

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231408924>

Triple ion formation in acetonitrile

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · JANUARY 1989

Impact Factor: 2.78 · DOI: 10.1021/j100339a079

CITATIONS

28

READS

10

5 AUTHORS, INCLUDING:



Masashi Hojo

Kochi University

114 PUBLICATIONS 1,501 CITATIONS

SEE PROFILE

crystal containing the glassy characteristics. V_f defined as the increment to the hypothetical crystal is not as good a factor for *o*-terphenyl as for the *o*-TP/TPCM mixture, and the glass transition of *o*-terphenyl cannot be regarded as a quasi-equilibrium second-order transition of the Ehrenfest type. The Adam-Gibbs parameter is not effective for *o*-terphenyl. For a summary of the present series,^{2,3} we may be allowed to state that the thermody-

namic factor governing the molecular mobility of molecular liquids including polymer liquids is the configurational internal energy or the configurational entropy.

Acknowledgment. We are grateful to Hironobu Okumura and Kouji Ujita for helpful correspondence.

Registry No. *o*-TP, 84-15-1.

Triple Ion Formation in Acetonitrile

Masashi Hojo,* Tohru Takiguchi, Minoru Hagiwara, Hironori Nagai, and Yoshihiko Imai

Department of Chemistry, Faculty of Science, Kochi University, Kochi 780, Japan

(Received: December 22, 1987; In Final Form: July 11, 1988)

The effect of halide ions on the cathodic waves of cations was examined by means of dc polarography in acetonitrile. The formation constants of $\text{Li}^+(\text{Cl}^-)_n$ ($n = 1-4$), $\text{NH}_4^+(\text{Cl}^-)_n$ ($n = 2$ and 3), $\text{Et}_3\text{NH}^+(\text{X}^-)_n$ ($\text{X} = \text{Cl}$ or Br , $n = 1$ and 2), etc., were obtained. The present and the previous polarographic studies indicated the symmetrical formation of triple ions from trialkylammonium halides, i.e., $K_2 \simeq K_3$, in the following reactions: $\text{M}^+ + \text{X}^- \rightleftharpoons \text{M}^+\text{X}^-$ (K_1), $2\text{M}^+ + \text{X}^- \rightleftharpoons (\text{M}^+)_2\text{X}^-$ (K_2), and $\text{M}^+ + 2\text{X}^- \rightleftharpoons \text{M}^+(\text{X}^-)_2$ (K_3), where M^+ stands for R_3NH^+ ($\text{R} = \text{Me}$, Et , and $n\text{-Bu}$) and X^- is Cl^- , Br^- , or I^- . The conductivity data of $\text{R}_3\text{NH}^+\text{X}^-$ in acetonitrile were quantitatively explained by the triple ions in addition to the ion-pair formation. Assuming that the limiting equivalent conductivity of the triple ions, Λ_T , is one-third of that of the simple ions, Λ_0 , the calculated Λ values of Et_3NHCl ($(0.4-6.0) \times 10^{-3} \text{ M}$) with $K_1 = 2.8 \times 10^4$ and $K_2 = K_3 = 3.0 \times 10^6$ fitted the observed values within 0.9% error, while the error was more than 9% at higher concentrations when only ion pairing was considered. Me_3NHCl and $n\text{-Bu}_3\text{NHCl}$ gave similar results. In the cases of bromide salts, less than 0.9% error in Λ values was given by the assumption of $\Lambda_T = \Lambda_0/2$.

Introduction

In a previous study,¹ we have examined the polarographic anodic (mercury dissolution) waves of halide ions in the presence of Li^+ , benzoic acid, *p*-bromophenol, and R_3NH^+ ($\text{R} = \text{Et}$, etc.) in acetonitrile. The formation of the $(\text{M}^+)_n\text{X}^-$ type species ($\text{M}^+ = \text{Li}^+$, benzoic acid, etc.; $n = 1$ or 2 ; $\text{X} = \text{Cl}$, Br , or I) was confirmed by a newly developed method. In the new method, the formation constants of "complexes" were evaluated by the positive shift in the half-wave potential ($E_{1/2}$) of the mercury dissolution wave from a base (L) in a large excess of (Lewis) acids.²⁻⁶ The method was first proposed by Reilley et al.⁷ in 1956 with a limiting feature for metal-EDTA (ethylenediaminetetraacetic acid) complexes in aqueous solutions. Casassas and Esteban⁸ presented a "general" equation for the method. Unfortunately, however, they introduced rather unrealistic conditions to the equation, which restricted the proper applications of the method.⁹ We have extended the new method further through the utilization of the cathodic wave of $[\text{HgL}]^{2+}$ instead of the mercury dissolution wave of L .⁴⁻⁶ Approximately the same formation constants of the $(\text{M}^+)_n\text{X}^-$ species as those by the anodic wave of X^- were obtained by the positive shift in the $E_{1/2}$ of the second cathodic wave of HgX_2 on the addition of the (Lewis) acids.⁹ The effect of the (Lewis) acids on the half-wave potentials of two cathodic waves of CuCl_2 and CuBr_2 gave similar results.⁹

In the first part of the present paper, the formation of $\text{M}^+(\text{X}^-)_n$ ($\text{M}^+ = \text{Li}^+$, NH_4^+ , Et_3NH^+ , $\text{C}_3\text{H}_5\text{NH}^+$, etc.; $\text{X} = \text{Cl}$, Br , or I ; $n = 1-4$) type species in acetonitrile will be reported. The usual polarographic method is employed to determine the formation constants of the complexes: the negative shift in $E_{1/2}$ of the cathodic wave of the M^+ cation on the addition of a large excess

of X^- was utilized. We have proposed the formation of alkali-metal complexes with carboxylate ions,² cyclic polyamines (cyclam⁶ and tetramethylcyclam⁵), and acyclic polyamines, such as ethylenediamine and triethylenetetramine,⁴ in acetonitrile by the conventional and the newly developed methods.

The coordination numbers of these complexes (Li^+ , Na^+ , or K^+ complexes) were all found to be 4. Now, it will be probable that four halide ions, especially chloride ions, coordinate an alkali-metal cation. Brooker¹⁰ stated that the coordination number of lithium ion has been the subject of several studies with differing conclusions. Incidentally, he also pointed out that tetrahedral coordination is not very common for hydrated ions with only $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ and possibly $[\text{Li}(\text{H}_2\text{O})_4]^+$ exhibiting this structure.

On the basis of the confirmation of the $\text{Li}^+(\text{Cl}^-)_4$, $\text{NH}_4^+(\text{Cl}^-)_3$, $\text{Et}_3\text{NH}^+(\text{X}^-)_2$, and $\text{C}_3\text{H}_5\text{NH}^+\text{X}^-$ species in acetonitrile, in the second part of the present paper we will deal with the triple ion formation from trialkylammonium halides, $\text{R}_3\text{NH}^+\text{X}^-$ ($\text{R} = \text{Me}$, Et , and $n\text{-Bu}$; $\text{X} = \text{Cl}$, Br , and I), by electrical conductivity data.

