+} and $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{L}^-$.

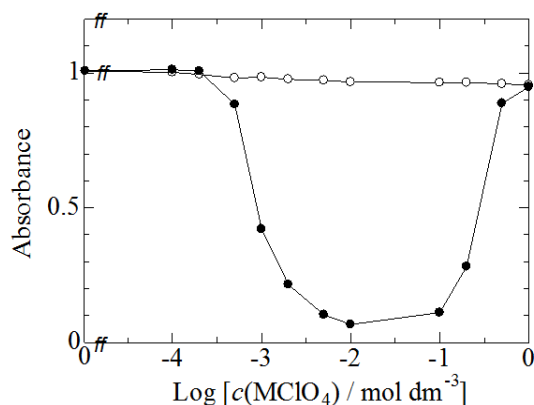


Fig. 4.15. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 290 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ bis(4-nitrophenyl)phosphate containing $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{Et}_3\text{N}$ with increasing of alkali metal ions: (○) LiClO_4 ; (●) NaClO_4 .

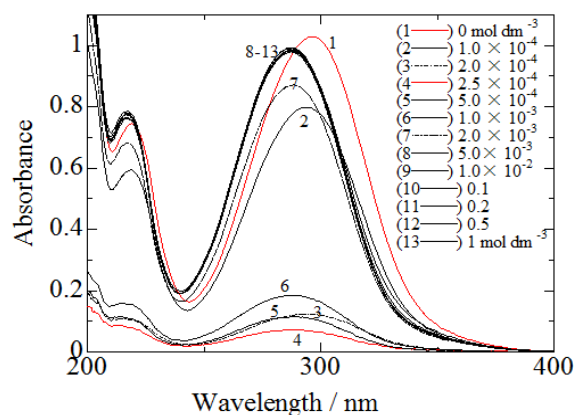


Fig. 4.16. UV spectra of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ bis(4-nitrophenyl)phosphate (0.1 cm path-length) containing $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Et}_3\text{N}$ with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$ in MeCN.

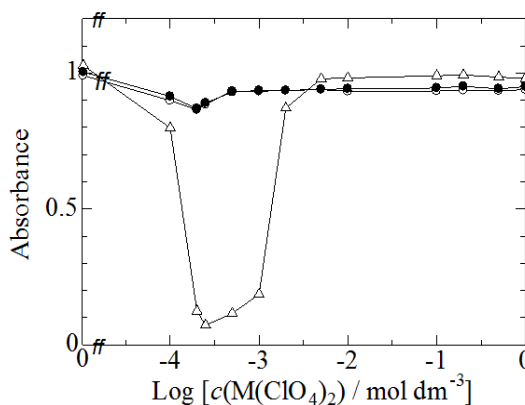
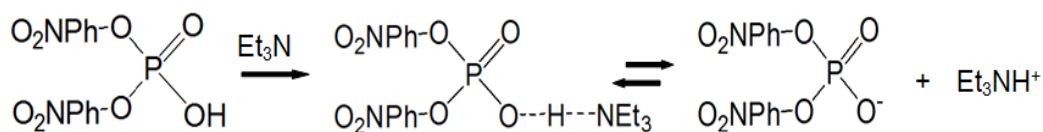
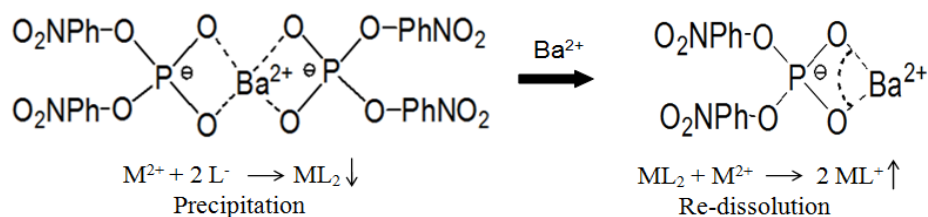


Fig. 4.17. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 290 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ bis(4-nitrophenyl)phosphate containing $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Et}_3\text{N}$ with increasing of alkaline earth metal ions in MeCN: (○) $\text{Mg}(\text{ClO}_4)_2$; (●) $\text{Ca}(\text{ClO}_4)_2$; (Δ) $\text{Ba}(\text{ClO}_4)_2$.



Scheme 4.4. The partial ionization of bis(4-nitrophenyl)phosphate by the addition Et_3N in MeCN.



Scheme 4.5. Successive formation of BaL_2 and BaL^+ for the bis(4-nitrophenyl)phosphate ion (L^-) in MeCN.

4.3.3.2. The influences of added H₂O and MeOH on the interaction between Na⁺ or Ba²⁺ and the mixture of HL with Et₃N

Fig. 4.18 shows the influences of added H₂O on the precipitation and the successive re-dissolution of NaL. With increasing contents of H₂O, the solubility of NaL increases distinctly. The pK_{sp} values are 6.70, 5.80, and 4.63 in 0.0, 1.0, and 2.0% H₂O, respectively. In 3.0% H₂O, no precipitation reaction is observed. Similarly, no apparent interaction can be detected also in 10% MeOH (*cf.* Table 4.1).

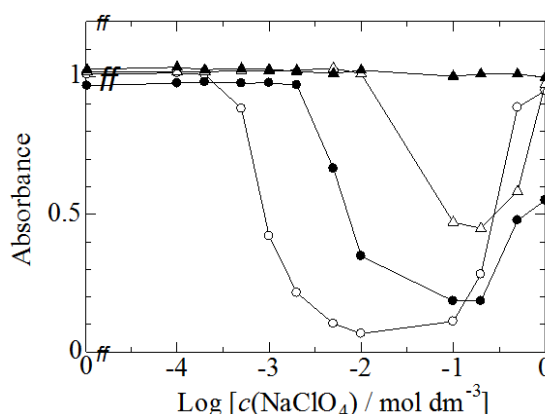


Fig. 4.18. Absorbance ($\lambda_{max} = \text{ca. } 290 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ bis(4-nitrophenyl)phosphate (0.1 cm path-length) containing $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ Et₃N in the presence of NaClO₄ in MeCN-H₂O mixtures: (○) 0; (●) 1.0; (Δ) 2.0 (▲) 3.0% (v/v) of H₂O.

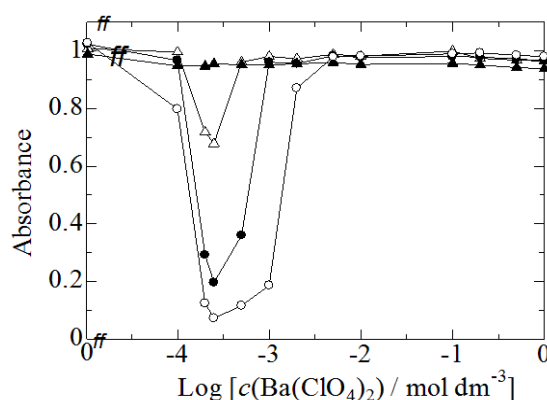


Fig. 4.19. Absorbance ($\lambda_{max} = \text{ca. } 290 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ bis(4-nitrophenyl)phosphate containing $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ Et₃N in the presence of Ba(ClO₄)₂ in MeCN-H₂O mixtures: (○) 0; (●) 0.50; (Δ) 1.0 (▲) 2.0% (v/v) of H₂O.

Fig. 4.19 shows the influences of added H₂O on the precipitation and the successive re-

dissolution of BaL_2 . The added 0.5% H_2O affects obviously both precipitation and re-dissolution between Ba^{2+} and the anion, despite the absorbance minimum appears at an equivalence of Ba^{2+} . Slight precipitation takes place in 1.0% H_2O . The “pseudo” solubility products ($\text{p}K_{\text{sp}}$) are 13.68, 12.36 and 10.72 in 0.0, 0.50, and 1.0% H_2O , respectively. The interaction is totally obscured by 2.0% H_2O . Compared with water, MeOH affects weakly the precipitation and re-dissolution (*cf.* Table 4.1). The interaction is totally hidden by 5.0% MeOH . The remarkable influences on Ba^{2+} of low contents of protic solvents should be caused by the stronger solvation toward the bis(4-nitrophenyl)phosphate ion.

4.4. Conclusion

The coordination ability of alkali metal (M^+) and alkaline earth metal (M^{2+}) ions with diphenylphosphinate, diphenylphosphate, and bis(4-nitrophenyl)phosphate ions has been confirmed not only in sole MeCN but also in the binary solvents with H_2O , MeOH , and EtOH . The precipitation and the successive re-dissolution reactions have been observed between every M^+ or M^{2+} and $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate. The “reverse coordination” or coordination constants suggest that the chemical interaction should increase in the order of $\text{Na}^+ < \text{Li}^+$ and $\text{Ba}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+}$. With $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate, however, only Ca^{2+} and Ba^{2+} (the strength order of $\text{Ba}^{2+} < \text{Ca}^{2+}$) can cause the obvious precipitation in MeCN . Nevertheless, we are confident that all the phosphinate and phosphate ions should interact with the alkali metal and alkaline earth metal ions through the chemical (coordination) force above the Coulombic force in poor solvating media. The results in the present study may give an important clue to recognize the kinetic mechanism in hydrolysis reactions under “non-aqueous solvent conditions” or in biological systems, based on the direct interaction between “indifferent” metal ions and the anion species released from substrates.

Table 4.1 Precipitation and re-dissolution reactions of the diphenylphosphinate ion ($n\text{-Bu}_4\text{N}^+\text{L}^-$) with alkali metal or alkaline earth metal perchlorates in MeCN .

$n\text{-Bu}_4\text{N}^+$ salt	Equilibrium constants ^a	Li^+	Na^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
Diphenylphosphinate		▲	▲	▲	▲	▲

ion	(pK _{sp})	8.28	8.06	11.89	11.35	10.43
(1.0×10 ⁻³ mol dm ⁻³)	(pK _{sp}) ^b	8.38	8.16	12.20	11.66	10.74
		○	△	○	○	○
	log K ₂ , log K ₁	5.88	5.20	4.36	4.11	3.63

Explanatory notes: Solid circles and triangles represent the complete and partial precipitation, respectively. The complete precipitation means here that the absorbance of a “ligand” anion (L⁻) reaches < 1/10 of the initial value at an equivalence 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 Solubility products (K_{sp}) and “reverse” coordination constants (K₂, K₁), *cf.* the experimental section in this paper.

^b 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. [46].

Table 4.2 Precipitation and re-dissolution reactions of the diphenylphosphinate ion with alkali metal ions in binary mixtures of MeCN-H₂O or MeCN-MeOH.

Metal ions ^a		Equilibrium constants ^b			
MeCN-H ₂ O [H ₂ O% (v/v)]		1.0	2.0	5.0	7.0
Li ⁺		▲	▲	No	
	(pK _{sp})	7.20	6.68	–	
	(pK _{sp})	7.30	6.78	–	
		○	○	No	
	log K ₂	4.93	4.98	–	
Na ⁺		▲	▲	▲	No
	(pK _{sp})	6.64	3.54	3.11	–
	(pK _{sp})	6.74	3.64	3.21	–
		○	○	No	No
	log K ₂	4.15	–	–	–
MeCN-MeOH [MeOH% (v/v)]		2.0	5.0	10	
Li ⁺		▲	▲	No	
	(pK _{sp})	7.30	6.83	–	
	(pK _{sp})	7.40	6.93	–	

		○	○	No
	$\log K_2$	5.02	5.21	–
		▲	▲	No
	(pK_{sp})	6.75	4.09	–
Na ⁺	(pK_{sp})	6.85	4.19	–
		○	○	No
	$\log K_2$	3.45	–	–

For the *Explanatory notes*, cf. Table 4.1.

^a MClO_4 .

^b Solubility products (K_{sp}) and “reverse” coordination constants (K_2), cf. the Experimental section.

Table 4.3 Precipitation and re-dissolution reactions of the diphenylphosphinate ion with alkaline earth metal ions in binary mixtures of MeCN-H₂O or MeCN-MeOH.

