



Coordination ability of alkali metal or alkaline earth metal ions with aromatic dicarboxylate, sulfonate, or disulfonate ions in acetonitrile

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ABSTRACT

In a poor solvating solvent, acetonitrile, the coordination ability of alkali metal (Li^+ , Na^+) and alkaline earth metal (Mg^{2+} , Ca^{2+} , Ba^{2+}) ions with carboxylate and sulfonate ions has been thoroughly examined, based on the precipitation of non-charged species and the successive re-dissolution of charged species. At first, the formation of $[\text{C}_6\text{H}_5\text{CO}_2\text{Ca}]^+$ (the calcium benzoate cation) in acetonitrile was evidenced by ESI-MS. Tetraethylammonium 3-nitrophthalate (3-nitro-1,2-benzenedicarboxylate, L^{2-}) of $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ was precipitated completely by the addition of $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{Ca}(\text{ClO}_4)_2$, although the absorption spectrum of L^{2-} was only slightly changed by $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{Ca}(\text{ClO}_4)_2$. In the presence of $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{Ca}(\text{ClO}_4)_2$, however, the precipitates re-dissolved drastically. The successively formed species between Ca^{2+} and L^{2-} were proposed to be CaL_2^0 , CaL^0 , and Ca_2L^{2+} . The lithium ion also caused the precipitation of non-charged species (Li_2L^0) as well as the re-dissolution of charged species (tentatively assigned to be Li_3L^+ or Li_4L^{2+}), however, the re-dissolution with Na^+ took place just hardly. We were able to observe the re-dissolution of precipitates for 4-nitrophthalate through the formation of positively charged species in the presence of excess amounts of the alkaline earth metal ions, but not of the alkali metal ions. Tetraethylammonium *p*-toluenesulfonate, and 1,5-, 2,6-, and 2,7-naphthalenedisulfonates were also examined. The “reverse” coordination constants have been successfully evaluated for some of all the systems, e.g., $K_2 = 3 \times 10^7$ ($2 \text{ Mg}^{2+} + \text{L}^{2-} \rightleftharpoons \text{Mg}_2\text{L}^{2+}$) and $K_3 = 2 \times 10^8$ ($3 \text{ Li}^+ + \text{L}^{2-} \rightleftharpoons \text{M}_3\text{L}^+$), where $\text{L}^{2-} = 2,7\text{-naphthalenedisulfonate}$.

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1. Introduction

In an aqueous solution, it is taken for granted that alkali metal or alkaline earth metal ions exhibit no coordination ability, aside from the chelate formation of alkaline earth metal ions (e.g., Mg^{2+} , Ca^{2+}) with a powerful chelate reagent, such as EDTA (ethylenediamine-*N,N,N',N'*-tetraacetic acid). The coordination ability of alkali metal or alkaline earth metal ions should be much weaker than that of transition metal ions because of their lack of partly filled d- or f-shells. In a review article, Fromm [1] stated that “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.”

At any rate, each metal ion is highly hydrated in dilute aqueous solution, and no reaction sites of a main-group metal ion are left for moderate complexing ligands or anions. Ligands or anions are also well hydrated in dilute aqueous solution, and are already restricted

to donate their electron pair to a metal cation. Therefore, it might be quite natural to regard that the ion pairing between a simple anion and an alkali metal or alkaline earth metal ion in dilute aqueous solution is based on absolute electrostatic interaction. The Debye–Hückel theory [2] has been constructed with a pure electrostatic model and still been developing [3].

In an aprotic solvent which has poor solvating ability, however, one can expect to observe actually the “weak” coordination ability of alkali metal and alkaline earth metal ions. Acetonitrile (MeCN) of a relatively high permittivity ($\epsilon_r = \text{ca. } 36$) [4] is not only an aprotic solvent but also a protophobic solvent [5], therefore, its solvation ability is very weak toward both anions and metal cations. The poor solvating ability of MeCN can be expressed by acceptor and donor numbers of 19.3 and 14.1, respectively [6], cf. 54.8 [6] and ca. 40 [7] for bulk water. In MeCN, Murray and Hiller [8a] postulated the formation of $\text{Li}_2(\text{acac})^+$ ($\text{acac} = \text{acetylacetonate}$) in the polarographic reduction of $\text{Fe}(\text{acac})_3$ with a large excess of LiClO_4 . Itabashi [8b] also suggested the formation of the M_2A^+ ($\text{M} = \text{Li}$ and Na , $\text{A} = \text{the acetate or benzoate ion}$) in the same solvent.

