Conductivities and Ion Association of Quaternary Ammonium Carboxylates in γ -Butyrolactone

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The conductivities for eighteen quaternary ammonium carboxylates in γ -butyrolactone have been measured at 25°C, which have been recently used as high performance liquid electrolytes in aluminum electrolytic capacitors. The limiting molar conductivities and the ion association constants of these electrolytes were calculated by the Shedlovsky extrapolation method. The single ion limiting molar conductivities of carboxylate ions were 24.8, 20.2 and 18.9 S cm² mol⁻¹ for bimalate, biphthalate and benzoate ion, respectively. The single ion limiting molar conductivities of quaternary ammonium ions decreased in the order: Me₄N⁺ 23.1 > Me₃EtN⁺ 22.7 > Me₂(CH₂)₄N⁺ 22.3 > Me₂Et₂N⁺ 22.0 > MeEt₃N⁺ 21.3 > Et₄N⁺ 20.6 S cm² mol⁻¹. The ion association constants increased as the ionic radius of a quaternary ammonium ion and the acidity of a carboxylic acid decreased.

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 acids^{4,5)}, particularly on the lithium salts⁶⁻⁸⁾ such as LiClO₄, LiBF₄, LiPF₆ and LiAsF₆, because γ -butyrolactone is an important solvent used for high energy lithium batteries.

On the other hand, quaternary ammonium salts of carboxylic acids in γ -butyrolactone have recently acquired a potential application in aluminum electrolytic capacitors⁹⁻¹¹⁾. However, the conductivity data for quaternary ammonium carboxylates have been reported only for acetonitrile (AN)¹²⁻¹⁴⁾, N,N-dimethylformamide (DMF)¹⁵⁻¹⁷⁾ and propylene carbonate (PC)¹⁸⁾.

This work is a systematic study on the transport properties of quaternary ammonium carboxylate/ γ -butyrolactone electrolytes, which are used in aluminum

electrolytic capacitors. The conductivity data of several quaternary ammonium bimalates, biphthalates and benzoates, which involve symmetric and asymmetric cations from tetramethylammonium to tetraethylammonium, are presented¹⁹⁾.

2 EXPERIMENTAL

Tetraethylammonium bimalate, biphthalate and benzoate were prepared by the neutralization of maleic acid (Tokyo Chemical Industry Co.), phthalic acid (Tokyo Chemical Industry Co.) and benzoic acid (Wako Pure Chemical Industries) with 40 wt % tetraethylammonium hydroxide aqueous solution (SACEM Inc., Ultapure grade). Tetramethylammonium bimalate, biphthalate and benzoate were prepared by the neutralization of the acids with tetramethylammonium bicarbonate aqueous solution obtained from the reaction of trimethylamine with dimethyl carbonate in methanol²⁰⁾. Asymmetric quaternary ammonium bimalates, biphthalates and benzoates were prepared similarly using asymmetric quaternary ammonium bicarbonate aqueous solutions obtained from the reaction of appropriate amines with dimethyl carbonate. Tetraethylammonium and tetrabutylammonium perchlorates (Tokyo Chemical Industry Co.) were

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recrystallized from high purity water and vacuum dried.

The exact concentrations of quaternary ammonium hydroxide and bicarbonate aqueous solutions were determined by potentiometric titration with a standard sulfuric acid aqueous solution using an auto titrator (Hiranuma Sangyo Co., COMTITE-8/UCB-7).

These salts were dissolved in γ -butyrolactone (Mitsubishi Petrochemical Co., F-GBL). The solutions were then vacuum dried until the water content dropped below 500 ppm, and were readjusted to desired concentrations by adding appropriate amount of the solvent.

The water contents in these stock solutions were measured by a moisture meter (Mitsubishi Kasei Co., CA-06). Their conductivities and densities at $25 \pm 0.1^\circ\text{C}$ were measured by a conductivity meter (Toa Electronics, CM-30S) and a digital density meter (PAAR, DMA 45), respectively. Impurities in these stock solutions were determined by a X-ray fluorescence spectrometer (Rigaku Industrial Corp., 3370E) for Cl and an atomic absorption spectrometer (Hitachi, Z-9000) for Na, K and Fe. These impurities were found less than 1 ppm.

