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Triple Ion and Quadrupole Formations from Trialkylammonium Sulfonates and Nitrate in Protophobic Aprotic Solvents with Higher Dielectric Constants

Masashi Hojo,* Yoshihiro Miyauchi, and Yoshihiko Imai
Department of Chemistry, Faculty of Science, Kochi University,
Akebono-cho, Kochi 780

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The formation of symmetrical triple ions (2 $M^+ + X^- \rightleftarrows M_2X^+$, ($K_2$); $M^+ + 2X^- \rightleftarrows MX_2^-$, ($K_3$); $K_2 = K_3$) and the quadrupole ($M_2X^+ + X^- \rightleftarrows M_2X_2$, ($K_4$); $MX_2^- + M^+ \rightleftarrows M_2X_2$, ($K_5$); $K_4 = K_5$), in addition to the ion pair formation ($M^+ + X^- \rightleftarrows MX$, ($K_1$)) from uni-univalent salts (MX) has been examined in acetonitrile (dielectric constant $\varepsilon = 35.95$), benzonitrile ($\varepsilon = 25.2$), nitrobenzene ($\varepsilon = 34.82$), and nitromethane ($\varepsilon = 36.67$) at 25 ° by means of conductometry. Tho molar conductivities (Λ) of tributylammonium methanesulfonate (n-$Bu_3NHCH_3SO_3$) of (0.4—6.0) $\times 10^{-3}$ M (1 M=1 mol dm^{-3}) in benzonitrile were explained by the formation of triple ions ($K^a_1 = 8.4 \times 10^4$, $K^a_2 = K^a_3 = 5.5 \times 10^5$, corrected by the activity coefficients of ions) within ±0.85% relative error, assuming that $\Lambda_T = \Lambda_O / 3$ (Λ_T: the limiting molar conductivity of the triple ions; Λ_O: that of the simiple ions). In nitrobenzene, however, the quadrupole formation must be invoked for the salt in the same concentration range ($K^a_1 = 1.38 \times 10^5$, $K^a_2 = K^a_3 = 4.75 \times 10^7$, $K^a_4 = K^a_5 = 8.5 \times 10^2$). The alternative formation constant of the quadrupole (2 $MX \rightleftarrows M_2X_2$, ($K_{41}$)) was evaluated as $K^a_{41} = 5.0$ instead of K^a_4. Triple ion formation was observed in acetonitrile and nitromethane, but not in an amphiprotic solvent, ethanol ($\varepsilon = 24.55$). The tendency for triple ion formation or higher aggregate formations from trialkylammonium salts was found to decrease as follows: $Cl^- > CH_3SO_3^-$, $Br^- >$ TsO^-, $NO_3^- > I^-$, $CF_3SO_3^- >$ (ClO_4^-). The difference in the aggregate forming ability is discussed from the view point of basicity of the anions, the strength for a proton acceptor in hydrogen bonding, and the localization of electrons in the anion molecule.

It was been widely accepted that the symmetrical triple ion formation from a uni-univalent salt could occur only in low permittivity media ($\varepsilon < 12$). Fuoss and Kraus[1)] introduced the concept of the triple ion in order to explain the minimum, conductometrically observed, in the relation between the molar conductivity (Λ) and the concentration (C) of tetraisopentylammonium nitrate in dioxane-water mixtures. The formation constant of the quadrupole ($2MX \rightleftarrows M_2X_2$) for triisopentylammonium picrate in benzene was obtained by cryoscopy,[2)] neglecting the concentrations of single and triple ions. Recently, Salomon et al.[3)] treated the minimum in the Λ-$C^{1/2}$ curves of $LiAsF_6$ and $LiClO_4$ in methyl acetate with alternative models either involving triple ions or neglecting triple ions. Previously, Songstad et al.[4)] suggested that triple ions can be neglected and that the observed increase in Λ is due to a decreasing ion association with an increase in the solution permittivity ($\varepsilon = \varepsilon_0 + \Delta C$).

The unilateral triple ion formation and not the bilateral (symmetrical) triple ion formation was introduced by Wooster in 1937.[5)] He dealt with the conductivity data of sodium diphenylketyl in liquid ammonia. Salmon treated the conductivity data of silver halides and pseudohalides in pyridine in terms of complex equilibria involving ion pairs, asymmetric triple ions, and quadrupoles.[6)] The homoconjugation formation (HA_2^-) from an acid (HA), which is sometimes observed in protophobic solvents, can be treated by the French–Roe method.[7)] This method was extended by Izutsu et al.[8)] for cases in which the dissociation of HA is appreciable.

We have developed a new polarographic method,[9,10)] in which the positive shift in the half-wave potential ($E_{1/2}$) of the anodic (mercury dissolution) wave with the addition of (Lewis) acids is made use of for the analysis. The new method has enabled us to find a number of new species, such as $RCOO^-(M^+)_2$ (R=Me, Ph; M=Li, Na), $(Li^+)_2Cl^-$, $(R_3NH^+)_2Br^-$ (R=Me, Et, n-Bu, etc.) in acetonitrile[9,10)] and other protophobic solvents.[11)] To the contrary, by the conventional polarographic analysis, we found $M^+(C_6H_5COO^-)_2$ (M=Li, Na, K), $Li^+(Cl^-)_n$ (n=1—4), $R_3NH^+(Br^-)_2$, etc. in acetonitrile.[9,12)] The symmetrical triple ion formation from $R_3NH^+X^-$ (R=Me, Et, n-Bu; X=Cl, Br) in acetonitrile was confirmed both by polarography and conductometry.[12)] In a previous paper,[13)] we have concluded that the triple ion formation from trialkylammonium halides in protophobic aprotic solvents of relatively high dielectric constants ($20 < \varepsilon < 65$) is caused mainly by the hydrogen bonding force. For the solvents, the triple ion formation from tributylammonium halides decreased in the following order: nitrobenzene>benzonitrile>acetone, acetonitrile >propylene carbonate. The conductivity data of CF_3COOLi in propylene carbonate were properly explained by the strong formation of the quadrupole, in addition to the symmetrical formation of the triple ion and the ion pair formation.[14)]

In the present study, by means of conductometry, we examined the triple ion formation or higher ion aggregates from trialkylammonium methanesulfonate, p-toluenesulfonates, and nitrate in acetonitrile, benzonitrile, nitrobenzene, and nitromethane. Lithium and tributylammonium trifluoromethanesulfonates were also briefly examined. The main purpose of this study was to demonstrate the common occurrance for triple ion formation from the salts of *strong* acids, except for perchloric acid.

