

LOW TEMPERATURE EFFECTS ON CONDUCTIVITIES OF LITHIUM AND  
QUATERNARY AMMONIUM SALTS IN PROPYLENE CARBONATE AND  $\gamma$ -  
BUTYROLACTONE

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Abstract

Propylene carbonate (PC) and  $\gamma$ -butyrolactone (GBL) are important dipolar aprotic solvents good to prepare electrolyte solutions of lithium perchlorate applicable to rechargeable high energy batteries, as we have shown before [1 - 5].

In this work solution conductances of  $\text{LiClO}_4$  and  $(\text{C}_2\text{H}_5)_4\text{NBr}$  in those solvents were measured at temperatures ranging from  $-30\text{ }^\circ\text{C}$  to  $+25\text{ }^\circ\text{C}$ . Limiting molar conductivities and association constants were evaluated through Viana and Calado [6] and Fuoss and Hsia's equations [7]. Some thermodynamic functions resulting from  $(K_A, T)$  variations are obtained and the results are discussed on this basis.

The accuracy and precision of the results is high and they are where possible comparable to others previously published [8, 9].

## Introduction

Lithium perchlorate and other lithium salts have been used to obtain an optimisation of electrolyte solutions in aprotic solvents for primary and rechargeable lithium batteries [1–5, 10] stable over a wide temperature range. This is based on large anions with delocalised charges, which minimize the ion-ion interactions, and hence good stability and electric conductivity [11 – 13] can be expected. Propylene carbonate (PC) and  $\gamma$ -butyrolactone (GBL) are good aprotic solvents to prepare that type of solutions because they are stable [10] as a result of their medium to high permittivities and low viscosities [1]. In such solutions a chemical model should take into account all types of interactions ion-ion, ion-solvent, etc to evaluate the mean activity coefficients of free ions  $\gamma_{\pm}$  (FI) and that of ion pairs (IP) which are included in the equation for ionic association constant  $K_A$  [14]. For 1:1 salts such expression is as follows:

$$C^+ + A^- \leftrightarrow IP, \quad K_A = \frac{1 - \alpha}{\alpha^2 c} \cdot \frac{\gamma(IP)}{\gamma_{\pm}^2(FI)} \quad (1).$$

Based on this model we have recently calculated the ionic association constants of lithium perchlorate and tetraethylammonium bromide in both solvents at 25 °C and under pressures from 1 atm to 2000 bar [1]. Such association is often stronger than solvation in energetic terms according to Evans and col. [12] for some specific reasons. Related to these problems a recent theory based on Bjerrum's electrostatic model was developed by Côté and col. [13, 15, 16] dealing with ion-ion and ion-solvent interactions to justify strong and stable associations for dilute solutions in aprotic solvents. Strong ionic associations in similar

systems were reported by Reichstädter and col. [17] for lithium and sodium perchlorates in 2-butanone being the results deeply discussed in several thermodynamic terms.

This paper is concerned with the determination of limiting molar conductivities and association constants of lithium perchlorate and tetraethylammonium bromide in the two referred solvents varying the temperature from –30 °C to +10 °C at one atmosphere. The two ions resulting from the last salt have not very different diameters and so this compound was only used for comparative reasons. These studies are completed with the determination of the thermodynamic functions resulting from ( $K_A$ ,  $T$ ) variations.

## Experimental

**1-Reagents:** Lithium perchlorate (Riedel-de Haën) puriss >99%, tetraethylammonium bromide (Fluka) puriss >99%, propylene carbonate and  $\gamma$ -butyrolactone (Aldrich) with 99.7% and 99.5% of purity respectively without further purification. However, they were kept in a dry box with silica-gel and  $PO_5$ , accrossed by a slow flux of dry nitrogen, oxygen free. The relevant physical properties of the solvents were, within the experimental errors, in good agreement with those reported in the literature [3,18] (table 1).