Portions of each stock solution were placed in 100 ml volumetric flasks and solutions for the conductivity measurements were prepared by successive weight dilutions. The conductivity measurements were carried out at $25 \pm 0.1^\circ\text{C}$ by a bridge (Toa Electronics, CM-25E) and a standard type conductivity cell with a cell constant 0.104 cm^{-1} (Toa Electronics, CG-2001PL).

The van der Waals' volumes of each ion were calculated from the molecular models constructed by a molecular modeling system (CHEMLAB-II, Molecular Design) on a computer (Digital Equipment Corp., VAX8350). Final optimization in the structure was performed by a MNDO molecular orbital calculation.

3 RESULTS AND DISCUSSION

The relevant properties of γ -butyrolactone used in this work are summarized in Table 1, where d , η , ϵ_r and κ are density, viscosity, relative permittivity and electrolytic conductivity, respectively⁹.

During the course of pursuing an electrolyte which exhibits the highest conductivity, the structural optimization of a cation in quaternary ammonium

carboxylate/ γ -butyrolactone electrolytes has been carried out. Triethylmethylammonium salts have shown lower conductivities than tetraethylammonium counterparts at higher solute concentrations, particularly for benzoate electrolytes as shown in Fig. 1, where electrolytic conductivities σ of each electrolyte are plotted against solute concentration C_w . In order to elucidate this phenomenon, the conductometric analysis of these electrolytes has been attempted.

Table 1. Physical properties of γ -butyrolactone at 25°C .

$d / \text{g cm}^{-3}$	η / P	$\epsilon_r / -$	$\kappa / \text{S cm}^{-1}$
1.1234	1.727×10^{-2}	41.77	2×10^{-8}

Fig. 1. Concentration dependence of the conductivities of quaternary ammonium carboxylate/ γ -butyrolactone electrolytes at 25°C .

- Et₄N bimalate
- MeEt₃N bimalate
- ▲ Me₄N bimalate
- Et₄N bipthalate
- MeEt₃N bipthalate
- △ Me₄N bipthalate
- Et₄N benzoate
- MeEt₃N benzoate
- △ Me₄N benzoate

3.1 Molar conductivities

The conductivities of the stock solutions of quaternary ammonium bimalates, biphthalates and benzoates are given in Table 2. The concentrations of the stock solutions were adjusted to 1 mol dm⁻³. The concentrations of tetramethylammonium bimalate, tetramethylammonium benzoate and trimethylethylammonium benzoate were adjusted to 0.1 mol dm⁻³ due to their low solubility in γ -butyrolactone as shown in Fig. 1.

These stock solutions were diluted successively and the molar concentrations C on a volume basis were calculated from the concentration on a weight basis and the density of each solution. The densities were calculated from equation 1, where d and d_0 are the densities of solution and solvent, respectively, m is the moles of solute per kg of solution, and D is a constant characteristic of the electrolyte. Density data for the stock solutions given in Table 3 were used to obtain values of D .

$$d = d_0 + Dm \quad (1)$$

The molar conductivities Λ were calculated from the experimental electrolytic conductivities σ after correction for the electrolytic conductivity of the solvent κ . The molar conductivities over the concentration range of 10⁻² to 10⁻³ mol dm⁻³ are given in Tables 4, 5, 6 and 7 for quaternary ammonium perchlorate, bimalate, biphthalate and benzoate electrolytes, respectively.

3.2 Analysis of conductivity data

The data were analyzed in terms of the Shedlovsky equation²¹⁾

$$\frac{1}{\Lambda S^{(z)}} = \frac{1}{\Lambda_0} + \frac{C \Lambda S^{(z)} f_{\pm}^2 K_A}{\Lambda_0^2} \quad (2)$$

where $S^{(z)}$, $f_{\pm}$, Λ_0 and K_A are the Shedlovsky function, a mean molar activity coefficient, a limiting molar conductivity and an association constant, respectively.

$$S^{(z)} = \left[z/2 + \sqrt{1 + (z/2)^2} \right]^2 \quad (3)$$

$$z = \frac{\sqrt{C \Lambda}}{\Lambda_0^{3/2}} \quad (4)$$

where S is the Onsager coefficient

$$S = \alpha \Lambda_0 + \beta \quad (5)$$

$$\alpha = \frac{8.204 \times 10^5}{(\epsilon_r T)^{3/2}} \quad (6)$$

$$\beta = \frac{82.49}{\eta(\epsilon_r T)^{1/2}} \quad (7)$$

Table 2. Conductivities of the 1 mol dm⁻³ - quaternary ammonium carboxylate/ γ -butyrolactone electrolytes at 25°C.

