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Effect of Substituents on the Triple Ion Formation from Various Ammonium or Guanidium Chlorides

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The triple ion formation from various ammonium or guanidium chlorides has been examined by conductometry in acetonitrile, benzonitrile, and propylene carbonate. The observed minimum in the $\Lambda - C^{1/2}$ curve of diethylcyclohexylammonium chloride in benzonitrile could be reproduced in terms of a large formation constant of quadrupole complexes by computer simulations.

It has been established that ion aggregates, triple ions and quadrupoles can be fromed, in addition to ion pairs between ions, in high dielectric constant media ($20 < \varepsilon < 65$).[1-4] Previously, the symmetrical triple ion formation was found to occur only in solvents with low dielectric constants.[5] We have used protophobic aprotic solvents such as acetonitrile and nitrobenzene with relatively high dielectric constants. The solvents can weaken Coulombic forces between anions and cations. The poor solvation ability of the solvents with both anions and cations may reveal minor interactions between (or among) solutes. Fouss and Kraus[5] have derived an equation, with which conductivity data can be analyzed for the symmetrical triple ion formation. On the other hand, our analytical method[1-4] for conductivity data can be used, even if higher ion aggregates than triple ions are present.

The triple ion formation from trialkylammonium cation and various anions in protophobic aprotic solvents has already been studied.[1-4,6] In the present study, we have examined conductometrically the triple ion formation of various ammonium or guanidium chlorides in acetonitrile (ε = 35.95), benzonitrile (ε = 25.2), and prolylene carbonate (ε = 64.4). The attention was focused on the relation between the triple ion formation and the acidity of the cationic acids (ammonium ions, etc).

Conductometric measurements were carried out with a Yanagimoto conductivity outfit (Model MY-8) at (25±0.02) °C. Details concerning the experiments and the analysis were described in previous papers.[2,4]

Molar conductivitis (Λ) of 1,3-diphenylguanidium chloride (C = (0.4 - 0.6) x 10^{-3} M (1 M = 1 mol dm^{-3}) showed that the salt behaved as a weak electrolyte. The molar conductivities could not be explained in terms of the ion pair formation, but of the ion pair (K^a_1 = 4.85 x 10^4) and symmetrical triple ion (K^a_2 = K^a_3 = 2.0 x 10^6) formations (the relative error of -0.65 - +0.61% for the entire concentration range). On the other hand, the triple ion formation was hardly observed for 1,1,3,3-tetramethylguanidinum chloride in the same solvent. 1,1,3,3-Tetramethylguanidine (pK_{BH^+} = 23.3)[7)] is a much stronger base than 1,3-diphenylguanidine (pK_{BH^+} = 17.9 in acetonitrile).[8)] The basicity of triethylamine decreases by the replacement of ethyl groups with phenyl groups. Therefore, much stronger formation of triple ions from N,N-diethylanilinium chloride than Et_3NHCl was expected. However, the triple ion formation from N,N-diethylanilinium chloride (K^a_1 = 1.865 x 10^5, K^a_2 = K^a_3 = 2.5 x 10^6) was only slightly stronger than that from Et_3NHCl.[9)] Triple ions formed to a similar extent from diethylcyclohexylammonium chloride (K^a_1 = 2.91 x 10^4, K^a_2 = K^a_3 = 1.50 x 10^6). N-Methyldioctylammonium chloride gave a smaller triple ion formation constant (K^a_1 = 3.20 x 10^4, K^a_2 = K^a_3 = 6.70 x 10^5). The relation between ion pair (K^a_1) and triple ion (K^a_2 = K^a_3) formation constants and the basicity of amines is shown in Fig. 1. We predicted that the weaker the basicity of amines is, the stronger the triple ion formation occurs. The experimental results showed "leveling-off" at pK_{BH^+} = 18 in acetonitrile. The "leveling-off" might be caused by the larger basicity of the chloride ion in acetonitrile, which results in the formation of BH^+Cl^- and B·····HCl.

