J. Chem. Eng. Data 1992, 37, 443–445

Conductance of Lithium and Sodium Perchlorates and of Some Quaternary Ammonium Halides and Perchlorates in a Propylene Carbonate + Tetrahydrofuran Mixture at 25 °C

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The electrical conductances of lithium and sodium perchlorates and of some quaternary ammonium halides and perchlorates in propylene carbonate (PC) + tetrahydrofuran (THF) (1:1 in volume) have been measured at 25 °C. The conductance data were analyzed by a minimization technique using the complete form of the Fuoss/Hsia (F/H) equation. All electrolytes were found to be anomalous in showing unusually higher molar conductances than in each solvent alone. The effect of the variation of the three parameters K_A, Λ_o, and a was fully investigated.

Introduction

Although considerable work has been reported on measurements of conductivity of various electrolytes in mixed organic solvents, the relationship between conductivity and solvent composition is not well understood. Various explanations were given for the abnormal conductance in mixed solvents. It is evident that electrical conductivity of electrolytes in mixed solvents is influenced firstly by the concentration of the electrolyte and secondly by the viscosity of the solvent medium. Beside that, attempts to use mixed organic solvents in high-energy batteries have been reported (*1, 2*).

In recent years much interest has been shown in the solvent properties of both propylene carbonate and tetrahydrofuran. Some lithium batteries (*3–5*) have adopted mixed organic electrolytes, such as a mixed solvent of propylene carbonate (PC) and 1,2-dimethoxyethane dissolving lithium perchlorate. PC has been adopted as the solvent for high-energy batteries by many researchers, and tetrahydrofuran (THF) has been used in an investigation of a secondary lithium electrode (*6*). In connection with these solvents, electrolytic conductances of the mixed systems of PC and THF (1:1 in volume) with lithium and sodium perchlorates and with some tetraalkylammonium salts were measured in this study. Relationships between viscosity and solvent composition in terms of nature and number of solvent moles in the mixture have been discussed (*7*). It was found that the molar conductivity of the PC + THF mixture was higher than that of each single solvent, and the maximum value of the molar conductivity was obtained at the mixture ratio of about 1:1.

Experimental Section

Conductance measurements were made at 25 °C with a Wayne-Kere B331 autobalance precision bridge. The conductivity cell used is that described elsewhere (*8*) with platinum electrodes which were lightly coated with platinum black before use, and the cell constant (as determined by a standard solution of KCl) was 0.169 93 ± 0.000 03 cm^{-1}.

Propylene carbonate and tetrahydrofuran were purified by the methods described elsewhere (*2, 9*), and the final water contents were below 100 ppm in PC and 200 ppm in THF. The conductivities (S cm^{-1}) of the final products were in the ranges (2–4) × 10^{-8}, (1–2) × 10^{-8}, and (3–5) × 10^{-6} for PC, THF, and their mixture (1:1), respectively, at 25 °C. Lithium and sodium perchlorates were used after drying under reduced pressure at 160–170 °C for 24 h, and tetraalkylammonium salts were dried under reduced pressure at 65–75 °C for 24 h, where all electrolytes were taken as analar (*7*).

Solutions for the conductivity measurements were prepared by weighing from the stock solutions and the solvents. Solvent mixtures were also made by weight. Preparation of the solutions and all the other manipulations were performed in a drybox.

Results and Discussion

The experimental molar conductances Λ_{exp} of lithium and sodium perchlorates and of tetraethylammonium iodide, bromide, chloride, and perchlorate as well as tetrabutylammonium perchlorate have been measured in this work at different molar concentrations C; the results are given in Tables I–IV. Figures 1 and 2 show Λ_{exp} vs $C^{1/2}$ for the same electrolytes. These data were analyzed by means of the Fuoss/Hsia equation (*10*):

$$\Lambda = [\Lambda_o - \Delta\Lambda][1 + \Delta X/X]/[1 + 3\phi/2] \qquad (1)$$