**Table 1.** Physical properties of the solvents at 25 °C

Solvent	$\rho/g\text{ cm}^{-3}$	$\eta/\text{cP}$	$\epsilon$	$\chi/S\text{ cm}^{-1}$
PC	1.189	2.513 <sup>(a, b)</sup>	64.92 <sup>(a, b)</sup>	$0.9 \times 10^{-7}$ <sup>(a)</sup>
GBL	1.120	1.727 <sup>(a, c)</sup>	41.77 <sup>(a, c)</sup>	$2.5 \times 10^{-7}$ <sup>(a)</sup>

<sup>a</sup>Ref. 9, <sup>b</sup>Ref. 19, <sup>c</sup>Ref. 20

**2-Solutions preparation:** Each salt was dissolved in propylene carbonate or in  $\gamma$ -butyrolactone to make 50 mL of each solution and they were kept within the dry box. The stock solution with a concentration of about  $0.1 \text{ mol dm}^{-3}$  were obtained by dilution from the mother solutions. Different concentrations prepared from the stock solutions, were obtained by weight.

**3-Conductivity measurements:** The conductivity measurements were carried out with a conductance bridge Wayne Kerr B905 working at a frequency of 1 kHz. The results expressed by six figures were obtained through Ingold cells type 980-K19, carrying platinum electrodes. Cell constants varied from  $0.97 \text{ cm}^{-1}$  to  $1.01 \text{ cm}^{-1}$ . A criostat Julabo FP.W 90 was used to obtain the conductivities at the lower temperatures. A precision of  $0.01 \text{ }^\circ\text{C}$  was always reached even for lower temperatures. Densities were determined with a Anton Paar, model DMA 60 densimeter, being them obtained with six figures.

### Results and discussion

As it was referred before, the advantages of choosing two aprotic solvents to prepare electrolyte solutions good for high energy batteries, are the medium to high permittivities and low viscosities which favours good stability [21, 22] within large temperature and pressure ranges, particularly at low temperatures as it is the case of this paper.

The conductivity determinations of lithium perchlorate and tetraethylammonium bromide, in both PC and GBL were performed within the temperature range from 243.15 K to 283.15 K at 1 atm, at concentrations ranging  $5 \times 10^{-4}$  to  $10^{-2} \text{ mol dm}^{-3}$ . The limiting molar conductivities were obtained through Kohlrausch-Onsager equation (2) presented by

Robinson and Stokes [2] and compared with the modified relationship (3), resulting from the Debye-Hückel theory [23].

$$\Lambda = \Lambda_0 - S\sqrt{ac} \quad (2)$$

$$\Lambda = \Lambda_0 - S \frac{\sqrt{ac}}{1 + \sqrt{ac}} \quad (3)$$

The obtained limiting molar conductivities for each solution are shown in table 2, and they always increase with temperature.

The thermodynamic association constants were evaluated as a function of the degree of dissociation according to the relationship (4), as well as through the Fuoss and Hsia's equation [7].

$$\Lambda = \Lambda_0 - \frac{K_A}{\Lambda_0} \Lambda^2 c f_{\pm}^2 \quad (4),$$

where  $K_A$  is the association constant,  $c$  molar concentration,  $\alpha$  is the dissociation degree and  $f_{\pm}$  the activity coefficient obtained through the relationship (5)

$$\log f_{\pm} = -A|Z_+Z_-|\sqrt{\mu} \quad (5).$$

Being the  $A$  is the Debye-Hückel coefficient,  $Z_+$  and  $Z_-$ , the ionic charges and  $\mu$  the ionic strength. So the association constants were calculated through curve gradient of

$\Lambda$  versus  $\Lambda^2 c_{\pm}^2$ . The data presented in table 3 show that  $K_A$  always increases with temperature, which is consequence of an endoenergetic behaviour.

**Table 2.** Limiting molar conductivities ( $\Lambda_0 / S \text{ cm}^2 \text{ mol}^{-1}$ ) as function of temperature of lithium perchlorate and tetraethylammonium bromide in GBL and PC ( $P = 1 \text{ atm}$ )