Metal ions ^a	Equilibrium constants ^b							
	MeCN-H ₂ O [H ₂ O% (v/v)]	0.5	1	2	3	4	5	10
		▲	▲	▲			▲	No
	(pK_{sp})	12.40	12.14	11.89			–	–
Mg ²⁺	(pK_{sp})	12.71	12.45	12.19			–	–
		○	○	○			○	No
	$\log K_1$	4.43	4.08	3.87		–	–	–
			▲	▲		▲	No	
	(pK_{sp})		11.31	10.96		10.05	–	
Ca ²⁺	(pK_{sp})		11.62	11.26		10.32		
			○	○		○	No	
	$\log K_1$		4.11	3.93		3.49	–	
			▲	▲	▲		No	
	(pK_{sp})		10.79	10.89	9.96		–	
Ba ²⁺	(pK_{sp})		11.10	11.19	10.25			
			○	○	○		No	
	$\log K_1$		3.89	3.96	–		–	
	MeCN-MeOH [MeOH% (v/v)]	2.0	5.0	10	15	20	25	30
Mg ²⁺				▲	▲	▲	▲	No

	(pK _{sp})		12.47	11.35	10.72	9.77	–
	(pK _{sp})		12.79	11.67	11.04	10.09	–
			○	○	○	○	No
	log K ₁		4.20	4.00	3.84	–	–
		▲	▲	No			
	(pK _{sp})	9.72	9.42	–			
Ca ²⁺	(pK _{sp})	10.03	9.74	–			
		○	○	No			
	log K ₁	–	–	–			
		▲	▲	▲	▲	▲	No
	(pK _{sp})	10.94	10.96	10.73	10.41	10.00	–
Ba ²⁺	(pK _{sp})	11.25	11.27	11.05	10.73	10.32	–
		○	○	○	○	○	No
	log K ₁	3.75	3.08	3.28	3.40	3.34	–

For the *Explanatory notes*, cf. Table 4.1.

^a M(ClO₄)₂.

^b Solubility products (K_{sp}) and “reverse” coordination constants (K₁), cf. the Experimental section.

Table 4.4 Precipitation and re-dissolution reactions on the diphenylphosphate ion (L[–]) or Et₃N-HL with alkali metal or alkaline earth metal perchlorates in MeCN.

Mixed solution	Equilibrium constants ^a	Li ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	Ba ²⁺
Diphenylphosphate		▲	▲	No	▲	●
(5.0×10 ^{–3} mol dm ^{–3} L [–] for	(pK _{sp})	– ^b	5.56	–	13.07	13.57
alkali metal ions)	(pK _{sp})	–	–	–	13.29	13.79
(5.0×10 ^{–4} mol dm ^{–3} L [–] for		○	○	No	○	○
alkaline earth metal ions)	log K ₂ , log K ₁	– ^b	3.73	–	4.72	3.61
					▲	●
	(pK _{sp})				12.71	13.78
Et ₃ N-HL	(pK _{sp})				12.93	14.00
(5.0×10 ^{–4} mol dm ^{–3})					○	○

log K_1

4.50

3.85

For the *Explanatory notes*, cf. Table 4.1.

^a Solubility products (K_{sp}) and “reverse” coordination constants (K_2 , K_1), cf. the Experimental section.

^b The pK_{sp} and log K_2 values are not evaluated because the precipitation of LiL in MeCN is not enough, cf. Fig. 4.8

Table 4.5 Influences of the concentration on the 1:1 mixture of Et₃N and diphenylphosphate (Et₃N-HL) on the precipitation and re-dissolution reactions for Ba(ClO₄)₂ in MeCN-MeOH.

Mixed solution	Equilibrium constants ^a	MeCN-MeOH [MeOH% (v/v)]				
		10	15	20	30	50
Et ₃ N-HL (5.0×10 ⁻⁴ mol dm ⁻³)		▲	▲	No		
	(pK_{sp})	12.74	(10.94)	–		
	(pK_{sp})	12.96	(11.16)	–		
		○	○	No		
	log K_1	3.90	(3.78)	–		
Et ₃ N-HL (5.0×10 ⁻³ mol dm ⁻³)			▲	▲	▲	No
	(pK_{sp})		11.26	8.97	8.52	–
	(pK_{sp})		11.97	9.68	9.24	–
			○	○	○	No
	log K_1		3.35	3.06	2.68	–

For the *Explanatory notes*, cf. Table 4.1.

^a Solubility products (K_{sp}) and “reverse” coordination constants (K_1), cf. the Experimental section.

References

- [1] L.S.B. Upadhyay, N. Verma, Biosens. Bioelectron. 68 (2015) 61.
- [2] L. Ronconi, P.J. Sadler, Coordin. Chem. Rev. 251 (2007) 1633.
- [3] D. Loca, M. Sokolova, J. Locs, A. Smirnova, Z. Irbe, Mater. Sci. Eng. C 49 (2015) 106.
- [4] Y. Zhang, A. Clearfield, Inorg. Chem. 31 (1992) 2821.
- [5] Z. Rohlik, P. Holzhauser, J. Kotek, J. Rudovsky, I. Nemec, P. Hermann, I. Lukes, J. Organomet. Chem. 691 (2006) 240.

- [6] M. Mitra, R. Ghosh, *Inorg. Chem. Commu.* 24 (2012) 95.
- [7] F.M. Menger, L.H. Gan, E. Johnson, D.H. Durstt, *J. Am. Chem. Soc.* 109 (1987) 2800.
- [8] P. Jurek, A.E. Martell, *Inorg. Chim. Acta* 287 (1999) 47.
- [9] J. Xie, B. Jiang, X. Kou, C. Hu, X. Zeng, *Transition Met. Chem.* 28 (2003) 782.
- [10] L.C. Manege, T. Ueda, M. Hojo, *Bull. Chem. Soc. Jpn.* 71 (1998) 589.
- [11] L.C. Manege, T. Ueda, M. Hojo, M. Fujio, *J. Chem. Soc. Perkin Trans. 2* (1998) 1961.
- [12] M. Hojo, T. Ueda, S. Inoue, Y. Kawahara, *J. Chem. Soc. Perkin Trans. 2* (2000) 1735.
- [13] M. Hojo, T. Ueda, E. Ueno, T. Hamasaki, D. Fujimura, *Bull. Chem. Soc. Jpn.* 79 (2006) 751.
- [14] M. Hojo, T. Ueda, E. Ueno, T. Hamasaki, T. Nakano, *Bull. Chem. Soc. Jpn.* 83 (2010) 401.
- [15] M. Hojo, S. Aoki, *Bull. Chem. Soc. Jpn.* 85 (2012) 1023.
- [16] L.D. Bayissa, Y. Ohmae, M. Hojo, *J. Mol. Liquids* 199 (2014) 294.
- [17] M. Hojo, T. Takiguchi, M. Hagiwara, H. Nagai, Y. Imai, *J. Phys. Chem.* 93 (1989) 955.
- [18] M. Hojo, H. Nagai, M. Hagiwara, Y. Imai, *Anal. Chem.* 59 (1987) 1770.
- [19] M. Hojo, Y. Miyauchi, A. Tanio, Y. Imai, *J. Chem. Soc. Faraday Trans. 24* (1991) 3847.
- [20] M. Hojo, T. Ueda, T. Inoue, M. Ike, *J. Phys. Chem. B* 117 (2007) 1759.
- [21] M. Hojo, H. Hasegawa, H. Yoneda, *J. Chem. Soc. Perkin Trans. 2* (1994) 1855.
- [22] M. Hojo, S. Ohta, K. Ayabe, K. Okamura, K. Kobiro. Z. Chen, *J. Mol. Liquids* 177 (2013) 145.
- [23] M. Hojo, H. Hasegawa, Y. Miyauchi, H. Moriyama, H. Yoneda, S. Arisawa, *Electrochim. Acta* 39 (1994) 629.
- [24] X. Chen, K. Ayabe, M. Hojo, Z. Chen, M. Kobayashi, *J. Mol. Liquids* 199 (2014) 445.
- [25] M. Hojo, T. Ueda, M. Ike, M. Kobayashi, H. Nakai. *J. Mol. Liquids* 145 (2009) 152.
- [26] M. Hojo, Y. Imai, *Bull. Chem. Soc. Jpn.* 56 (1983) 1963.
- [27] M. Hojo, *Pure Appl. Chem.* 80 (2008) 1539.
- [28] Z. Chen, M. Hojo, *J. Phys. Chem. B*, 101 (1997) 10896.
- [29] M. Hojo, T. Ueda, M. Nishimura, H. Hamada, *J. Phys. Chem. B* 103 (1999) 8965.
- [30] M. Hojo, A. Watanabe, T. Mizobuchi, Y. Imai, *J. Phys. Chem.* 94 (1990) 6073.
- [31] R.R. Holmes, R.O. Day, Y. Yoshida, J.M. Holmes, *J. Am. Chem. Soc.* 114 (1992) 1771.
- [32] R.M. Fuoss, C.A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 2387.

- [33] H. Weingartner, V.C. Weiss, W. Schroer, J. Chem. Phys. 113 (2000) 762.
- [34] S. Petrucci, E. M. Eyring, J. Phys. Chem. 95 (1991) 1731.
- [35] R.L. Jarek, S.K. Shin, J. Am. Chem. Soc. 119 (1997) 10501.
- [36] M. Hojo, Y. Kondo, K. Zei, K. Okamura, Z. Chen, M. Kobayashi, Bull. Chem. Soc. Jpn. 87 (2014) 98.
- [37] M. Hojo, T. Ueda, A. Inoue, S. Tokita, J. Mol. Liquids 148 (2009) 109.
- [38] M. Hojo, T. Ueda, M. Yamasaki, A. Inoue, S. Tokita, M. Yanagita, Bull. Chem. Soc. Jpn. 75 (2002) 1569.
- [39] G.V. Oshovsky, D.N. Reinhoudt, W. Verboom, J. Am. Chem. Soc. 128 (2006) 5270.
- [40] M. Hojo, H. Hasegawa, Z. Chen, Bull. Chem. Soc. Jpn. 69 (1996) 2215.
- [41] M. Iida and Y. Hata, Bull. Chem. Soc. Jpn. 65 (1992) 707.
- [42] 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.
- [43] V. Gutmann, The Donor-Acceptor Approach to Molecular Interactions, Plenum, New York, 1978.
- [44] P. Eberspächer, E. Wismeth, R. Buchner, J. Barthel, J. Mol. Liquids 129 (2006) 3.
- [45] Y. Marcus, J. Solution Chem. 13 (1984) 599.
- [46] A.K. Covington, T. Dickinson, Physical Chemistry of Organic Solvent Systems, Plenum, London, 1973.

Appendix

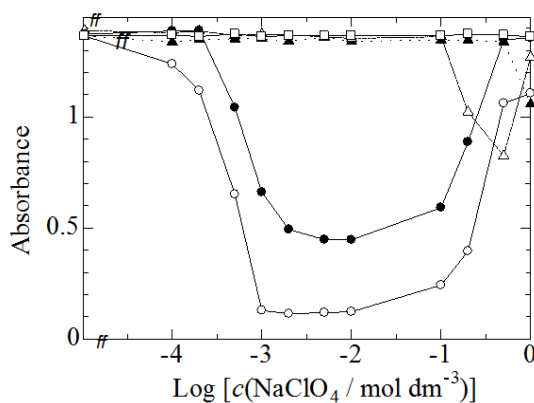


Fig. 4A.1. Changes in absorbance ($\lambda_{\max} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of NaClO_4 in MeCN- H_2O mixtures: (\circ) 0; (\bullet) 1.0; (Δ) 2.0; (\blacktriangle) 5.0; (\square) 7.0% (v/v) of H_2O .