The concept of triple ion formation was first introduced by Fuoss and Kraus¹¹ as early as 1933 to explain the minimum in the relation between the equivalent conductivity (Λ) and the concentration (C) of tetraisoamylammonium nitrate in dioxane-water mixtures (dielectric constant $\epsilon < 12$). They assumed the triple ion formation from a neutral molecule and a simple ion ($\text{AB} + \text{B}^- \rightleftharpoons \text{AB}_2^-$ and $\text{AB} + \text{A}^+ \rightleftharpoons \text{A}_2\text{B}^+$) by the action of electrostatic forces. Sellers et al.¹² interpreted the conductance behavior of weak acids and bases in nonaqueous solvents in terms of complex equilibria. They suggested that $\text{H}(\text{HA})_n^+$ ($n \geq 1$, $\text{HA} = \text{an acid}$) type species should be considered for a possibility as part of a general equilibrium scheme and that the formation of HAH^+ would turn out to provide an alternate explanation for certain literature data. On the basis of IR and Raman spectra, Bacelon et al.¹³ proposed the formation of triple ions ($\text{Li}^+\text{NCS}^-\text{Li}^+$ and

(1) Hojo, M.; Nagai, H.; Hagiwara, M.; Imai, Y. *Anal. Chem.* **1987**, *59*, 1770; *Chem. Lett.* **1987**, 449.

(2) Hojo, M.; Imai, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1963.

(3) Hojo, M.; Imai, Y. *Anal. Chem.* **1985**, *57*, 509.

(4) Hojo, M.; Imai, Y. *J. Electroanal. Chem.* **1986**, *209*, 297.

(5) Hojo, M.; Hagiwara, M.; Nagai, H.; Imai, Y. *J. Electroanal. Chem.* **1987**, *234*, 251.

(6) Hojo, M.; Imai, Y. *Anal. Sci.* **1985**, *1*, 185.

(7) Reilley, C. N.; Scribner, W. G.; Temple, C. *Anal. Chem.* **1956**, *28*, 450.

(8) Casassas, E.; Esteban, M. *J. Electroanal. Chem.* **1985**, *194*, 11.

(9) Hojo, M.; Sasayama, H.; Izumida, H.; Imai, Y., to be published.

(10) Brooker, M. H. In *The Chemical Physics of Solvation. Part B: Spectroscopy of Solvation*; Dogonadze, R. R., Kalman, E., Kornyshev, A. A., Ulstrup, J., Eds.; Elsevier: Amsterdam, 1986; Chapter 4, p 160.

(11) Fuoss, R. M.; Kraus, C. A. *J. Am. Chem. Soc.* **1933**, *55*, 2387.

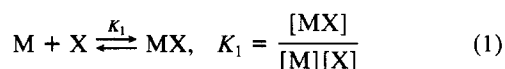
(12) Sellers, N. G.; Eller, P. M. P.; Caruso, J. A. *J. Phys. Chem.* **1972**, *76*, 3618.

(13) Bacelon, P.; Corset, J.; Loze, C. *J. Solution Chem.* **1980**, *9*, 129.

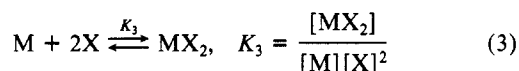
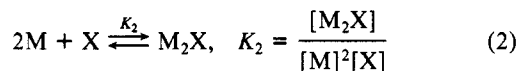
SCN⁻Li⁺NCS⁻) from LiSCN in nitromethane, which has a relatively high dielectric constant ($\epsilon = 36.7$ at 25 °C). Beronius and Lindback¹⁴ investigated the formation of triple ions, using conductance data of LiBr in 1-octanol ($\epsilon = 9.85$ at 25 °C). However, Grigo¹⁵ asserted that it was possible to fit conductance data by Beronius and Lindback¹⁴ without the additional assumption of triple ion formation. On the other hand, Salomon and Uchiyama¹⁶ showed the triple ion formation by fitting the full Fuoss-Hsia equation to the conductivity data. At the same time, they found some limitations in its applications.

Dawson et al.¹⁷ measured the conductances of ammonium and substituted ammonium halides in *N*-methylacetamide, an amphiprotic solvent with a high dielectric constant of 165.5 at 40 °C. In an amphiprotic solvent, the activity of both the ammonium cations and halide anions may be reduced by the interaction (or solvation) between the ions and the solvent through hydrogen bonding. On the other hand, in a protophobic aprotic solvent, such as nitromethane, acetone, or acetonitrile, the activities of both ions do not decrease because of the weak solvation. Therefore, we can predict that the triple ion formation from substituted ammonium halides will be observed conductometrically in acetonitrile, even if the dielectric constant is relatively high (35.95 at 25 °C). We have already confirmed the formation of RCOO⁻(M⁺)₂ (R = CH₃ and C₆H₅, M = Li and Na) as well as [M(C₆H₅COO)₂]⁻ (M = Li, Na, and K), although the solubilities of RCOOM salts are very small in acetonitrile.²

For the analysis of the conductance data of trialkylammonium halides (MX) in acetonitrile, the following formulation was made. The dielectric constant of acetonitrile is high enough to dissociate the salts to some extent. The ion-pair formation reaction is expressed by



omitting the ionic charges, and triple ion formation reactions are



The mass balance of a salt is

$$C_s = [M] + [MX] + \frac{1}{2}([M_2X] + [MX_2]) \quad (4)$$

where C_s is the analytical concentration of the salt. If $K_2 = K_3$, then $[M] = [X]$ because of the symmetry in eq 2 and 3. In this case, eq 4 can be reduced to a very simple form:

$$3K_3[X]^3 + K_1[X]^2 + [X] - C_s = 0 \quad (5)$$

The third-order equation was solved by the trial-and-error method until the relative error became less than $\pm 0.05\%$ for each C_s value. The preferable values of K_1 and K_3 ($K_2 = K_3$) were estimated by the polarographic data in the previous study¹ and in the first section of the present paper.

Once the $[X]$ values are calculated, the concentration of each species can be easily obtained.

$$[MX] = K_1[X]^2 \quad (6)$$

$$[M_2X] = K_2[X]^3 = [MX_2] = K_3[X]^3 \quad (7)$$

The total value of the equivalent conductivity, Λ , is given by the summation of those of the simple ions ($[M] = [X]$) and the triple ions ($[M_2X] = [MX_2]$):

$$\Lambda = \frac{[X]}{C_s} \Lambda_0 + \frac{[MX_2]}{C_s} \Lambda_T \quad (8)$$

where Λ_0 represents the sum of the limiting equivalent conductivity for the simple ions and Λ_T is the sum of the limiting equivalent conductivity of the two kinds of triple ions ($\Lambda_T = \lambda_{0(M_2X^+)} + \lambda_{0(MX_2^-)}$). The activity coefficients of all the species were assumed to be unity to avoid complications in the analysis. The association between M_2X^+ and MX_2^- (formation of $(MX)_3$) was ignored because of the relatively high dielectric constant of the solvent.

