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Observation of the Triple Cation Formation from Substituted-Benzoate Ions in Acetonitrile by Spectrophotometry

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For 2,4-dinitrobenzoate ion (A^-) in acetonitrile, the ion pair (Li^+A^-) and the triple cation ($(Li^+)_2A^-$) formation constants were obtained by distinct changes of UV absorption spectra with increasing concentration of $LiClO_4$.

A number of normal coordination complexes in crystals and solutions of alkali metals (M^+L_n: L = the ligand, n ⩾ 1) have been reported.[1,2] However, the formation of the species, $(M^+)_mL$ (m ⩾ 2), in solutions might be regarded to be extraordinary. Murray and Hiller[3] postulated the formation of $Li_2(acac)^+$ (acac = acetylacetonate) in the polarographic reduction of $Fe(acac)_3$ with a large excess of $LiClO_4$ in acetonitrile. Itabashi[4] suggested the formation of the $[CH_3COOLi_2]^+$ species in the same solvent. We have identified the $[M_2A]^+$ (M = Li and Na, A = the acetate or benzoate ion) by a new polarographic method in acetonitrile.[5] The formation constants of complexes, such as $(Li^+)_2Cl^-$ and $(HA)_2Cl^-$ (HA = acetic or benzoic acid) were also obtained.[6] Furthermore, conductivity data of CF_3COOLi in propylene carbonate[7] and LiSCN in nitromethane[8] were completely explained by the ion pair (MX), symmetrical triple ion (M_2X and MX_2), and quadrupole (M_2X_2) formation reactions.

The purpose of the present study is to examine the triple cation (M_2X) formation from various benzoate ions and alkali metal ions in acetonitrile by spectrophotometry.

Commercially obtained acetonitrile (Nacalai Tesque, Inc., SP grade) was used as received. Tetraethylammonium benzoates were prepared by a method similar to that previously mentioned.[5] UV and visible absorption spectra were measured by a Hitachi double-beam spectrophotometer (model U-2000) with a Hitachi graph-plotter (model 672) in 1-cm quartz cuvettes at room temperature.

For the analysis of the spectrophotometric data, the following formulation was made.[8] When a large excess of cation (M: $MClO_4$) are added to a certain concentration of anions (X: Et_4NX), two ions of M may react to a simple ion of X. The (overall) formation constants (K_1 and K_2) of the ion pair (MX) and the triple cation (M_2X) are expressed as $K_1 = [MX]/([M][X])$ and $K_2 = [M_2X]/([M]^2[X])$, respectively. The mass balances for M and X are $C_M = [M] + [MX] + 2[M_2X]$ and $C_X = [X] + [MX] + [M_2X]$, respectively. Above four equations derive a third-order equation for [M].

$$K_2[M]^3 + \{K_1 - K_2(C_M - 2C_X)\}[M]^2 + \{1 - K_1(C_M - C_X)\}[M] - C_M = 0 \quad (1)$$

The concentration of M can be calculated for each C_M concentration (C_X: constant) with known K_1 and K_2 values. The equation, $[X] = (2C_X - C_M + [M])/(2 + K_1[M])$, gives the concentration of X.

The entire absorbance is made of the summation of absorbances of the free anion, the ion pair, and the triple cation, if the free cation has no absorption at a certain wavelength.

$$A/cm = \varepsilon_0[X] + \varepsilon_1[MX] + \varepsilon_2[M_2X], \quad (2)$$

where ε_0, ε_1, ε_2 (M^{-1} cm^{-1}, 1 M = 1 mol dm^{-3}) are the molar absorption coefficients of X, MX, and M_2X, respectively. The values of K_1 and K_2 can be adjusted to minimize deviations of calculated A values to the observed ones. The formation of M_2X may be ignored when the concentration of M is not a large excess to that of X ($[M] \approx [X]$). The correction with activity coefficients of ions was made, which were evaluated by the Debye-Hückel equation (a = 5Å).