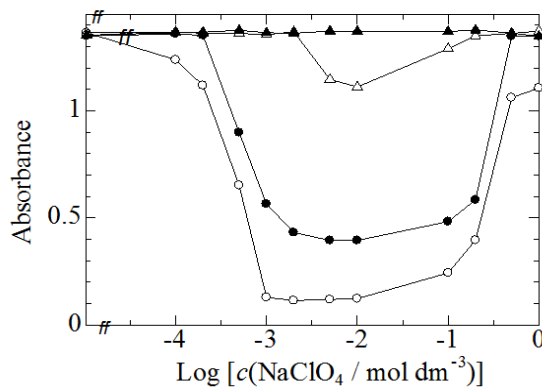


Fig. 4A.2. Changes in absorbance ($\lambda_{\max} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of NaClO_4 in MeCN-MeOH mixtures: (\circ) 0; (\bullet) 2.0; (Δ) 5.0; (\blacktriangle) 10% (v/v) of MeOH.

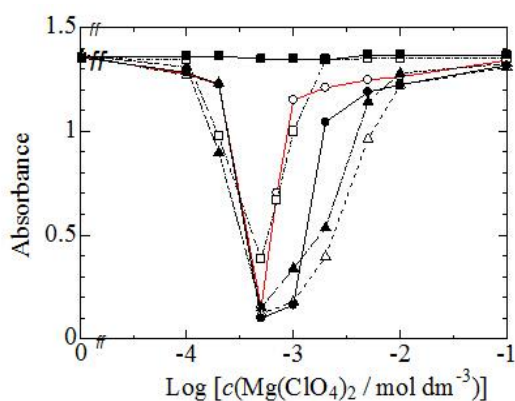


Fig. 4A.3. Changes in absorbance ($\lambda_{\max} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of $\text{Mg}(\text{ClO}_4)_2$ in MeCN- H_2O mixtures: (\circ) 0; (\bullet) 0.5; (Δ) 1.0; (\blacktriangle) 2.0; (\square) 5.0; (\blacksquare) 10% (v/v) of H_2O .

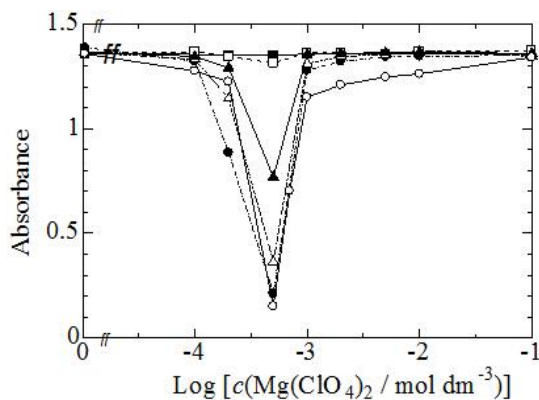


Fig. 4A.4. Changes in absorbance ($\lambda_{\max} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of $\text{Mg}(\text{ClO}_4)_2$ in MeCN-MeOH mixtures: (\circ) 0; (\bullet) 10; (Δ) 20; (\blacktriangle) 25; (\square) 30; (\blacksquare) 50% (v/v) of MeOH.

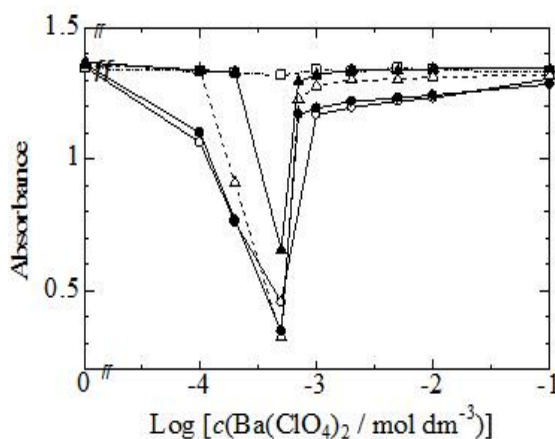


Fig. 4A.5. Changes in absorbance ($\lambda_{\max} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$ in MeCN- H_2O mixtures: (\circ) 0; (\bullet) 1.0; (Δ) 2.0; (\blacktriangle) 3.0; (\square) 5.0% (v/v) of H_2O .

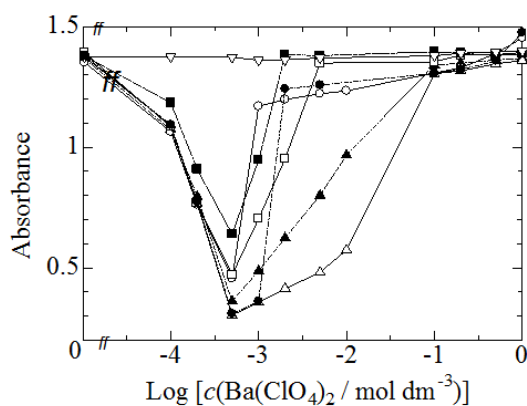


Fig. 4A.6. Changes in absorbance ($\lambda_{\max} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$ in MeCN-MeOH mixtures: (\circ) 0; (\bullet) 2.0; (Δ) 5.0; (\blacktriangle) 10; (\square) 15; (\blacksquare) 20; (∇) 30% (v/v) of MeOH.

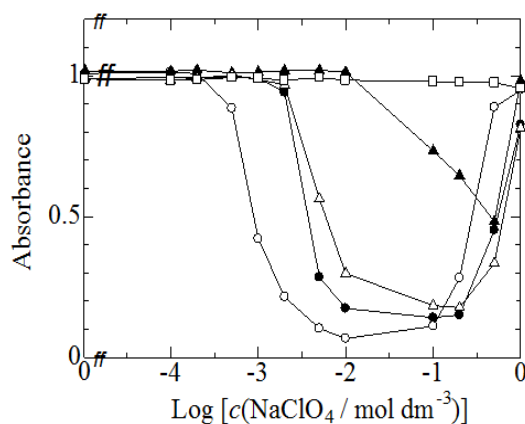


Fig. 4A.7. Absorbance ($\lambda_{\max} = \text{ca. } 290 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ bis(4-nitrophenyl)phosphate (1.0 mm path-length) containing $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Et}_3\text{N}$ in the presence of NaClO_4 in MeCN-MeOH mixtures: (\circ) 0; (\bullet) 2.0; (Δ) 3.0 (\blacktriangle) 5.0; (\square) 10% (v/v) of MeOH.

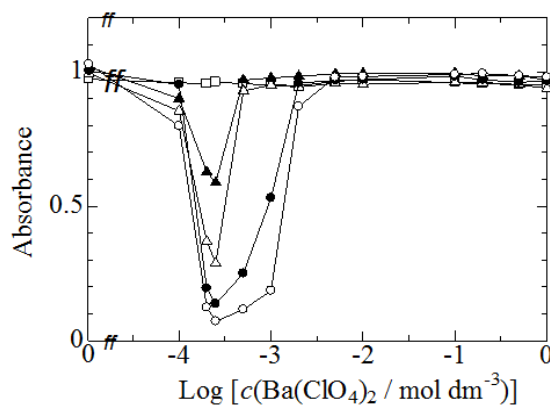


Fig. 4A.8. Absorbance ($\lambda_{\max} = \text{ca. } 290 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ bis(4-nitrophenyl)phosphate containing $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Et}_3\text{N}$ in the presence of $\text{Ba}(\text{ClO}_4)_2$ in MeCN-MeOH mixtures: (\circ) 0; (\bullet) 1.0; (Δ) 2.0; (\blacktriangle) 3.0; (\square) 5.0 (v/v) of MeOH.

Table 4A.1 Precipitation and re-dissolution reactions of diphenylphosphate containing an equivalent amount of Et_3N with barium ions in MeCN- H_2O , MeCN-MeOH, and MeCN-EtOH mixtures.

Metal ions ^a	Equilibrium Constants					
	MeCN-H ₂ O (v/v, H ₂ O %)	1.0	2.0	3.0	5.0	10
Ba ²⁺		●	●	▲	▲	No
	(p <i>K</i> _{sp})	14.45	13.26	12.40	10.49	—
	(p <i>K</i> _{sp})	14.67	13.47	12.61	10.69	—
		○	○	○	○	No

$\log K_1$		4.25	3.95	3.08	–	–
MeCN-MeOH (v/v, MeOH %)		10	15	20		
Ba ²⁺		▲	▲	No		
	(p <i>K</i> _{sp})	12.74	10.94	–		
	(p <i>K</i> _{sp})	12.96	11.16			
		○	○	No		
	$\log K_1$	3.90	3.78	–		
MeCN-EtOH (v/v, EtOH %)		5.0	10	20	30	50
Ba ²⁺		▲	▲	▲	▲	No
	(p <i>K</i> _{sp})	13.92	13.34	12.57	11.39	–
	(p <i>K</i> _{sp})	14.15	13.57	12.81	11.65	–
		○	○	○	○	No
	$\log K_1$	4.45	3.83	3.95	–	–

For the *Explanatory notes*, cf. Table 4.1.

^a MClO₄.

Chapter 5 Specific coordination between alkali metal or alkaline earth metal ions with naphthalenedicarboxylate ions in acetonitrile-water or acetonitrile-methanol binary mixtures

ABSTRACT

In binary acetonitrile-water (MeCN-H₂O) and acetonitrile-methanol (MeCN-MeOH) solvents, the specific interactions between alkali metal (Li⁺, Na⁺) or alkaline earth metal ions (Mg²⁺, Ca²⁺, Ba²⁺) and 1,4- or 2,3-naphthalenedicarboxylate (L²⁻) ions had been examined by UV-visible spectroscopy. As for 1,4-naphthalenedicarboxylate (1×10^{-4} mol dm⁻³), an excess amounts of Na⁺ and Li⁺ causes formation of “reverse-coordinated” species of M₃L⁺ in 10% MeOH-MeCN. Precipitation extent of Li₂L takes place to a large extent than that of Na₂L in 10% MeOH-MeCN. As well, CaL can be formed more than BaL in 10% or 15% H₂O-MeCN. For 2,3-naphthalenedicarboxylate (1×10^{-4} mol dm⁻³), the formed Na₂L and Li₂L cannot be re-dissolved even by 1.0 mol dm⁻³ Na⁺ or Li⁺ in 5.0% H₂O-MeCN. Even in 30% H₂O, the precipitation could take place between Ca²⁺ or Ba²⁺ and L²⁻. The precipitation extent increases in the order of Ca²⁺ > Ba²⁺ > Mg²⁺. The solubility products (pK_{sp}) and the “reverse” coordination constants (log K₃ and log K₂) have been evaluated in MeCN containing various content of MeOH or H₂O.

Keywords: “reverse” coordination; binary solvent; triple ion formation; solubility product; UV-visible spectroscopy.

5.1. Introduction

Aromatic polycarboxyl compounds have been extensively applied as ligand in studying on the coordination complexes, owing to carboxylate group have multiform coordination modes such as monodentate, chelating, and bridging upon metalation [1]. Commonly, many papers focus on constructing transition metal [1-5] and lanthanide metal complexes [6-7] with carboxylates. Due to lacking of partly filled d- or f-shells, alkali metal or alkaline earth metal ions have weaker coordination ability than transition metal ions [8], though they have advantage of being non-toxic, cheap and soluble in aqueous media for applying in pharmaceuticals, dyes and pigments.

Murray and Hiller [9] first suggested involvement of two lithium ions in a ligand loss during one-electron reduction of $\text{Fe}(\text{acac})_3$ in acetonitrile (MeCN) containing LiClO_4 as the supporting electrolyte. Itabashi [10] also suggested the formation of $[\text{CH}_3\text{COOLi}_2]^+$ in MeCN. Based on a pyridinedicarboxylate ligand [11], a coordination polymer $[\text{Li}_6(\text{pda})_3 \cdot 2\text{EtOH}]$ was synthesized which is used as anode for Li-ion battery.

