CHEMISTRY LETTERS, pp. 37-40, 1993.

Triple Ion Formation from Lithium and Sodium Tropolonates in Ethanol

Masashi HOJO,* Chinatsu FUJIME, and Hitoshi YONEDA
Department of Chemistry, Faculty of Science, Kochi University,
Akebono-cho, Kochi 780

Electrical conductivities of lithium and sodium tropolonates in ethanol were completely explained by the formation of higher ion aggregates in addition to ion pairs.

Protophobic aprotic solvents, such as acetonitrile and nitrobenzene, have relatively high dielectric constants (ε_r) and very small solvation ability towards both anions and cations. We have demonstrated the formation of triple ions (M_2X^+ and MX_2^-) and the quadrupole (M_2X_2) from monovalent electrolytes (MX) in protophobic aprotic solvents ($20 < \varepsilon_r < 65$) by means of polarography,[1,2] spectrophotometry,[3,4] and conductometry.[2,4-7] These higher ion aggregates were regarded to be caused by hydrogen bonding or coordination forces as well as electrostatic forces. Causes of the failure in the Shedlovsky analysis and related methods for abnormal weak electrolytes have been discussed from the standpoint of higher ion aggregates.[6,7] On the other hand, in protic solvents such as ethanol, electrolytes can be strongly solvated; therefore, no higher ion aggregate has been observed by our investigations so far.

Tropolone (2-hydroxyl-2,4,6-cycloheptatrien-1-one) and its derivatives have attracted both organic[8,9] and inorganic[10] chemists by the characteristic behavior for many years. Recently, theoretical[11] and experimental[12] examinations were performed for tropolone and its derivatives. Tropolone is a weak acid (pK_a = 6.7) in the aqueous solution.[8] In the present paper, we would like to present the first instance of the higher ion aggregates in a protic solvent, ethanol (ε_r = 24.55[5] at 25 °C). Spectrophotometry was employed to examine the potential of triple cation formation for the tropolonate ion in ethanol. Then, conductivities of lithium and sodium tropolonates in ethanol were explained by the symmetrical triple ion (and the quadrupole) model.[6,7] Lithium benzoate, LiTTA, and NaTTA (TTA = thenoyltrifluoroacetonate) were also examined in this connection.

Experiments with tropolonates were performed under shading the light for avoiding the possible effects of light. Other details concerning conductometric[5)] and spectrophotometric[4)] measurements have been shown elsewhere. The analysis and calculation were performed by following the methods described previously.[3,4,6,7)]

Tetrabutylammonium tropolonate ($n\text{-}Bu_4N\ C_7H_5O_2$) in ethanol gave three main absorption peaks at λ_{max} = 402, 336, and 242 nm; the absorption coefficients ($\varepsilon/dm^3\ cm^{-1}\ mol^{-1}$) of the peaks were 7.8×10^3, 1.0×10^4, and 2.2×10^4, respectively (cf. Ref. 9). When $LiClO_4$ was added to the 1.0×10^{-4} mol dm^{-3} tropolonate solution, isosbestic points observed were shifted distinctly by the increase of Li^+ concentration (cf. Ref. 3). We had the equilibrium constants of $K_1 = 3.0 \times 10^4$ ($Li^+ + X^- \rightleftharpoons Li^+X^-$) and $K_2 = 2.5 \times 10^6$ ($2Li^+ + X^- \rightleftharpoons (Li^+)_2X^-$ where X^- = tropolonate ion).

