Temperature Effects on Conductivities and Association Constants of Lithium and Tetra-Ethylammonium Salts in Six Aprotic Solvents of Medium to High Permittivities from – 30 ºC to + 10 ºC

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Abstract

A few non-aqueous dipolar aprotic solvents of medium to high permittivities, low viscosities and large temperature intervals between freezing and boiling points have been used to prepare electrolyte solutions applicable to primary and rechargeable high energy batteries. Lithium perchlorate is a salt often chosen to obtain those systems.

In this work low temperature effects on conductivities and association constants of $LiClO_4$ and Et_4NBr in six different solvents have been analyzed, using the tetraethylammonium bromide salt for comparative reasons. The temperature interval was -30 ºC to 10 ºC. A few thermodynamic functions resulting from K_A, T variations were determined being the results discussed on this basis.

The accuracy and precision of results are high; whenever possible they are compared with others previously published.

Keywords: low temperature effects, limiting molar conductivity, association constants, electrolyte solutions, ionic associations.

Introduction

Lithium perchlorate and other lithium salts have been used to obtain an optimization of electrolyte solutions in organic aprotic solvents for primary and rechargeable lithium batteries [1-6] stable over a wide temperature range. Large

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anions with delocalized charges are generally chosen to minimize ion-ion interactions, and hence good stability and high electric conductivity [7-9] can be expected. In this work, the elected solvents were propylene carbonate (PC), γ-butyrolactone (GBL), acetonitrile (AN), dimethyl-formamide (DMF), dimethylacetamide (DMA) and *N*-methylpirolidinone (NMP), all being good to prepare stable electrolyte solutions [2,5] as a result of their medium to high permittivities, low viscosities, particularly at low temperatures [3,4] as is the case of this work.

The adopted chemical model for association constants should take into account all types of interactions, namely ion-ion and ion-solvent on which the evaluation of the mean activity coefficients of free ions $\gamma_\pm$ (FI) and those of ion pairs (IP) should be included in the equation of ionic association constant (K_A) [2]. For 1:1 salts the following equation is generally applicable

$$K_A = \frac{1-\alpha}{\alpha^2 c} \cdot \frac{\gamma(IP)}{\gamma_\pm^2(FI)} \tag{1}$$

where α is the dissociation (or ionization) degree.

Based on this equation, we have recently determined the ionic association constants of two salts in either propylene carbonate (PC) or γ-butyrolactone (GBL) at 25 ºC and pressures ranging from 1 atm to 2 000 bar [3].

Evans and co-workers have shown that ionic association is often stronger than solvation when expressed in energetic terms though ion-ion interactions are in some cases lower than those observed with isodielectric protic liquids for some specific structural reasons [8,9]. A recent theory based on Bjerrum´s electrostatic model was developed by Côté and co-workers [10, 11] dealing with ion-ion and ion-solvent interactions and through it strong and stable associations in dilute solutions in aprotic solvents are interpreted. Strong ionic associations in similar systems are reported by Reichstädter and co-workers [12] for lithium and sodium perchlorates in 2-butanone being the results deeply discussed in thermodynamic terms.

This paper is concerned with the determination of limiting molar conductivities and association constants of lithium perchlorate and tetraethylammonium bromide in the above referred solvents at temperatures ranging from -30 ºC to 10 ºC at one atmosphere. The second salt being a strong electrolyte in all solvents was chosen because it has a much larger cation radius than lithium ion being that one structurally quite different from this one. Both anions are quite large and so having well delocalized negative charges and so ion-ion interactions, though depending on permittivities and structure of the solvents[9], are generally low. Different thermodynamic functions were obtained from K_A, T variations and most of them well illustrate different types of behaviors. U.V. and visible spectroscopies as well as N.M.R. spectra were taken into account in relation to our results, the same way as it is referred by Jackson and Gilkerson [13] and Gilkerson and Kendric [14].

Experimental

Reagents

Lithium perchlorate (Riedel-de Haën) purity > 99%, tetraethylammonium bromide (Fluka) purity > 99%, propylene carbonate, γ-butyrolactone, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, acetonitrile and *N*-methylpyrrolidinone (Aldrich) with 99.7%, 99.5%, > 99.5%, > 99.8%, > 99.0% and > 99.0% of purity respectively. They were used without further purification. However, they were kept in a glove box, under a slow flux of dry nitrogen, oxygen free, after passing through silica gel and P_2O_5. The relevant physical properties of the solvents were, within the experimental errors, in good agreement with those reported in the literature [15, 16] (Table 1).

