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Conductometric Studies on the Triple Ion and Quadrupole Formations from Lithium and Tributylammonium Trifluoroacetates in Protophobic Aprotic Solvents

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The observed conductivity data of CF_3COOLi in propylene carbonate were properly explained by the strong formation of the quadrupole (M_2X_2, $M = Li^+$ and $X = CF_3COO^-$), in addition to the symmetrical formation of the triple ions (M_2X^+ and MX_2^-) and the ion pair formation.

The concept of the triple ion formation from a uni-univalent salt in low permittivity media ($\varepsilon < 12$) was first introduced by Fuoss and Kraus in 1933.[1)] However, Grigo fitted conductances in a low permittivity solvent without invoking triple ions with a theory.[2)] On the other hand, Salomon and Uchiyama[3)] showed the triple ion formation by fitting the extended full Fuoss-Hsia equation to the conductivity data. Very recently, Salomon et al.[4)] treated the minimum observed in the $\Lambda - C^{1/2}$ of $LiAsF_6$ in methyl acetate in terms of alternative models either involving triple ions or neglecting triple ions.

We have demonstrated the formation of $[M_2X]^+$ and $[MX_2]^-$ type species in acetonitrile by means of polarography.[5-7)] The symmetrical formation of triple ions from trialkylammonium halides (Cl^- and Br^-) in acetonitrile was confirmed both by polarography and conductometry.[8)] In the previous paper,[9)] we have reported that the triple ion formation from the trialkylammonium halide (MX) is caused mainly by the hydrogen bonding forces between (or among) the solutes in protophobic aprotic solvents with higher dielectric constants ($25 < \varepsilon < 65$).

In the present paper, by means of conductometry, we will demonstrate the quadrupole formation reaction, in addition to the triple ion and ion pair formations from lithium trifuoroacetate (CF_3COOLi) in propylene carbonate. The quadrupole and triple ion formations are shown for tributylammonium trifluoroacetate ($n\text{-}Bu_3NH^+CF_3COO^-$) in acetonitrile and benzonitrile.

The third-order equation (1) was solved for each analytical concentration of the salt (C_s) in order to analyze conductivity data.[8)]

$$3\,K_2\,[X]^3 + K_1\,[X]^2 + [X] - C_s = 0 \tag{1}$$

where K_1 is the ion pair formation constant and K_2 is the overall formation constant of a triple ion ($2M^+ + X^- \rightleftarrows M_2X^+$, K_2). The alternative triple ion formation constant ($M^+ + 2X^- \rightleftarrows MX_2^-$, K_3) was assumed to have the same value. When [X] (= [M]: the concentration of the simple ion) is calculated , the concentration of each species can be obtained: $[MX] = K_1[X]^2$, $[M_2X] = K_2[X]^3 = [MX_2] = K_3[X]^3$. The total value of the equivalent conductivity, Λ, is given by the summation of those of the simple ions (Λ_0) and the triple ions (Λ_T). The Λ_T value was assumed to be the one-third of the Λ_0 value.[8,9)]

$$\Lambda = \frac{[X]}{C_s}\,\Lambda_0 + \frac{[MX_2]}{C_s}\,\Lambda_T \tag{2}$$

When the quadrupole formation must be considered, the following fourth-order equation[9)] is solved:

$$4\,K_4\,K_2\,[X]^4 + 3\,K_2\,[X]^3 + K_1\,[X]^2 + [X] - C_s = 0 \tag{3}$$

where K_4 is the formation constant of the quadrupole (M_2X_2) from the triple ion (M_2X^+ or MX_2^-) and the simple ion (X^- or M^+). The concentration of M_2X_2 equals $K_4[M_2X][X] + K_5[MX_2][M]$ (assuming $K_4 = K_5$).

At first, the activity coefficients of all the species were assumed to be unity. Then, the activity coefficients of ions were calculated by the Debye-Hückel limiting law ($-\log f_\pm = A\,\mu^{1/2}$). The ionic strength was evaluated by the sum of [X] and $[MX_2]$. The activity coefficients of uncharged species were assumed to be unity.

The conductometric measurements were carried out with a Yanagimoto conductivity outfit (model MY-8) at 25±0.02 °C.

The conductivity data of the salts were treated by the Shedlovsky method, and the results are listed in Table 1. Tetraethylammonium, tributylammonium, and lithium perchlorates and tetraethylammonium trifluoro-

Table 1. The Λ_0 and apparent K_a values of salts in propylene carbonate

Salt	Shedlovsky		
	Λ_0	K_a a)	Λ_0(calcd) b)
Et_4NClO_4	33.01	2.71	
$n\text{-}Bu_3NHClO_4$	29.20	0.67	
$LiClO_4$	26.29	3.02	
Et_4NCF_3COO	31.91	0	
$n\text{-}Bu_3NHCF_3COO$	28.25	5.48×10^2	28.10
$LiCF_3COO$	71.99	2.70×10^4	25.19

a) Association constant, $M^+ + X^- \rightleftarrows MX$ (K_a). b) By Kohlrausch's law.

acetate behaved as strong electrolytes in propylene carbonate. The association constants (K_a) of tributylammonium and lithium trifluoroacetates showed that these salts were rather weak electrolytes. The Λ_0 value of n-Bu_3NHCF_3COO (28.25) directly given by the Shedlovsky method was close to the value (28.10), given indirectly after the calculation with Kohlrausch's law. On the other hand, the apparent Λ_0 value directly given by the Shedlovsky method was much larger than that indirectly given by the calculation with Kohlrausch's law for $LiCF_3COO$. The inconsistency in Λ_0 values may indicate that some additional reactions other than ion pair formation occur in the solution.