Experimental Section

Reagents. Commercially obtained acetonitrile (Wako Pure Chemicals, GR grade) was purified as previously described.¹⁸ The water content of the solvent was determined as 0.01% by gas chromatography. The specific conductance, κ was much less than $4 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$. The preparation and purification methods of LiClO₄, NaClO₄, Me₄NClO₄, Et₄NClO₄, and *n*-Bu₄NClO₄ were mentioned previously.¹⁹ NH₄ClO₄ obtained from Alfa Products and KClO₄ from Wako were used without further purification. The perchlorate salts of trialkylammonium (Me₃NH⁺, Et₃NH⁺, and *n*-Bu₃NH⁺), diethylammonium (Et₂NH₂⁺), anilinium (PhNH₃⁺), *N,N*-dimethylanilinium (PhNMe₂H⁺), and pyridinium (C₅H₅NH⁺) were prepared as described previously.¹ Tetraethylammonium bromide (Et₄NBr) and tetrabutylammonium iodide (*n*-Bu₄NI) were prepared and purified by the usual method.²⁰ Other tetraethylammonium halides (Et₄NCl, GR grade), triethylammonium chloride (Et₃NHCl), and pyridinium chloride (C₅H₅NHCl, EP grade) were also obtained from Wako. Triethylammonium bromide (Et₃NHBr) was prepared from 10 mL of triethylamine (Wako, GR grade) and the equivalent amount of HBr (Wako, GR grade) in 50 mL of methanol. This solution was evaporated to dryness under reduced pressure at less than 50 °C. The salt was recrystallized from methanol and was washed with ethyl ether. Trimethylammonium bromide (Me₃NHBr) was prepared and purified in a similar way. Tributylammonium bromide (*n*-Bu₃NHBr) was prepared and washed with *n*-hexane. Tributylammonium chloride (*n*-Bu₃NHCl) was prepared from tributylamine and hydrochloric acid (both from Wako) in methanol. The salt was obtained after evaporating the solvent. Dimethylammonium chloride (Et₂NH₂Cl) was prepared from diethylamine (Wako, GR grade) and HCl in methanol. The salt was washed with ethyl ether. Trimethylammonium iodide (Me₃NHI) was prepared from 10 mL of trimethylamine (30% in water; Wako, GR grade) and HI (Wako, GR grade) in methanol. The salt was recrystallized from the mixture of methanol and water (1:1). Triethylammonium and tributylammonium iodides were prepared in a similar way and were washed with ethyl ether and water, respectively. All chemicals were dried under vacuum over P₂O₅. Other chemicals commercially obtained were used as received.

Apparatus. A Yanagimoto polarograph (Model P-1000) and a Watanabe X-Y recorder (Model WX-4410-L0) were used for the polarographic measurements. The rate of the potential sweep was 5 mV/s. The dropping mercury electrode had the following open-circuit characteristics: $m = 1.28 \text{ mg/s}$ and $\tau = 2.9 \text{ s}$ in a 0.1 M Et₄NClO₄-MeCN solution at $h = 50 \text{ cm}$. The drop time was regulated to be 1.0 s by means of a Yanagimoto P-1000-ST drop timer. The reference electrode was a Ag/0.1 M AgClO₄-MeCN electrode. All the polarographic measurements were carried out at 25 ± 0.2 °C.

The conductometric measurements were carried out with a Yanagimoto conductivity outfit (Model MY-8) in a Yanagimoto conductivity cell (type C). The temperature was controlled at 25 ± 0.02 °C by a Yamato constant-temperature water bath (Model BK-33) and a Yamato Neocool Dip (Model BD-15). The

(14) Beronius, P.; Lindback, T. *Acta Chem. Scand., Ser. A* **1978**, *32*, 423.
(15) Grigo, M. *J. Solution Chem.* **1982**, *8*, 529.

(16) Salomon, M.; Uchiyama, M. *C. J. Solution Chem.* **1987**, *16*, 21.

(17) Dawson, L. R.; Wilhoit, E. D.; Sears, P. G. *J. Am. Chem. Soc.* **1956**, *78*, 1569.

(18) Fujinaga, T.; Okazaki, S.; Hojo, M. *J. Electroanal. Chem.* **1980**, *113*, 89.

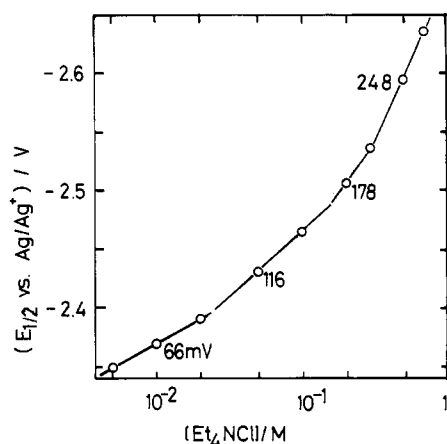
(19) Fujinaga, T.; Okazaki, S.; Hojo, M. *Bull. Inst. Chem. Res., Kyoto Univ.* **1978**, *56*, 139.

(20) Fujinaga, T.; Izutsu, K. In *Hisui Yoeki Hanno*; Ise, N., Tokura, N., Fujinaga, T., Eds.; Kagaku-dojin: Kyoto, 1970; Part II, Chapter 1, p 122.

TABLE I: Direct Current Polarographic Data of Alkali-Metal, Ammonium, Trialkylammonium, and Pyridinium Ions in Acetonitrile Containing Various Supporting Electrolyte Anions at 25 °C

supporting electrolyte ^a	$E_{1/2}$ /V	$I_1/\mu\text{A}$	slope ^c	$E_{1/2}$ /V	$I_1/\mu\text{A}$	slope
	[LiClO ₄] = 0.52 mM			[NaClO ₄] = 0.47 mM		
Et ₄ N ⁺ ClO ₄ ⁻	-2.30	1.3	61	-2.19	1.4	58
Et ₄ N ⁺ I ⁻	-2.31	1.4 ₅	63	-2.19 ₅	1.4	58
Et ₄ N ⁺ Br ⁻	-2.35	1.4 ₅	67	-2.22	1.4	62
Et ₄ N ⁺ Cl ⁻	-2.47	1.3	74	<i>d</i>		
	[NH ₄ ClO ₄] = 0.52 mM			[C ₅ H ₅ NHClO ₄] = 0.50 mM		
Et ₄ N ⁺ ClO ₄ ⁻	-2.19	1.6	65	-1.64 ₅	1.4 ₅	53
Et ₄ N ⁺ I ⁻	-2.21	1.4 ₅	62	-1.67	1.4 ₅	44
Et ₄ N ⁺ Br ⁻	-2.28 ₅	1.3 ₅	59	-1.74	1.3 ₅	47
Et ₄ N ⁺ Cl ⁻	-2.38 ₅	1.1 ₅	58	-1.79 ₅	1.2	68
	[Me ₃ NHClO ₄] = 0.50 mM			[Et ₃ NHClO ₄] = 0.51 mM		
Et ₄ N ⁺ ClO ₄ ⁻	-2.20 ^e	1.14 ^e	91	-2.28	1.5 ₅	93
Et ₄ N ⁺ I ⁻	-2.20 ₄	1.5 ₃	68	-2.36	1.5	96
Et ₄ N ⁺ Br ⁻	-2.30 ₇	1.5 ₅	88	-2.48	1.6	110
Et ₄ N ⁺ Cl ⁻	-2.39 ₄	1.1 ₅	99	-2.58	1.5 ₂	109

^a0.1 M tetraethylammonium salts. ^bVersus Ag/0.1 M AgClO₄-MeCN electrode. ^c- E vs log [$i/(i_d - i)$]. ^dNo wave appeared because of precipitation. ^eThe drop time was shortened to be 0.1 s in order to remove the polarographic maximum.

**Figure 1.** Effect of Cl⁻ on the $E_{1/2}$ of the cathodic wave of Li⁺, [LiClO₄] = 0.55 mM. Et₄NClO₄ was added to adjust the ionic strength to be 0.1 M when less than 0.1 M.

Shedlovsky analysis was performed by an NEC personal computer (Model PC-9801VM or PC-8801).

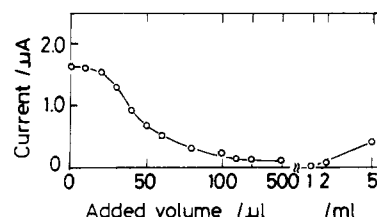
Results and Discussion

Formation of $M^+(X^-)_n$ Type Species. At a dropping mercury electrode, lithium perchlorate (0.52 mM) gave a reversible cathodic wave at -2.3 V in acetonitrile containing 0.1 M Et₄NClO₄ as the supporting electrolyte. With other supporting electrolyte anions, I⁻, Br⁻, and Cl⁻, the half-wave potential ($E_{1/2}$) of Li⁺ reduction shifted negatively, as is shown in Table I. The reduction of Na⁺ and K⁺ was not affected by the kind of the supporting electrolyte anion, except that the cathodic wave of Na⁺ was shifted slightly to the negative potential by 0.1 M Br⁻ and that the waves of Na⁺ and K⁺ disappeared completely with 0.1 M Cl⁻. All the waves showed diffusion-control character ($i_1 \propto h^{1/2}$).

