



# Chemical interaction between alkaline earth metal ions and the benzoate or 2,6-naphthalenedicarboxylate ion in acetonitrile and alcohols

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## ABSTRACT

The chemical interactions of alkaline earth metal ions ( $M^{2+} = Ca^{2+}, Ba^{2+}$ ) with the benzoate ( $L^-$ ) and the 2,6-naphthalenedicarboxylate ( $L^{2-}$ ) ions have been examined by means of UV–visible spectroscopy in acetonitrile (MeCN) and several alcohols. In MeCN, the absorption band at around 220 nm of  $L^-$  ( $1.0 \times 10^{-3}$  mol dm $^{-3}$ ) firstly has decreased and almost disappeared in the presence of  $5.0 \times 10^{-4}$  mol dm $^{-3}$   $M^{2+}$  and then suddenly recovered at  $1.0 \times 10^{-3}$  mol dm $^{-3}$   $Ca^{2+}$  or  $5.0 \times 10^{-2}$  mol dm $^{-3}$   $Ba^{2+}$ . The successive phenomena should be caused by the  $ML_2$  precipitation and the re-dissolution with the formation of the cationic species of  $ML^+$  from  $ML_2$ . The specific chemical interaction between  $L^-$  and  $Ba^{2+}$  can take place not only in MeCN but also amphiprotic solvents, such as, ethanol, 1-propanol, 2-propanol, and 1-butanol. However, the addition of  $\geq 10\%$   $H_2O$  or  $\geq 50\%$  MeOH to MeCN has inhibited the precipitation between  $L^-$  and  $Ba^{2+}$ . Between the  $L^{2-}$  and  $Ba^{2+}$  ions, both precipitation and re-dissolution have been observed in binary mixed solvents, MeCN-ROH of 50–100% MeOH and of 70% EtOH. The solubility products ( $pK_{sp}$ ) and the coordination or “reverse” coordination constants ( $\log K_1$  and  $\log K_2$ ) between  $L^-$  or  $L^{2-}$  and  $Ba^{2+}$  have been evaluated in MeCN, the alcohols, and the binary mixtures of MeCN- $H_2O$  or MeCN-MeOH. Where,  $K_1 = [BaL^+]/([Ba^{2+}][L^-])$  and  $K_2 = [Ba_2L^{2+}]/([Ba^{2+}]^2[L^{2-}])$  for the chemical equilibria,  $Ba^{2+} + L^- \rightleftharpoons ML^+$  and  $2Ba^{2+} + L^{2-} \rightleftharpoons Ba_2L^{2+}$ , respectively.

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## 1. Introduction

In aqueous solution, alkali metal or alkaline earth metal salts in relatively low concentrations dissociate almost completely, and the behavior has been successfully explained by Debye–Hückel theory [1]. In low permittivity media ( $\epsilon_r < 10$ ), Fuoss and Kraus [2] have discovered that some uni-univalent salts give a minimum on the relation curve between  $\Lambda$  and  $\sqrt{c}$  where  $\Lambda$  is the molar conductivity and  $c$  is the molar concentration of electrolyte. They rationalized the appearance of the minimum by postulating the existence of triple ions. They introduced the idea of triple ion formation from an ion  $A^+$  or  $B^-$  with an ion pair:  $A^+ + AB \rightleftharpoons A_2B^+$  and  $B^- + AB \rightleftharpoons AB_2^-$  by the electrostatic force.

Though some investigators [3] insist that the technical term of “triple ions” should be restricted to the electrostatic interaction, we will use this term also for the triple ions formed through coordination or hydrogen bonding forces as well as by the electrostatic force. Indeed, we have demonstrated that in aprotic media of relatively higher permittivity ( $20 < \epsilon_r < 65$ ), e.g. acetone, acetonitrile (MeCN), or propylene carbonate [4]. The chemical interaction between alkali metal ( $M^+$ ) or alkaline earth metal ( $M^{2+}$ ) ions and some anions could take place even in protic media,