Based on the triple ion theory proposed by Fuoss and Fraus [12], our laboratory keep on studying the specific association behavior of alkali metal (M^+) and alkaline earth metal ions (M^{2+}) in non-aqueous solution over thirty years [13]. By means of voltammetry, conductometry, UV-visible and NMR spectroscopy, we have demonstrated that M^+ or M^{2+} may react with some simple anion (L^-), *e.g.* halides [14], sulfonate [15], carboxylate [16], tropolonate [17], to form precipitates and “reverse-coordinated” species through specific process of precipitation ($\text{M}^+ + \text{L}^- \rightarrow \text{ML}$) and successive re-dissolution ($\text{ML} + \text{M}^+ \rightarrow \text{M}_2\text{L}^+$). The coordination bonding forces as well as Coulombic forces was assigned to the aggregation of metal ions with anions in higher permittivity media ($20 < \epsilon_r < 65$) [18].

Stable carbocations can be produced from trityl halides by addition of perchlorates of Li^+ , Na^+ , Mg^{2+} and Ba^{2+} in MeCN, because of the interaction between halides and metal ions could pull out the halide ions from the partly ionized C^+-X^- bond, causing the formation of trityl ions [19-21]. As well, on basis of the specific interaction between M^+ or M^{2+} and anions, the solvolysis (or hydrolysis) reaction rate of typical $\text{S}_\text{N}1$ substrates ($\text{R}-\text{X}$) can be increased at higher concentration of salt even in “aqueous” solution. Also, we have explained the large salt effects on the indicator acidity and on the proton transfer from tropolone [22] or nitrophenols [23] to amine bases in MeCN in terms of the chemical interaction between the anions and M^+ or M^{2+} .

Ion aggregation behavior has been extensively studied in aqueous-organic or organic-organic mixed solvents [24] which are of considerable importance in understanding organic reaction mechanism [25] and the nature of molecular interaction [26]. We have proposed that the properties of bulk water are altered into those of “dihydrogen ether” $\text{R}[\text{H}]-\text{O}-[\text{H}]\text{R}$ when the huge network of bulk water is distorted by added organic solvents and concentrated salts [27-29].

In previous work, to further convince the coordination ability of M^+ and M^{2+} , the specific interaction of those metal ions and 1,4- or 2,3-naphthalenedicarboxylate ion have been investigated

in MeCN-MeOH and MeCN-H₂O mixed solvents. The solubility products and “reverse” coordination constants have been successfully evaluated for the systems.

5.2. Experimental

5.2.1. Chemicals

1,4- And 2,3-naphthalenedicarboxylic acid was purchased from TCI. Tetrabutylammonium 1,4-naphthalenedicarboxylate $[(n\text{-Bu}_4\text{N}^+)_2 \text{C}_{12}\text{H}_6\text{O}_4^{2-}]$ was prepared from tetrabutylammonium hydroxide ($n\text{-Bu}_4\text{NOH}$, Wako) and the equivalence of 1,4-naphthalenedicarboxylic acid (1.0 g) in methanol. The solution was evaporated to dryness at 50 °C, and the salt was dried in vacuo at 50 °C. Tetrabutylammonium 2,3-naphthalenedicarboxylate was prepared from 2,3-naphthalenedicarboxylic acid in a similar way.

Metal perchlorates without hydrate water, LiClO_4 , 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 °C to obtain anhydrous $\text{Ca}(\text{ClO}_4)_2$. Acetonitrile and methanol from Wako were used as received. Water was purified by means of a MilliQ system (Millipore Corp.). The percentage of the solvent in binary solvents is all expressed by the volume fraction [% (v/v)] in the present paper.

5.2.2. Apparatus and procedure

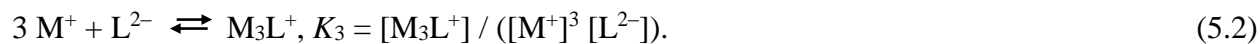
UV-visible absorption spectra were measured at room temperature using a Shimadzu double-beam spectrophotometer (model UV-2550) in 0.05 and 0.1 cm path-length quartz cuvettes. When precipitation occurred, the solution was sonicated for a few minutes in a Branson ultrasonic bath (model Yamato 2510, 42 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 a precipitation reaction.

5.2.3. Evaluation of “reverse” coordination formation constants

The “reverse” coordination formation constants between the alkali metal cations (M^+) and the “ligand” anions (L^{2-}) are evaluated by the UV-visible spectroscopic data as the method previously proposed [16] as follows:

(a) In the case of ion charges of 1:2 (M^+ and L^{2-})

The reactions and equilibrium constants for precipitation dissolution (solubility products, K_{sp}) and “reverse” coordination (K_3) at higher M^+ concentrations, compared to L^{2-} , are expressed by Eqs. 5.1 and 5.2, respectively.



The solubility s of M_2L or the total “ligand” concentration, c_t , in solution (and not in precipitation) is expressed by Eq. 5.3.

$$s = c_t = [L^{2-}] + [M_3L^+] = K_{sp} [M^+]^{-2} (1 + K_3 [M^+]^3). \quad (5.3)$$

Neglecting the formation of the $[M_4L^{2+}]$ species, the observed absorbance A_{bs} of L^{2-} (and M_3L^+) can be rationalized by Lambert-Beer’s law as, $A_{bs} = \varepsilon c l \sim \varepsilon s l$ (5.4)

Where ε , c , and l are the molar absorptivity ($\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$) of L^{2-} (or M_3L^+), the concentration (mol dm^{-3}), and the path-length (cm), respectively. Eq. 5.5 is given by introducing Eq. 5.3 into Eq. 5.4.

$$A_{bs} = \varepsilon l c_t = \varepsilon l K_{sp} [M^+]^{-2} (1 + K_3 [M^+]^3). \quad (5.5)$$

With higher M^+ concentrations and larger K_3 values, equation 5.5 can be arranged to be $A_{bs} = \varepsilon l K_{sp} K_3 [M^+]$.

(b) In the case of ion charges of 2:2 (M^{2+} and L^{2-})

The evaluating method of the “reverse” coordination formation constants between the alkaline earth metal cations (M^{2+}) and the “ligand” anions (L^{2-}) is shown in Chapter 2.

5.3. Results and discussion

5.3.1. Specific interactions between 1,4-naphthalenedicarboxylate (L^{2-}) and alkali metal ions (Li^+ , Na^+) in MeCN-MeOH mixtures.

Acetonitrile of a relatively high permittivity ($\epsilon_r = \text{ca. } 36$, [30]) is not only an aprotic solvent but also a protophobic solvent [31]. Due to its weak solvation ability ($\text{DN} = 14.1$, $\text{AN} = 19.3$, [32]) the salt of 1,4- and 2,3-naphthalenedicarboxylate tetrabutylammonium cannot be dissolved completely in sole MeCN, thus the coordination behaviors of carboxylates with alkali metal or alkaline earth metal ions are examined in MeCN containing protic solvent of MeOH and H_2O .

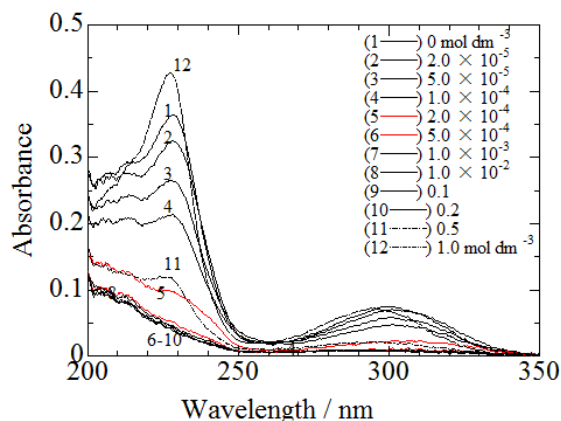
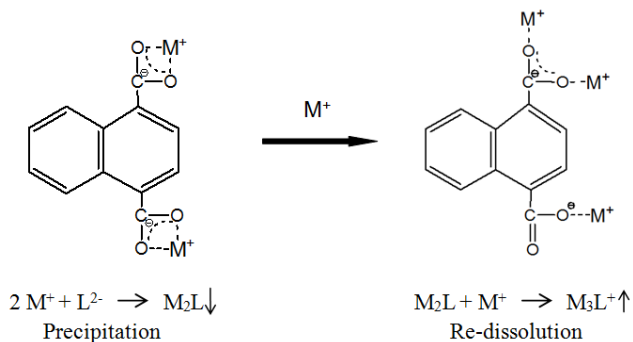


Fig. 5.1. UV spectra of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion (0.1 cm path-length) with increasing concentration of LiClO_4 in MeCN containing 2.0% (v/v) MeOH.



Scheme 5.1. Successive formation of M_2L and M_3L^+ ($\text{M} = \text{Li, Na}$) for 1,4-naphthalenedicarboxylate.

Fig. 5.1 shows the UV spectra of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion $[(\text{Bu}_4\text{N}^+)_2\text{L}^{2-}]$ with increasing concentration of LiClO_4 in MeCN containing 2.0% MeOH. The L^{2-} ion gives a distinct peak around 228 nm ($\epsilon/\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3 = \text{ca. } 3.7 \times 10^4$) and the aromatic band around 300 nm is very weak. The band at 228 nm gradually decreases with increasing concentration of LiClO_4 , and disappears in the presence of $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Li}^+$, accompanying white precipitates (Li_2L). However, the absorbance of the solution increases and finally exceeds the original value by addition of $1.0 \text{ mol dm}^{-3} \text{ Li}^+$, showing a slight blue shift ($\lambda_{\text{max}} = 227.0$), which

owing to the form the “reverse-coordinated” species of Li_3L^+ by the successive re-dissolution of Li_2L (Scheme 5.1). The phenomenon of first precipitation and successive re-dissolution proves that the specific interaction could take place between Li^+ and 1,4-naphthalenedicarboxylate ion in MeCN-MeOH mixtures.

Fig. 5.2 shows the trend of precipitation and re-dissolution of lithium ions and L^{2-} with increasing content of MeOH (2.0 – 20%) in MeCN. In 10% MeOH, the precipitation still occurs completely, even takes place to a larger extent than in 2.0% MeOH: the values of the product solubility ($\text{p}K_{\text{sp}}$) are evaluated as 11.64 and 13.27 in 2.0 and 10% MeOH, respectively (*cf.* Table 5.1), even though the precipitates re-dissolves to a larger extent by addition of $0.5 \text{ mol dm}^{-3} \text{ LiClO}_4$: the absorbance are 0.103 and 0.313 in 2.0 and 10% MeOH, respectively. In previous study, it have been observed that 10% MeOH totally inhabited the interaction between Li^+ and 1,3,6-naphthalenetrisulfonate ion (Chapter 3) or diphenylphosphinate ion (Chapter 4). However, even in 15% MeOH, the precipitation could largely take place. No precipitation and re-dissolution could be observed in 20% MeOH.

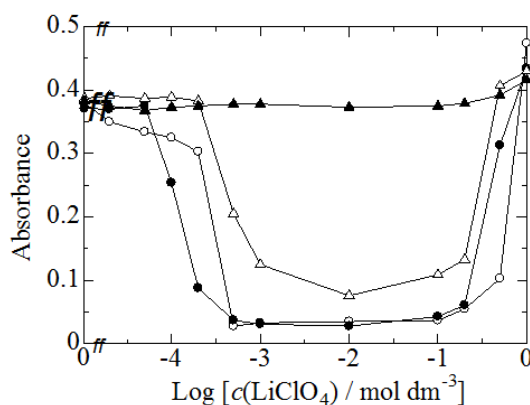


Fig. 5.2. Absorbance ($\lambda_{\text{max}} = \text{ca. } 228 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion in the presence of LiClO_4 in MeCN-MeOH mixtures: (○) 2.0; (●) 10; (△) 15; (▲) 20% (v/v) of MeOH.

The UV spectrum changes of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion with increasing concentration of NaClO_4 in 2.0% MeOH-MeCN are shown in Fig. 5.3. As well as LiClO_4 , $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ NaClO}_4$ causes the absorbance peak disappear and $0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$ results in successive absorbance increase, the precipitates re-dissolve completely in presence of $1.0 \text{ mol dm}^{-3} \text{ NaClO}_4$.