Figure 1 shows molar conductivities ($\Lambda/S\ cm^2\ mol^{-1}$) of Lithium tropolonate ($C = (0.4 - 6.0) \times 10^{-3}$ mol dm^{-3}). The observed Λ values (Λ_{obsd}) of all the concentration range were explained by the ion pair

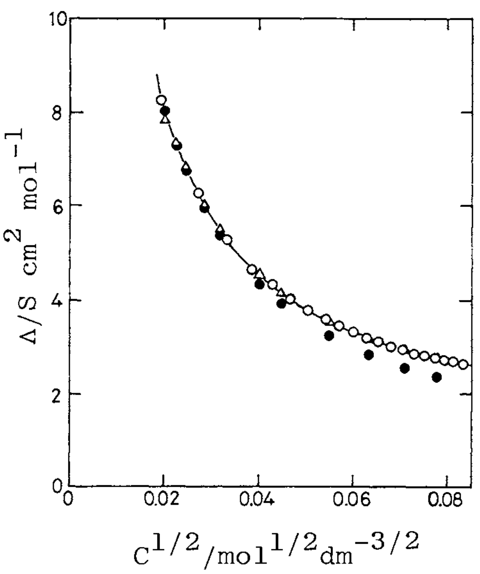

Fig. 1. Observed and calculated Λ values of lithium tropolonate in ethanol at 25°C: (○) observed; (●) calculated with the ion pair only; (△) calculated with ion pair and triple ion, $K^a{}_1{}' = 3.72 \times 10^4$, $K^a{}_2{}' = 2.5 \times 10^6$, $\Lambda_0 = 34.50$, and $\Lambda_T/\Lambda_0 = 0.693$.

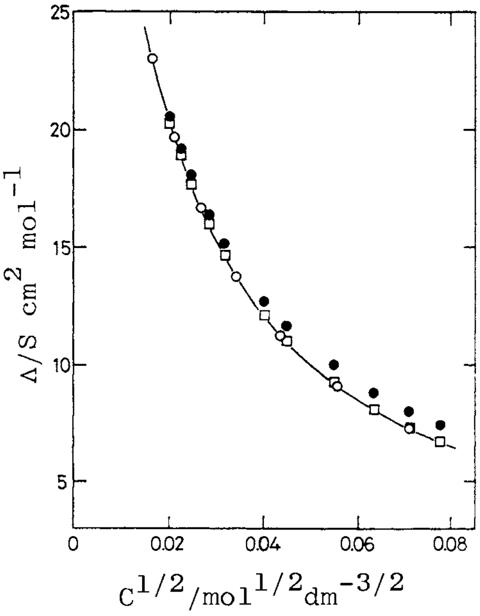

Fig. 2. Observed and calculated Λ values of sodium tropolonate in ethanol at 25°C: (○) observed; (●) calculated with the ion pair only; (□) calculated with ion pair, triple ion, and quadrupole, $K^a{}_1{}' = 4.0 \times 10^3$, $K^a{}_2{}' = 3.3 \times 10^5$, $K^a{}_4{}' = 4.0 \times 10^3$, $\Lambda_0 = 38.08$, and $\Lambda_T/\Lambda_0 = 0.693$.

Talbe 1. Λ_0 and K_a Values by the Shedlovsky Analysis and the Comparison with the Real Values

	Shedlovsky			
	Λ_0 a)	K_a b)	Λ_0(calcd) c)	$K^a{}_1{}'$ d)
Li Tropolonate	15.78	4.81×10^3	34.50	3.72×10^4
Na Tropolonate	47.65	8.21×10^4	38.08	4.00×10^3
Li C_6H_5COO	36.24	2.80×10^2	35.20	2.27×10^2

a) Limiting molar conductivity by the direct Shedlovsky analysis. b) Apparent association constant. c) Calculated by Kohlrausch's additivity law with strong electrolytes. d) The real ion pair formation constant, (accompanied by higher ion aggregates).