The negative shift in the $E_{1/2}$ for Li⁺ with halide ions can be attributed to the complex formation between Li⁺ and halide ions. Figure 1 shows the shift in $E_{1/2}$ of Li⁺ reduction with the change in Et₄NCl concentration. The following equation²¹ was used for the analysis of the data

$$(E_{1/2})_c = (E_{1/2})_s - \frac{0.059}{n} \log K_p - \frac{0.059}{n} p \log [X^-] \quad (9)$$

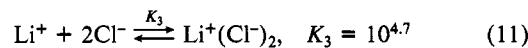
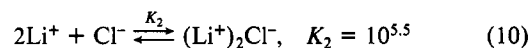
where $(E_{1/2})_c$ is the $E_{1/2}$ of the reduction of M⁺ (alkali-metal or

**Figure 2.** Amperometric titration curve of 0.5 mM NH₄ClO₄ (10 mL) with 0.1 M Et₄NCl-MeCN. The supporting electrolyte was 0.1 M Et₄NClO₄. The change in the total volume was corrected.

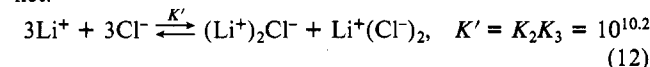
ammonium ions) in the presence of X⁻ (halide ions), and $(E_{1/2})_s$ is the $E_{1/2}$ in the absence of X⁻; n is the number of electrons involved in the electrochemical reduction of M⁺ or M⁺(X⁻)_p ($n = 1$). K_p stands for the overall formation constant of the complex: $K_p = [M^+(X^-)_p]/[M^+][X^-]^p$ for the reaction $M^+ + pX^- \rightleftharpoons M^+(X^-)_p$. The diffusion coefficients of the complex and the free cation were assumed to be equal, and the activity coefficients of all the species in the solution were also assumed to be unity for simplicity. The incomplete dissociation of R₄NX and MClO₄ at higher concentrations was ignored.

The formation of the complex ions, up to [LiCl₄]³⁻, was suggested by the slope ($\Delta E_{1/2}/\Delta \log [X^-]$) of 66, 116, 178, and 248 mV, as is shown in Figure 1. The overall formation constants (K_p) of the Li⁺(Cl⁻)_p are listed in Table II. The irreversibility in the Li⁺ reduction in the presence of Cl⁻ could be ignored. The complexation ability of I⁻ to Li⁺ seemed to be small, judging from the minor shift in $E_{1/2}$ with 0.1 M I⁻ (cf. Table I).

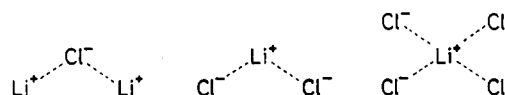
By the way, eq 12 about the formation of triple ions can be justified by the combination of the data in the previous work,¹ eq 10, and the present work, eq 11.



net:



In this case, K_2 and K_3 are close to each other in value.



Ammonium perchlorate (0.52 mM) also gave a single cathodic wave at -2.19 V with 0.1 M Et₄NClO₄ as the supporting electrolyte. The $E_{1/2}$ of NH₄⁺ reduction was affected by Br⁻ and Cl⁻ (cf. Table I). These waves were all diffusion controlled. The wave height (1.2–1.6 μA) was almost independent on the kind of the supporting electrolyte anion. The solubility of NH₄Cl in MeCN is so small that even the NH₄Cl-MeCN solution saturated at 25 °C gave a rather small wave (~0.75 μA) at ca. -2.2 V. Figure 2 shows the amperometric titration curve of NH₄ClO₄ with 0.1 M Cl⁻. The wave height for the NH₄⁺ reduction gradually decreased with the increase in the amount of Cl⁻. The wave disappeared completely at 1 mL of 0.1 M Cl⁻. (The equivalence point for the NH₄Cl formation equals 50 μL of 0.1 M Cl⁻.) Upon further addition of Cl⁻, the wave came out again, and its wave height increased with increasing amount of Cl⁻. The reappearance of the cathodic wave suggested the formation of NH₄⁺(Cl⁻)_n ($n \geq 2$).

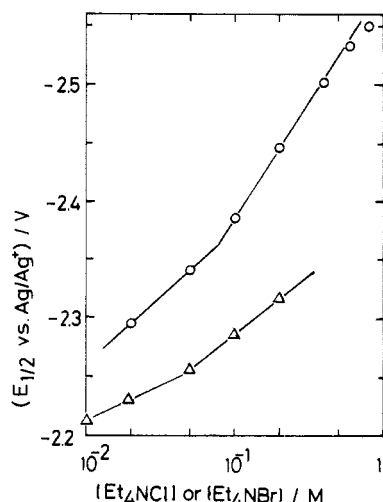
The effect of Cl⁻ on the $E_{1/2}$ of NH₄⁺ reduction wave is shown in Figure 3. The reversibility of the NH₄⁺ reduction seemed to be high enough in dc polarography, according to the log plot slope in Table I. In cyclic voltammetry at a hanging mercury drop electrode, the cathodic and anodic peaks of NH₄⁺ in aprotic solvents have been observed at high scan rates ≥ 0.3 V/s.²² By

(21) Heyrovsky, J.; Kuta, J. *Principles of Polarography*; Academic: New York, 1966; Chapter 8, pp 147–160.

(22) Angelis, K.; Brezina, M.; Koryta, J. *J. Electroanal. Chem.* **1973**, *45*, 504.

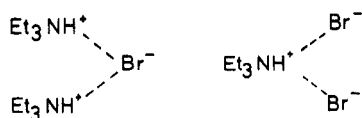
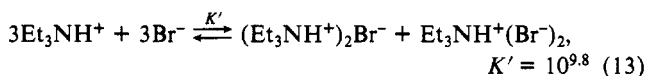
TABLE II: Overall Formation Constants ($\log K_p$) of the Complexes between the Cations and Halide Ions ($\text{Li}^+(\text{X}^-)_p$, $\text{R}_3\text{NH}^+(\text{X}^-)_p$, etc.) in Acetonitrile at 25 °C

cation	Cl^-				Br^-		I^-	
	$p = 1$	$p = 2$	$p = 3$	$p = 4$	$p = 1$	$p = 2$	$p = 1$	$p = 2$
Li^+	3.0	4.7	5.5	6.1	(1.8)			
NH_4^+		5.1	6.4		2.4	3.6		
Me_3NH^+		5.7			(2.5)	4.0		
Et_3NH^+	5.4	7.1			(3.4)	5.0	(2.1)	(3.3)
$\text{C}_3\text{H}_5\text{NH}^+$	3.5				2.6			

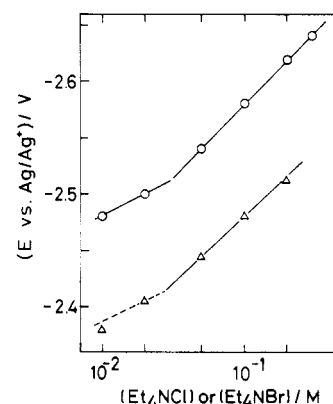
**Figure 3.** Effects of Cl^- and Br^- on the $E_{1/2}$ of the cathodic wave of NH_4^+ , $[\text{NH}_4\text{ClO}_4] = 0.5 \text{ mM}$: (O) Et_4NCl ; (Δ) Et_4NBr . See Figure 1 for the ionic strength.

the analysis of the data in Figure 3, the formation of $\text{NH}_4^+(\text{Cl}^-)_2$ and $\text{NH}_4^+(\text{Cl}^-)_3$ was confirmed by the formation constants of $10^{5.1}$ and $10^{6.4}$, respectively. The formation constants of $\text{NH}_4^+(\text{Br}^-)_n$ ($n = 1$ and 2) were also obtained. However, the formation constants of $\text{NH}_4^+(\text{I}^-)_n$ could not be obtained polarographically (cf. Tables I and II).