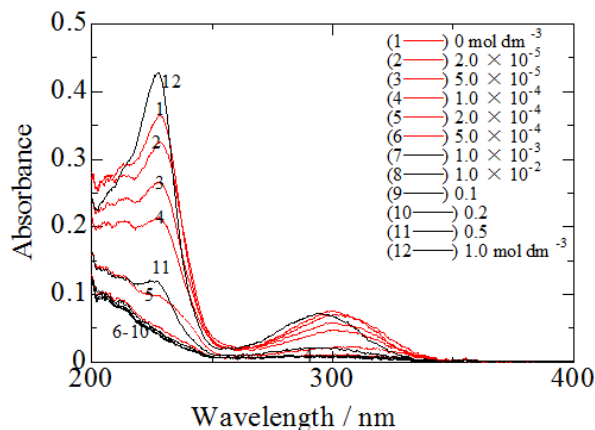


Fig. 5.3. UV spectra of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion (0.1 cm path-length) with increasing concentration of NaClO_4 in MeCN containing 2.0% (v/v) MeOH .

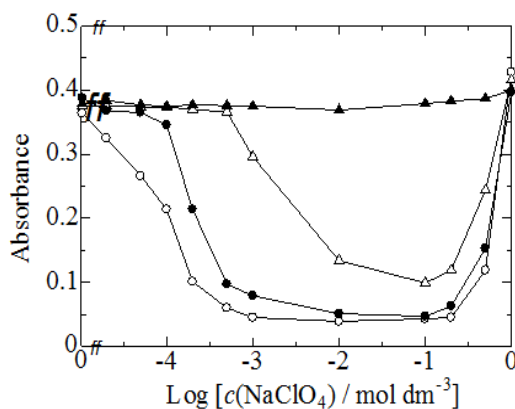


Fig. 5.4. Absorbance ($\lambda_{\text{max}} = \text{ca. } 228 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion in the presence of NaClO_4 in MeCN - MeOH mixtures: (○) 2.0; (●) 5.0; (Δ) 10; (▲) 20% (v/v) of MeOH .

The precipitation between Na^+ and L^{2-} is unexpectedly weaker than that of Li_2L (Fig. 5.4 and Fig. 5.3) in MeCN - MeOH mixtures, the re-dissolution or “reverse” coordination is also easier to take place. In 10% MeOH , the precipitation of Na_2L ($\text{p}K_{\text{sp}} = 9.24$, Table 5.1) becomes incomplete, while that of Li_2L ($\text{p}K_{\text{sp}} = 13.27$, Table 5.1) takes place completely. Because of its larger size, sodium ion is considered to be more difficult to react with precipitates. In sole MeCN , MeCN - H_2O , and MeCN - MeOH mixed solvent, the precipitation of sodium 1,3,6-naphthalenetrisulfonate took place to a larger extent than that of lithium 1,3,6-naphthalenetrisulfonate (Chapter 3). However, in acetone, the Li^+ ion has a stronger tendency than Na^+ to associate with diphenylphosphate ion [15]. No apparent interaction between Na^+ and L^{2-} is observed in 20% MeOH .

5.3.2. Specific interactions between 1,4-naphthalenedicarboxylate (L^{2-}) and alkaline earth metal ions (Mg^{2+} , Ca^{2+} , Ba^{2+}) in MeCN- H_2O mixtures.

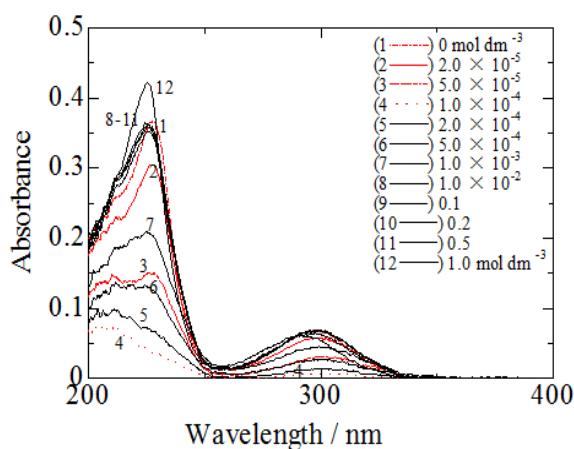
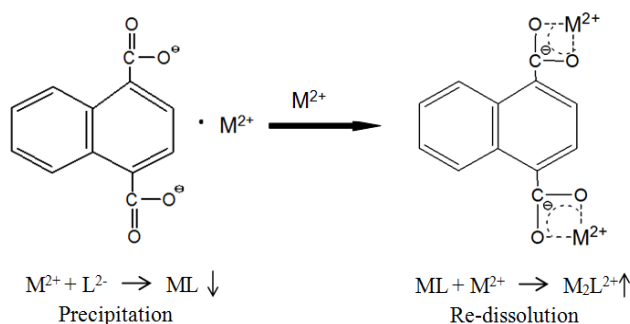


Fig. 5.5. UV spectra of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion (0.1 cm path-length) with increasing concentration of $Mg(ClO_4)_2$ in MeCN containing 5.0% (v/v) H_2O .



Scheme 5.2. Successive formation of ML and M_2L^{2+} ($M = Mg, Ca, Ba$) for 1,4-naphthalenedicarboxylate in MeCN containing 2.0% and 5.0% H_2O .

Fig. 5.5 shows the spectral changes of $1.0 \times 10^{-4} \text{ mol dm}^{-3} L^{2-}$ with increasing concentration of $Mg(ClO_4)_2$ in 5.0% H_2O -MeCN. Firstly, the absorbance of L^{2-} decreases gradually, the peak at 228 nm almost disappears at the equivalent point of Mg^{2+} , the absorbance begins to increase with addition of $5.0 \times 10^{-4} \text{ mol dm}^{-3} Mg^{2+}$, finally a “reverse-coordinated” species of Mg_2L^{2+} completely forms by a large excess concentration of Mg^{2+} (Scheme 5.2).

Fig. 5.6 shows the precipitation and the successive re-dissolution of MgL in MeCN- H_2O (2.0 – 15%) mixtures. Complete precipitation occurs at 2.0 and 5.0% H_2O . In 2.0% H_2O -MeCN, the absorbance minimum appears at 5.0×10^{-5} but not $1.0 \times 10^{-4} \text{ mol dm}^{-3} Mg^{2+}$, may be due to the low solubility of formed species, MgL_2^{2-} . With increasing content of water, the solubility of

precipitation increases: the pK_{sp} values are 10.21, 10.00 and 8.34 for 2.0, 5.0 and 10.0% H_2O , respectively (*cf.* Table 5.2). No apparent interaction is observed in 15% H_2O .

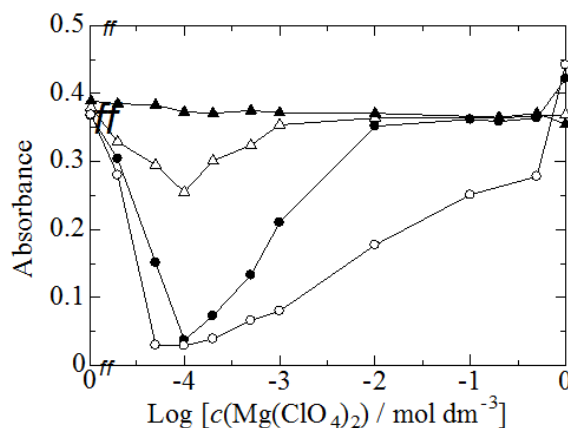


Fig. 5.6. Absorbance ($\lambda_{max} = \text{ca. } 228 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion in the presence of $Mg(ClO_4)_2$ in MeCN- H_2O mixtures: (○) 2.0; (●) 5.0; (Δ) 10; (▲) 15% of H_2O (v/v).

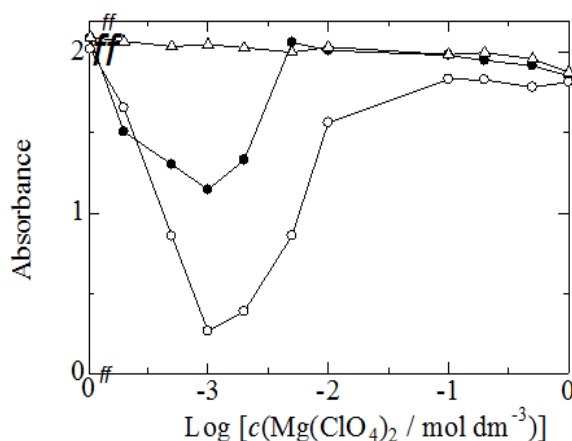


Fig. 5.7. Absorbance ($\lambda_{max} = \text{ca. } 228 \text{ nm}$, 0.05 cm path-length) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion in the presence of $Mg(ClO_4)_2$ in MeCN- H_2O mixtures: (○) 10; (●) 15; (Δ) 20% of H_2O (v/v).

However, the precipitation between 10-fold concentration of $1.0 \times 10^{-3} \text{ mol dm}^{-3} L^{2-}$ and Mg^{2+} could be observed in 15% H_2O (Fig. 5.7). By performing experiments with higher concentration of L^{2-} , we can obtain the equilibrium constants in mixtures containing a larger amount of H_2O . The solubility product of MgL and formation constant of MgL^{2+} in 15% H_2O are given to be 6.52 and 6.03, respectively (Table 5.2). Meanwhile, the equilibrium values evaluated from different L^{2-} concentration in 10% H_2O are well consistent.

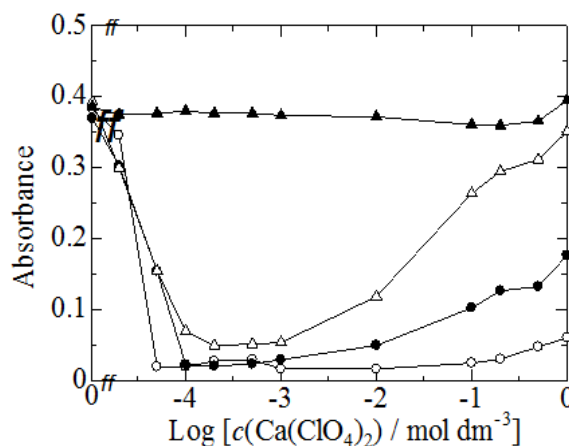


Fig. 5.8. Absorbance ($\lambda_{\max} = \text{ca. } 228 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion in the presence of $\text{Ca}(\text{ClO}_4)_2$ in MeCN- H_2O mixtures: (\circ) 2.0; (\bullet) 10; (Δ) 15; (\blacktriangle) 20% (v/v) of H_2O .

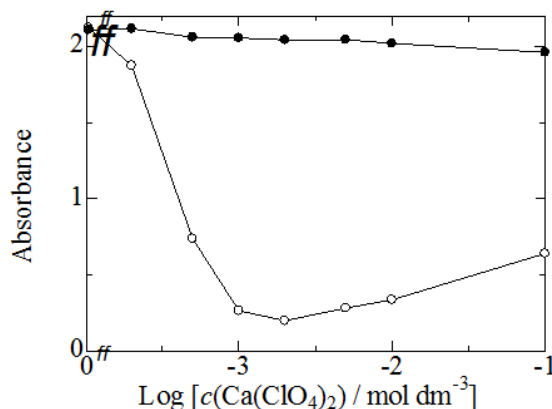


Fig. 5.9. Absorbance ($\lambda_{\max} = \text{ca. } 228 \text{ nm}$, 0.05 cm path-length) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion in the presence of $\text{Ca}(\text{ClO}_4)_2$ in MeCN- H_2O mixtures: (\circ) 20; (\bullet) 30% (v/v) of H_2O .