Tetraethylammonium benzoate ($C_6H_5COOEt_4N$) gave a strong peak (or a shoulder) at λ_{max} = 215 nm ($\log \varepsilon$ = 3.96) and smaller peaks around 255 - 270 nm in acetonitrile. The peak height of each peak was linear to the concentration ((0 - 2.0) x 10^{-3} M). The addition of $LiClO_4$ or $NaClO_4$ of (0.4 - 2.0) x 10^{-3} M to the benzoate ion (2.0 x 10^{-3} M) gave the decrease of absorbance. White precipitation of lithium and sodium benzoates was observed at the higher concentrations near equivalent amount of the alkali metals. Therefore, the solution was aged for 10 min over ultrasonic wave generator, and was centrifuged (2 500 rpm) for 30 min. The spectrum of the supernatant was measured. The absorbance at 261.5 nm (a distinct peak, $\log \varepsilon$ = 2.76) decreased almost linearly up to the equivalent point (1:1) by the addition of Na^+. With the increase of the Li^+ concentration, however, the absorbance decreased with a convex curve up to half-equivalent point, and then, with a concave curve. Similar abnormal decrease has been reported for the Li^+-benzoate system in the polarographic study, and was attributed to the formation of the lithium dibenzoate complex.[5)]

In the presence of an excess amount (5.0 x 10^{-3} M) of $LiClO_4$ to the 2.0 x 10^{-3} M benzoate, the absorbance at 225 nm (probably based on lithium benzoate in the solution) decreased further. However, by the addition of a large excess of $LiClO_4$, the absorbance increased as is shown in Fig. 1. The λ_{max} of the peak shifted to the shorter wave length (e.g., λ_{max} = 222 nm at 0.3 M $LiClO_4$). The increase of the absorbance with increasing concentration of $LiClO_4$ can be caused by the alternation of Li^+A^- to $(Li^+)_2A^-$.

$$C_6H_5COOLi \ + \ Li^+ \longrightarrow C_6H_5COO\text{-}(Li^+)_2 \qquad (3)$$

The addition of Et_4NClO_4 to the equivalent mixture of Li^+ and A^- did not increase the absorbance at all. The effect of an excess amount of $NaClO_4$ was smaller than that of $LiClO_4$ (cf. Fig. 1).

Similar increase of absorbance was observed for 4-chloro-, 4-nitro-, and 3,5-dichlorobenzoates by the addition of a large excess of $LiClO_4$ or $NaClO_4$. Sodium perchlorate gave a stronger effect than lithium perchlorate on 3,5-dichlorobenzoate, whereas both alkali metal ions gave almost the same effect on 4-chlorobenzoate.

The addition of $LiClO_4$ to a 2,4-dinitrobenzoate solution (2.0×10^{-4} M) gave no precipitation. Figure 2 shows spectral changes with the molar ratio (up to 1:1) of $LiClO_4$ to 2,4-dinitrobenzoate. A distinct isosbestic point was observed at 297 nm. The isosbestic point at 297 nm, however, shifted to 291 nm by the presence of more than 2.0×10^{-4} M of Li^+ (Fig. 3). The coexistence of A^- and Li^+A^- should make the isosbestic point at 297 nm, and the coexistence of Li^+A^- and $(Li^+)_2A^-$ at 291 nm. The formation constants of the ion pair (K_1) and the triple cation (K_2) were calculated by eqs. 1 and 2 to be 4.0×10^5 and 6.0×10^7, respectively, with $\varepsilon_0 = 8.4 \times 10^3$, $\varepsilon_1 = 9.5 \times 10^3$, and $\varepsilon_2 = 1.12 \times 10^4$ M^{-1} cm^{-1} at 244 nm. The values of ε_1 and ε_2 were evaluated from the absorbances in the presence of equivalent amount of Li^+ and 0.2 M Li^+, respectively. The relative error in the calculated absorbance to the observed one was -1.9 - +1.0% over the entire concentration range of $LiClO_4$ (2.0×10^{-4} - 0.2 M).