In Figure 4 is shown the effect of Cl^- and Br^- on the $E_{1/2}$ of the cathodic wave of the Et_3NH^+ ion. The slope, $\Delta E_{1/2} / \Delta \log [\text{Cl}^-]$, was 65 and 130 mV for 10–20 and 50–300 mM Cl^- , respectively. These slope values give $p = 1$ and 2 in eq 9, which means that the coordination numbers of Cl^- toward Et_3NH^+ are 1 and 2. The (overall) formation constants of $\text{Et}_3\text{NH}^+\text{Cl}^-$ and $\text{Et}_3\text{NH}^+(\text{Cl}^-)_2$ were obtained to be $10^{5.4}$ and $10^{7.1}$, respectively, ignoring the partial irreversibility of the waves. The effect of Br^- on the wave was much weaker than that of Cl^- . The (overall) formation constants of $\text{Et}_3\text{NH}^+\text{Br}^-$ and $\text{Et}_3\text{NH}^+(\text{Br}^-)_2$ were $10^{3.4}$ and $10^{5.0}$, respectively. Therefore, with the aid of the previous study,¹ the formation constant of the triple ions between the triethylammonium ion and the bromide ion was also evaluated, as follows:



The effect of I^- on the Et_3NH^+ reduction wave was not so clear. Other trialkylammonium ions, Me_3NH^+ and $n\text{-Bu}_3\text{NH}^+$, were affected by the halide ions in a way similar to Et_3NH^+ . Here, we would like to add that the effect of $n\text{-Bu}_4\text{NCl}$ and Et_4NCl on the Me_3NH^+ reduction wave was the same; i.e., R_4N^+ cations had no effect on this system. Comparing Table II and the data in ref 1, the K_2 and K_3 values in eq 2 and 3 of the interaction between trialkylammonium ions and the chloride or bromide ion were rather close to each other. Thus, the formation of $\text{R}_3\text{NH}^+(\text{X}^-)_2$ ($\text{X} = \text{Cl}$ and Br) was maximum, and $\text{R}_3\text{NH}^+(\text{X}^-)_3$ was not observed polarographically.

**Figure 4.** Effects of Cl^- and Br^- on the $E_{1/2}$ of the cathodic wave of Et_3NH^+ , $[\text{Et}_3\text{NHClO}_4] = 0.5 \text{ mM}$: (O) Et_4NCl ; (Δ) Et_4NBr . See Figure 1 for the ionic strength.

However, in the case of the diethylammonium ion (Et_2NH_2^+), the formation of up to $\text{Et}_2\text{NH}_2^+(\text{Cl}^-)_3$ was suggested. The formation of $\text{PhNH}_3^+(\text{Br}^-)_2$ and $\text{PhNH}_3^+(\text{Br}^-)_3$ was found with formation constants of $10^{5.8}$ and $10^{7.2}$, respectively. The formation constants of $\text{PhNMe}_2\text{H}^+(\text{Br}^-)_2$ and $\text{PhNMe}_2\text{H}^+\text{I}^-$ were $10^{6.0}$ and $10^{2.7}$, respectively. The effect of Cl^- on the anilinium ion and the N,N -dimethylanilinium ion could not be fully examined because the acidity of the anilinium ions is so strong that they reacted with Cl^- (a base) to produce another cathodic wave in acetonitrile. On the other hand, the interaction between pyridinium ion ($\text{C}_5\text{H}_5\text{NH}^+$) and X^- was rather unique, if compared with the ammonium ion or the substituted ammonium ions: only $\text{C}_5\text{H}_5\text{NH}^+\text{X}^-$ did form and $\text{C}_5\text{H}_5\text{NH}^+(\text{X}^-)_2$ was not observed.

Conductometric Identification of Triple Ions from Trialkylammonium Halides. By the polarographic study in the previous section, it was shown that the interaction between the trialkylammonium ions and the halide ions is symmetrical in acetonitrile: both $(\text{M}^+)_2\text{X}^-$ and $\text{M}^+(\text{X}^-)_2$ type species are formed with formation constants of similar values. On the other hand, the interaction between the pyridinium ion and the halide ions is not symmetrical: the formation of $\text{Py}^+(\text{X}^-)_2$ type species could not be observed, whereas, the $(\text{Py}^+)_2\text{X}^-$ species was easily found in acetonitrile.¹ The interaction between the dialkylammonium ions and the halides seems not to be symmetrical because the formation of $\text{Et}_2\text{NH}_2^+(\text{Cl}^-)_3$ as well as $\text{Et}_2\text{NH}_2^+(\text{Cl}^-)_2$ was suggested. In the present section, the conductivity of trialkylammonium halides in acetonitrile will be examined on the basis of the symmetrical formation of triple ions, i.e., $[(\text{M}^+)_2\text{X}^-] = [\text{M}^+(\text{X}^-)_2]$.

In Figure 5 is shown the relationship between the equivalent conductivity (Λ) and the square root of the concentration ($C^{1/2}$) of tetraethylammonium perchlorate and halides and triethylammonium perchlorate over the range $(0.38\text{--}7) \times 10^{-3} \text{ M}$. These salts are all strong electrolytes in acetonitrile. The approximate values of the equivalent conductivity at infinite dilution or limiting equivalent conductivity (Λ_0) were obtained and are listed in Table III. Next, the Arrhenius–Ostwald relationship,²³ i.e., $1/\Lambda = 1/\Lambda_0 + C\Lambda_0/K_a$, was examined for these salts. The plot of $1/\Lambda$ vs $C\Lambda_0$ gave straight lines for the first 10 points. The approximate values of Λ_0 and the association constant, K_a , were obtained. A modified method from the Arrhenius–Ostwald relationship by

(23) Popovych, O.; Tomkins, R. P. T. *Nonaqueous Solution Chemistry*; Wiley: New York, 1981; pp 255–256.