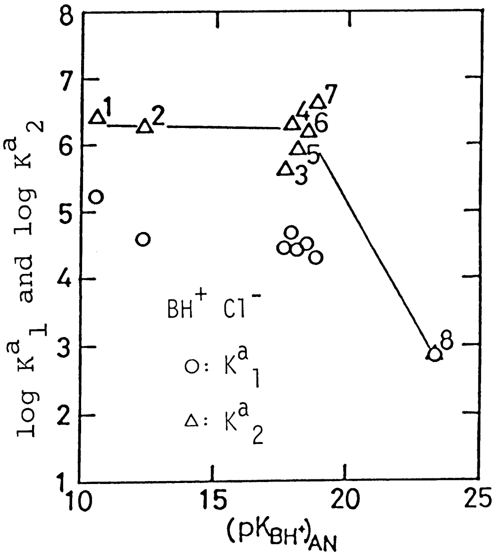

Fig. 1. The relation between ion pair (○) and triple ion (△) formation constants of chlorides and the basicity of amines (pK_{BH^+} values) in acetonitrile: (1) N,N-diethylaniline (the pK_{BH^+} value of aniline); (2) pyridine; (3) trimethylamine; (4) 1,3-diphenylguanidine; (5) tributylamine; (6) triethylamine, (7) diethylamine; (8) 1,1,3,3-tetramethylguanidine.

In benzonitrile, the larger triple ion formation constants were obtained for the salts than those in acetonitrile. The quadrupole formation should be taken into account to explain the conductivities even in the low concentration range ((0.4 - 6.0) x 10^{-3} M). The formation constants of K^a_1 = 4.52 x 10^6, K^a_2 = K^a_3 = 3.50 x 10^9, and K^a_4 = K^a_5 = 5.0 x 10^4 were given for 1,3-diphenylguanidium chloride. 1,1,3,3-Tetramethylguanidium chloride also showed the triple ion and quadrupole formation.

As for diethylcyclohexylammonium chloride in the high concentration range (C = (0.4 - 12.0) x 10^{-2} M), the molar conductivities gave a minimum at C = 3.7 x 10^{-2} M in benzonitrile (Fig. 2). The observed conductivities were well explained in terms of K^a_1 = 1.05 x 10^6, K^a_2 = K^a_3 = 2.0 x 10^8, and K^a_4 = K^a_5 = 1.5 x 10^4 (the relative error of -0.72 - +0.53%), after correcting activity coefficients of the ions with the Debye-Hückel equation.[10)] The minimum in the Λ - $C^{1/2}$ curve has been reported for n-Bu_3NHCl in nitrobenzene and benzonitrile.[2)] We have suggested[4,6)] that an

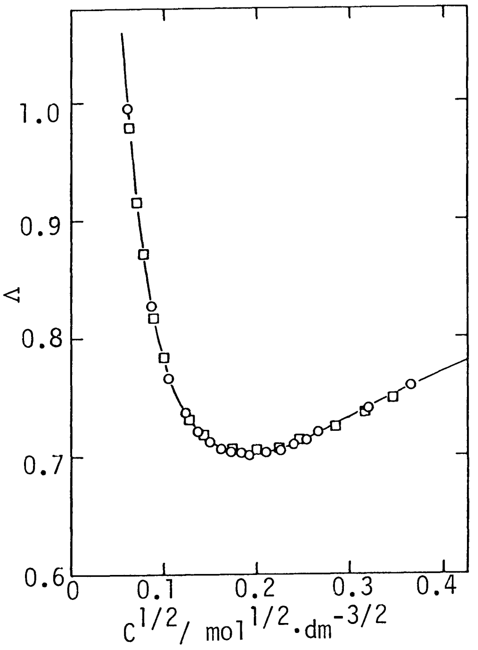

Fig. 2. Observed and calculated Λ values of diethylcyclohexylammonium chloride (C = (0.4 - 12.0) x 10^{-2} M) in benzonitrile: (○) observed; (□) calculated with the ion pair (K^a_1 = 1.05 x 10^6), the triple ion (K^a_2 = K^a_3 = 2.0 x 10^8), and the quadrupole (K^a_4 = K^a_5 = 1.5 x 10^4) formation constants, Λ_0 = 50.43, and Λ_T = $\Lambda_0/3$.