Theoretical

A third-order equation 1[12,13] was solved for each analytical concentration (C_S) of a salt (MX) in order to calculate the concentration of the simple ion ([X]) in the solution, in which, the symmetrical triple ion formation occurs.

$$3K_2[X]^3 + K_1[X]^2 + [X] - C_S = 0, \qquad (1)$$

where K_1 is the 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 be the same value. Once, [X] (=[M]) was calculated, the concentration of each species could be obtained: $[MX]=K_1[X]^2$, $[M_2X]=K_2[X]^3=[MX_2]=K_3[X]^3$. The total values of the molar conductivity, Λ, is determined by a summation of those of the simple ions (Λ_O) and the triple ions (Λ_T),

$$\Lambda = \frac{[X]}{C_S}\Lambda_O + \frac{[MX_2]}{C_S}\Lambda_T, \qquad (2)$$

where Λ_T was assumed to be one-third of the Λ_O values.[12,13] When the triple ion formation could be neglected, the first term in Eq. 1 was omitted ($K_2=K_3=0$). When both the triple ion and quadrupole formation must be considered, the following fourth-order equation was solved,[13]

$$4K_4K_2[X]^4 + 3K_2[X]^3 + K_1[X]^2 + [X] - C_S = 0, \qquad (3)$$

where K_4 is the formatioin 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 $K_4[M_2X][X]+K_5[MX_2][M]$ (assumed $K_4=K_5$).

At first, the activity coefficients of all the species were assumed to be unity. Then, the activity coefficients of ions were calculated[13] by the Debye–Hückel limiting law ($-\log f_\pm = A\,\mu^{1/2}$). In spite of the relatively high dielectric constants of the solvents, the association between M_2X^+ and X^-, or MX_2^- and M^+ (the formation of the quadrupole: M_2X_2) should be considered for the high concentrations of some salts. The alternative process of the quadrupole formation is the association between ion pairs:

$$2MX \rightleftarrows M_2X_2, \qquad K_{41} = \frac{[M_2X_2]}{[MX]^2}. \qquad (4)$$

In this case, Eq. 3 must be rearranged to

$$2K_{41}K_1^2[X]^4 + 3K_2[X]^3 + K_1[X]^2 + [X] - C_S = 0. \qquad (5)$$

Experimental

Commercially obtained nitromethane (Wako Pure Chemicals, GR grade) was purified by drying with molecular sieves (Wako type 5A) for several days and distilling in vacuo (40—50 mmHg, 1 mmHg=133.322 Pa). The purification methods of acetonitrile,[15] benzonitrile, nitrobenzene, and ethanol[13] were described in previous papers. Specific conductivities of acetonitrile and nitromethane were ca. 7×10^{-8} and ca. 9×10^{-8} S cm^{-1}, respectively, and those of the other solvents were shown in a previous paper.[13] The dielectric constants and viscosity of nitromethane at 25 °C are $\varepsilon=36.67$ and $\eta=0.00627$ P, respectively.[16] The viscosities of acetonitrile,[12] benzonitrile, nitrobenzene, and ethanol[13] were also given in the previous papers.

The preparation and purification methods of $LiClO_4$, Et_4NClO_4, n-Bu_4NClO_4, Et_3NHClO_4, and n-Bu_3NHClO_4 were mentioned previously.[12] Tetraethylammonium methanesulfonate ($Et_4NCH_3SO_3$) was prepared from tetraethylammonium hydroxide (20 wt% aqueous solution, Aldrich Chemical) and the equivalent amount of methanesulfonic acid (Wako, GR grade) in methanol. The solution was evaporated to dryness under reduced pressure at less than 50 °C. Produced white crystals were washed with diethyl ether several times (cf. Ref. 17). Tetraethylammonium *p*-toluenesulfonate (Et_4NTsO) and trifluoromethanesulfonate ($Et_4NCF_3SO_3$) were prepared in a similar way from *p*-toluenesulfonic acid (Wako, GR grade) and trifluoromethanesulfonic acid (Wako, GR grade). Tetrabutylammonium methanesulfonate (n-$Bu_4NCH_3SO_3$) was prepared from tetrabutylammonium hydroxide (ca. 10% aqueous solution, Wako GR grade) and methanesulfonic acid in methanol. Tetraethylammonium nitrate (Et_4NNO_3) was prepared from Et_4NOH and nitric acid (Wako, GR grade) in water. Produced white crystals were treated in a similar way. Tributylammonium methanesulfonate (n-$Bu_3NHCH_3SO_3$), *p*-toluenesulfonate (n-Bu_3NHTsO), and trifluoromethanesulfonate (n-$Bu_3NHCF_3SO_3$) were prepared from tributylamine (Wako, GR grade) and the corresponding acid in methanol. White crystals, obtained after evaporation at less than 50 °C, were recrystallized or washed with diethyl ether. Triethylammonium *p*-toluenesulfonate (Et_3NHTsO) was prepared from triethylamine (Wako, GR grade) and *p*-toluenesulfonic acid in the similar way, but the nitrate was prepared from aqueous solution. By the way, tributylammonium nitrate and triethylammonium, methanesulfonate were not obtained as a solid at room temperature, and were not used in the present study. Lithium trifluoromethanesulfonate ($LiCF_3SO_3$) was prepared from Li_2CO_3 (Wako, GR grade) and trifluoromethanesulfonic acid in cold water. The solution was evaporated to dryness at less than 60 °C. All of chemicals were dried under vacuum over P_2O_5.

