PRESSURE EFFECTS ON CONDUCTIVITY STUDIES OF LITHIUM AND QUATERNARY AMMONIUM SALTS IN PROPYLENE CARBONATE AND γ-BUTYROLACTONE

César A. N. VIANA and Mavitidi DILO
Centro de Electroquímica e Cinética e Departamento de Química e Bioquímica da Universidade de Lisboa, Instituto Bento da Rocha Cabral, Calçada Bento da Rocha Cabral,14, 1250-047 Lisboa, Portugal

ABSTRACT

Propylene carbonate (PC) and γ-butyrolactone (GBL) are important dipolar approtic solvents used to prepare non-aqueous electrolytes for high energy lithium batteries [1-4]. A few salts have been tried in these solvents because they permit to work at lower and higher temperatures than the melting and boiling points of water respectively. Actually these solvents have much larger liquid temperature intervals than water and they are generally very stable and safe as it was demonstrated by Kita and Hasegawa in recent papers [5,6].

In this paper conductivity determination of lithium perchlorate ($LiClO_4$) as well as of tetra-ethylammonium bromide (Et_4NBr) solutions in those two solvents have been obtained under different pressures. The resulting volumes of activation are positive for both salts and generally decrease as pressure increases for lower concentrations. The contrary is observed for higher concentrated solutions. The association equilibrium constants were also determined and they are almost constant or slightly decrease with pressure and decrease with concentration. All the experiments were carried out at 25 °C ± 0.01 °C.

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Introduction

Experimental and theoretical researches on the thermodynamics of electrolytic solutions have mainly been performed with aqueous solutions. The specific electrical condutivity of most non-aqueous solvents is lower than that of water and so conductance measurements of electrolytes in those solvents can be made at lower concentrations without loss of accuracy. Propylene carbonate (PC) and γ-butyrolactone (GBL) are promising solvents to prepare non-aqueous electrolytes in high energy lithium batteries, capable of working at very high temperatures and pressures and / or also at low temperatures. Lithium and tetra-alkylammonium salts are good materials to produce high electrolytic conductivities in such solvents at higher concentrations, acquiring excellent qualities as electrochemical solutions.

Experimental

1-Reagents: Lithium perchlorate (Riedel-de Haën) puriss >99% , bromide tetra-ethylammonium (Fluka) puriss >99%, propylene carbonate and γ-butyrolactone (Aldrich) with 99.7% and 99.5% of purity respectively without further purification.

2-Solutions preparation: Each salt was dissolved in propylene carbonate and / or γ-butyrolactone to make 50 mL of solution. The mother solution was diluted to about 0.1 mol dm^{-3} by the solvent to make the stock solution.

3-Conductivity measurements: The conductivity measurements were carried out at 25 °C ± 0.01 °C and pressure range of 1 - 2000 bar by a conductance bridge Wayne Keer B905 working at frequency of 1kHz. The cell constants were obtained through the aqueous solutions of potassium chloride 0.01M at 25 °C ± 0.01 °C with values between 0.25125 cm^{-1} and 0.25972 cm^{-1}.

Results and discussion

The advantages, concerning the used solvents are, namely, very high relative permitivities, low melting points and high boiling points, which means large liquid zone between the following limits (table I):

Table I: Physical properties of PC and GBL at 25 °C

SOLVENTS PHYS.PROPER.	PC	GBL
Melting Point / °C	-49	-44
Boiling Point / °C	240	204 - 205
Relative Permitivity	65	42

These two substances are not too volatile in large temperature interval, which, connected with other properties, namely the high permitivities favours them as very stable and safe as well as good ionizing solvents. On the other hand, the very broad liquid zone allows them to be used in many applications of the referred batteries, particularly for preparing solutions where high ionized substances to work at low or high temperatures are required.

It was recently demonstrated by Makoto Ue [12] that an electrolyte composed by $LiClO_4$ or Et_4NClO_4 in PC shows a well - balanced performance of high electrolytic conductivity, a wide stable potential window, and durability against hydrolysis.

In this paper, conductivity determinations of the two salts, lithium perchlorate and tetra- ethylammonium bromide, both in PC and GBL have been performed at 25 °C ± 0.01 °C and within the pressure range 1 atm to 2000 bar. The precision of the obtained results can be shown saying that the conductivity measurements have been determined with six figures and the concentrations with five and they can be compared with the few other results obtained at 1 atm. (table II).

Table II: Values of limiting molar conductivity of $LiClO_4$ salt in PC and GBL (P = 1 atm , T = 25 °C)

Systems	Λ_0 / S $cm^2 mol^{-1}$	
$LiClO_4$ + PC	29.7306 (a)	26.4010 (b)
$LiClO_4$ + GBL	44.2242 (a)	40.3037 (b)

(a) our results; (b) results of Makoto Ue[12].

