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Comparison of Ionic Association between Tertiary and Quaternary Ammonium Carboxylates in γ -Butyrolactone

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1 INTRODUCTION

The conductometric analysis of nonaqueous electrolytes¹⁻³⁾ containing γ -butyrolactone (GBL) solvent has been focused on tetraalkylammonium and alkali metal salts of strong acids⁴⁻¹⁰⁾, particularly on the lithium salts such as LiClO_4 , LiBF_4 , LiPF_6 and LiAsF_6 , because γ -butyrolactone is an important dipolar aprotic solvent used for high energy lithium batteries.

On the other hand, tertiary and quaternary ammonium salts of carboxylic acids in γ -butyrolactone have been used as liquid electrolytes in aluminum electrolytic capacitors¹¹⁻¹⁴⁾.

In the previous paper¹³⁾, we have reported the conductometric analysis on the quaternary ammonium carboxylates in γ -butyrolactone. The study was extended to the tertiary ammonium carboxylates in order to clarify the difference in ionic association between tertiary and quaternary ammonium salts.

The conductometric analysis of tertiary ammonium salts in γ -butyrolactone has not been reported and only the data for diethylammonium salicylate^{15, 16)} (secondary ammonium salt) have been published.

2 EXPERIMENTAL

Triethylammonium bimalate, biphtalate and benzoate were prepared *in situ* by the neutralization of maleic acid, phthalic acid and benzoic acid with triethylamine in γ -butyrolactone. Triethylammonium perchlorate was prepared by the titration of aqueous perchloric acid with triethylamine followed by recrystallization and vacuum drying.

The water content in the mother solutions (less than 100 ppm) was measured by a moisture meter and the concentrations of the solutions were calibrated. The

conductivity measurements were carried out by the method previously reported¹³⁾.

3 RESULTS AND DISCUSSION

The molar conductivities Λ of the mother solutions (C ; 1 mol dm^{-3}) and diluted solutions (10^{-2} to $10^{-3} \text{ mol dm}^{-3}$) are given in Table 1 and Fig. 1, respectively.

The molar conductivities of the tertiary ammonium salts are evidently lower than those of the quaternary ammonium counterparts having the same formula weights due to ionic association.

Analysis of conductivity data

The conductivity data were analyzed by means of the Fernández-Prini expansion of the Fuoss-Hsia equation²⁾:

$$\Lambda = \Lambda_0 - S(C\gamma)^{1/2} + E(C\gamma)\ln(C\gamma) + J_1(C\gamma) - J_2(C\gamma)^{3/2} - K_A(C\gamma) f_{\pm}^2 \Lambda \quad [1]$$

where Λ_0 , K_A , γ and $f_{\pm}$ are the limiting molar conductivity, the association constant, the degree of dissociation and the mean molar activity coefficient, respectively. All the coefficients S , E , J_1 and J_2 depend on the solvent properties and the charge on the ions, and J_1 and J_2 also depend on the distance R of closest approach of ions.

The mean molar activity coefficient was calculated by the Debye-Hückel equation³⁾:

$$\ln f_{\pm} = -A(C\gamma)^{1/2} / [1 + BR(C\gamma)^{1/2}] \quad [2]$$

The association constant was evaluated according to the mass action equation³⁾:

$$K_A = (1 - \gamma) / C\gamma^2 f_{\pm}^2 \quad [3]$$

where the activity coefficient for the neutral ion pair is assumed to equal unity.

Although the distance parameters $R(J_1)$ and $R(J_2)$, which are derived from J_1 and J_2 , must be compatible with R in equation 2, there exists inconsistency between distance parameters. Justice recommended that $R(J_1)$ and R be set equal to the Bjerrum critical distance $q^{17)}$.

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Fernández-Prini suggested further that the best results for slightly associated electrolytes are obtained by fixing these parameters, and they are set equal to q , when association is assumed to be of electrostatic nature^{2,18)}.

Setting the distance parameter R equal to the Bjerrum critical distance q , a two-parameter (Λ_0 and K_A) equation 1 was solved by an iterative least square method²⁾. The standard error of estimate σ_A is defined by the following equation²⁾:

$$\sigma_A = [\sum(\Lambda_{\text{obsd}} - \Lambda_{\text{calcd}})^2 / (n - 2)]^{1/2} \quad [4]$$

Limiting molar conductivities and association constants

The results are given in Table 2, where the parameters for diethyldimethylammonium salts were obtained by reanalyzing the conductivity data in Ref. 13.

Lower limiting molar conductivities were obtained

Table 1 Molar conductivities in GBL at 1 mol dm⁻³ and 25°C.

Λ
Et ₃ NH ⁺	4.1	3.2	0.4
Me ₂ Et ₂ N ⁺	13.7*	10.8*	6.0*

in S cm² mol⁻¹. * Ref. 13.

Fig. 1 Kohlrausch plots for tertiary and quaternary ammonium carboxylates in GBL at 25°C.

for tertiary ammonium salts due to the large association constants. Therefore, their limiting molar conductivities were estimated from the data of Et₃NHClO₄, which showed a slight association ($\Lambda_0 = 48.9$ S cm² mol⁻¹, $K_A = 11.0$ dm³ mol⁻¹). The obtained differences of $\Lambda_0(\text{Et}_3\text{NHClO}_4) - \Lambda_0(\text{Et}_4\text{NClO}_4)^{19)} = 1.1$ S cm² mol⁻¹ and $\lambda_0(\text{Et}_2\text{Me}_2\text{N}^+) - \lambda_0(\text{Et}_4\text{N}^+) = 1.4$ S cm² mol⁻¹¹³⁾ give $\lambda_0(\text{Et}_3\text{NH}^+) - \lambda_0(\text{Et}_2\text{Me}_2\text{N}^+) = -0.3$ S cm² mol⁻¹. The estimated values are given in parentheses in Table 2.

The revised single ion limiting molar conductivities are also presented in Table 3.

The association constants of the triethylammonium salts were more than 20 times higher than those of the corresponding diethyldimethylammonium salts. Extraordinarily large ionic association prohibited the simple calculation for the triethylammonium benzoate.

This behavior can be ascribed to the hydrogen bond effect of a protic cation. It is evident that there is a large difference in ionic association between protic cation (tertiary ammonium ion) and non-protic cation (quaternary ammonium ion) in dipolar aprotic solvents.

Table 2 Derived parameters in GBL at 25°C.

Salt		Λ_0	K_A	σ_A
Et ₃ NH		43.6 (46.1)	226	0.099
Me ₂ Et ₂ N		46.4	10	0.140
Et ₃ NH		39.7 (42.2)	228	0.047
Me ₂ Et ₂ N		42.5	10	0.110

Λ_0 in S cm² mol⁻¹, K_A in dm³ mol⁻¹.

Table 3 Single ion limiting molar conductivities in GBL at 25°C.

λ_0^+		λ_0^-
Et ₃ NH ⁺	20.4	25.7
Me ₂ Et ₂ N ⁺	20.7	21.8
Et ₄ N ⁺	19.3*	ClO ₄ ⁻ 28.5*

in S cm² mol⁻¹. * Ref. 19.

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