σ / mS cm ⁻¹			
Me ₄ N ⁺	2.7*	10.1	1.5*
Me ₃ EtN ⁺	12.9	10.5	1.6*
	13.3	10.5	5.9
Me ₂ Et ₂ N ⁺	13.7	10.8	6.0
MeEt ₃ N ⁺	13.7	10.8	6.8
Et ₄ N ⁺	13.8	10.5	8.3

* 0.1 mol dm⁻³

Table 3. Densities of the 1 mol dm⁻³ - quaternary ammonium carboxylate/ γ -butyrolactone electrolytes at 25°C.

d / g cm ⁻³			
Me ₄ N ⁺	1.1241*	1.1404	1.1231*
Me ₃ EtN ⁺	1.1279	1.1379	1.1230*
	1.1362	1.1453	1.1260
Me ₂ Et ₂ N ⁺	1.1249	1.1346	1.1157
MeEt ₃ N ⁺	1.1227	1.1324	1.1149
Et ₄ N ⁺	1.1200	1.1300	1.1128

* 0.1 mol dm⁻³

The mean molar activity coefficient $f_{\pm}$ was calculated by the Debye-Hückel equation

$$\log f_{\pm} = -\frac{A\sqrt{\gamma C}}{1 + Ba\sqrt{\gamma C}} \quad (8)$$

$$A = \frac{1.8246 \times 10^6}{(\epsilon_r T)^{3/2}} \quad (9)$$

$$B = \frac{50.29 \times 10^8}{(\epsilon_r T)^{1/2}} \quad (10)$$

where a is the distance of closest approach in cm and γ is the degree of dissociation in the mass action equation.

$$K_A = \frac{1 - \gamma}{C\gamma^2 f_{\pm}^2} \quad (11)$$

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

The degree of dissociation γ is correlated with the Shedlovsky function by the following equation.

$$\gamma = \frac{\Delta}{\Lambda_0} S(z) \quad (12)$$

The ion-size parameter a in the equation 8 was estimated by summing up ionic radii r 's of a cation and an anion, which were calculated by equation 13 using the van der Waals' volume V of each ion. The ionic radii of quaternary ammonium ions and carboxylate ions are given in Table 8. The estimated values for quaternary ammonium ions are very close to those obtained by a similar method²². The ionic radius of perchlorate ion was assumed to be 2.00 Å⁴³.

$$r = \left(\frac{3V}{4\pi} \right)^{1/3} \quad (13)$$

A set of parameters Λ_0 and K_A are derived from the intercept and slope of the straight line on the plot of $1/\Lambda S(z)$ vs. $C\Lambda S(z)f_{\pm}^2$. A BASIC program was used to solve the above procedures, where an initial value of Λ_0 was calculated from the Arrhenius-Ostwald relation ($S(z) = f_{\pm} = 1$ in equation 2) and iterations were continued until the error in Λ_0 became less than 0.001. A typical result is given in Table 9. Derived parameters are summarized in Tables 10, 11 and 12.

Table 4. Molar concentrations and molar conductivities of quaternary ammonium perchlorate/ γ -butyrolactone electrolytes at 25°C.

$10^3 C$ / mol dm ⁻³	Λ / S cm ² mol ⁻¹	$10^3 C$	Λ
Et ₄ N ClO ₄		Bu ₄ N ClO ₄	
9.7352	40.213	9.7407	39.780
7.7479	40.989	8.2007	40.433
5.9551	41.960	6.3841	41.272
3.6390	43.220	4.3085	42.400
1.9542	44.587	1.9471	44.046
1.0916	45.647	0.9751	45.174

Table 5. Molar concentrations and molar conductivities of quaternary ammonium bimalate/ γ -butyrolactone electrolytes at 25°C.