Conductometric measurements were carried out with a Yanagimoto conductivity outfit (Model MY-8) in a Yanagimoto conductivity cell (Type C) at (25±0.02) °C. Details concerning the experiments and the analysis were described in a previous paper.[13]

Results and Discussion

Tributylammonium Methanesulfonate, Tributyl-, and Triethylammonium *p*-toluenesulfonates. In Table 1 are shown the limiting molar conductivity (Λ_O) and the association constants (K_a), given by an analysis using the Shedlovsky method.[12,18] The association constants of all of the tetraalkylammonium salts and of all the perchlorates have small values, showing that these salts behave as rather strong electrolytes in protophobic aprotic solvents, acetonitrile, benzonitrile, nitrobenzene, and nitromethane. While, the (apparent) association constant values of trialkylammonium methanesulfonate ($R_3NHCH_3SO_3$) and *p*-toluenesulfonates (R_3NHTsO) are large in all protophobic solvents. These trialkylammonium salts are weak electrolytes in these solvents.

Table 1. Λ_0 and Apparent K_a Values of Trialkyl-, Tetraalkylammonium and Lithium Salts in Several Protophobic Aprotic Solvents and Ethanol by the Shedlovsky Method

Salt	Shedlovsky		
	Λ_0[a]	K_a[b]	Λ_0 (calcd)[c]
(Acetonitrile)			
$LiClO_4$	178.73	1.07×10	
$Et_4NCH_3SO_3$	180.81	1.05×10	
n-$Bu_3NHCH_3SO_3$	155.94	2.16×10^3	159.9
Et_4N TsO	165.09	2.12	
Et_3NH TsO	164.29	1.67×10^3	167.5
n-Bu_3NH TsO	145.69	1.71×10^3	144.2
$Et_4NCF_3SO_3$	186.42	5.03	
$LiCF_3SO_3$	174.15	1.28×10^2	172.0
Et_4NNO_3	196.60	1.12×10	
Et_3NHNO_3	201.91	1.21×10^3	199.0
(Benzonitrile)			
Et_4NClO_4	54.64	6.31×10	
Et_3NHClO_4	55.42	2.69×10^2	
$LiClO_4$	47.66	2.44×10^2	
$Et_4NCH_3SO_3$	50.65	1.45×10^2	
n-$Bu_3NHCH_3SO_3$	17.20	8.24×10^3	44.52
Et_4N TsO	46.70	1.45×10^2	
n-Bu_3NH TsO	18.36	8.57×10^3	40.57
$Et_4NCF_3SO_3$	52.15	6.19×10	
$LiCF_3SO_3$	39.67	2.13×10^3	45.17
Et_4NNO_3	55.53	9.74×10	
Et_3NHNO_3	32.94	1.14×10^4	56.31
(Nitrobenzene)			
Et_4NClO_4	38.68	1.97×10	
Et_3NHClO_4	39.00	3.17×10^2	
$Et_4NCH_3SO_3$	35.28	4.36×10	
n-$Bu_3NHCH_3SO_3$	5.31	1.03×10^3	30.80
Et_4N TsO	32.27	4.60×10	
Et_3NH TsO	9.28	2.66×10^3	32.59
n-Bu_3NH TsO	6.93	1.92×10^3	27.79
$Et_4NCF_3SO_3$	36.74	1.65×10	
n-$Bu_3NHCF_3SO_3$	32.19	1.15×10^3	32.26
Et_4NNO_3	39.94	3.08×10	
Et_3NHNO_3	16.29	5.20×10^3	40.26
(Nitromethane)			
n-Bu_4NClO_4	102.51	0	
Et_4NClO_4	116.99	4.24	
n-Bu_3NHClO_4	106.79	3.95×10	
Et_3NHClO_4	119.11	4.44×10	
$Et_4NCH_3SO_3$	103.71	4.61	
n-$Bu_3NHCH_3SO_3$	82.47	3.34×10^3	93.46
Et_4N TsO	95.56	7.39	
n-Bu_3NH TsO	79.12	2.89×10^3	85.28
Et_4NNO_3	115.91	3.13	
Et_3NHNO_3	114.12	2.35×10^3	117.9
(EtOH)			
n-$Bu_4NCH_3SO_3$	42.17	5.21×10	
n-$Bu_3NHCH_3SO_3$	42.57	1.89×10^2	42.27

a) Molar conductivity ($cm^2\,S\,mol^{-1}$). b) Association constant. $M^+ + X^- \rightleftarrows MX$ (K_a). c) The Λ_0 value calculated by Kohlrausch's law.

The Λ_0 values of weak electrolytes in the protophobic solvents, directly obtained by the Shedlovsky method, were often much smaller than those obtained indirectly by Kohlrauch's law. For instance, in benzonitrile, the direct Shedlovsky analysis of *n*-Bu_3NHTsO gave a Λ_0 of 18.36, while a calculation with Kohlrausch's law gave the Λ_0 of 40.57 (Λ_0(*n*-Bu_3NHTsO)=Λ_0(*n*-Bu_3NHClO_4)+Λ_0(Et_4NTsO)−Λ_0(Et_4NClO_4)). The Λ_0 value of *n*-Bu_3NHClO_4 was adapted from the previous work.[13] This kind of shortage in Λ_0 values has been reported for some salts or acids in protophobic aprotic solvents. French and Roe[7] described the situation as follows: Moore and Johns[19] by a method of graphical extrapolation, suggested a value of 7.5 for the limiting molar