TABLE III: Δ_0 and Apparent K_a Values of Trialkyl- and Tetraalkylammonium Salts in Acetonitrile by Three Different Methods of Analysis

salt	Δ vs $C^{1/2}$ Δ_0^a	Arrhenius–Ostwald			Shedlovsky	
		Δ_0	K_a^b	$\Delta_0(\text{calcd})^c$	Δ_0	K_a
Me_4NClO_4	202.1	197.2	52.3		201.3	13.2
Et_4NClO_4	195.5	189.6	52.8		193.2	11.1
$n\text{-Bu}_4\text{NClO}_4$	169.4	164.9	42.8		169.3	5.5
$\text{Me}_3\text{NHClO}_4$	209.7	202.8	37.8		209.0	14.6
$\text{Et}_3\text{NHClO}_4$	197.1	190.1	46.4		195.6	20.1
$n\text{-Bu}_3\text{NHClO}_4$	172.8	167.7	46.4		172.3	12.1
Et_4NCl	188.6	183.0	45.6		187.9	13.7
$n\text{-Bu}_4\text{NCl}$	162.5	158.3	42.9		162.9	6.1
Me_3NHCl		133.3	1.01×10^4	196.2	137.1	1.07×10^4
Et_3NHCl		131.1	1.26×10^4	183.5	125.0	1.15×10^4
$n\text{-Bu}_3\text{NHCl}$		129.9	1.32×10^4	161.1	115.2	1.02×10^4
Et_4NBr	189.0	183.6	43.0		188.6	11.4
$n\text{-Bu}_4\text{NBr}$	165.7	160.5	46.4		164.6	7.5
Me_3NHBr		191.6	2.13×10^3	196.8	193.8	2.33×10^3
Et_3NHBr		178.6	2.75×10^3	184.1	183.0	3.10×10^3
$n\text{-Bu}_3\text{NHBr}$		156.3	2.39×10^3	163.3	167.4	2.97×10^3
Et_4NI	192.5	187.5	41.5		192.3	8.5
$n\text{-Bu}_4\text{NI}$	169.8	165.0	44.9		169.6	8.9
Me_3NHI	219.5	206.6	2.59×10^2	200.7	209.2	2.29×10^2
Et_3NHI	202.0	188.3	2.65×10^2	188.0	194.4	2.87×10^2
$n\text{-Bu}_3\text{NHI}$	177.0	164.7	2.37×10^2	167.8	176.5	2.89×10^2

^a Equivalent conductivity ($\text{cm}^2/(\Omega \text{ mol})$). ^b Association constant, $\text{M}^+ + \text{X}^- = \text{MX}$ (K_a). ^c The Δ_0 value calculated by Kohlrausch's law.

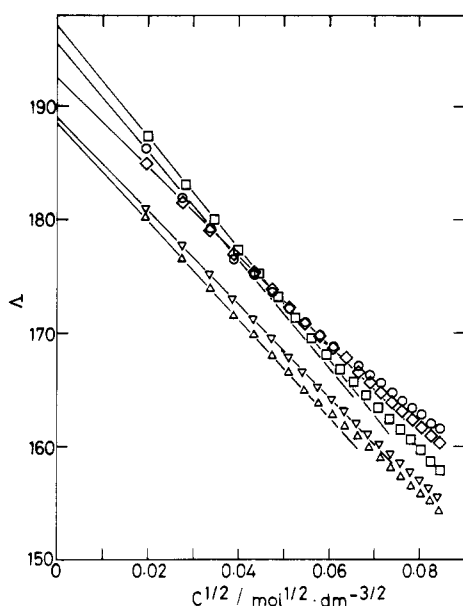


Figure 5. Δ vs $C^{1/2}$ relation of strong electrolytes in acetonitrile at 25 °C: (O) Et_4NClO_4 ; (□) $\text{Et}_3\text{NHClO}_4$; (Δ) Et_4NCl ; (▽) Et_4NBr ; (◇) Et_4NI .

Shedlovsky was also applied. The Shedlovsky equation^{23,24} is expressed as follows

$$1/\Delta S = 1/\Delta_0 + C\Delta S f_{\pm}^2 K_a / \Delta_0^2 \quad (14)$$

where S is the Shedlovsky function and f_{\pm} is the mean activity coefficient of ions. The f_{\pm} value was estimated by the Debye–Hückel equation, using 5 Å for the ionic diameter. The values of the dielectric constant and viscosity of acetonitrile were taken as 35.95 and 0.3412 cP, respectively.²⁵ The Δ_0 and K_a values were obtained after the computer calculation for the first 10 points (lower concentrations, $(0.38\text{--}3.5) \times 10^{-3}$ M). The iteration process was terminated when values of limiting equivalent conductivity converged to 0.1% or better. For the strong electrolytes, the Δ_0 values obtained by the Δ vs $C^{1/2}$ relation were very close to those obtained by the Shedlovsky method. All the Δ_0 values obtained

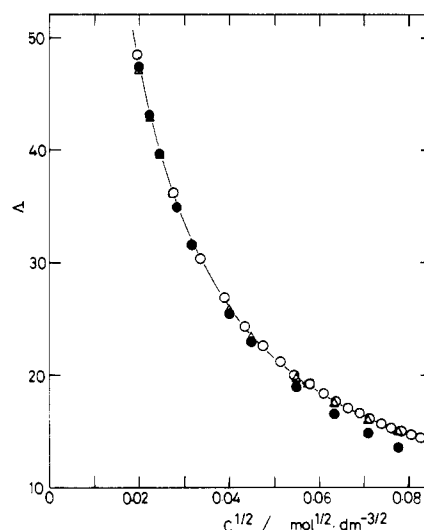


Figure 6. Observed and calculated Δ values of Et_3NHCl : (O) observed; (Δ) calculated with both the ion-pair and the triple ions, $K_1 = 2.8 \times 10^4$, $K_2 = K_3 = 3.0 \times 10^6$, $\Delta_0 = 183.5$, $\Delta_T = \Delta_0/3 = 61.2$; (●) calculated without the triple ions, $K_1 = 2.8 \times 10^4$, $\Delta_0 = 183.5$.

by the Arrhenius–Ostwald relationship were smaller (ca. 2%) than those from the Shedlovsky method. However, the literature²⁶ reports the limiting single ion conductivities (λ_0^+ and λ_0^-) in acetonitrile which are almost coincident with the Δ_0 values by the Arrhenius–Ostwald relationship in our study (99–101% for tetraethylammonium halides). Therefore, we will make use of the Δ_0 values by the Arrhenius–Ostwald relationship for the later calculations.

The conductivities of trialkylammonium halides ($(0.38\text{--}7) \times 10^{-3}$ M) in acetonitrile were treated by the above three methods. The apparent values of Δ_0 and K_a of the halides are listed in Table III.

The apparent association constants of triethylammonium chloride, bromide, and iodide are given to be 1.26×10^4 , 2.75×10^3 , and 2.65×10^2 , respectively, by the Arrhenius–Ostwald relation. The apparent Δ values obtained by the Arrhenius–Ostwald relation were much smaller than those obtained indirectly

(24) Fuoss, R. M.; Shedlovsky, T. *J. Am. Chem. Soc.* **1949**, *71*, 1496.

(25) Kay, R. L.; Hales, B. J.; Cunningham, G. P. *J. Phys. Chem.* **1967**, *71*, 3925.

(26) Spiro, M. In *Physical Chemistry of Organic Solvent Systems*; Conington, A. K., Dickinson, T., Eds.; Plenum: London, 1973; p 678, and references therein.