$10^3 C$	Λ	$10^3 C$	Λ
Me ₄ N bimalate		Me ₃ EtN bimalate	
9.7352	40.213	9.7407	39.780
7.7479	40.989	8.2007	40.433
5.9551	41.960	6.3841	41.272
3.6390	43.220	4.3085	42.400
1.9542	44.587	1.9471	44.046
1.0916	45.647	0.9751	45.174
N ^{Me} ₂ bimalate		Me ₂ Et ₂ N bimalate	
9.9679	39.485	9.9887	38.972
8.3737	40.087	7.9113	39.903
6.5422	40.946	5.8964	40.734
4.5274	41.985	3.9468	41.826
2.5150	43.212	1.9774	42.990
1.2196	44.488	1.0196	44.147
MeEt ₃ N bimalate		Et ₄ N bimalate	
9.9253	38.839	9.8916	38.779
7.9012	39.512	7.7222	39.507
6.0870	40.199	5.8570	40.171
4.1749	41.148	3.7297	41.177
2.0363	42.576	2.0008	42.324
1.0099	43.628	1.0265	43.235

Table 6. Molar concentrations and molar conductivities of quaternary ammonium biphthalate/ γ -butyrolactone electrolytes at 25°C.

10^3C	Λ	10^3C	Λ
Me ₄ N biphthalate		Me ₃ EtN biphthalate	
9.9677	35.536	10.0582	36.038
7.9319	36.647	8.0444	36.781
6.1130	37.360	6.0054	37.546
4.1578	38.405	4.0345	38.832
2.1405	39.976	2.0391	39.885
1.1319	40.859	1.0332	40.972
biphthalate		Me ₂ Et ₂ N biphthalate	
9.7567	35.963	9.8348	35.606
7.9368	36.624	7.9977	36.233
6.0204	37.386	6.1726	37.032
4.0393	38.467	4.2241	37.992
1.9767	39.723	2.0479	39.299
1.0320	40.599	1.0576	40.215
MeEt ₃ N biphthalate		Et ₄ N biphthalate	
9.9849	35.136	9.9316	34.514
8.3456	35.561	8.1159	35.077
6.4731	36.193	5.9566	35.923
4.4558	37.071	4.0016	36.680
2.4753	38.239	2.6788	37.304
1.2917	39.327	1.4889	38.237

Table 7. Molar concentrations and molar conductivities of quaternary ammonium benzoate/ γ -butyrolactone electrolytes at 25°C.

10^3C	Λ	10^3C	Λ
Me ₄ N benzoate		Me ₃ EtN benzoate	
9.9975	29.505	9.9984	30.483
8.3015	30.570	7.9466	31.898
6.1986	32.230	5.9711	33.324
4.3194	34.097	4.1141	34.875
2.0599	36.527	2.0683	36.919
1.0337	37.943	1.0424	37.903
benzoate		Me ₂ Et ₂ N benzoate	
10.0056	31.191	10.0892	31.705
8.0117	32.350	7.9887	32.744
5.9877	33.666	6.0493	33.868
4.0557	35.205	4.1092	35.233
1.9935	37.111	2.0969	37.046
1.0259	37.840	1.1204	37.881
MeEt ₃ N benzoate		Et ₄ N benzoate	
9.9857	32.424	10.1772	32.689
7.9811	33.351	8.2609	33.372
6.1242	34.319	6.3718	34.084
4.1484	35.503	4.4023	34.954
2.0322	36.905	2.4429	36.117
1.0127	37.682	1.2805	36.971

Table 8. Estimated ionic radii from van der Waals' volumes.

Cation	$r_+ / \text{\AA}$		Anion	$r_- / \text{\AA}$
Me ₄ N ⁺	2.89	2.83*1		2.64
Me ₃ EtN ⁺	3.05
3.08			2.99
Me ₂ Et ₂ N ⁺	3.19			
MeEt ₃ N ⁺	3.32			2.83
Et ₄ N ⁺	3.42	3.39*1		
Bu ₄ N ⁺	4.20	4.15*1		

*1 Data from literature²²⁾

Table 9. The calculated result for tetramethylammonium benzoate/ γ -butyrolactone electrolyte.