Systems T/K	LiClO <sub>4</sub> + GBL	Et <sub>4</sub> NBr + GBL	LiClO <sub>4</sub> + PC	Et <sub>4</sub> NBr + PC
243.15	10.09 ± 0.09	15.30 ± 0.25	4.14 ± 0.03	6.69 ± 0.07
253.15	13.11 ± 0.09	20.06 ± 0.37	6.23 ± 0.04	10.15 ± 0.13
263.15	16.44 ± 0.10	25.42 ± 0.47	8.72 ± 0.07	14.30 ± 0.21
268.15	18.24 ± 0.13	28.32 ± 0.52	10.13 ± 0.08	16.64 ± 0.27
273.15	20.09 ± 0.15	31.35 ± 0.58	11.64 ± 0.10	19.11 ± 0.33
278.15	21.78 ± 0.11	34.43 ± 0.65	13.20 ± 0.12	21.72 ± 0.39
283.15	24.13 ± 0.20	37.64 ± 0.73	14.83 ± 0.13	24.46 ± 0.46

**Table 3.** Association constants ( $K_A / \text{mol}^{-1} \text{ dm}^3$ ) as function of temperature of lithium perchlorate and tetraethylammonium bromide in GBL and PC ( $P = 1 \text{ atm}$ )

Systems T/K	LiClO <sub>4</sub> + GBL	Et <sub>4</sub> NBr + GBL	LiClO <sub>4</sub> + PC	Et <sub>4</sub> NBr + PC
243.15	16.6212	16.5783	15.5534	12.7025
253.15	17.6826	17.2904	15.1219	13.9218
263.15	19.1325	18.6094	15.2403	15.6108
268.15	19.3296	19.3032	15.6912	16.4553
273.15	19.8627	20.1501	16.3459	17.2940
278.15	19.0069	20.4900	16.5973	18.1357
283.15	21.1126	21.6838	16.9252	19.0405

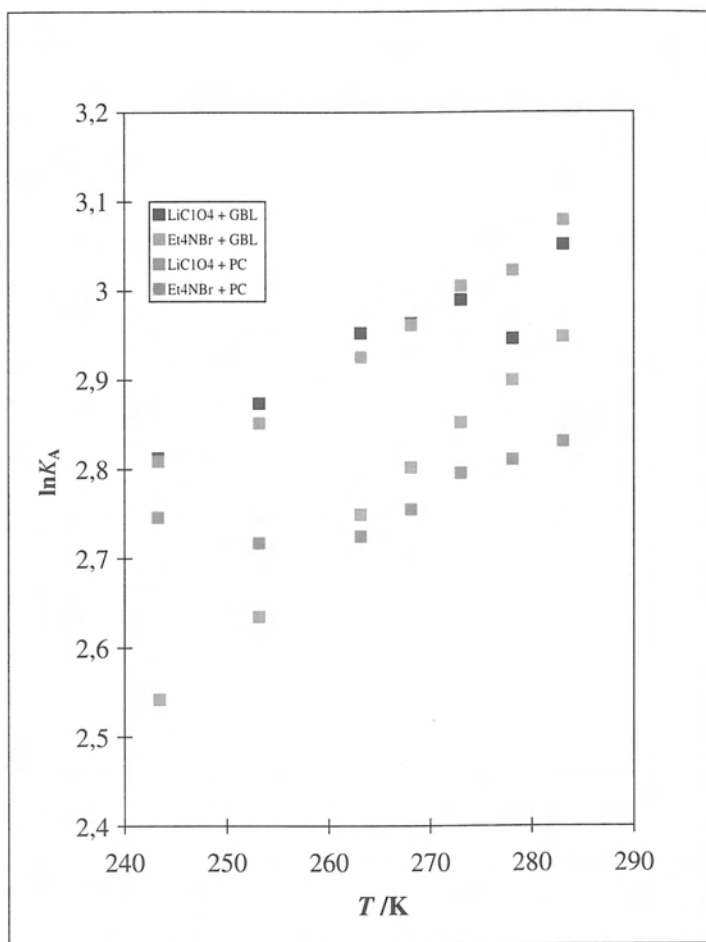


Figure.1: Variation of  $\ln K_A$  as function of temperature of lithium perchlorate and tetraethylammonium bromide in GBL and PC at 1 atm