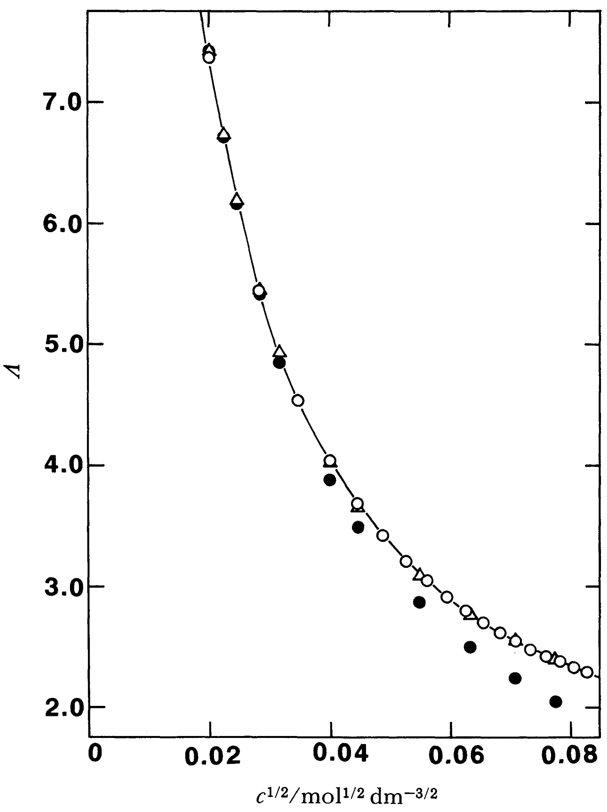


Fig. 1. Observed and calculated Λ values of *n*-$Bu_3NHCH_3SO_3$ ((0.38—7.0)×10^{-3} M) in benzonitrile: (○) observed, (△) calculated with the ion pair and triple ion formations, K_1=7.5×10^4, K_2=K_3=1.0×10^7, Λ_0=44.52, and Λ_T=Λ_0/3; (●) calculated only with the ion pair formation.

conductance of picric acid in acetone, whereas Kraus and Reynolds[20] subsequently gave the limiting mobility in acetone of the picrate ion alone as 78.5. We have also reported the inconsistency in Λ_0 values for trialkylammonium halides[12,13] and lithium trifluoroacetate[14] in protophobic aprotic solvents. The inconsistency in Λ_0 values must be a good indication that ion aggregates above the ion pair between an anion and a cation occur in solutions.

Figure 1 shows the Λ vs. $C^{1/2}$ relation of tributylammonium methanesulfonate in benzonitrile. The Λ values, calculated with Eqs. 1 and 2, coincided with the observed values within less than ±0.9% over the analytical concentration of $(0.4—6.0)\times10^{-3}$ M (1 M= 1 mol dm^{-3}) with $K_1=7.5\times10^4$, $K_2=K_3=1.0\times10^7$, $\Lambda_0=44.52$, $\Lambda_T=\Lambda_0/3$. Ignoring triple ion formation, a calculation involving ion pair formation caused large negative deviations to the observed Λ values (the relative error of −15% at $C_S=6.0\times10^{-3}$ M). In the above discussion, the activity coefficients of ions have not been corrected. A recalculation with the equilibrium constants corrected by the activity coefficients ($K^a_1=K_1/f_\pm^2$, $K^a_2=K_2/f_\pm^2$) gave a good fit (the relative error of −0.71—+0.84%) over the concentration range of $(0.4—6.0)\times10^{-3}$ M (cf. Table 2). With the K^a_1 and K^a_2, the equilibrium concentrations of the simple ions, the ion pair, and the triple ions were calculated to be 1.09×10^{-4}, 8.72×10^{-4}, and 6.23×10^{-6} M, respectively at $C_S=1.0\times10^{-3}$ M. The relation between the equilibrium concentration of each species ([X], [MX], or [MX$_2$]) and the analytical salt concentration (C) is shown in Fig. 2. When the salt concentration is very low (C_S or $C\leqq5\times10^{-4}$ M), the equilibrium concentration of triple ions can be negligible, compared to those of the simple ions and the ion pair. The ion pair formation constant (K_1 or K^a_1) was first evaluated using the Λ value at $C_S=4.0\times10^{-4}$ M. After a determination of the K_1 value, the K_2 value was evaluated by using the Λ values at higher concentrations. By the way, the Λ values at higher concentrations could not be fitted only with the ion pair formation constant, even after correction of the activity coefficient. Furthermore, even the triple ion formation could not explain the Λ_{obsd} values at extremely high salt concentrations (cf. Fig. 3).

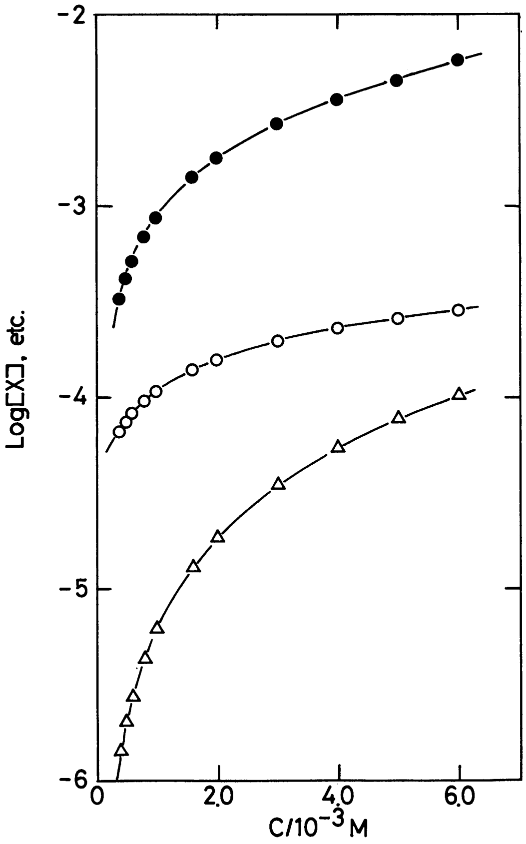


Fig. 2. The equilibrium concentrations of the species from n-Bu$_3$NHCH$_3$SO$_3$ in benzonitrile: (○) the simple ions, [M]=[X]; (●) the ion-pair, [MX]; (△) the triple ions, [M$_2$X]=[MX$_2$]. $K^a_1=8.41\times10^4$ and $K^a_2=K^a_3=5.5\times10^6$.