TABLE IV: Comparison of the Calculated Δ Values with the Observed Δ Values for Trimethylammonium Halides in Acetonitrile

$10^3 C_s^a$	$10^4 [X]$	$10^5 [MX_2]$	Δ_{calcd}	Δ_{obsd}^a	rel error/%	rel error ^b /%
Me ₃ NHCl, $K_1 = 2.4 \times 10^4$, $K_2 = K_3 = 1.5 \times 10^6$, $\Delta_0 = 196.2$, $\Delta_T = \Delta_0/3 = 65.4$						
0.4	1.090	0.1943	53.80	(54.2) ^c	-0.7	(-0.5)
0.5	1.238	0.2846	48.96	49.1	-0.3	(-0.1)
0.6	1.371	0.3865	45.25	45.3	-0.1	(+0.1)
0.8	1.608	0.6237	39.95	40.0	-0.1	(-0.1)
1.0	1.816	0.8983	36.22	36.3	-0.2	(-0.4)
1.6	2.336	1.912	29.43	29.55	-0.4	(-1.2)
2.0	2.627	2.719	26.66	26.8	-0.5	(-1.7)
3.0	3.242	5.111	22.32	22.4	-0.4	(-2.7)
4.0	3.756	7.948	19.72	19.8	-0.4	(-3.9)
5.0	4.206	11.16	17.96	18.0	-0.2	(-4.9)
6.0	4.609	14.69	16.67	16.62	+0.3	(-5.6)
8.0	5.319	22.57	14.89	14.78	+0.7	(-7.6)
Me ₃ NHBr, $K_1 = 2.22 \times 10^3$, $K_2 = K_3 = 2.0 \times 10^5$, $\Delta_0 = 196.8$, $\Delta_T = \Delta_0/2 = 98.4$						
0.4	2.509	0.316	124.20	123.3	+0.7	(+1.9)
0.6	3.325	0.735	110.27	109.4	+0.8	(+2.3)
1.0	4.635	1.991	93.18	93.0	+0.2	(+2.2)
2.0	7.013	6.898	72.41	72.7	-0.4	(+1.6)
4.0	10.245	21.51	56.70	56.0	-0.5	(-2.1)
6.0	12.615	40.15	47.96	48.0	-0.1	(-2.0)
Me ₃ NHI, $K_1 = 2.59 \times 10^2$, $\Delta_0 = 206.7$						
0.2	1.906		197.0	198.0		-0.5
0.4	3.654		188.8	188.5		+0.2
0.6	5.278		181.8	181.3		+0.3
1.0	8.241		170.3	170.6		-0.2
2.0	14.53		150.2	152.7		-1.6
3.6	22.68		130.2	135.3		-3.8

^aThe total concentration of a salt and the Δ value, read from the Δ vs $C^{1/2}$ curve. ^bThe relative error of the calculated Δ value to the observed value, when only the ion-pair formation ($M^+ + X^- \rightleftharpoons MX$) is accounted for. ^cAn extrapolated value.

by the calculation with Kohlrausch's law for the chloride salt: $\Delta = 131.1$, directly obtained; $\Delta_0 = 183.5$, by Kohlrausch's law ($\Delta_0(\text{Et}_3\text{NHCl}) = \Delta_0(\text{Et}_3\text{NHClO}_4) + \Delta_0(\text{Et}_4\text{NCl}) - \Delta_0(\text{Et}_4\text{NClO}_4)$). A similar phenomenon occurred for the bromide; however, the Δ_0 values obtained by both methods were almost the same ones for the iodide. Trimethyl- and tributylammonium halides gave results similar to those of triethylammonium halides. The Shedlovsky method showed a tendency similar to the Arrhenius-Ostwald method with often slightly larger values of the apparent Δ_0 and K_a than the Arrhenius-Ostwald values for $R_3\text{NHX}$.

At least in the present cases, we believe that some additional reactions other than the ion-pair formation between $R_3\text{NH}^+$ and X^- could be a cause for the fact that the (apparent) Δ_0 values obtained directly for $R_3\text{NHX}$ by the Arrhenius-Ostwald or the Shedlovsky method are smaller than the Δ_0 values obtained indirectly after the Kohlrausch calculation with the Δ_0 values of

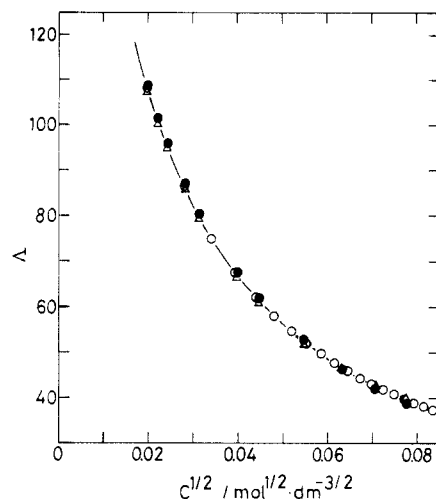
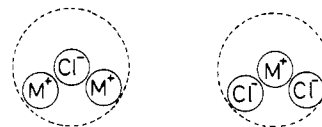


Figure 7. Observed and calculated Δ values of Et_3NHBr : (O) observed; (Δ) calculated with both the ion-pair and the triple ions, $K_1 = 2.98 \times 10^3$, $K_2 = K_3 = 2.0 \times 10^5$, $\Delta_0 = 184.1$, $\Delta_T = \Delta_0/2 = 92.05$; (\bullet) calculated without the triple ions, $K_1 = 2.98 \times 10^3$, $\Delta_0 = 184.1$.

strong electrolytes. The larger the migration particles, the smaller the value in conductivity.

Figure 6 shows the Δ vs $C^{1/2}$ relation from the observed and calculated values for Et_3NHCl in acetonitrile. The Δ values calculated by eq 8 coincided with the observed value within 0.9% error, at most, over the initial concentration (C_s) range of $(0.4\text{--}6.0) \times 10^{-3}$ M Et_3NHCl . For example, at $C_s = 1.0 \times 10^{-3}$ M, the values of $K_1 = 2.8 \times 10^4$, $K_2 = K_3 = 3.0 \times 10^6$, $\Delta_0 = 183.5$, and $\Delta_T = 61.2$ gave the Δ_{calcd} value of 31.7, which has a -0.3% relative error compared with the Δ_{obsd} value of 31.8. The concentrations of simple ions, ion pair, and triple ions are calculated to be 1.680×10^{-4} , 7.903×10^{-4} , and 1.42×10^{-5} M, respectively. The formation constants of ion pair (K_1) and triple ions (K_2 and K_3) are, at first, estimated by the polarographic data: $\log K_2 = 6.7$ and $\log K_1 = 4.3$ (from the correlation between $\log K_1$ and $\log K_2$ values) in ref 1; $\log K_3 = 7.1$ and $\log K_1 = 5.4$ in Table II. The reasonable Δ_0 values of Et_3NHCl were evaluated by Kohlrausch's law with the Δ_0 values of strong electrolytes (by the Arrhenius-Ostwald relationship, shown in Table III). The limiting equivalent conductivity of triple ions, Δ_T , was assumed to be one-third of that of simple ions, Δ_0 . Fuoss and Kraus made the same assumption for the triple ions from tetraisoamylammonium nitrate in low dielectric constant media.¹¹ We think that the assumption is reasonable from the viewpoint of the mean diameter of the triple ions as the result of free rotation. By the way, it

**TABLE V: Ion-Pair (K_1) and Triple Ion ($K_2 = K_3$) Formation Constants of Trialkylammonium Halides from Conductometric Data**

	Δ_0^a	Δ_T^b	K_1	$K_2 = K_3$	rel error ^c /%	rel error ^d /%
Me ₃ NHCl	196.2	65.4	2.4×10^4	1.5×10^6	-0.7 to +0.3	(-5.6 to +0.1)
Me ₃ NHBr	196.8	98.4	2.22×10^3	2.0×10^5	-0.5 to +0.8	(-2.0 to +2.3)
Me ₃ NHI ^e	206.7 ^f (200.7)		2.59×10^2			(-3.8 to +0.3)
Et ₃ NHCl	183.5	61.2	2.8×10^4	3.0×10^6	-0.9 to +0.5	(-9.2 to +0.2)
Et ₃ NHBr	184.1	92.0 ₅	2.98×10^3	2.0×10^5	-0.8 to +0.9	(-2.0 to +1.1)
Et ₃ NHI	188.0		2.65×10^2			(-2.4 to +0.5)
<i>n</i> -Bu ₃ NHCl ^g	161.1	53.7	2.2×10^4	2.0×10^6	-0.5 to +0.7	(-5.5 to +0.9)
<i>n</i> -Bu ₃ NHBr	163.3	81.6 ₅	2.64×10^3	1.0×10^5	-0.4 to +0.4	(-1.6 to +1.1)
<i>n</i> -Bu ₃ NHI	167.8		2.6×10^2			(-2.5 to +1.3)