The limiting molar conductivities were obtained through the quadratic equation used by Viana and Calado [8]

$$\Lambda = \Lambda_0 + a_1 c + a_2 c^{1/2}$$

though the Fuoss and Hsia equation [10] has been tried without showing more precise results than those obtained through that one. An adjust programme applied to the coefficients a_1 and a_2 was used and the resulting limiting molar conductivities obtained out of it

are presented in table III. It shows that Λ_0 always decrease as pressure increases for all the solutions(table III and fig.I).

Table III: Limiting molar conductivities(Λ_0/S cm^2 mol^{-1}) as function of pressure T = 298.15 K

Systems P / bar	$LiClO_4$ + GBL	$LiClO_4$ + PC	Et_4NBr + GBL	Et_4NBr + PC
1	44.2242±0.73	29.7307±0.46	59.8531±2.03	38.3639±0.51
100	42.4839±0.64	28.9744±0.31	57.8432±1.43	36.3879±0.37
200	40.7408±0.50	27.6701±0.58	55.7808±1.38	34.6436±0.36
300	38.8722±0.53	26.0181±0.61	52.7254±1.09	32.5581±0.37
400	37.2801±0.61	24.5856±0.57	50.3012±1.18	30.7981±0.29
500	35.7692±0.38	23.1747±0.55	48.2178±0.97	29.2068±0.29
1000	29.9758±0.52	18.2754±0.42	39.2193±0.84	22.6024±0.45
1500	24.4308±0.52	13.6405±0.29	32.3837±0.56	17.3103±0.26
2000	20.6053±0.16	10.8629±0.31	27.8280±0.65	13.2999±0.15

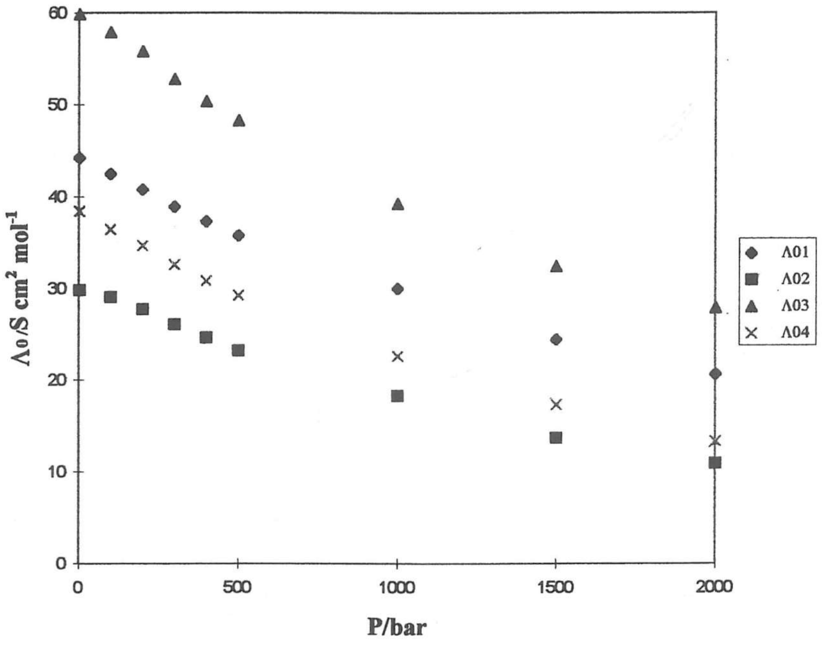

Figure 1: Limiting molar condutivities vs Pressure of Lithium Perchlorate and Tetra-ethylammonium Bromide in GBL and PC at 298.15 K

Λ_{01} =$LiClO_4$ + GBL; Λ_{02}=$LiClO_4$ + PC; Λ_{03}= Et_4NBr + GBL; Λ_{04}= Et_4NBr + PC

The association constants were calculated through the gradient of linear part of the curves $1 - \Lambda/\Lambda_0$ versus $(\Lambda/\Lambda_0)^2$ extrapolated to $c = 0$ for the most dilute solutions (fig.2). These curves result from the application of the following equation

$$K_A = [(1 - \Lambda/\Lambda_0) / (\Lambda/\Lambda_0)^2 c]$$

which for the lower values of concentration leads to a linear variation.