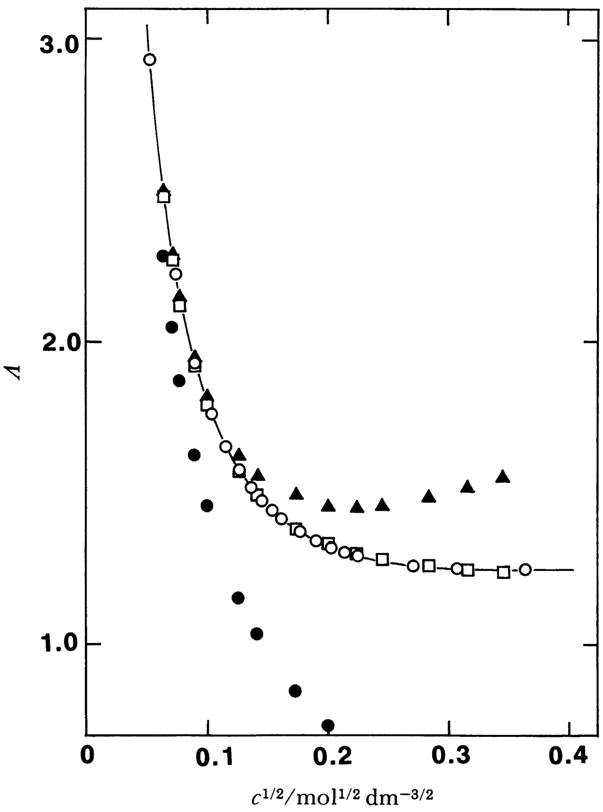


Fig. 3. Observed and calculated Λ values of n-Bu$_3$NHCH$_3$SO$_3$ at higher concentration ($(0.27—13.3)\times10^{-2}$ M) in benzonitrile: (○) observed; (□) calculated with the ion pair, triple ion, and quadrupole formations, $K_1=9.0\times10^4$, $K_2=K_3=9.5\times10^6$, $K_4=K_5=8.2\times10^2$, $\Lambda_0=44.52$, and $\Lambda_T=\Lambda_0/3$; (▲) calculated with the ion pair and triple ion formations; (●) calculated only with the ion pair formation.

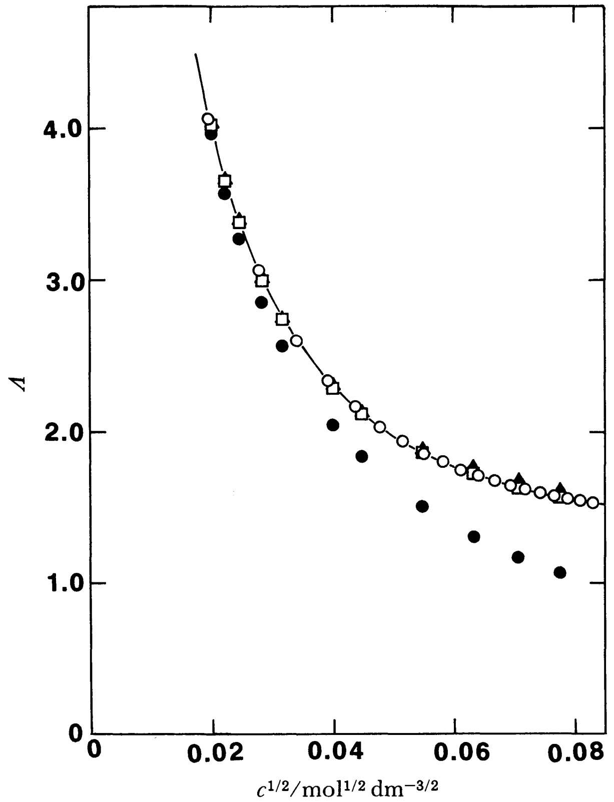


Fig. 4. Observed and calculated Λ values of n-$Bu_3NHCH_3SO_3$ in nitrobenzene: (○) observed; (□) calculated with the ion pair, triple ion, and quadrupole formations, $K_1=1.31\times10^5$, $K_2=K_3=5.8\times10^7$, $K_4=K_5=8.0\times10^2$, $\Lambda_0=30.8$, and $\Lambda_T=\Lambda_0/3$; (▲) calculated with the ion pair and triple ion formations; (●) calculated only with the ion pair formation.

The Λ vs. $C^{1/2}$ relation for tributylammonium methanesulfonate in nitrobenzene is shown in Fig. 4. In this case, triple ion formation did not fully account for the conductivity data. Quadrupole formation was introduced in order to explain the Λ_{obsd} of n-$Bu_3NHCH_3SO_3$ ((0.4—6.0)$\times10^{-3}$ M) in nitrobenzene. The calculation by Eqs. 2 and 3 gave a good fit (the relative error in the calculated value to the observed Λ value of −0.87—+0.84%), with values of $K_1=1.31\times10^5$, $K_2=K_3=5.8\times10^7$, $K_4=K_5=8.0\times10^2$, $\Lambda_0=30.80$, and $\Lambda_T=\Lambda_0/3$. If the quadrupole formation was ignored, the error increased to −0.52—+3.52%. In addition, neither the quadrupole nor triple ion formations were accounted. Then, the calculation only with K_1 gave a large error (−31.48——0.72%).