The evaluation of thermodynamic function resulting from ion pair (IP) equilibria was based on the well-known relation

$$\Delta G^0 = -RT \ln K_A = \Delta H^0 - T\Delta S^0 \quad (6)$$

According to the results the standard association free energy variations  $\Delta G^0$  fit a quadratic dependence on the temperature,

$$\Delta G^0 = a_0 + a_1T + a_2T^2 \quad (7)$$

from which standard enthalpies and entropies have been obtained from the following relations

$$\Delta S^0 = -a_1 - 2a_2T \quad (8)$$

$$\Delta H^0 = a_0 - a_2T^2 \quad (9)$$

where  $a_0$ ,  $a_1$  and  $a_2$  are represented in table (4)

Table 4. Coefficients  $a_i$  of the fitted temperature dependences of Gibbs energy

Systems	$a_0$	$a_1$	$a_2$
LiClO <sub>4</sub> + GBL	6524.44	-62.8592	0.05198
Et <sub>4</sub> NBr + GBL	-6314.52	38.5313	-0.14756
LiClO <sub>4</sub> + PC	-19936.2	134.705	-0.31044
Et <sub>4</sub> NBr + PC	1141.83	-9.05434	-0.06885

### Conclusions

Poor solvated or unsolvated anions are present in all solutions on account of their small charge density. Lithium cation should be extensively solvated while the contrary should happen to tetraethylammonium ion due to its large volume and low charge over it.

As it can be seen in figure 1, the ( $K_A$ ,  $T$ ) variations are linear for both GBL solution while non-linear for PC solution certainly due to some specific interactions in the latter cases. A similar situation was observed by Côté and co-workers [11].

A deeper analysis can be obtained through the values of other thermodynamic functions. These results are shown in figures (2 - 4) and generally positive enthalpy variations and also positive  $\Delta S^0$  from which negative  $\Delta G^0$  are resulting.

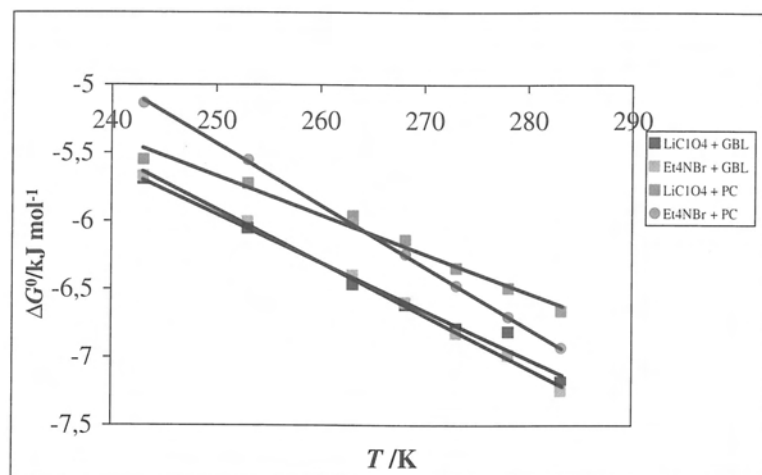


Figure 2: Variation of Gibbs energy as function of temperature of  $\text{LiClO}_4$  and  $\text{Et}_4\text{NBr}$  in GBL and PC at 1 atm

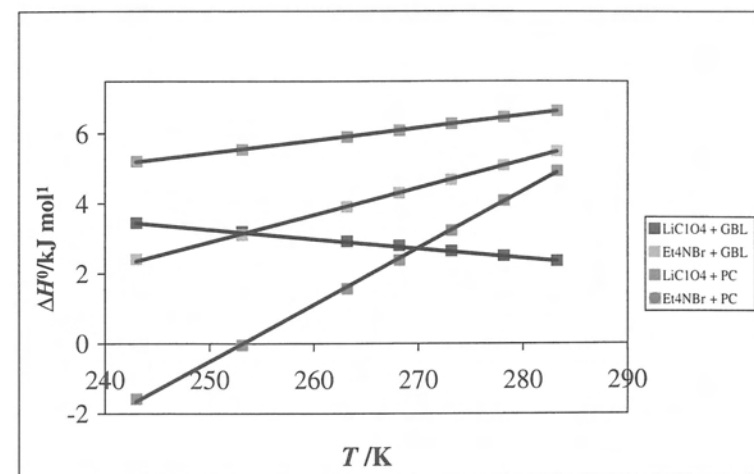


Figure 3: Variation of enthalpies as function of temperature of  $\text{LiClO}_4$  and  $\text{Et}_4\text{NBr}$  in GBL and PC at 1 atm