As well, the L^{2-} absorbance minimum appears at an half equivalent amount of Ca^{2+} ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$) in 2.0% H_2O (Fig. 5.8), and the precipitates of CaL would not be re-dissolved by the addition of a large excess concentration of Ca^{2+} . In 10% H_2O , precipitation occurs completely and CaL partially re-dissolves to Ca_2L^{2+} by the addition of $1.0 \text{ mol dm}^{-3} \text{ Ca}^{2+}$. In 15% H_2O -MeCN, the precipitation becomes incomplete but still take place to a large extent. Even 15% H_2O only affect the precipitate on a small scale, the $\text{p}K_{\text{sp}}$ values of CaL in 2.0, 10, and 15% H_2O are given to be 10.57, 10.41, and 9.51, respectively. However, the re-dissolution is largely promoted by 15% H_2O , the precipitates are almost completely re-dissolved by the addition of $1.0 \text{ mol dm}^{-3} \text{ Ca}^{2+}$ (Scheme 5.2). 20% H_2O inhibits the specific interaction between Ca^{2+} and L^{2-} . The equilibrium

constants in 20% H₂O are obtained as 7.81 and 5.29 for pK_{sp} and $\log K_2$ (*cf.* Table 5.2) by observing the interaction of $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ L}^{-2}$ with Ca^{2+} of wide concentration range, which precipitation actually takes place to a larger extent in 20% H₂O (Fig. 5.9).

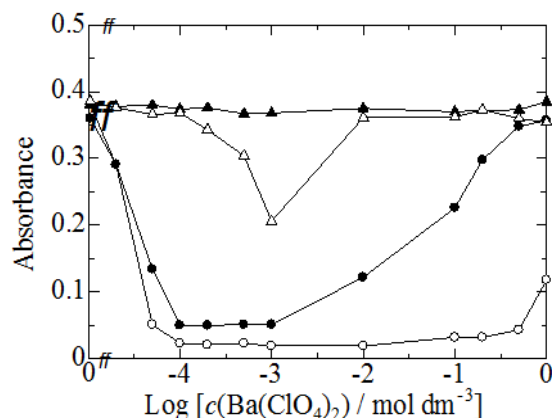


Fig. 5.10. Absorbance ($\lambda_{\max} = \text{ca. } 228 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion in the presence of $\text{Ba}(\text{ClO}_4)_2$ in MeCN-H₂O mixtures: (○) 2.0; (●) 10; (Δ) 15; (▲) 20% (v/v) of H₂O.

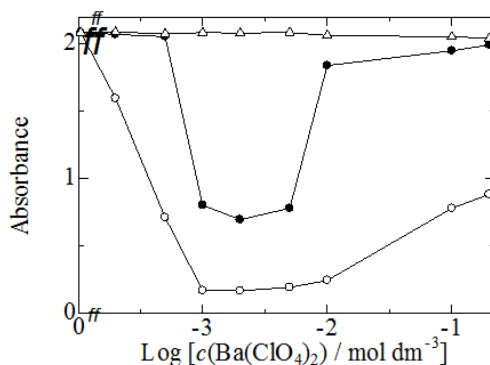


Fig. 5.11. Absorbance ($\lambda_{\max} = \text{ca. } 228 \text{ nm}$, 0.05 cm path-length) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ion in the presence of $\text{Ba}(\text{ClO}_4)_2$ in MeCN-H₂O mixtures: (○) 15; (●) 20; (Δ) 30% (v/v) of H₂O.

The precipitation extent of BaL is smaller than that of CaL (Fig. 5.10). In 10% H₂O-MeCN, the precipitates of BaL re-dissolves to Ba_2L^{2+} (Scheme 5.2) completely. In 15% H₂O, the precipitation of BaL slightly takes place, the solubility products of CaL and BaL are evaluated as 9.50 and 7.30 (*cf.* Table 5.2), respectively. However, it have been observed that the precipitation interactions of barium with diphenylphosphinate and 1,5-naphthalenedisulfonate could take place

to a larger extent than that of Ca^{2+} . The effect of Ca^{2+} on formation of the trityl cation from trityl halides were exceptionally large than Ba^{2+} [19]. The equilibrium constants in higher content of water as 20% and 30% can be obtained by performing the experiment in $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ L}^{2-}$ (Fig. 5.11 and Table 5.2).

In previous study [16], the coordination ability of 3- and 4-nitrophthalate ions with Mg^{2+} , Ca^{2+} and Ba^{2+} have been examined in MeCN. The precipitation extent increases in the order of $\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$. However, the precipitation of 1,4-naphthalenedicarboxylate with alkaline earth metal ions is as the order of $\text{Ca}^{2+} > \text{Ba}^{2+} > \text{Mg}^{2+}$ (*cf.* Table 5.2). Reversely, the “reverse” coordination ability increases in the order $\text{Ca}^{2+} < \text{Ba}^{2+} < \text{Mg}^{2+}$.

5.3.3. Specific interactions between 2,3-naphthalenedicarboxylate (L^{2-}) and alkali metal ions (Li^+ , Na^+) in MeCN- H_2O mixtures.

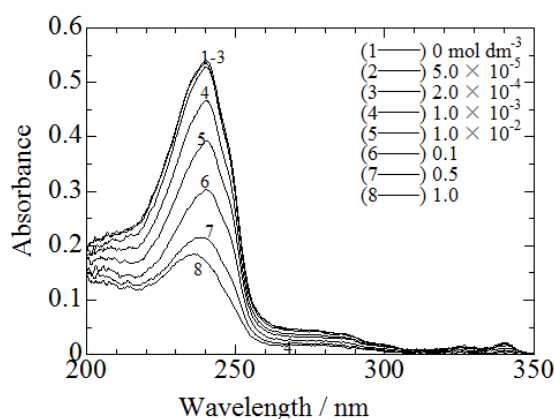


Fig. 5.12. UV spectra of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 2,3-naphthalenedicarboxylate ion (0.1 cm path-length) with increasing concentration of NaClO_4 in MeCN containing 5.0% (v/v) H_2O .

The 2,3-naphthalenedicarboxylate ion ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$) gives a strong peak at around 239 nm ($\epsilon/\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3 = \text{ca. } 5.4 \times 10^4$) in MeCN containing with 5.0% (v/v) H_2O , which is shown in Fig. 5.12. With increasing concentration of NaClO_4 , the absorbance gradually decreases but never recovers again, the absorbance appears as 0.184 at $1.0 \text{ mol dm}^{-3} \text{ Na}^+$. The additional water inhibits the interaction between ions, more sodium ions needed to form precipitates. From other point of view, it also proves that ionic strength cannot affect the association of Na_2L in this system.

Fig. 5.13 shows the precipitation and the successive re-dissolution of Na_2L in $\text{MeCN-H}_2\text{O}$ (2.0 – 10%) mixtures. In 2.0% H_2O , the L^{2-} absorbance decreases with increasing concentration of NaClO_4 , and reaches its minimum at $0.5 \text{ mol dm}^{-3} \text{ Na}^+$, the precipitates of Na_2L cannot be completely re-dissolved by $1.0 \text{ mol dm}^{-3} \text{ Na}^+$. The solubility products in 2.0 and 5.0% H_2O are given to be 11.87 and 11.43, respectively (*cf.* Table 5.3). No apparent interaction is observed in 10% H_2O .

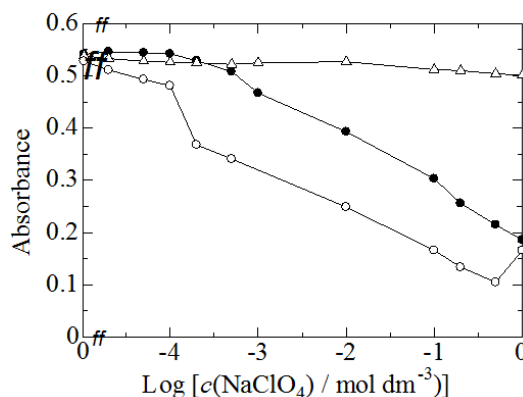


Fig. 5.13. Absorbance ($\lambda_{\text{max}} = \text{ca. } 239 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 2,3-naphthalenedicarboxylate ion in the presence of NaClO_4 in $\text{MeCN-H}_2\text{O}$ mixtures: (\circ) 2.0; (\bullet) 5.0; (Δ) 10% (v/v) of H_2O .

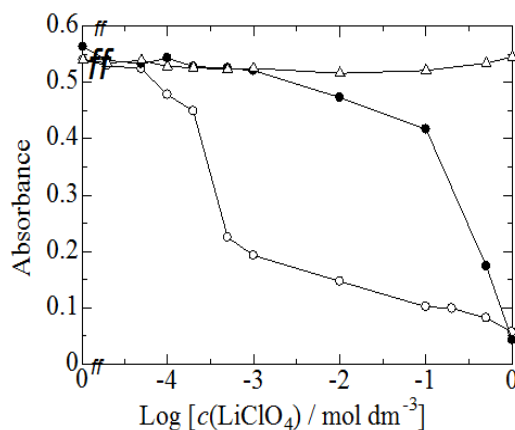


Fig. 5.14. Absorbance ($\lambda_{\text{max}} = \text{ca. } 239 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 2,3-naphthalenedicarboxylate ion in the presence of LiClO_4 in $\text{MeCN-H}_2\text{O}$ mixtures: (\circ) 2.0; (\bullet) 5.0; (Δ) 10% (v/v) of H_2O .

Fig. 5.14 shows the specific interaction between lithium ion and L^{2-} in $\text{MeCN-H}_2\text{O}$ (2.0 – 10%) mixtures. The precipitates of LiL_2 could take place in 2.0 and 5.0% H_2O , but cannot be re-dissolved by an excess amount of Li^+ . In 2.0% H_2O , the absorbance minimum of L^{2-} shows as 0.105 at $0.5 \text{ mol dm}^{-3} \text{ Na}^+$ but 0.057 at $1.0 \text{ mol dm}^{-3} \text{ Li}^+$. 10% H_2O inhibits the interaction between

Li^+ and L^{2-} .

5.3.4. Specific interactions between 2,3-naphthalenedicarboxylate (L^{2-}) and alkaline earth metal ions (Mg^{2+} , Ca^{2+} , Ba^{2+}) in $\text{MeCN-H}_2\text{O}$ mixtures.

The precipitation and the successive re-dissolution of MgL in 2.0 – 10% $\text{H}_2\text{O-MeCN}$ is shown in Fig. 5.15. Incomplete precipitation occurs at 2.0 and 5.0% H_2O . In 2.0% H_2O , the absorbance minimum appears at an equivalent amount of Mg^{2+} ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$), the precipitates of MgL successively re-dissolves to Mg_2L^{2+} with addition of an excess amount of Mg^{2+} (Scheme 5.3). With increasing content of water, the solubility of precipitates increases: the $\text{p}K_{\text{sp}}$ values are 8.82, 8.29 for 2.0, 5.0% H_2O , respectively (*cf.* Table 5.4). No apparent interaction is observed in 10% H_2O .

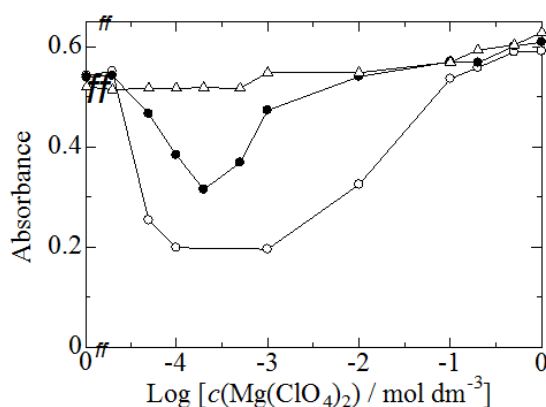
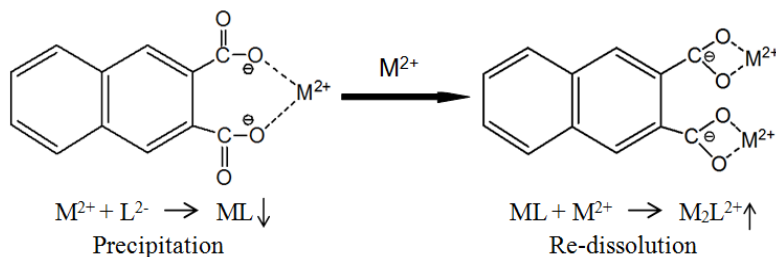


Fig. 5.15. Absorbance ($\lambda_{\text{max}} = \text{ca. } 239 \text{ nm}$) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 2,3-naphthalenedicarboxylate ion in the presence of $\text{Mg}(\text{ClO}_4)_2$ in $\text{MeCN-H}_2\text{O}$ mixtures: (\circ) 2.0; (\bullet) 5.0; (Δ) 10% (v/v) of H_2O .