($M^+ + X^- \rightleftarrows MX$, $K^a{}_1{}'$) and the symmetrical triple ion ($2M^+ + X^- \rightleftarrows (M^+)_2X^-$, $K^a{}_2{}'$; $M^+ + 2X^- \rightleftarrows M^+(X^-)_2$, $K^a{}_3{}'$, assuming $K^a{}_2{}' = K^a{}_3{}'$) with the relative error of ±0.8%. The ratio of Λ_T to Λ_0 were assumed to be 0.693, where Λ_T and Λ_0 stand for the limiting molar conductivities of triple ions ($M_2X^+MX_2{}^-$) and simple ions (M^+X^-), respectively. The calculation with the ion pair formation alone caused the large negative error in Λ_{calcd} to Λ_{obsd} at the higher salt concentration, e.g., -15.2% at 6.0×10^{-3} mol dm^{-3}, although Λ_{calcd} fitted Λ_{obsd} at a few points in lower concentrations.

To the contrary, sodium tropolonate gave the positive error in Λ_{calcd} with considering only the ion pair (cf. Fig. 2) at higher salt concentrations. The other example of positive error in Λ_{calcd} to Λ_{obsd} at higher concentrations has been reported in propylene carbonate.7) Conductivities in that case7) have been completely explained by the strong quadrupole formation ($M_2X^+ + X^- \rightleftarrows M_2X_2$, $K^a{}_4{}'$ or $M^+ + MX_2{}^- \rightleftarrows M_2X_2$, $K^a{}_5{}'$; $K^a{}_4{}' = K^a{}_5{}'$) in addition to the ion pair ($K^a{}_1{}'$) and the triple ion ($K^a{}_2{}' = K^a{}_3{}'$) formation. The conductivities of sodium tropolonate in ethanol could not be explained by the triple ion formation which caused further deviations in Λ_{calcd} from Λ_{obsd}. With the quadrupole formation ($K^a{}_4{}' = K^a{}_5{}' = 4.0 \times 10^3$) in addition to triple ions and the ion pair, Λ_{calcd} fitted Λ_{obsd} within ±0.7% relative error.

Lithium benzoate (Li C_6H_5COO) was also examined by conductometry in ethanol. The association constant (K_a) by the Shedlovsky analysis indicated that the salt associated weakly in ethanol (cf. Table 1). The Λ_0 value (36.24), directly obtained by the Shedlovsky analysis was almost coincident with Λ_0(calcd), calculated by Kohlrausch's additivity law. The K_a value was naturally coincident with the ion pair formation constant ($K^a{}_1{}'$), calculated by the Λ_{obsd} of the entire concentration range, $(0.4 - 6.0) \times 10^{-3}$ mol dm^{-3}. The K_a values by the

Shedlovsky method utilized the data of (0.4 - 4.0) x 10^{-3} mol dm^{-3}. Thus, the conductivities of LiC_6H_5COO in ethanol were explained by the ion pair formation only: $\Lambda_0 \approx \Lambda_0$(calcd) and $K_a \approx K^a{}_1'$.

As described above, however, the ion pair and the symmetrical triple ion formation accounted for the conductivities of lithium tropolonate in ethanol. In this case, the Λ_0 value (15.78) was smaller than Λ_0(calcd) = 34.50, and the K_a value (4.8 x 10^3) was also much smaller than $K^a{}_1'$ (3.72 x 10^4): $\Lambda_0 < \Lambda_0$(calcd) and $K_a \ll K^a{}_1'$. Values of Λ_0 and K_a have been determined by the least-squares method of the Shedlovsky plots ($1/\Lambda S$ vs. $C\Lambda Sf_{\pm}{}^2$). On the other hand, conductivities of sodium tropolonate showed the strong quadrupole formation ($K^a{}_4'$ = 4.0 x 10^3). The values of Λ_0 and K_a (by the direct Shedlovsky analysis) were much larger than the real values: $\Lambda_0 > \Lambda_0$(calcd) and $K_a \gg K^a{}_1'$. The causes of the failure in the Shedlovsky analysis have been discussed in the previous papers.[6,7]

Conductivities of LiTTA and NaTTA in ethanol could be explained by the triple ion formation. Results of α- and β-diketonate salts in protophobic aprotic solvents will be reported later.

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(Received September 9, 1992)