where all symbols are defined in the original paper. All calculations were performed on an ACOS 800 computer using the values of Λ_o, a, and K_A independently which produce a theoretical curve (Λ_{calcd} against $C^{1/2}$) giving the best fit to the measured conductance (Λ_{exp}) at a series of known concentrations of solute. The criterion of "fit" is that the sum of the squares S^2 of the differences between Λ_{calcd} and Λ_{exp} at each concentration should be a minimum, and hence the standard deviation σ is also a minimum which is given by

$$S^2 = \sum_1^N [\Lambda_{calcd} - \Lambda_{exp}]^2 \qquad \sigma = (S^2/N)^{1/2} \qquad (2)$$

where N represents the number of experimental points.

The values of the derived parameters for all salts, Λ_o, a, and K_A are summarized in Table V together with the standard deviation σ.

The common characteristic point of analyzing data for all electrolytes is that their molar conductivities are higher than those in each single solvent. The very significant factors affecting the conductance of ionic solutions would be the dielectric constant and the viscosity in connection with the solvation of the ions and the solvent–solvent interaction. The same trend was found by Matsuda and Satake (*7*).

It could be assumed that the increase in molar conductivitiy of the solution with the addition of THF to PC is caused

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0021-9568/92/1737-0443$03.00/0

Table I. Experimental Conductance Data at 25 °C

$LiClO_4$		$NaClO_4$	
$C \times 10^{-4}$/ (mol dm^{-3})	Λ_{exp}/ (S cm^2 mol^{-1})	$C \times 10^{-4}$/ (mol dm^{-3})	Λ_{exp}/ (S cm^2 mol^{-1})
1.1466	49.360	2.0758	53.098
4.9043	48.579	3.0931	52.179
9.3184	47.215	5.6372	51.785
11.7460	46.739	7.2372	51.186
14.0781	46.687	9.3011	50.847
18.9732	46.339	11.4081	50.279
21.2491	45.968	14.4344	49.795
23.5447	45.779	17.0955	49.374
25.8915	45.424	19.7944	48.919
27.9497	45.100	22.1546	48.579
29.9486	44.794	24.1900	48.155
		26.3020	48.072
		28.9611	47.938
		31.1458	47.525
		33.2458	47.384
		35.1905	47.244
		37.2370	47.055
		39.0343	46.779
		41.0737	46.745
		44.1610	46.473

Table II. Experimental Conductance Data at 25 °C

$(C_2H_5)_4NI$		$(C_2H_5)_4NClO_4$	
$C \times 10^{-4}$/ (mol dm^{-3})	Λ_{exp}/ (S cm^2 mol^{-1})	$C \times 10^{-4}$/ (mol dm^{-3})	Λ_{exp}/ (S cm^2 mol^{-1})
10.8673	54.403	6.3834	74.575
13.0403	53.968	12.7875	72.446
15.2613	53.481	18.2320	71.102
17.3707	52.995	19.9053	70.774
19.5647	52.719	21.9655	70.427
21.7169	52.402	24.0184	69.963
23.8773	52.208	26.1526	69.621
25.8885	51.801	27.9414	69.286
27.8374	51.609	29.6721	69.012
29.7897	51.369	31.5288	68.703
31.7874	51.209	33.6210	68.444
33.6989	51.046	35.4515	68.227
35.5214	50.856	37.6032	67.859
37.6294	50.707	39.5411	67.592

Table III. Experimental Conductance Data at 25 °C

$(C_2H_5)_4NCl$		$(C_2H_5)_4NBr$	
$C \times 10^{-4}$/ (mol dm^{-3})	Λ_{exp}/ (S cm^2 mol^{-1})	$C \times 10^{-4}$/ (mol dm^{-3})	Λ_{exp}/ (S cm^2 mol^{-1})
23.1747	50.260	3.5216	55.415
25.7289	49.713	8.3448	53.639
28.2321	49.364	10.3614	53.016
30.3044	49.084	12.3769	52.682
32.3153	48.694	14.4577	52.189
34.1642	48.374	16.7009	51.952
36.3873	48.129	19.1188	51.435
38.5026	47.908	21.8241	50.929
40.5991	47.717	24.5143	50.603
42.9923	47.297	26.6278	50.170
		28.7746	49.947
		31.1269	49.545
		33.3556	49.291
		35.3705	48.954
		37.4489	48.709
		39.8014	48.466
		42.1380	48.287
		44.2554	48.176