Based on various data with electrochemical and spectroscopic techniques in aprotic protophobic solvents, we have convinced [9]

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that an alkali metal ion (M^+), especially Li^+ , can interact with simple mono-anions (L^-) to form not only a “normal” coordination-type species, ML_2^- [10], but also cationic or “reverse” coordinated [11] species, M_2L^+ , in addition to 1:1 ion-pair or a salt, ML^0 . The ML^+ ($M = \text{bivalent}$) as well as M_2L^+ ($M = \text{univalent}$) type species of carboxylate [12,13] and sulfonate ions [11] has been evidenced. The motive force of such a chemical interaction has been utilized for the color development or changes of indicators or dyes of carboxylic [14–16] and sulfonic types [17].

The concept of the specific chemical interaction between M^+ or M^{2+} and simple anions has been applied for elucidating the solvolysis (or hydrolysis) reaction mechanism: the exponential increases in the solvolysis (hydrolysis) rate constants of haloalkanes (and related compounds, RX) in the presence of metal salts should be based on the direct chemical interaction between the leaving-group anion (X^-) and the metal cations to generate the carbocation (R^+) as the reaction intermediate even in “aqueous” solution [18], providing that it contains a large quantity of organic solvents and salts: e.g., $RX + M^{2+}(ClO_4^-)_2 \rightleftharpoons R^+||ClO_4^- + MX^+||ClO_4^-$. For long time, the “special” salt effect in solvolysis of organic compounds had been interpreted just qualitatively by the exchange between two ion-pairs: $R^+||X^- + M^+||ClO_4^- \rightleftharpoons R^+||ClO_4^- + M^+||X^-$ [19]. By means of IR, powder X-ray diffraction, and thermal analyses (TG and DTA), we have characterized $BaCl^+(ClO_4^-)$ crystals formed from acetonitrile solution [20].

In the present study, the chemical interaction between alkali metal or alkaline earth metal ions and aromatic carboxylate or sulfonate ions (cf. Chart 1 for the acid forms) is examined mainly by means of UV spectroscopy. The chemical interaction between dicarboxylates or disulfonates and alkaline earth metal ions is highlighted because such a bivalent anion has never been examined in our group yet. The effects of the basicity of the anions, the solubility of non-charged species, and additional water in the solvent are discussed. We would like to mention that Rudolph et al. [21] have detected a Raman band which is tentatively assigned to $Mg_2SO_4^{2+}$ in an aqueous solution of $MgSO_4$ at high temperature ($<200^\circ C$).

An important aim of the present study is to establish further that carboxylate and sulfonate ions can interact chemically with non-transition metal ions in solution; which can support our proposal [18] that the salt effects on the solvolysis of S_N1 to S_N2 haloalkane substrates can be accounted for without relying on conventional reaction schemes [19] or the arbitrary function of various ion pairs. We would like to stress that, very recently, our mechanistic scheme has been firmly accepted [18f].

2. Experimental section

2.1. Chemicals

Tetraethylammonium 3- and 4-nitrophthalates were prepared as follows: 1.0 g of 3-nitrophthalic acid (3-nitro-1,2-benzenedicarboxylic acid, Aldrich) was dissolved in methanol, and was titrated by Et_4NOH (20 wt.% in H_2O , Aldrich) in methanol up to an equivalent point. The solution was evaporated to dryness at $50^\circ C$, and the salt was dried in vacuo at $50^\circ C$. 4-Nitrophthalic acid (4-nitro-1,2-benzenedicarboxylic acid, Aldrich) was also treated in a same way to obtain the 4-derivative salt. The numbers of hydrated water in the tetraethylammonium salts were determined to be 2.5 and 3.0 for 3- and 4-nitrophthalates, respectively, by means of the 1H NMR method. Tetraethylammonium salts from *p*-toluenesulfonic acid (monohydrate, Wako), 1,5-, 2,6-, and 2,7-naphthalenedisulfonic acids were prepared in a method similar to that for the nitrophthalates. However, the salts from mono- and disulfonic acids were dried at $150^\circ C$, and conductometric titrations with trifluoromethanesulfonic acid indicated that the hydrated waters of the salts can be negligible. 1,5-Naphthalenedisulfonic acid tetrahydrates was purchased from Aldrich, but 2,6- and 2,7-naphthalenedisulfonic acids were prepared from sodium salts as follows: thirty-five grams of sodium 2,6- or 2,7-naphthalenedisulfonate, purchased from Taicang, Hualian Chemical, China, was dissolved in pure water of 2 l, and the sodium ions were exchanged to protons with an ion-exchange column, each by each of 200 ml. The Na^+ concentration was determined by an atomic absorption spectrophotometer, and was kept to be less than $0.1 \mu g/ml$. The elute solution was evaporated to dryness in a rotary evaporator at $<35^\circ C$, and crystals were dried in vacuo at $35^\circ C$.