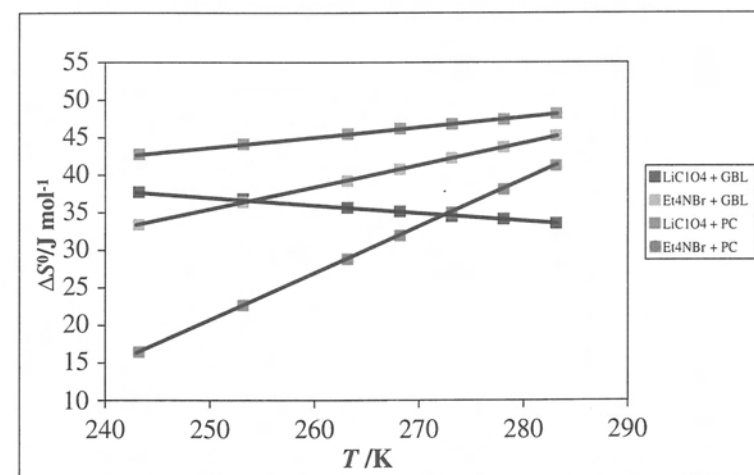
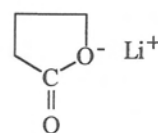


Figure 4: Variation of association entropies as function of temperature of  $\text{LiClO}_4$  and  $\text{Et}_4\text{NBr}$  in GBL and PC at 1 atm

$\Delta S^0$  is generally higher for tetraethylammonium bromide than for lithium perchlorate which is resulting from smaller ionic association as a consequence of both anion and cation having small charge density. Such situation corresponds to more ion freedom as it was demonstrated by Gilkerson and co-workers [24, 25] using U.V. and visible spectroscopies as well as N.M.R. methods.

In relation to lithium perchlorate the delocalised charge over a large anion certainly corresponds to small solvation on it. However lithium ion is small so creating a high electric field. Both large solvation and ion association could be expected. According to the entropy variations it slightly decreases as temperature increases when GBL is used as a solvent. Such result is certainly a consequence of some increasing of organizations mainly due to solvation of the solvent molecules group over the lithium ion.



On the other hand when PC is used as a solvent a large increase of  $\Delta S^0$  with temperature is observed which corresponds to small ion association and a better quality as electrolyte solution than the one in GBL. As a complementary to it, a  $\Delta H^0$  variation from negative to positive is observed as temperature increases.

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#### References

1. Viana, C.A.N. and Dilo, M., *This journal*, **18**, 23 (2000), Dilo, M., *Master Thesis*, Lisboa (1997)
2. Robinson, R. A. and Stokes, R. H., "Electrolyte Solution", 2nd ed. revised, Butterworths, London, (1970).
3. Covington, A.K. and Dickinson, T. "Physical Chemistry of Organic Solvent Systems", Editors, Plenum Press, London, (1973).
4. Popvyeh, O. and Tomkin, R.P.T. "Nonaqueous Solution Chemistry" John Wiley & Sons, Inc., New York, (1981)
5. Barthel, J., Gores, H. J. and Wachter, R., *Topics in Current Chemistry*, **111**, 33 (1983).
6. Viana, C.A.N. and Calado, A. R. T., *Portugaliae Electrochimica Acta*, **6**, 149 (1988).
7. Fuoss, R.M. and Hsia, K.L., *Proc. Nat. Acad. Sci.*, **57**, 1550 (1967).
8. Salomon, M. and Plichta, E. J., *Electrochem. Acta*, **6**, 731 (1984)
9. Ue, M., *J. Electrochem. Soc.*, **12**, 141 (1994).
10. D'Aprano, A., Sesta, B., Mauro, V. and Salomon, M., *J. Chem. Solution*, **29**, 1075 (2000).
11. Côté, J.-F., Perron, G. and Desnoyers, J.E.; *J. Solution Chem.*, **27**, 707 (1998).
12. Evans, D.F., Thomas, J., Nadas, J. A. and Matesich, M.A., *J. Phys Chem.*, **75**, 1714 (1971).
13. Côté, J.-F.; Desnoyers, J.E. and Justice, J.-C., *J. Solution Chem.*, **25**, 113 (1996).