by the effect of the low viscosity of THF on the Waldens product. However, the reason for the low molar conductivity of the THF-rich solution cannot be interpreted by this viscosity theory. It has been reported that the dielectric constant decreases with the THF content and the above observation would be attributed to specific solvation (*11–13*) or to the decrease in the Waldens product (*14*).

Table IV. Experimental Conductance Data for $(C_4H_9)_4NClO_4$ at 25 °C

$C \times 10^{-4}$/ (mol dm^{-3})	Λ_{exp}/ (S cm^2 mol^{-1})	$C \times 10^{-4}$/ (mol dm^{-3})	Λ_{exp}/ (S cm^2 mol^{-1})
1.9303	51.052	25.5361	46.724
3.2823	50.500	29.3108	46.453
5.7398	50.117	31.5947	46.085
9.2938	49.699	33.4692	45.985
11.1657	48.700	36.4245	45.726
15.7200	47.804	39.1073	45.406
17.6223	47.414	41.5006	45.248
21.5812	47.170		

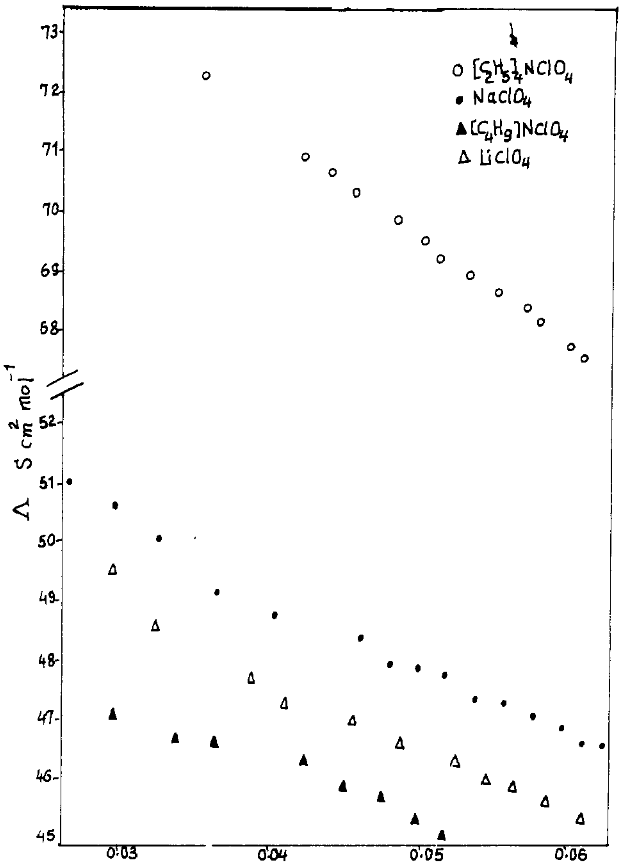

Figure 1. Λ_{exp} (S cm^2 mol^{-1}) of sodium, lithium, tetraethylammonium, and tetrabutylammonium perchlorates versus $C^{1/2}$ (mol dm^{-3}) at 25 °C.

Some precise viscosity and conductance measurements on solutions of the same electrolytes studied here have been made in PC only (*15–18*). The significance of the viscosity coefficient in interpreting the conductance data obtained has been discussed. The conductance data indicated negligible ion association in all these electrolytes. Furthermore, it was found that, in the event of ion–ion contacts, the bare ions rather than their solvated cospheres are presumably involved as indicated from the calculated *a* parameters.