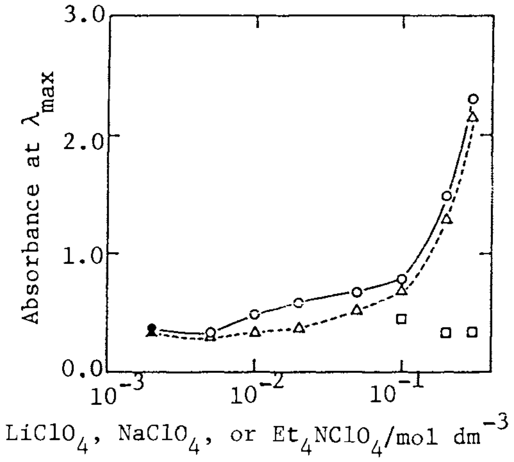

Fig. 1. The absorbance change of the benzoate ion (2.0×10^{-3} M $C_6H_5COOEt_4N$) by the addition of an excess of $LiClO_4$ (○), $NaClO_4$ (△), and Et_4NClO_4 (□, containing 2.0×10^{-3} M $LiClO_4$). Solid marks show the equivalent amount.

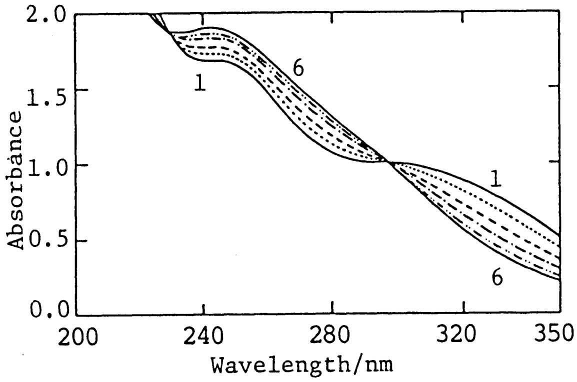

Fig. 2. UV spectral changes with the molar ratio (up to 1:1) of $LiClO_4$ to 2,4-dinitrobenzoate ions (2.0×10^{-4} M) in acetonitrile: (——1) 0; (·······) 0.2; (–––) 0.4; (–·–) 0.6; (–··–) 0.8; (——6) 1.0.

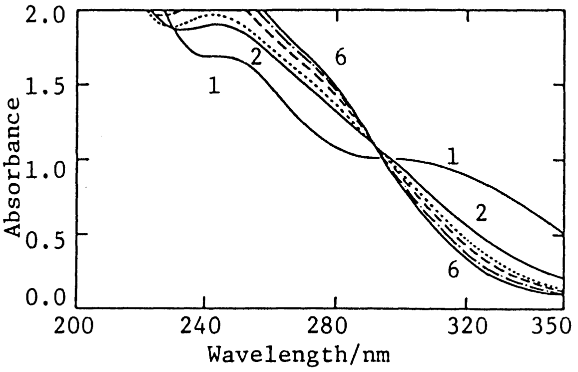

Fig. 3. UV spectral changes of 2,4-dintrobenzoate (2.0×10^{-4} M) by the addition of an excess amount of $LiClO_4$: (——1) 0; (——2) 2.0×10^{-4}; (······) 1.0×10^{-3}; (–––) 1.0×10^{-2}; (–··–) 4.0×10^{-2}; (——6) 0.1 and 0.2 M of $LiClO_4$.

The effect of $NaClO_4$ up to 1:1 equivalent point on the 2.0×10^{-4} M 2,4-dinitrobenzoate solution was not large enough to be examined fully. The addition of 2.0×10^{-4} - 0.2 M $NaClO_4$ gave an isosbestic point at 297 nm. Assuming the coexistence of only A^- and Na^+A^- in the solution, the ion pair formation constant was obtained to be $K_1 = 4.5 \times 10^3$ (the relative error of -0.2 - +1.3%) with $\varepsilon_0 = 8.4 \times 10^3$ and $\varepsilon_1 = 9.0 \times 10^3$ M^{-1} cm^{-1} at 244 nm. The value of ε_1 was evaluated by the absorbance at $[NaClO_4] = 0.1$ M. The absorbances of $LiClO_4$ and $NaClO_4$ were small enough to be ignored (the absorbance: 0.007 and 0.012 at 280 and 240 nm, respectively, for $LiClO_4$; 0.010 and 0.014 at 280 and 240 nm, respectively, for $NaClO_4$). For 3,4-dinitro- and 3,5-dinitrobenzoates, the spectral changes in the presence of $LiClO_4$ were not so large; further analyses have not been performed.

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