14. Barthel, J., Gores, H. -J., Neueder, R. and Schmid, A., *Pure Appl. Chem.*, **71**, 1715 (1999).
15. Côté, J. -F., Perron, G., Desnoyers, J.E., Benson, G. C. and Lu, B. C. -Y, *J. Solution Chem.*, **27**, 685 (1998).
16. Côté, J. -F., Perron, G. and Desnoyers, J.E., *J. Solution Chem.*, **28**, 395 (1999).
17. Reichstädter, L., Fischchervá, E. and Frischer, O., *J. Chem. Solution*, **1**, 35 (1999).
18. Handbook of Chemistry and Physics, 82<sup>nd</sup> ed., C. R. C. press, London, (2001)
19. Jansen, M. and Yeager, H. L., *J. Phys. Chem.*, **77**, 3089 (1973)
20. Salomon, M. and Plichta, E. J., *Electrochem. Acta*, **30**, 113 (1985)
21. Kita, F.A., Snoda, T. and Kobayashi, H. "In new sealed Rechargeable batterie and supercapacitors", B. M. Barnett, E. Dowgiallo, G. Halper, Y. Matsuda, and Z-i Takehara, Editors, PV93-23, P.321, The Electrochemical Society Proceeding series, Pennington, NJ (1993)
22. Hasegawa, K. and Arakawa, Y., *J. Power Sources*, **44**, 523 (1993).
23. Debye, P. and Hückel, E., *Phys. Z.* **24**, 185 (1923).
24. Jackson, M. D. and Gilkerson, W. R., *J. Am. Chem. Soc.*, **101**, 328 (1979).
25. Gilkerson, W. R. and Kendrick, K. L., *J. Phys. Chem.*, **88**, 5352 (1984)

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## THE SENSITIZATION OF SELF-ASSEMBLED MONOLAYER FORMED BY OCTADECANETHIOL FOR THE PHOTO-ELECTRIC OXIDATION OF CH<sub>3</sub>OH ON THE TiO<sub>2</sub> NANOPOROUS FILM ELECTRODE

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### Abstract

Octadecanethiol self-assembled monolayer (OCSAM), which was first employed as one sensitizer for TiO<sub>2</sub> nanoporous film electrode in the oxidation of methanol, was firstly investigated using electrochemical and photoelectrochemical methods. The photocurrent generated by using TiO<sub>2</sub> nanoporous film electrode modified by OCSAM (18SH/TiO<sub>2</sub>) is about 1.95 times larger than that without modification. In addition, the maximum absorption peak has shifted towards the infrared region for about 30nm when the TiO<sub>2</sub> nanoporous film electrode modified with OCSAM. This paper has testified that the increased photocurrent could not be attributed to the photooxidization of octadecanethiol or the ethanol solvent simply. It was proposed that the change of surface structure of TiO<sub>2</sub> nanoporous film electrode should be responsible for the phenomenon in some degree.

**Keywords:** Octadecanethiol; Self-assembled monolayer; Sensitization; TiO<sub>2</sub> nanoporous film electrode; Photoelectrooxidation

### Introduction

So far there are many papers dealing with TiO<sub>2</sub> electrode or TiO<sub>2</sub> nanoporous film electrode with an intention to improve the light-to-electricity conversion efficiency. The dye-sensitized photoelectrochemical cells have been widely investigated because of their characteristics of differentiating light absorption and charge separation. Many organic substance was tried to improve the conversion efficiency [1-4]. Some noble metals, such as platinum and ruthenium, were also employed to sensitize the TiO<sub>2</sub> electrode [5,6]. Summarily, dye, nanoporous film, and noble metal are the three main sensitizers for TiO<sub>2</sub> electrode. Nanoporous sulfide was also used to sensitize the TiO<sub>2</sub> nanoporous films electrode and TiO<sub>2</sub> self-assembled monolayer electrode [7, 8], where the light absorption of TiO<sub>2</sub> photoanodes could be extended into the visible region. In a word, the investigation of improving the conversion efficiency of light to electricity for TiO<sub>2</sub> has never been terminated.