The equilibrium constans were corrected using the activity coefficients ($K^a{}_1=K_1/f_\pm{}^2$, $K^a{}_2=K_2/f_\pm{}^2$, and $K^a{}_4=K_4/f_\pm{}^2$). The equibibrium constants corrected by the activity coefficients were adjusted in order to minimize any error in the Λ values. With values of $K^a{}_1=1.38\times10^5$, $K^a{}_2=K^a{}_3=4.75\times10^7$, $K^a{}_4=K^a{}_5=8.5\times10^2$, $\Lambda_0=30.8$, $\Lambda_T=\Lambda_0/3$, the error was minimized to −0.74—+0.87% over the entire concentration range. An analysis with Eqs. 2 and 5 gave the same values of $K^a{}_1$ and $K^a{}_2=K^a{}_3$, and $K^a{}_{41}=5.0$ (the relative error of −0.76—+0.86%) instead of $K^a{}_4$. Figure 5 shows the equilibrium concentrations of the species in the solution. The triple ions ($[M_2X]=[MX_2]$) exceed the simple ions ($[M]=[X]$) at $C=3.5\times10^{-3}$ M.

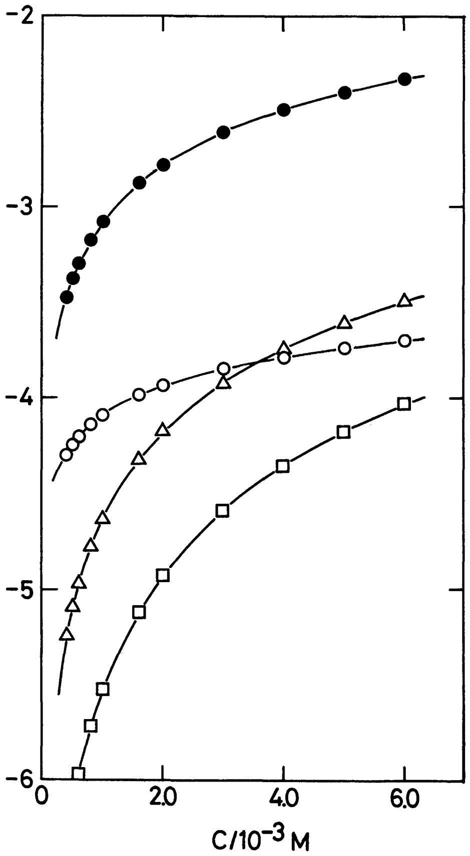


Fig. 5. The equilibrium concentrations of the species from n-$Bu_3NHCH_3SO_3$ in nitrobenzene: (○) the simple ions; (●) the ion-pair; (△) the triple ions; (□) the quadrupole, $[M_2X_2]$. $K^a{}_1=1.38\times10^5$, $K^a{}_2=4.75\times10^7$, and $K^a{}_4=K^a{}_5=8.5\times10^2$.

In nitromethane and acetonitrile, no good fit in the Λ values was found for n-$Bu_3NHCH_3SO_3$ of (0.4—6.0)$\times10^{-3}$ M without a correction involving the activity coefficient. However, after correcting the activity coefficients of ions, the calculated values fitted the Λ_{obsd} values. By an analysis using Eqs. 2 and 5, the $K^a{}_{41}$ values were calculated to be 5.0 and 4.0 in nitromethane and acetonitrile, respectively. The extent of the triple ion formation in these two solvents was smaller than that in nitrobenzene. As a summary for the methanesulfonate, the observed Λ values over the concentration range of (0.4—6.0)$\times10^{-3}$ M were explained by the ion pair, triple ion, and quadrupole formations in the solvents, except in benzonitrile. In benzonitrile, the Λ values could be explained by ion pair and triple ion formations.

Tributylammonium methanesulfonate caused only ion pair formation in an amphiprotic solvent, ethanol,

Table 2. Equilibrium Constants, K^a_1, $K^a_2=K^a_3$, and $K^a_4=K^a_5$, Corrected by the Activity Coefficients

Salt	K^a_1	$K^a_2=K^a_3$	(K^a_2/K^a_1)[a]	$K^a_4=K^a_5$	Relative error/%[b]
(Acetonitrile)					
n-Bu$_3$NHCH$_3$SO$_3$	2.50×10^3	2.70×10^5	108	(50)	−0.92—+0.44
n-Bu$_3$NH TsO	1.80×10^3	1.95×10^5	108		−0.68—+0.66
Et$_3$NH TsO	1.95×10^3	1.50×10^5	76.9		−0.72—+0.65
LiCF$_3$SO$_3$	2.10×10^2				−0.34—+0.43
Et$_3$NHNO$_3$	1.30×10^3	6.10×10^4	46.9		−0.57—+0.34
(Benzonitrile)					
n-Bu$_3$NHCH$_3$SO$_3$	8.41×10^4	5.50×10^6	65.4		−0.71—+0.84
n-Bu$_3$NH TsO	6.15×10^4	3.35×10^6	54.5		−0.26—+0.29
LiCF$_3$SO$_3$	3.80×10^3	1.00×10^4	(2.6)		−0.64—+0.96
Et$_3$NHNO$_3$	4.22×10^4	1.20×10^6	28.4		−0.44—+0.26
(Nitrobenzene)					
n-Bu$_3$NHCH$_3$SO$_3$	1.38×10^5	4.75×10^7	344	850	−0.74—+0.87
n-Bu$_3$NH TsO	8.20×10^4	1.90×10^7	232		−0.75—+0.74
Et$_3$NH TsO	6.95×10^4	1.30×10^7	187		−0.42—+0.62
n-Bu$_3$NHCF$_3$SO$_3$	1.325×10^3	6.00×10^4	45.3	(25)	−0.22—+0.20
Et$_3$NHNO$_3$	4.98×10^4	6.00×10^6	120		−0.88—+0.98
(Nitromethane)					
n-Bu$_3$NHCH$_3$SO$_3$	5.00×10^3	6.00×10^5	120	(70)	−0.59—+0.63
n-Bu$_3$NH TsO	3.85×10^3	4.00×10^5	104	(50)	−0.57—+0.41
Et$_3$NHNO$_3$	2.82×10^3	1.50×10^5	53.2		−0.45—+0.53
(EtOH)					
n-Bu$_3$NHCH$_3$SO$_3$	4.19×10^2				−1.00—+0.92

a) $K^a_2/K^a_1=a_{\mathrm{M_2X}}/(a_{\mathrm{MX}}\cdot a_{\mathrm{M}})$ and $K^a_3/K^a_1=a_{\mathrm{MX_2}}/(a_{\mathrm{MX}}\cdot a_{\mathrm{X}})$. b) The relative error in the calculated Λ value to the observed Λ value (over the range of $(0.4—6.0)\times10^{-3}$ M salt concentration).