Scheme 5.3. Successive formation of ML and M_2L^{2+} ($\text{M} = \text{Mg, Ca, Ba}$) for the 2,3-naphthalenedicarboxylate ion.

Fig. 5.16 shows the precipitation and the successive re-dissolution of CaL in the binary $\text{MeCN-H}_2\text{O}$ (10 – 50%) solvents. In 10% H_2O , 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 CaClO_4 . In 20% H_2O , Ca^{2+} can react with L^{2-} to cause partial precipitation of CaL. The absorbance minimum of 0.099 is given in the presence of $2.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ca}^{2+}$, the “reverse-coordinated” species cannot be formed by $1.0 \text{ mol dm}^{-3} \text{ Ca}^{2+}$ even in 20% H_2O . The precipitation of CaL only occurs slightly at 1.0×10^{-3} and $1.0 \times 10^{-2} \text{ mol dm}^{-3} \text{ Ca}^{2+}$ in 30% H_2O . The solubility product of CaL for 2,3-naphthalenedicarboxylate ion is given as 10.37 (*cf.* Table 5.4), which is close to the value of 10.41 for 1,4-naphthalenedicarboxylate ion (*cf.* Table 5.2). However, the interaction between Ca^{2+} and 1,4-naphthalenedicarboxylate ion is totally inhibited in 20% H_2O -MeCN, though slight precipitation for 2,3-naphthalenedicarboxylate ion could take place in 30% H_2O . No apparent interaction of L^{2-} with Ca^{2+} is observed in 50% H_2O .

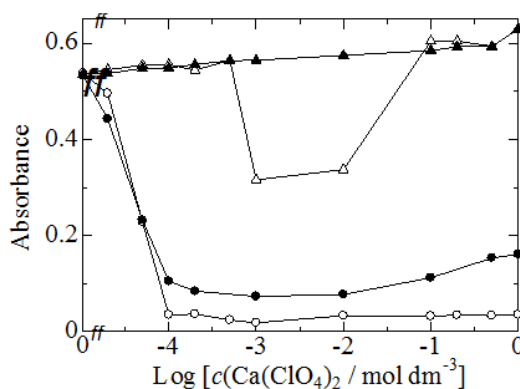


Fig. 5.16. Absorbance (λ_{max} = ca. 239 nm) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 2,3-naphthalenedicarboxylate ion in the presence of $\text{Ca}(\text{ClO}_4)_2$ in MeCN- H_2O mixtures: (○) 10; (●) 20; (Δ) 30; (▲) 50% (v/v) of H_2O .

Fig. 5.17 shows the UV spectral changes of 2,3-naphthalenedicarboxylate ion with increasing concentration of $\text{Ba}(\text{ClO}_4)_2$. When $\text{Ba}(\text{ClO}_4)_2$ is added to the solution, the L^{2-} absorbance gradually decreases, and the peak reaches its minimum at $2.0 \times 10^{-4} \text{ mol dm}^{-3}$, accompanying white precipitates (BaL). The solubility of BaL is very small, showing partial re-dissolution by the addition of $1.0 \text{ mol dm}^{-3} \text{ Ba}^{2+}$, which can also be seen in Fig. 5.18. The “reverse-coordinated” species of Ba_2L^{2+} formed from BaL is shown in scheme 5.3.

Fig. 5.18 shows the precipitation and re-dissolution of BaL in MeCN- H_2O mixtures. In 10% H_2O , the precipitation completely takes place between Ba^{2+} and L^{2-} , and could not be re-dissolved by the addition of $1.0 \text{ mol dm}^{-3} \text{ Ba}^{2+}$. With increasing content of H_2O , the precipitation becomes incomplete, and the re-dissolution is promoted (*cf.* Table 5.4). No apparent interaction is observed

in 50% H₂O.

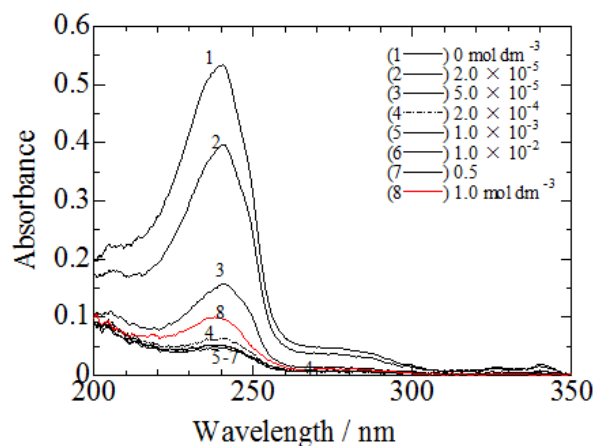


Fig. 5.17. UV spectra of 1.0×10^{-4} mol dm⁻³ 2,3-naphthalenedicarboxylate ion (0.1 cm path-length) with increasing concentration of Ba(ClO₄)₂ in MeCN containing 10% (v/v) H₂O.

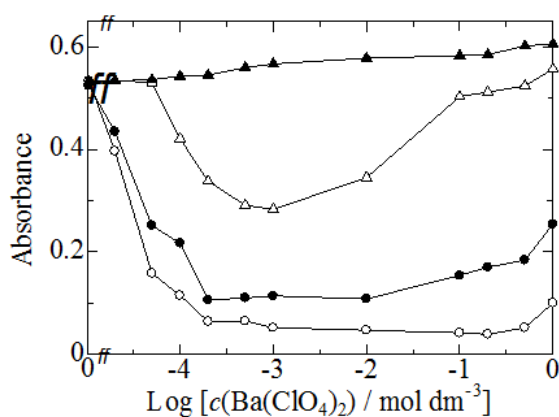


Fig. 5.18. Absorbance (λ_{max} = ca. 239 nm) of 1.0×10^{-4} mol dm⁻³ 2,3-naphthalenedicarboxylate ion in the presence of Ba(ClO₄)₂ in MeCN-H₂O mixtures: (○) 10; (●) 20; (Δ) 30; (▲) 50% (v/v) of H₂O.

5.4. Conclusion

In the present study, the specific coordination of alkali metal (M⁺) or alkaline earth metal ions (M²⁺) with the 1,4- and 2,3-naphthalenedicarboxylate ions have been observed in MeCN-MeOH and MeCN-H₂O binary mixtures. We have demonstrated that the precipitation of the non-charged species, *i.e.* M₂L and ML and the successive formation of the “reverse-coordinated” species (M₃L⁺ and ML⁺) take place in aprotic-protic solvents. The interaction behaviors suggest that the “reverse” coordination should increase in the order of Li⁺ < Na⁺ and Ca²⁺ < Ba²⁺ < Mg²⁺, showing difference from the results of previous study (Chapter 2, 3 and 4). Even in 30% H₂O, the precipitation of CaL or BaL (1.0×10^{-4} mol dm⁻³ 2,3-naphthalenedicarboxylate) could take place. However, 20% H₂O

totally inhibits the interaction be observed between Ca^{2+} or Ba^{2+} and $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate. The “reverse” coordination constants ($\log K_3$, $\log K_2$) have been successfully evaluated for all the systems. By performing the experiment with higher concentration of L^{2-} ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$), we can obtain the equilibrium constants in the solvents of higher content H_2O .

Table 5.1 Precipitation and re-dissolution reactions of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 1,4-naphthalenedicarboxylate ions with Li^+ and Na^+ ions in MeCN-MeOH mixtures.

Metal ions ^a	Equilibrium Constants ^b	MeCN-MeOH (v/v, MeOH %)				
		2.0	5.0	10	15	20
Li^+		●		●	▲	No
	($\text{p}K_{\text{sp}}$)	11.64		13.27	10.54	–
	($\text{p}K_{\text{sp}}$) ^c	11.78		13.41	10.68	–
		○		○	○	No
	$\log K_3$	7.28		9.43	6.73	–
Na^+		●	●	▲		No
	($\text{p}K_{\text{sp}}$)	13.07	12.17	9.24		–
	($\text{p}K_{\text{sp}}$) ^c	13.21	12.31	9.38		–
		○	○	○		No
	$\log K_3$	8.81	8.06	5.31		–

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 re-dissolution of precipitation, respectively. The mark “No” indicates no precipitation or no re-dissolution.

^a MClO_4 .

^b Solubility products (K_{sp}) and “reverse” coordination constants (K_3), *cf.* the Experimental section in Ref. [16]. The uncertainties (errors) in K_{sp} values and “reverse” coordination constants may be less than ± 0.01 and ± 0.05 , respectively, in this table and Tables 5.2 – 5.4.

^c 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. [34].

Table 5.2 Precipitation and re-dissolution reactions of 1.0×10^{-4} or $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ 1,4-

naphthalenedicarboxylate ions with alkaline earth metal ions in MeCN-H₂O mixtures.

Metal ions (mol dm ⁻³) ^a	Equilibrium Constants ^b	MeCN-H ₂ O (v/v, H ₂ O %)					
		2.0	5.0	10	15	20	30
Mg ²⁺ (1.0 × 10 ⁻⁴)		●	●	▲	No		
	(pK _{sp})	10.21	10.00	(8.34)	–		
	(pK _{sp}) ^c	10.57	10.34	(8.65)	–		
		○	○	○	No		
	log K ₂	7.81	7.92	(7.59)	–		
Mg ²⁺ (1.0 × 10 ⁻³)				▲	▲	No	
	(pK _{sp})			7.77	6.52	–	
	(pK _{sp}) ^c			8.77	7.44	–	
				○	○	No	
	log K ₂			6.70	6.03	–	
Ca ²⁺ (1.0 × 10 ⁻⁴)		●		●	▲	No	
	(pK _{sp})	10.57		10.41	9.5	–	
	(pK _{sp}) ^c	10.93		10.72	9.79	–	
		No		△	○	No	
	log K ₂	–		6.09	6.34	–	
Ca ²⁺ (1.0 × 10 ⁻³)						▲	No
	(pK _{sp})					7.81	–
	(pK _{sp}) ^c					8.67	
						△	No
	log K ₂					5.29	–
Ba ²⁺ (1.0 × 10 ⁻⁴)		●		●	▲	No	
	(pK _{sp})	10.43		9.71	(7.30)	–	
	(pK _{sp}) ^c	10.79		10.02	(7.59)		
		No		○	○	No	
	log K ₂	–		6.51	–	–	
Ba ²⁺ (1.0 × 10 ⁻³)					▲	▲	No
	(pK _{sp})				8.17	6.83	–
	(pK _{sp}) ^c				9.09	7.69	–
					△	○	No
	log K ₂				5.74	4.80	–

For the *Explanatory notes*, cf. Table 5.1.

^a M(ClO₄)₂.

^b Solubility products (K_{sp}) and “reverse” coordination constants (K_2), *cf.* the Experimental section in Ref. [16].

^c *Cf.* Table 5.1, note c for the thermodynamic solubility products (K_{sp}) corrected with the activity coefficients of ions.

Table 5.3 Precipitation and re-dissolution reactions of 1.0×10^{-4} mol dm⁻³ 2,3-naphthalenedicarboxylate ions with Li⁺ or Na⁺ ion in MeCN-H₂O mixtures.