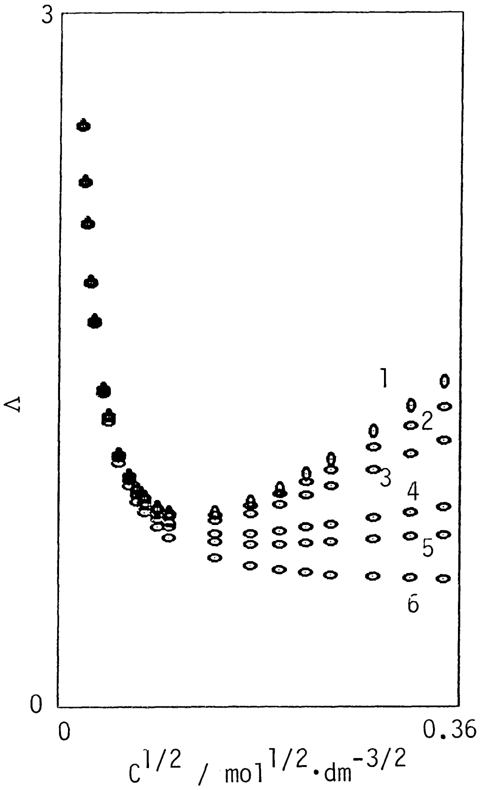

Fig. 3. The computer simulation of Λ - $C^{1/2}$ curves (C = 4.0 x 10^{-4} - 0.12 M) in benzonitrile with K^a_1 = 1.05 x 10^6, K^a_2 = K^a_3 = 2.0 x 10^8, and various K^a_4 = K^a_5 values: (1) 0; (2) 1.0 x 10^3; (3) 3.0 x 10^3; (4) 1.0 x 10^4; (5) 1.5 x 10^4; (6) 3.0 x 10^4.

extremely large K_2 value (triple ion formation) and a relatively small K_4 value (quadrupole formation) could be a means to make a $\Lambda - C^{1/2}$ curve minimum. Computer simulation curves shown in Fig. 3 supported our prediction. The K^a_4 value of 3.0×10^4 gave no longer the minimum, although K^a_4 values of 0 to 1.5×10^4 gave minima.

In propylene carbonate, smaller constants of the triple ion formation than in acetontrile were given for the chlorides. 1,3-Diphenylguanidium chloride gave rather large values than expected: $K^a_1 = 1.195 \times 10^4$ and $K^a_2 = K^a_3 = 1.7 \times 10^6$.

References

1) M. Hojo, T. Takiguchi, M. Hagiwara, H. Nagai, and Y. Imai, J. Phys. Chem., 93, 955 (1989).
2) M. Hojo, A. Watanabe, T. Mizobuchi, and Y. Imai, J. Phys. Chem., 94, 6073 (1990).
3) M. Hojo, Y. Miyauchi, I. Nakatani, T. Mizobuchi, and Y. Imai, Chem. Lett., 1990, 1035.
4) M. Hojo, Y. Miyauchi, and Y. Imai, Bull. Chem. Soc. Jpn., 63, 3288 (1990).
5) R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc., 55, 2387 (1933).
6) M. Hojo, Y. Miyauchi, A. Tanio, and Y. Imai, Bull. Chem. Soc. Jpn., submitted for publication.
7) I. M. Kolthoff, M. K. Chanttoni, Jr., and S. Bhowmik, J. Am. Chem. Soc., 90, 23 (1968).
8) J. F. Coetzee and G. R. Padmanabhan, J. Am. Chem. Soc., 87, 5005 (1965).
9) The K_1 and $K_2 = K_3$ values of Et_3NHCl in Ref. 1 were recalculated by correcting activity coefficients of ions with the Debye-Hückel limiting law to be $K^a_1 = 3.02 \times 10^4$ and $K^a_2 = K^a_3 = 1.3 \times 10^6$.
10) The equation $-\log f_\pm = A\,\mu^{1/2}/(1 + Ba\mu^{1/2})$ (a = 5 Å) was used for the higher concentration range up to 0.12 M (μ = ca. 4.6×10^{-3}).

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