Table 3. Comparison of the Calculated Λ Values with the Observed Λ Values for Tributylammonium p-Toluenesulfonate (n-Bu$_3$NHTsO) in Nitrobenzene

$10^3\times C_s$[a]	$10^4\times$[X]	$10^4\times$[M$_2$X]	Λ_{calcd}	Λ_{obsd}[a]	Relative error/%[b]	Relative error/%[c]
0.4	0.64148	0.063351	4.6034	4.57	+0.73	(+0.14)
0.5	0.72148	0.090134	4.1770	4.17	+0.17	(−0.90)
0.6	0.79340	0.119864	3.8598	3.85	+0.26	(−1.33)
0.8	0.92012	0.186960	3.4128	3.41	+0.08	(−2.57)
1.0	1.03075	0.262826	3.1079	3.13	−0.71	(−4.42)
1.6	1.30426	0.532475	2.5736	2.59	−0.63	(−7.59)
2.0	1.45593	0.740689	2.3661	2.39	−1.00	(−10.00)
3.0	1.77325	1.33821	2.0558	2.06	−0.20	(−14.11)
4.0	2.03524	2.02329	1.8825	1.90	−0.92	(−19.00)
5.0	2.26214	2.77825	1.7720	1.775	−0.17	(−22.22)
6.0	2.46431	3.59167	1.6959	1.685	+0.65	(−24.21)

a) The total concentration of n-Bu$_3$NHTsO and the Λ value, read out from the Λ vs. $C^{1/2}$ curve. b) The relative error of the calculated Λ value to the observed value with $K_1=7.7\times10^4$, $K_2=K_3=2.4\times10^7$, $\Lambda_0=27.79$, $\Lambda_\mathrm{T}=\Lambda_0/3$. c) When only the ion-pair formation ($\mathrm{M^+ + X^- \rightleftarrows MX}$, $K_1=7.7\times10^4$) is accounted.

as shown in Table 2. The Λ_0 values, directly given by the Shedlovsky method, are coincident with that calculated by Kohlrausch's law (cf. Table 1). Ions in ethanol can be strongly solvated by ethanol through hydrogen bonding. To the contrary, both anions and cations are weakly solvated or in an "active" state in protophobic solvents. The higher ion aggregates from tributylammonium methanesulfonate in protophobic solvents could be observed, even at relatively low salt concentrations.

Table 3 shows a comparison of Λ_{calcd} with Λ_{obsd} of tributylammonium p-toluenesulfonate in nitrobenzene. The Λ_{calcd} values over the concentration range of $(0.4—6.0)\times10^{-3}$ M fitted the Λ_{obsd} values, considering ion pair and triple ion formations. After correcting the activity coefficient, a good fit (the relative error of ±0.75%) was obtained with the equilibrium constants (Table 2). However, the situation changed when the concentration of the salt increased: triple ion formation could no longer account for the Λ_{obsd} values. Obviously, the quadrupole or the higher aggregates above the triple ions should be introduced into the system. The Λ_{obsd}

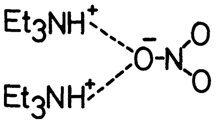
values at higher concentrations ($C_S \geqslant 4.0 \times 10^{-2}$ M) could not be explained within 2% relative error, even by the ion pair, triple ion, and quadrupole formations. The higher ion aggregate (e.g. M_3X_3: $M_2X^+ + MX_2^- \rightleftarrows M_3X_3$, ($K_6$)) could account for the Λ_{obsd} values. However, further discussions may not be verified without correcting the activity coefficient, viscosity, and other factors at very high salt concentrations. Viscosity data of nitrobenzene containing triethylammonium acetates have been reported by Pawelka and Haulait-Pirson.[21] The data of n-Bu_3NHTsO (C_S=(0.4—12.0)$\times 10^{-2}$ M) in benzonitrile were explained by the quadrupole formation ($K_1=5.25\times10^4$, $K_2=K_3=5.06\times10^6$, and $K_4=K_5=7\times10^2$), although the ion pair and triple ion formation caused a relative error of +25% at $C_S=1.0\times10^{-2}$ M in benzonitrile.

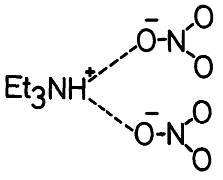
The effect of the chain length of substituted-ammonium cations was examined. Triethylammonium p-toluenesulfonate gave a smaller triple ion formation constant (K^{a}_2) than the tributylammonium salt in acetonitrile and nitrobenzene. The ratio of $K^{\mathrm{a}}_2/K^{\mathrm{a}}_1$ of the tributyl- and triethylammonium salt was 108 and 76.9, respectively in acetonitrile. The dissociation constants of the monoprotonated bases ($\mathrm{p}K_{\mathrm{HA^+}}$) for triethylamine and tributylamine in acetonitrile have been reported to be 18.5 and 18.1 respectively.[22] The acidities of the cations might be concerned with the ion pair and triple ion formation constants.