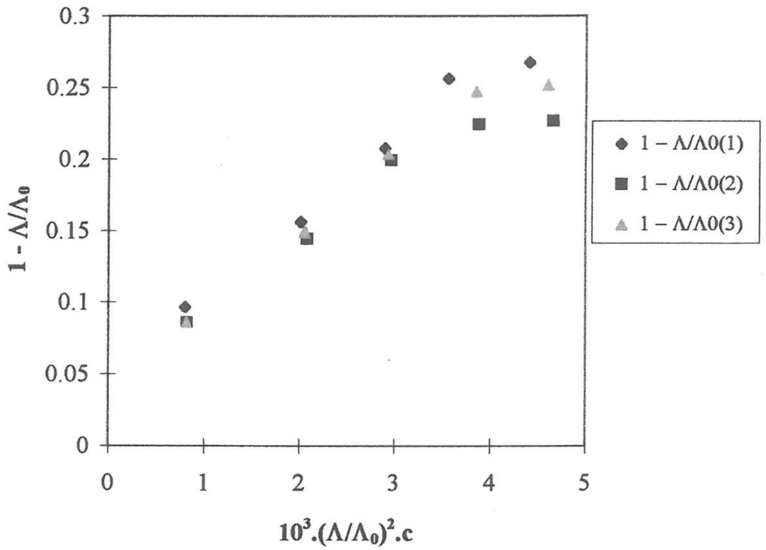

Figure 2: Variation of $1 - \Lambda/\Lambda_0$ vs $10^3(\Lambda/\Lambda_0)^2$ *c* of Tetra-ethylamonium Bromide in PC at 298.15 K and at 1 atm, 100 bar and 200 bar

1 = 1 atm, 2 = 100bar, 3 = 200bar

Table IV: Association Constants (K_A/ $mol^{-1}dm^3$) as function of Pressure

Systems / P/ bar	Et_4NBr + PC	Et_4NBr + GBL	$LiClO_4$ + PC	$LiClO_4$ + GBL
1	50.5882±0.48	84.1366±1.18	45.2501±0.51	43.9250±0.61
100	42.8748±0.37	80.6984±1.12	48.7188±0.44	40.9680±0.50
200	44.1579±0.40	83.1672±1.08	48.4864±0.73	39.8337±0.42
300	42.1270±0.41	79.0887±0.89	46.5976±0.78	39.6424±0.46
400	41.6065±0.85	79.0387±1.18	43.9498±0.78	39.0137±0.51
500	41.1437±0.32	75.1558±0.83	42.8828±0.72	37.9362±0.37
1000	36.5568±0.65	69.6472±0.92	43.3887±0.73	32.9242±0.39
1500	36.5653±0.50	72.4483±0.74	37.3098±0.60	37.3768±0.65
2000	38.1546±0.31	75.3718±1.07	44.2069±0.93	40.2602±0.25

The table IV shows the associaton constants as a function of pressure and the main deviations of them are observed for lower pressures.

The volumes of activation were calculated through the thermodynamic relationship

$$(\Delta V^{\neq})_T = -RT(\ \partial \ln \Lambda / \partial P\ )_T$$

using a similar equation due to Golinkin and Hyne [11],

$$\ln \Lambda\ = a + bP + cP^2$$

results

$$\Delta V^{\neq} = -RT\,(\ b\ +\ 2cP),$$

which the whole list of it is presented in table V

Table V: Volumes of activation ($cm^3.mol^{-1}$) as function of pressure

	Concentrations of $LiClO_4$ + PC / ($mol.dm^{-3}$)				
P/bar	0.00104	0.00284	0.00456	0.00639	0.00821
1	12.7663	12.4941	11.2060	12.1471	12.1470
100	12.7570	12.5312	11.3331	12.2449	12.1853
200	12.7475	12.5688	11.4615	12.2449	12.2240
300	12.7381	12.6038	11.5899	12.2941	12.2627
400	12.7287	12.6438	11.7183	12.3432	12.3013
500	12.7193	12.6814	11.8467	12.3923	12.3400
1000	12.6723	12.9437	12.4887	12.6380	12.5334
1500	12.6251	13.0567	13.1308	12.8836	12.7267
2000	12.5780	13.2443	13.7728	13.1293	12.9201