Metal ions ^a	Equilibrium Constants ^b	MeCN- H ₂ O (v/v, H ₂ O %)		
		2.0	5.0	10
Li ⁺		▲	▲	No
	(pK_{sp})	11.73	11.48	–
	(pK_{sp}) ^c	11.86	11.61	–
		No	No	No
	log K_3	–	–	–
Na ⁺		▲	▲	No
	(pK_{sp})	11.87	11.43	–
	(pK_{sp}) ^c	12.00	11.56	–
		No	No	No
	log K_3	–	–	–

For the *Explanatory notes*, *cf.* Table 5.1.

^a MClO₄.

^b Solubility products (K_{sp}) and “reverse” coordination constants (K_3), *cf.* the Experimental section in Ref. [16].

^c *Cf.* Table 5.1, note c for the thermodynamic solubility products (K_{sp}) corrected with the activity coefficients of ions.

Table 5.4 Precipitation and re-dissolution reactions of 1.0×10^{-4} mol dm⁻³ 2,3-naphthalenedicarboxylate ions with alkaline earth metal ions in MeCN-H₂O mixtures.

Metal ions ^a	Equilibrium Constants ^b	MeCN- H ₂ O (v/v, H ₂ O %)					
		2.0	5.0	10	20	30	50
Mg ²⁺		▲	▲	No			
	(p <i>K</i> _{sp})	8.82	8.29	–			
	(p <i>K</i> _{sp}) ^c	9.18	8.63	–			
		○	○	No			
	log <i>K</i> ₂	6.52	7.18	–			

		●	▲	▲	No
Ca ²⁺	(pK _{sp})	10.37	9.41	7.23	–
	(pK _{sp}) ^c	10.68	9.68	7.47	–
		No	△	○	No
	log K ₂	–	5.17	4.96	–
Ba ²⁺	(pK _{sp})	9.34	8.77	8.20	–
	(pK _{sp}) ^c	9.65	9.04	8.44	–
		No	△	○	No
	log K ₂	–	–	5.58	–

For the *Explanatory notes*, cf. Table 5.1.

^a M(ClO₄)₂.

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

^c Cf. Table 5.1, note c for the thermodynamic solubility products (K_{sp}) corrected with the activity coefficients of ions.

References

- [1] X.J. Jiang, J.H. Gu, M. Dua, J.S. Li, Polyhedron 28 (2009) 3759.
- [2] A. Pichon, C.M. Fierro, M. Nieuwenhuyzen, S.L. James, CrystEngComm 9 (2007) 449.
- [3] Q.R. Fang, G.S. Zhu, Z. Jin, M. Xue, X. Wei, D.J. Wang, S.L. Qiu, Angew. Chem. Int. Ed. 45 (2006) 6126.
- [4] J.L.C. Rowsell, O. M. Yaghi, J. Am. Chem. Soc. 128 (2006) 1304.
- [5] J.Y. Lee, D. H. Olson, L. Pan, T.J. Emge, J. Li, Adv. Funct. Mater, 17 (2007) 1255.
- [6] M. Hu, H. Zhao, E.C. Sañudo, M. Chen, Polyhedron 101 (2015) 270.
- [7] M. Fang, X. Li, P. Cui, B. Zhao, J. Solid State Chem. 223 (2015) 138.
- [8] K.M. Fromm, Coord. Chem. Rev. 252 (2008) 856.
- [9] R.W. Murray and L.K. Hiller Jr., Anal. Chem. 39 (1967) 1221.
- [10] E. Itabashi, J. Electroanal. Chem. 36 (1972) 179.
- [11] L. Gou, H.X. Zhang, X.Y. Fan, D.L. Li, Inorg. Chim. Acta 394 (2013) 10.
- [12] R.M. Fuoss, C.A. Kraus, J. Am. Chem. Soc. 55 (1933) 2387.
- [13] M. Hojo, Pure Appl. Chem. 80 (2008) 1540.

- [14] M. Hojo, H. Nagai, M. Hagiwara, Y. Imai, *Anal. Chem.* 59 (1987) 1770.
- [15] M. Hojo, H. Hasegawa, Y. Miyauchi, H. Moriyama, H. Yoneda, S. Arisawa, *Electrochim. Acta*, 39 (1994) 629.
- [16] M. Hojo, S. Ohta, K. Ayabe, K. Okamura, K. Kobiro, Z. Chen, *J. Mol. Liquids* 177 (2013) 145.
- [17] M. Hojo, T. Ueda, T. Inoue, M. Ike, *J. Phys. Chem. B* 111(2007) 1759.
- [18] M. Hojo, T. Ueda, M. Nishimura, H. Hamada, *J. Phys. Chem. B* 103 (1999) 8965.
- [19] M. Hojo, H. Hasegawa, H. Tsurui, K. Kawamura, S. Minami, A. Mizobe, *Bull. Chem. Soc. Jpn.* 71 (1998) 1619.
- [20] M. Hojo, T. Ueda, M. Yamasaki, *J. Org. Chem.* 64 (1999) 4939.
- [21] M. Hojo, T. Ueda, M. Yamasaki, A. Inoue, S. Tokita, M. Yanagita, *Bull. Chem. Soc. Jpn.* 75 (2002) 1569.
- [22] M. Hojo, H. Hasegawa, H. Yoneda, *J. Chem. Soc., Perkin Trans. 2* (1994) 1855.
- [23] M. Hojo, H. Hasegawa, A. Mizobe, Y. Ohkawa, Y. Miimi, *J. Phys. Chem.* 99 (1995) 16609.
- [24] R.S. Sah, B. Sinha, M.N. Roy, *Fluid Phase Equilib.* 307 (2011) 216.
- [25] J.A. Krom, J.T. Petty, A. Streitwieser, *J. Am. Chem. Soc.* 115 (1993) 8024.
- [26] P.S. Nikam, M. C.Jadhav, M. Hasan, *J. Chem. Eng. Data* 41 (1996) 1028.
- [27] L.C. Manege, T. Ueda, M. Hojo, *Bull. Chem. Soc. Jpn.* 71 (1998) 589.
- [28] L.C. Manege, T. Ueda, M. Hojo, M. Fujio, *J. Chem. Soc., Perkin Trans. 2* (1998) 1961.
- [29] M. Hojo, S. Aoki, *Bull. Chem. Soc. Jpn.* 85 (2012) 1023.
- [30] J.A. Riddick, W.B. Bunger, T.K. Sakano, *Organic Solvent, Physical Properties and Methods of Purification*, 4th ed., John Wiley & Sons, New York, 1986.
- [31] I.M. Kolthoff, M.K. Chantooni Jr., *General Introduction to Acid-Base Equilibria in Nonaqueous Organic Solvents*, in: *Treatise on Analytical Chemistry, Part 1, Theory and Practice*, Vol. 2, Section D, John Wiley & Sons, New York, 1979, p. 239.
- [32] V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum, New York, 1978.
- [33] X. Chen, K. Ayabe, M. Hojo, Z. Chen, M. Kobayashi, *J. Mol. Liq. J. Mol. Liquids* 199 (2014) 445.

- [34] A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, London, 1973.

Chapter 6 Summary

This study have examined the coordination ability of alkali metal (M^+), alkaline earth metal (M^{2+}) and indium ions with the common ligand of sulfonates, phosphates and carboxylates not only in aprotic solvent but also protic solvent as primary alcohols and binary protic-aprotic solvents, through observing the specific coordination phenomena of those metal ions and the Conjugate Anions. The obtained results are as follows:

1. Regardless in aprotic solvent MeCN, mono-, di- or tri- sulfonates can interact with alkaline earth metal ions to form precipitates and “reverse-coordinated” species even in primary alcohols of relatively high donicity.
2. The coordination ability of M^+ and M^{2+} ions with diphenylphosphinate, diphenylphosphate, and bis(4-nitrophenyl)phosphate ions has been confirmed not only in sole MeCN but also in the binary solvents with H_2O , MeOH, and EtOH.
3. In binary MeCN-MeOH and MeCN- H_2O , the specific interaction could take place between M^+ , M^{2+} and 1,4- or 2,3-naphthalenedicarboxylate ions to different extent.
4. The coordination force also attributed to the higher ion-aggregation in addition to coulombic forces.
5. The “reverse” coordination formation constants have been successfully evaluated for all systems.
6. Based on the direct interaction between metal ions and the anion species deviated from substrates, the results may give an important clue to recognize the kinetic mechanism in hydrolysis reactions under “non-aqueous solvent conditions” or in biological systems.

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Achievement*Papers*

1. X. Chen, K. Ayabe, M. Hojo, Z. Chen, M. Kobayashi, Specific coordination phenomena of alkaline earth metal ions with aromatic sulfonate ions in alcohols and binary solvents of acetonitrile-alcohols, *Journal of Molecular Liquids* 199 (2014), 445-453.
2. 北條正司, 陳小卉. プロトン性溶媒及び二成分アセトニトリル-プロトン性混合溶媒中におけるアルカリ土類金属イオン-芳香族スルホン酸イオン間の配位現象の解明. *分析化学*, 64 (2015) 247-260.
3. X. Chen, M. Hojo, Z. Chen, M. Kobayashi, Coordination phenomena of alkali metal, alkaline earth metal, and indium ions with 1,3,6-naphthalenetrisulfonate ion in protic and aprotic solvents, *Journal of Molecular Liquids* 214 (2016), 369-377.
4. X. Chen, M. Hojo, Z. Chen, Complexing ability between alkali metal or alkaline earth metal ions with phosphoric acid in acetonitrile and binary solvents with protic solvents, *Journal of Molecular Liquids*, in press.
5. The specific interaction between alkali metal or alkaline earth metal ions with naphthalenedicarboxylate ions in acetonitrile-water or acetonitrile-methanol binary mixtures. (Under preparation)

Oral Presentations

1. Xiaohui Chen, Masashi Hojo. Coordination Ability of alkali metal, alkaline earth metal and the group III metal ions with 1,3,6-naphthalenetrisulfonate in non-aqueous solvents. The 2nd International Symposium on Green Science (Kochi University, Mar. 2014).
2. Xiaohui Chen. Coordination Ability of alkali metal, alkaline earth metal and the group III metal ions with 1,3,6-naphthalenetrisulfonate in non-aqueous solvents. 2014 Conference on Physical Chemistry (Shenzhen, China, Jan. 2014).
3. Masashi Hojo, Xiaohui Chen, Keita Ayabe, Zhidong Chen, Masato Kobayashi. Specific coordination phenomena of alkaline earth metal ions with aromatic sulfonate ions in alcohols and binary solvents of acetonitrile-alcohols. 37th Symposium on Solution Chemistry of Japan (Saga

University, Nov. 2014)

4. Xiaohui Chen and Masashi Hojo. Complexing ability of alkali metal and alkaline earth metal ions with organic phosphinate or phosphates in acetonitrile and binary solvents with protic solvents.

日本分析化学会第64年会 (九州大学, 2015 年 9 月)

5. Xiaohui Chen. Specific coordination phenomena of alkali metal, alkaline earth metal, and the III group metal ions with the conjugate anions from organic acids in non-Aqueous solvents.

International seminar (Changzhou University, China, Dec. 2015)

Poster

1. Xiaohui Chen and Masashi Hojo. Coordination ability of alkali metal, alkaline earth metal and the group III metal ions with 1,3,6-naphthalenetrisulfonate in non-aqueous solvents. 日本分析化学会第62年会 (近畿大学東大阪キャンパス, 2013 年 9 月)

2. Xiaohui Chen and Masashi Hojo. The specific interaction between alkaline earth metal ions and sulfonate or phosphate ions in protic and aprotic solvents. 日本分析化学会第63年会 (広島大学東広島キャンパス, 2014 年 9 月)

3. Xiaohui Chen and Masashi Hojo. Specific coordination phenomena of alkaline earth metal ions with aromatic sulfonate ions in protic and aprotic solvents. 中国四国支部分析化学若手セミナー (高知大学, 2014 年 7 月)

4. Xiaohui Chen and Masashi Hojo. Complexing ability of alkali Metal and alkaline earth metal ions with organic phosphinate or phosphates in acetonitrile and binary solvents with protic solvents.

38th Symposium on Solution Chemistry of Japan (高知市文化プラザ, 2015 年 10 月)