Lithium and Tributylammonium Trifluoromethanesulfonates. The higher ion aggregates from lithium and tributylammonium trifluoromethanesulfonates ($LiCF_3SO_3$ and n-$Bu_3NHCF_3SO_3$) were examined in acetonitrile, benzonitrile, or nitrobenzene. The Λ_0 and K_{a} values of the trifluoromethanesulfonates, obtained by the Shedlovsky method, are listed in Table 1. Tetraethylammonium trifluoromethanesulfonate behaved as a strong electrolyte in all of the solvents. The K_{a} values showed that the lithium and the tributylammonium salts are weak electrolytes in benzonitrile and nitrobenzene, respectively. The lithium salt seemed to be a moderate weak electrolyte in acetonitrile. In benzonitrile, the Λ_0 value of $LiCF_3SO_3$, directly obtained by the Shedlovsky method, was definitely smaller than that calculated by Kohlrausch's law. The Λ_{calcd} values of $LiCF_3SO_3$ in acetonitrile only with the ion pair formation (K^{a}_1) were fitted to the Λ_{obsd} values over the entire concentration range of (0.4—6.0)$\times10^{-3}$ M within ±0.5% relative error (cf. Table 2). On the other hand, in benzonitrile, a better fit was given by the addition of triple ion formation to the ion pair formation. The Λ values of n-$Bu_3NHCF_3SO_3$ in nitrobenzene could not be accounted for by ion pair formation, even if corrections were made using the activity coefficient. The triple ion and quadrupole formations gave excellent fits (cf. Table 2).

Trifluoromethanesulfonic acid (CF_3SO_3H) is one of the strongest acids in both aqueous and nonaqueous solvents. In acetic acid,[23] CF_3SO_3H has been found to be stronger than perchloric acid by conductivity. However, Sampoli et at.[24] have described that CF_3SO_3H appears to be weaker than $HClO_4$, and obviously stronger than CH_3SO_3H in aqueous solutions. The ion pair formation constant of $LiCF_3SO_3$ in acetonitrile was reported by Fujinaga and Sakamoto.[25] In the present study, only the ion pair formation was again observed from $LiCF_3SO_3$ in acetonitrile. The higher ion aggregates from trifluoromethanesulfonates, however, were discovered in nitrobenzene or benzonitrile. The difference between acetonitrile and nitrobenzene or benzonitrile can be explained by the donor and acceptor numbers[26] given by Gutmann. In protophilic solvents, the trifluoromethanesulfonate anion must be a very weak base because the conjugate acid behaves as a strong acid[27] in a protophilic solvent, dimethyl sulfoxide. However, we think that the $CF_3SO_3^-$ anion should be an effectively strong "base" or hydrogen-bonding acceptor in protophobic solvents, especially in nitrobenzene or benzonitrile, now that the triple ions or the higher aggregates were observed from the trifluoromethanesulfonate salts in the higher permittivity media. In our systems, incidentally, the hydrogen bonding or complex formation ability of the perchlorate ion was neglected, even though such an interaction has been suggested.[28]

Triethylammonium Nitrate. Triethylammonium nitrate in benzonitrile, nitrobenzene, or nitromethane showed the similar shortage in the Λ_0 values (cf. Table 1), as did the methanesulfonates and the p-toluenesulfonate. The equilibrium constants corrected by the activity coefficients of ions, and the relative error in Λ values are shown in Table 2. The Λ_{obsd} values of triethylammonium nitrate in the concentration range (0.4—6.0)$\times10^{-3}$ M in the protophobic aprotic solvents, including acetonitrile, are sufficiently accounted for by the ion pair and the symmetrical triple ion formation.





Very recently, the proton affinity of nitric acid was examined in the gas phase by Cacace et al.[29] They obtained strong evidence for the existence of two isomers, characterized by the $(HO)_2NO^+$ and the $H_2O\cdot NO_2^+$ structures, and for the higher stability of the latter. We have tentatively adapted the $H_2O\cdot NO_2^+$ structure for a triple ion from Et_3NHNO_3 in the protophobic aprotic solvents. On the other hand, Pawlak et al. have reported the stability constants of complex ions HCl_2^-, $H(NO_3)_2^-$, and $H(HSO_4)_2^-$ in acetone.[30] The presence of a quadrupole from $LiNO_3$ in tetrahydrofuran was suggested by conductivity³¹⁾ and ultrasonic absorption³²⁾ studies. The quadrupole, in addition to the triple ions and the ion pair, was invoked for higher concentrations ($(0.1—1.2)\times10^{-1}$ M) of Et_3NHNO_3 in benzonitrile and nitrobenzene (K_4=K_5=4×10^2 and 4.5×10^2, respectively). The minimum in the Λ_{obsd} was not observed up to 0.12 M of the salt in these solvents, though the Λ_{obsd} remained constant at higher concentrations (e.g., Λ=1.99 and 1.71 at C_S=2.18×10^{-2} and 12.2×10^{-2} M, respectively in nitrobenzene). We have reported the minimum in the Λ–$C^{1/2}$ curve for n-Bu_3NHCl and not for the bromide in benzonitrile or nitrobenzene.¹³⁾ We think that the minimum in Λ_{obsd} can be given only by extremely large K_2 (or K_2/K_1) and smaller K_4 values.

According to the K^a_2 (or K^a_2/K^a_1) values in the present and previous¹³⁾ papers, the tendency of the triple ion or the higher aggregate formations from the trialkylammonium salts decreases as follows: Cl^-> $CH_3SO_3^-$, Br^->TsO^-, NO_3^->I^-, $CF_3SO_3^-$>(ClO_4^-). The difference between the methanesulfonate and the p-toluenesulfonate or nitrate may be caused by a difference in the localization of electrons in the anion molecule. Fujinaga and Sakamoto³³⁾ have concluded the strength of some sulfonic acids and perchloric acid in dipolar aprotic solvents: $HClO_4$>CF_3SO_3H>FSO_3H> $CH_3C_6H_4SO_3H$>CH_3SO_3H. The stronger the acids, the less the triple ions formed. Allerhand and Rague Schleyer³⁴⁾ have reported on the strength of the halide anion as a proton acceptor in hydrogen bonding: Cl^->F^->Br^->I^-. This order coincides with our results¹³⁾ for chloride, bromide, and iodide.

Conclusion

Without the minimum in Λ–$C^{1/2}$ curves, the trialkylammonium salts (R_3NHX) of *strong* acids (HX) should form symmetrical triple ions and quadrupoles in poorly solvating solvents. The formation of triple ions or higher ion aggregates from trialkylammonium salts must effect the solvent extraction of acids with amines in organic solvents.

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