In Fig. 1 is shown the relation between the observed Λ values and $C^{1/2}$ of $LiCF_3COO$. The Λ values calculated only with the ion pair formation differed from the observed values (the relative error of +31.7% at $C_s = 6.0 \times 10^{-3}$ M (1 M = 1 mol/dm^3)). Jansen and Yeager[10)] have reported the similar positive deviations for the same system by the analysis of the Fouss-Hsia (ion pair) equation. They tried to fit the observed values with the Kraus[1,11)] and the Wooster[12)] equations in vain. The conductance function which assumed the formation of only ion pair and ion pair dimers (quadrupole) gave the poor fit. Therefore, they concluded that lithium trifluoroacetate forms a variety of ion aggregate species in propylene carbonate. Our calculation with Eqs. 1 and 2 also caused the large relative error in Λ values. However, the Λ values calculated with Eqs. 2 and 3 fitted completely the observed Λ values (the relative error of less than ±2.0% for $C_s = (0.4\text{-}6.0) \times 10^{-3}$ M with the values of $K_1 = 1.5 \times 10^3$, $K_2 = 1.3 \times 10^5$, and $K_4 = 1.9 \times 10^3$). In the above discussion, the changes of the activity coefficients of ions with the changing concentration of the salt were ignored. The introduction of the activity coefficient caused slight changes in the equilibrium constants (cf. Table 2). By the way, the apparent K_a value obtained by the Shedlovsky method should differ from the K_1 or K^a_1 value if the higher aggregate

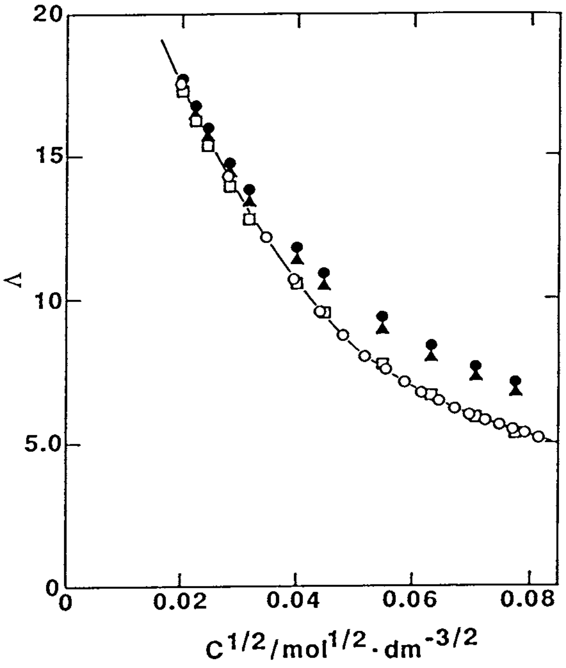

Fig. 1. The observed and calculated Λ values of CF_3COOLi in propylene carbonate: (○) observed; (●) calculated only with the ion pair; (▲) calculated with the ion pair and the triple ions; (□) calculated with the ion pair, triple ion and the quadrupole, $K_1 = 1.51 \times 10^3$, $K_2 = 1.30 \times 10^5$, $K_4 = 1.9 \times 10^3$, $\Lambda_0 = 25.19$, and $\Lambda_T = \Lambda_0/3$.

Table 2. Equilibrium constants, K^a_1, K^a_2, and K^a_4 corrected by the activity coefficients

Salt	K^a_1	K^a_2	(K^a_2/K^a_1)	K^a_4	(K^a_4/K^a_1)	Error[a)]/%
	[Acetonitrile]					
n-Bu_3NHCF_3COO	3.65×10^3	5.0×10^5	137	4.0×10^2	0.11	-0.53 – +0.63
	[Benzonitrile]					
n-Bu_3NHCF_3COO	2.025×10^5	1.0×10^7	49.4	6.0×10^3	0.03	-0.60 – +0.51
	[Propylene Carbonate]					
n-Bu_3NHCF_3COO	6.08×10^2	(5×10^3)	(8.2)			-0.33 – +0.28
$LiCF_3COO$	1.59×10^3	1.1×10^5	69.2	3.0×10^3	1.89	-1.69 – +1.90

a) The relative error of the calculated value to the observed Λ value.

formations are significant.

The observed Λ values of n-Bu_3NHCF_3COO in benzonitrile were properly explained by the ion pair, triple ion, and quadrupole formations. The relative error was -0.04 – +1.98% without the quadrupole formation, and was -6.54 – +0.28% only with the ion pair formation (K^a_1). The Λ_0 value directly obtained by the Shedlovsky method (14.87) was much smaller than the Λ_0(calcd) value (47.1). The shortage or the excess in Λ_0 values may be caused by the relative strength of the triple ion and quadrupole formation (K^a_2/K^a_1 and K^a_4/K^a_1).

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