$10^3 C$	Λ	z	$S(z)$	γ	$f_{\pm}$	$C\Lambda S(z) f_{\pm}^2$	$1/\Lambda S(z)$	Λ_0	K_A
9.9975	29.505	0.1361	1.1457	0.8113	0.8017	0.2172	0.0296	39.805	46.978
8.3015	30.570	0.1262	1.1345	0.8324	0.8131	0.1903	0.0288	41.738	42.282
6.1986	32.230	0.1120	1.1185	0.8652	0.8301	0.1540	0.0277	41.661	43.457
4.3194	34.097	0.0962	1.1009	0.9010	0.8500	0.1172	0.0266	41.664	43.413
2.0599	36.527	0.0687	1.0711	0.9391	0.8874	0.0635	0.0256	41.664	43.415
1.0337	37.943	0.0496	1.0509	0.9570	0.9158	0.0346	0.0251	$(a = 5.72 \text{ \AA})$	

Table 10. Derived limiting molar conductivities.

Λ_0 / $S \text{ cm}^2 \text{ mol}^{-1}$	$\text{[COO}^-\text{COOH]}$	$\text{[COO}^-\text{COOH]}$	$\text{[COO}^-\text{COOH]}$
Me_4N^+	48.14	43.48	41.66
Me_3EtN^+	47.53	43.27	41.37
N^+Me_2	47.10	42.90	41.03
$\text{Me}_2\text{Et}_2\text{N}^+$	46.45	42.53	40.89
MeEt_3N^+	45.84	41.67	40.27
Et_4N^+	45.43	40.75	39.46

Table 11. Derived ion association constants.

K_A / $\text{mol}^{-1} \text{ dm}^3$	$\text{[COO}^-\text{COOH]}$	$\text{[COO}^-\text{COOH]}$	$\text{[COO}^-\text{COOH]}$
Me_4N^+	8.36	9.64	43.42
Me_3EtN^+	7.48	6.45	31.34
N^+Me_2	6.68	5.55	24.04
$\text{Me}_2\text{Et}_2\text{N}^+$	5.94	5.50	19.84
MeEt_3N^+	4.59	4.13	11.24
Et_4N^+	3.00	2.42	5.51

Table 12. Derived parameters for perchlorates.

	Λ_0	K_A
$\text{Et}_4\text{N ClO}_4$	49.98	2.66
$\text{Bu}_4\text{N ClO}_4$	43.81	1.75

3.3 Single ion limiting molar conductivities

Conductivity data of Et_4NClO_4 and Bu_4NClO_4 in γ -butyrolactone were also analyzed in order to generate single ion limiting molar conductivities from Table 10, because the single ion limiting molar conductivity of Bu_4N^+ is known⁴⁾. However, this reported value seems to be too small, because the transport number t_o^+ (Bu_4NClO_4) and the relative difference between $\lambda_o^+(\text{Et}_4\text{N}^+)$ and $\lambda_o^+(\text{Bu}_4\text{N}^+)$ designated as Δ are deviated from those obtained for other dipolar aprotic solvents as shown in Table 13. Assuming t_o^+ (Bu_4NClO_4) is a more consistent value 0.329, which is calculated from the other reported data²³⁾, $\lambda_o^+(\text{Bu}_4\text{N}^+)$ was reassigned. As the result, $\lambda_o^+(\text{Et}_4\text{N}^+)$ was proven to be 20.6, which is almost the same as the reported value⁴⁾.

Table 13. Mobility data of ions in dipolar aprotic solvents at 25°C.