In comparison with our parameters Λ_o, a, and K_A given in Table V, it is clear that all Λ_o values obtained here are higher than those measured in PC or in THF separately. This may be attributed to the decrease in the viscosity coefficient as well as to some sort of solvation, so that solvated cospheres rather than their bare ions are presumably involved. This behavior could be more indicated from the high values of *a* parameters (distances of closest approach of ions) obtained here which do not agree with the crystallographic radii. The values of K_A given in the same table show good evidence of considerable ion association. It is concluded that there is a significant ion–solvent interaction in these systems.

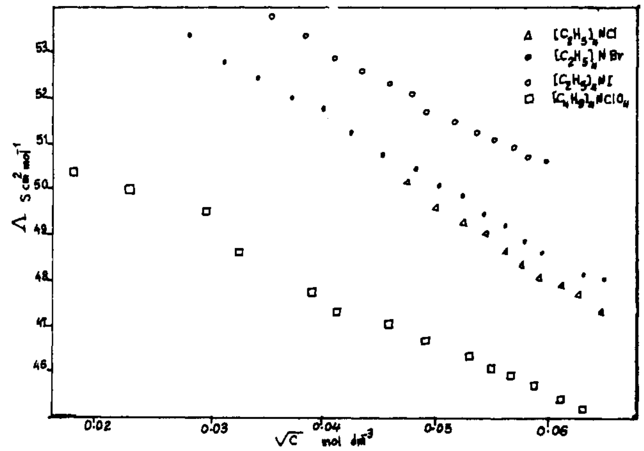

Figure 2. Λ_{exp} (S cm^2 mol^{-1}) of tetraethylammonium chloride, bromide, and iodide and of tetrabutylammonium perchlorate versus $C^{1/2}$ (mol dm^{-3}) at 25 °C.

Table V. Best Fit Values for Λ_o, K_A, and a Parameters

electrolyte	Λ_o/ (S cm^2 mol^{-1})	K_A/ (mol L^{-1})	a/A°	σ
$LiClO_4$	52.01	95	13	0.096
$NaClO_4$	60.03	85	12	0.071
$(C_2H_5)_4NI$	58.11	45	12	0.086
$(C_2H_5)_4NClO_4$	86.02	90	10	0.087
$(C_2H_5)_4NCl$	58.80	57	12	0.067
$(C_2H_5)_4NBr$	58.01	74	10	0.074
$(C_4H_9)_4NClO_4$	54.05	50	12	0.082

Plots of Λ against $C^{1/2}$ in PC + THF (1:1 in volume) containing various perchlorates are shown in Figure 1. In the range of concentrations studied, the order of molar conductivities of electrolytes is

$$(C_2H_5)_4NClO_4 > NaClO_4 > (C_4H_9)_4NClO_4 > LiClO_4$$

This order would be the same as that of molar conductivities of the cations, and the molar conductivities were almost the same as that in the infinite dilution.

Also, plots of Λ against $C^{1/2}$ in PC + THF (1:1 in volume) containing various tetraethylammonium electrolytes are shown in Figure 2. The order of molar conductivities covering the range of concentrations studied is

$$(C_2H_5)_4NClO_4 > (C_2H_5)_4NI > (C_2H_5)_4NBr > (C_2H_5)_4NCl > (C_4H_9)_4NClO_4$$

In general, large cations show a normal size–mobility dependence, but alkali-metal ions produce a reverse trend, in terms of bare-ion radii. Anions have much higher mobilities than cations, relative to their crystallographic size, indicating relatively low solvation of anions by a PC + THF mixture. Furthermore, comparison of the limiting conductances of the perchlorates suggests that the mobility of lithium ion is lower than that of $(C_4H_9)_4N^+$ and $(C_2H_5)_4N^+$, indicating that the lithium ions in a PC + THF mixture are substantially more solvated than in PC only.

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Received for review April 8, 1992. Accepted June 6, 1992.

Registry No. $LiClO_4$, 7791-03-9; $NaClO_4$, 7601-89-0; $(C_2H_5)_4NI$, 68-05-3; $(C_2H_5)_4NClO_4$, 2567-83-1; $(C_2H_5)_4NBr$, 71-91-0; $(C_2H_5)_4NCl$, 56-34-8; $(C_4H_9)_4NClO_4$, 1923-70-2.