surprisingly. In primary alcohols, the chemical interactions have been observed between  $M^+$  or  $M^{2+}$  and sulfonates (*p*-toluenesulfonate [5], 1,5-naphthalenedisulfonate [5], and 1,3,6-naphthalenetrisulfonate [6]). By means of various methods [7–11], we have derived the ion aggregation scheme between  $M^+$  and anions ( $L^-$ ) during increasing concentration of  $MClO_4$  toward  $R_4N^+L^-$ : (1) the formation of triple-anions or normal coordination species ( $ML_2^-$ ) in the presence of less than half concentration of  $M^+$  to  $L^-$ ; (2) the precipitation (non-charged species,  $ML$ ) between an equivalent of  $M^+$  and  $L^-$ ; (3) the successive re-dissolution of precipitates through the formation of triple-cations or “reverse” coordinated species ( $M_2L^+$ ) in the presence of more than twice concentration of  $M^+$  to  $L^-$ . So far, we have reported the specific interaction between  $M^+$  or  $M^{2+}$  and various anions, such as halides [12,13], tropolonates [8], thiocyanate [14], phosphates [15], sulfonates [5,6,16], and carboxylates [17] in various media. The solubility products and formation constants of the “reverse” coordination have been successfully evaluated.

The studies of specific interaction between  $M^+$  or  $M^{2+}$  and anions could give an important clue to recognize the mechanism in hydrolysis reactions under “non-aqueous condition” or in biologic systems. With our proposal [18–22], the salt effects on the solvolysis of  $S_N1$  substrates and related substrates can be accounted for without relying on conventional reaction schemes [23–26] or the arbitrary functions of various ion pairs. Meanwhile, we have developed a method for color development

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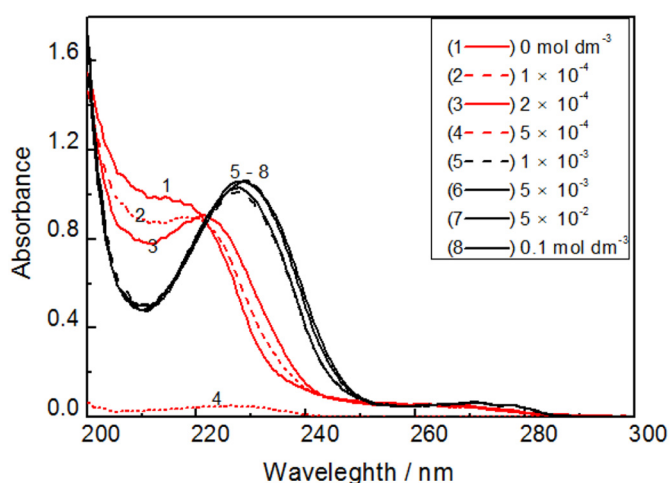


Fig. 1. UV spectra of  $1.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$  benzoate ion (0.1 cm path-length) with increasing concentration of  $\text{Ca}(\text{ClO}_4)_2$  in MeCN.

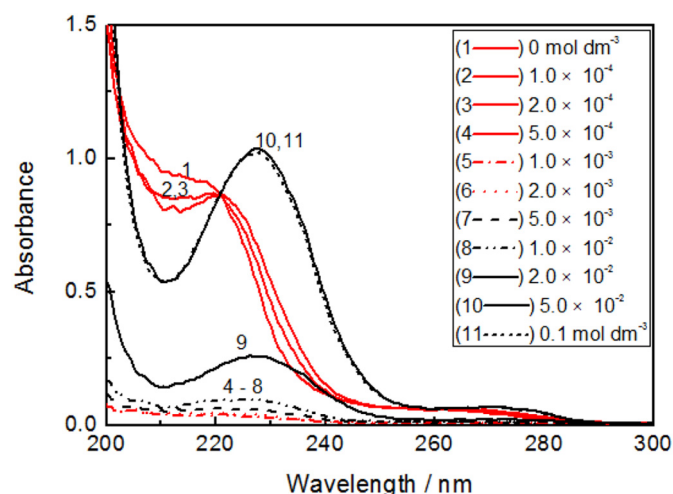


Fig. 2. UV spectra of  $1.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$  benzoate ion (0.1 cm path-length) with increasing concentration of  $\text{Ba}(\text{ClO}_4)_2$  in MeCN.

of indicators or dyes of sulfonic and carboxylic types [27,28] which depends upon the specific coordination interactions between alkali metal or alkaline earth metal ions and anions. Besides, the triple ion theory has been applied to explain phenomena in lithium batteries [29–31], ion-aggregation [32–34], and supramolecular chemistry [35].