	GBL*1	GBL*2	DMF*3	DMSO*4	PC*5
$\lambda_o^+(\text{Bu}_4\text{N}^+)$	14.4	11.8	25.4	11.8	9.0
$\lambda_o^+(\text{Et}_4\text{N}^+)$	20.6	20.4	35.4	17.5	13.2
$\lambda_o^-(\text{ClO}_4^-)$	29.4	26.2	52.4	24.1	18.4
$t_o^+(\text{Bu}_4\text{NClO}_4)$	0.329	0.311	0.326	0.329	0.328
Δ^6	0.142	0.226	0.129	0.159	0.153

*1 Present results

*2 λ_o data from literature⁶⁾

*3 λ_o data from literature²⁾

*4 Dimethylsulfoxide, λ_o data from literature²⁾

*5 λ_o data from literature²⁴⁾

*6 $\Delta = \frac{\lambda_o^+(\text{Et}_4\text{N}^+) - \lambda_o^+(\text{Bu}_4\text{N}^+)}{\lambda_o^+(\text{Bu}_4\text{N}^+) + \lambda_o^-(\text{ClO}_4^-)}$

The resulting consistent set of the single ion limiting molar conductivities of quaternary ammonium ions and carboxylate ions are given in Table 14.

Walden products $\lambda_o\eta$ of each ion are plotted against the reciprocal of ionic radius r in Fig. 2. The theoretical behavior calculated from Stokes' law in equation 14 is given by the bottom line for perfect stick ($A_s = 0.82$) and by the top line for perfect slip ($A_s = 1.23$).

$$\lambda_o\eta = \frac{A_s}{r} \quad (14)$$

Table 14. Single ion molar conductivities in γ -butyrolactone at 25°C.

λ_o^+ / S cm ² mol ⁻¹	λ_o^- / S cm ² mol ⁻¹
Me ₄ N ⁺ 23.1	24.8
Me ₃ EtN ⁺ 22.7	20.2
22.3	18.9
Me ₂ Et ₂ N ⁺ 22.0	
MeEt ₃ N ⁺ 21.3	
Et ₄ N ⁺ 20.6

Fig. 2. Walden products as a function of the reciprocal of ionic radius.

All quaternary ammonium ions including tetramethylammonium ion follow the theoretical behavior for perfect slip. Bimalcate, biphthalate and benzoate ions also approach the behavior for perfect slip. This result suggests that all ions discussed here are able to move without adhesion to γ -butyrolactone. The inversion of the order in the mobility between biphthalate and benzoate ion, which cannot be seen in the aqueous solution²⁵, may be explained by the lower conductivity of benzoate solution over the experimental concentration range due to the ion association discussed later.

3.4 Association constants

Derived ion association constants in Table 11 are plotted against ionic radii of cations as shown in Fig. 3. The K_A values increase in the order, Et₄N⁺ < MeEt₃N⁺ < Me₂Et₂N⁺ < Me₂(CH₂)₄N⁺ < Me₃EtN⁺ < Me₄N⁺ with decreasing cation size. This tendency can be predicted theoretically by the Bjerrum equation

$$K_B = \frac{3.531 \times 10^{13}}{(\epsilon_r T)^3} \int_2^b \chi^{-4} \exp(\chi) d\chi \quad (15)$$

$$b = \frac{1.671 \times 10^{-3}}{a\epsilon_r T} \quad (16)$$

where the ion association constant K_B increases as the ion-size parameter a decreases.

Fig. 3. Effect of cation size on ion association constants.

Calculated K_B values are shown by the broken curves in Fig. 3. The fact that the K_B values are smaller than the experimental K_A values indicates the existence of ion-dipole and dipole-dipole interaction besides an electrostatic force due to the delocalizability of the carboxylate ions.

A large dependence of cation size on the ion association constant observed for benzoate solutions cannot be explained theoretically. However this result is closely related to the low ionization constant K_a of benzoic acid in γ -butyrolactone compared with maleic acid and phthalic acid.

The ionization constants of carboxylic acids are given in Table 15²⁶⁾, where the values in γ -butyrolactone are estimated by the data that pK_a values in γ -butyrolactone are smaller than those in propylene carbonate by 2 units²⁷⁾.

Lower conductivities of triethylmethylammonium salts than tetraethylammonium counterparts at higher concentrations (Fig. 1) can be predicted by the tendency of K_A values obtained at low concentrations.

Table 15. Ionization constants of carboxylic acids in dipolar aprotic solvents at 25°C.

pK_a	GBL* ¹	DMA* ²	AN	PC
maleic acid	10	4	-	-
phthalic acid	11	5	14	-
salicylic acid	14	7	17	15
benzoic acid	18	11	21	20

*¹ Estimated values

*² Dimethylacetamide

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