	Concentrations of $LiClO_4$ + GBL / (mol.dm^{-3})				
	0.00101	0.00282	0.00458	0.00642	0.00819
1	10.1381	9.07297	9.07302	8.77587	8.97403
100	10.0728	9.08912	9.09423	8.82888	9.01197
200	10.0069	9.10543	9.11564	8.88243	9.05030
300	9.94092	9.12174	9.13706	8.93597	9.08862
400	9.87498	9.13805	9.15848	8.98952	9.12695
500	9.80904	9.15436	9.17990	9.04306	9.16527
1000	9.44793	9.27281	9.28699	9.31078	9.35689
1500	9.14965	9.31748	9.39407	9.57850	9.54851
2000	8.81996	9.39903	9.50116	9.84623	9.74013
	Concentrations of Et_4NBr + PC / (mol.dm^{-3})				
	0.00098	0.00283	0.00461	0.00643	0.00821
1	12.5190	12.7664	12.8407	11.5280	11.4030
100	12.5644	12.7717	12.8400	11.6325	11.4042
200	12.6103	12.7770	12.8393	11.7381	11.4055
300	12.6562	12.7823	12.8386	11.8437	11.4067
400	12.7021	12.7876	12.8379	11.9485	11.4080
500	12.7480	12.7929	12.8335	12.0549	11.4093
1000	12.9776	12.7664	12.8299	12.5829	11.4155
1500	13.2071	12.8460	12.8263	13.1109	11.4218
2000	13.4367	12.8725	12.6067	13.6390	11.4281
	Concentrations of Et_4NBr + GBL / (mol.dm^{-3})				
	0.00102	0.00281	0.00459	0.00641	0.00822
1	11.4264	9.61821	9.49443	10.6089	9.89062
100	11.2880	9.62221	9.51519	10.5274	9.86794
200	11.1482	9.62626	9.53617	10.4451	9.84504
300	11.0083	9.63030	9.55714	10.3628	9.82213
400	10.8685	9.63435	9.57811	10.2805	9.79923
500	10.7287	9.63840	9.59908	10.1982	9.77632
1000	10.0300	9.61817	9.70394	9.78673	9.66180
1500	9.33061	9.67885	9.80880	9.37523	9.54727
2000	8.63156	9.69908	9.91365	8.96373	9.43274

The values of the volumes of activations are always positive, generally decreasing as pressure increases for lower concentrations.To higher concentrations it goes the other way around.

CONCLUSIONS

The main conclusions are as follows:

1-The decreasing of conductivity as function of concentration.

2-The results were well adjusted to the **VIANA** and **CALADO's** three parameter empirical equations [8] being the comparable results very similar to the ones previously reported by Makoto Ue [12], as well as those obtained by us [7,9] when Fuoss and Hsia equation [10] was used.

3-The positive values of volumes of activation and the high association constants show that the salts should be very little solvated in the two solvents, which connected with relatively high permitivity and the very small volatility recommend such materials as very good electrolytic solvents.

4-The two salts show excellent electrochemical behaviour in both solvents, not only at 1 atm. but also at all the pressures to 2000 bar.

5-The gradient of the curves in Fig.2 are always the same for all the pressures through the linear part of the three curves. It means that at lower concentrations K_A is constant for all the pressures. In these regions $\gamma_{\pm}$ is very approximately constant, near one. Analogous behaviour was observed for all the systems and for all the pressures.

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PITTING CORROSION OF ALUMINIUM IN HALIDE SOLUTIONS CONTAINING SOME ANIONIC SURFACTANTS

S.A.Abd El-Maksoud[1], A.A.El-Shafei[2] and A.S.Fouda[2]

1 Chemistry Department, Faculty of Education, El-Arish, Sinai, Egypt

2 Chemistry Department, Faculty of Science, El-Mansoura University, Egypt.

ABSTRACT

The pitting corrosion of Aluminium was studied in 0.1 M halide solutions in various concentrations of decyl and dodecyl sodium sulphate. The results obtained from the potentiodynamic measurement show that the pitting corrosion is inhibited by the presence of organic compounds in this medium. The percentage inhibition was found to increase with increasing the concentration of the organic compounds in the medium at constant halide concentration.

For solutions of constant halide concentration, the pitting potential varies with the logarithm of the inhibitor concentration according to a linear relationship. These results are interpreted in terms of competitive adsorption between halide ions and organic anions at the passive metal-solution interface. It was found that the efficiency of inhibition for a given halide concentration decreases in the order of dodecyl sodium sulphate > decyl sodium sulphate. At constant inhibitor concentration, the pitting corrosion was found to decrease in the order: $Cl^- > Br^- > I^-$.

Key words: Pitting corrosion, Aluminium, Potentiodynamic, Passivation, Surfactants.

INTRODUCTION

Pitting corrosion is an extremely localized attack, which result in deep, localized cavities in the metal. Two basic conditions must be fulfilled for the initiation and propagation of pitting corrosion. First, the metal surface should be covered with a passive film. Second, the medium should contain an aggressive species. Pitting potential can be readily evaluated in the laboratory with such techniques as potentiostatic, potentiodynamic anodic polarization and cyclic voltammetry[1,2]. The pitting potential depends on the concentration of aggressive ions, pH of the solution, temperature, metal composition and heat treatment [3-7].

Many authors [2,8-13] have studied the effect of aggressive anions on pit initiation. The linear relationship between the pitting potential and the logarithmic of aggressive ion concentration is expressed according to the equation [14]:

$$E_p = a_1 - b_1 \log [Cl^-] \qquad (1)$$

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