Tetrabutylammonium benzoate ($n-Bu_4NC_6H_5CO_2$, $>98\%$) and sodium *p*-toluenesulfonate (95%) were purchased from Aldrich. Metal perchlorates without water, $LiClO_4$ (Wako), $NaClO_4$, $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$ (all Aldrich), were used as received. Calcium perchlorate tetrahydrates from Aldrich was dried in vacuo at $150^\circ C$ to obtain anhydrous $Ca(ClO_4)_2$. Tetraethylammonium perchlorate was prepared as mentioned previously [22]. Commercially obtained acetonitrile (MeCN) solvents of GR and super dehydrated grades (Wako), containing <0.001 and $<0.1\%$ (v/v) H_2O , were used as received. Other chemicals were purchased from Wako or Aldrich, and were used as received. Water was purified by means of a MilliQ system (Millipore Corp.).

2.2. Apparatus, component analysis, and solubility

ESI-MS (electrospray ionization mass spectroscopy) was conducted with a JEOL 700 mass spectrometer. UV-visible absorption spectra were measured at room temperature using a Shimadzu double-beam spectrophotometer (model UV-2550) in 0.5 and 1.0 mm path-length quartz cuvettes. When precipitation occurred, the solution was sonicated for a few minutes and the supernatant solution was measured after centrifugation. Sometimes, a long aging time was needed to complete a precipitation reaction. 1H measurements were carried out in a single NMR tube at room temperature with a JEOL FT-NMR spectrometer (model JNM-LA400). An NMR solvent, acetonitrile- d_3 of 99.8 atom% D containing TMS, was obtained from Aldrich. Electric conductance of solution was measured in a conductivity cell at $25 \pm 0.02^\circ C$ with a Hewlett-Packard LCR meter (model 4263A). The solubility of sodium *p*-toluenesulfonate was measured in acetonitrile solvents of two types and also the solvent with added water. Solutions containing ca. $1 \times 10^{-2} \text{ mol dm}^{-3}$ $CH_3C_6H_4SO_3Na$ were shaken for 24 h at room temperature. The UV absorbance around 222–223 nm of the supernatant solution after centrifugation was compared with that of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ tetraethylammonium *p*-toluenesulfonate in MeCN.

For the component analyses of the metal precipitates, the concentrations of metal ions in 0.1 mol dm^{-3} HCl aqueous solutions of the precipitates were determined by a Hitachi polarized Zeeman atomic

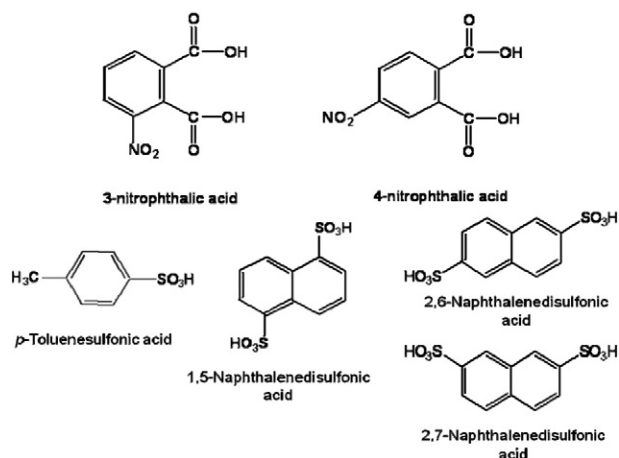


Chart 1. Aromatic dicarboxylic and sulfonic acids examined in the present study.

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