^aThe Δ_0 value obtained by the (Kohlrausch's law) calculation of the Δ_0 data from the Arrhenius-Ostwald relationship, e.g., $\Delta_0(\text{Et}_3\text{NHCl}) = \Delta_0(\text{Et}_3\text{NHClO}_4) + \Delta_0(\text{Et}_4\text{NCl}) - \Delta_0(\text{Et}_4\text{NClO}_4)$. ^bThe limiting equivalent conductivity of triple ions ($[M_2X]^+[MX_2]^-$), $\Delta_T = \Delta_0/3$ for chloride salts and $\Delta_T = \Delta_0/2$ for bromide salts. ^cThe relative error (over the range of $(0.4\text{--}6.0) \times 10^{-3}$ M salt concentration) in the calculated Δ value to the observed Δ value. ^dThe value when triple ion formation is ignored. ^eFor $(0.2\text{--}3.6) \times 10^{-3}$ M salt concentration. ^fThe value obtained from the Δ vs $C^{1/2}$ relation. ^gFor $(0.4\text{--}5.0) \times 10^{-3}$ M salt concentration.

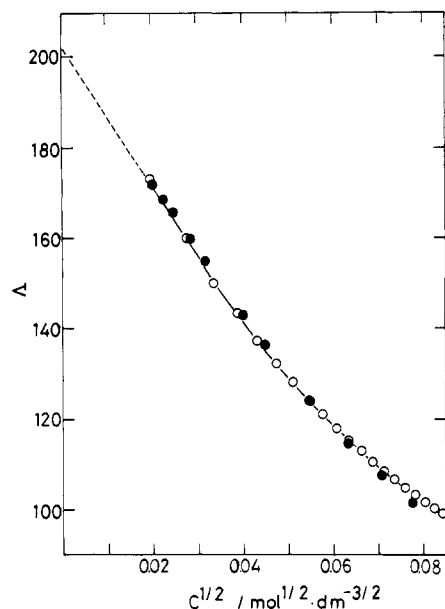


Figure 8. Observed and calculated Λ values of Et_3NHI : (○) observed; (●) calculated only with the ion pair, $K_1 = 2.65 \times 10^2$, $\Lambda_0 = 188.0$.

is not necessary to divide the Λ_0 or Λ_T value into two parts because $[\text{M}^+] = [\text{Cl}^-]$ and $[(\text{M}^+)_2\text{Cl}^-] = [(\text{M}^+(\text{Cl}^-)_2)]$ as the result of $K_2 = K_3$ in eq 2 and 3. And we would like to mention that the Λ vs $C^{1/2}$ curves showed a smooth decrease and no minimum was observed up to 4.3×10^{-2} and 5.7×10^{-2} M for $n\text{-Bu}_3\text{NHCl}$ and $n\text{-Bu}_3\text{NHBr}$, respectively, in acetonitrile.

The bromide salt of Et_3NH^+ gave similar results as Et_3NHCl (Figure 7). The deviation in the calculated Λ values being small (at $C_s = 6.0 \times 10^{-3}$ M, relative error of -2.0%) without the triple ions, the Λ_{calcd} value was fitted to the Λ_{obsd} within -0.8% and $+0.9\%$ error with the triple ion formation. The assumption that $\Lambda_T = \Lambda_0/2$ made a good fit, and not $\Lambda_T = \Lambda_0/3$ for bromides. Beronius and Lindback¹⁴ reached a value of $\Lambda_T = 0.43\Lambda_0$ for the best fit in Λ values of LiBr in 1-octanol.

As for Et_3NHI , the triple ions in addition to the ion-pair formation did not improve the fit in the Λ values, though the deviations were not so small (-2.4% to $+0.5\%$ relative error over the range $C_s = (0.4\text{--}6.0) \times 10^{-3}$ M) without the triple ions (Figure

8). Not only the poor fit but also the deviations in Λ could be caused by the very high ionic concentrations due to the small association constant of $\text{Et}_3\text{NH}^+\text{I}^-$ in acetonitrile: $K_1 = 2.65 \times 10^2$, $[\text{Et}_3\text{NH}^+] = [\text{I}^-] = 8.213 \times 10^{-4}$ M, while $[\text{Et}_3\text{NHI}] = 1.788 \times 10^{-4}$ M at $C_s = 1.0 \times 10^{-3}$ M. The high ionic concentration usually causes the deviation from the Arrhenius–Ostwald relationship by the increase in the relaxation and the electrophoretic effect²⁷ or even from the Onsager equation.

Table IV shows a comparison of the Λ_{calcd} with Λ_{obsd} for trimethylammonium halides (Me_3NHX) in acetonitrile. The results are very similar to that of Et_3NHX . The Λ_0 values of Me_3NHX were calculated with the help of Λ_0 of ethyl-substituted ammonium salts because Λ_0 values of Me_4NX were not measured. The results of $n\text{-Bu}_3\text{NHX}$ were also very similar to those of Et_3NHX . In Table V are listed the ion-pair and triple ion formation constants of nine trialkylammonium halides from conductometric data. The conductivities of pyridinium and diethylammonium chlorides were also measured in acetonitrile. However, the asymmetric interaction between $\text{C}_5\text{H}_5\text{NH}^+$ or Et_2NH_2^+ and Cl^- , mentioned above, prevented further investigations with the simple analysis.

Conclusion

The triple ion formation from trialkylammonium halides in a protophobic solvent with a relatively high dielectric constant was confirmed by both polarography and conductometry. The hydrogen bonding between trialkylammonium ions and halides ions as well as the Coulombic attraction seems to be the main force in triple ion formation.

Acknowledgment. We thank Associate Professor Ikko Sakamoto of Shimane University for his kind offering of the computer program of the Shedlovsky method.

Registry No. LiCl , 7447-41-8; NH_4Cl , 12125-02-9; Et_3NHCl , 554-68-7; Et_3NHBr , 636-70-4; Et_4NClO_4 , 2567-83-1; Et_4NI , 68-05-3; Et_4NBr , 71-91-0; Et_4NCl , 56-34-8; LiClO_4 , 7791-03-9; NaClO_4 , 7601-89-0; NH_4ClO_4 , 7790-98-9; $\text{C}_5\text{H}_5\text{NHClO}_4$, 15598-34-2; $\text{Me}_3\text{NHClO}_4$, 15576-35-9; $n\text{-Bu}_4\text{NClO}_4$, 1923-70-2; Me_4NClO_4 , 2537-36-2; $n\text{-Bu}_3\text{NHClO}_4$, 14999-66-7; Me_3NHCl , 593-81-7; $n\text{-Bu}_3\text{NHCl}$, 6309-30-4; $n\text{-Bu}_4\text{NCl}$, 1112-67-0; $n\text{-Bu}_4\text{NBr}$, 1643-19-2; Me_3NHBr , 2840-24-6; $n\text{-Bu}_3\text{NHBr}$, 37026-85-0; $n\text{-Bu}_4\text{NI}$, 311-28-4; $n\text{-Bu}_3\text{NHI}$, 34193-29-8; Me_3NHI , 20230-89-1; Et_3NHI , 4636-73-1.

(27) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1959; Chapter 7, pp 133–173.