As the extension of the studies, we examine the specific aggregation between alkaline earth metal ( $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ) with the benzoate and 2,6-naphthalenedicarboxylate ions by means of UV spectroscopy not only in aprotic (MeCN) but also amphiprotic (alcohols) or binary MeCN-ROH media. The solubility products and coordination or “reverse” coordination constants are successfully evaluated for  $\text{Ba}^{2+}$  systems. One of the main purposes of the present study is to confirm that alkaline earth metal ions can interact with carboxylate ions through strong coordination interaction as well as the electrostatic force in amphiprotic media.

## 2. Experimental

### 2.1. Chemicals

Calcium perchlorate tetrahydrates, barium perchlorate, and tetrabutylammonium benzoate ( $n\text{-Bu}_4\text{N}^+\text{C}_7\text{H}_5\text{O}_2^-$ ,  $\geq 98.0\%$ ) were obtained from Aldrich. Barium trifluoromethanesulfonate,  $\text{Ba}(\text{CF}_3\text{SO}_3)_2$ , of 99% was the product of Strem Chemicals. 2,6-Naphthalenedicarboxylic acid was purchased from TCI. Commercially obtained solvents of GR grades (Wako), acetonitrile (MeCN), methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-PrOH, and butanol (1-BuOH), were used as received. *t*-Butyl (2-methyl-2-propanol) and isopentyl alcohols (3-methyl-1-butanol) were also obtained from Wako. The water contents in the solvents are guaranteed to be  $<0.1\%$  for MeCN and MeOH;  $<0.2\%$  for the other alcohols. 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.

Before use, calcium perchlorate tetrahydrates was dried *in vacuo* at  $150^\circ\text{C}$  in order to obtain anhydrous  $\text{Ca}(\text{ClO}_4)_2$ . Tetrabutylammonium 2,6-naphthalenedicarboxylate [ $(n\text{-Bu}_4\text{N}^+)_2\text{C}_{12}\text{H}_6\text{O}_4^{2-}$ ] was prepared from 2,6-naphthalenedicarboxylic acid as follows: A 1.0 g of 2,6-naphthalenedicarboxylic acid was dissolved in methanol, and was titrated by tetrabutylammonium hydroxide ( $0.5 \text{ mol dm}^{-3}$   $n\text{-Bu}_4\text{NOH}$ , Wako) up to an equivalence point. The solution was evaporated to dryness at  $50^\circ\text{C}$ , and the salt was dried *in vacuo* at  $50^\circ\text{C}$ . The salt of  $(n\text{-Bu}_4\text{N}^+)_2\text{C}_{12}\text{H}_6\text{O}_4^{2-}$  is sparingly soluble in MeCN, therefore, the salt-MeCN solutions were prepared from the salt dissolved in  $\text{H}_2\text{O}$  or alcohols. In this case, finally, the MeCN solvent contained 5% of  $\text{H}_2\text{O}$  or ROH.

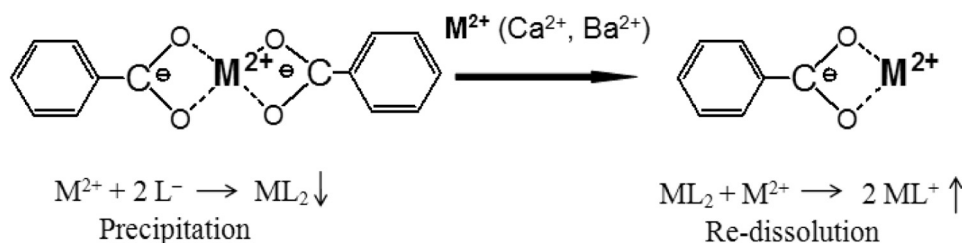
### 2.2. Apparatus and procedure

UV–visible absorption spectra were measured at room temperature using a Shimadzu double-beam spectrophotometer (model UV-2550) in 0.1 and 0.05 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 at room temperature was needed to complete a precipitation reaction.

### 2.3. Evaluation of coordination or “reverse” coordination constants

The evaluation method of solubility products ( $\text{p}K_{\text{sp}}$ ) and “reverse” coordination formation constants ( $\log K_1$  and  $\log K_2$ ) between  $\text{M}^{2+}$  and the “ligand” anions ( $\text{L}^-$ ,  $\text{L}^{2-}$ ) has been proposed previously [16], which is shown as follows:

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



Scheme 1. Successive formation of  $\text{ML}_2$  and  $\text{ML}^+$  ( $\text{M} = \text{Ca}$  and  $\text{Ba}$ ) for the benzoate ion ( $\text{L}^-$ ) in MeCN.

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