Solutions preparation

Each salt was dissolved in each solvent to make 50 mL of each solution and they were kept within the dry box. The stock solutions with concentration of about 0.1 mol dm^{-3} were obtained by dilution from the different mother solutions.

Different concentrations obtained by weight were prepared from the stock solutions.

Table 1. Physical properties of the solvents at 25 ºC.

Solvent	Properties			
	ρ / g cm^{-3}	η / cP	ε	χ / S cm^{-1}
PC	1.189	2.513[a,b]	64.92[a,b]	0.9×10^{-7} [a]
GBL	1.120	1.727[a,c]	41.77[a,c]	2.5×10^{-7} [a]
AN	0.786	0.300[d]	36.00[d]	—
DMF	0.945	0.800[d]	37.00[d]	—
DMA	0.937	0.900[d]	38.00[d]	—
NMP	1.026	1.700[d]	32.00[d]	—

[a]Ref. 5; [b]Ref. 17; [c]Ref. 18; [d]Ref. 19.

Conductivity and density 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 platinized platinum electrodes. Cell constants varied from 0.97 cm^{-1} to 1.01 cm^{-1}. A cryostat *Julabo FP.W* 90 was used to obtain the conductivities at the lower temperatures. An uncertainty of 0.01 ºC was always reached even at lower temperatures. Densities were determined with a densimeter *Anton Paar,* model *DMA* 60, always controlled to ± 0.01 ºC, the results being obtained with six figures.

Resultados and discussion

As it was referred before, the advantages of choosing six aprotic solvents to prepare electrolyte solutions good for high energy batteries are the medium to high permittivities and low viscosities which favors good stability [20,21] within

large temperature and pressure ranges, particularly at low temperatures as it is the case of this paper.

Table 2. Limiting molar conductivities as a function of temperature of lithium perchlorate in different solvents (P = 1 atm).

	Systems					
T / K	$LiClO_4$ + GBL	$LiClO_4$ + PC	$LiClO_4$ + DMF	$LiClO_4$ + AN	$LiClO_4$ + DMA	$LiClO_4$ + NMP
243.15	10.09 ± 0.09	4.14 ± 0.03	24.63 ± 1.00	70.84 ± 2.64	—	—
253.15	13.11 ± 0.09	6.23 ± 0.04	30.38 ± 1.22	80.97 ± 3.08	—	11.27 ± 0.13
258.15	—	—	—	—	22.88 ± 0.36	12.87 ± 0.14
263.15	16.44 ± 0.10	8.72 ± 0.07	36.19 ± 1.43	91.04 ± 3.31	25.45 ± 0.41	14.56 ± 0.16
268.15	18.24 ± 0.13	10.13 ± 0.08	39.28 ± 1.51	95.93 ± 3.53	28.79 ± 0.31	16.27 ± 0.19
273.15	20.09 ± 0.15	11.64 ± 0.10	42.41 ± 1.66	101.31 ± 3.60	30.81 ± 0.52	18.19 ± 0.20
278.15	21.78 ± 0.11	13.19 ± 0.12	45.55 ± 1.74	106.47 ± 3.64	33.57 ± 0.55	20.05 ± 0.22
283.15	24.13 ± 0.20	14.83 ± 0.13	48.83 ± 1.95	112.36 ± 3.51	36.36 ± 0.62	21.93 ± 0.26

The conductivity determinations of lithium perchlorate and tetraethylammonium bromide, in these solvents, were performed within the temperature range from 243.15 K to 283.15 K at 1 atm, at concentrations ranging from 5×10^{-4} to 1×10^{-2} mol dm^{-3}. The limiting molar conductivities were obtained using Kohlrausch-Onsager eq. (2) presented by Robinson and Stokes [22] and compared with the modified relationship (3), resulting from the Debye-Hückel theory [23].

$$\Lambda = \Lambda_0 - S\sqrt{\alpha c} \tag{2}$$

$$\Lambda = \Lambda_0 - S\frac{\sqrt{\alpha c}}{1 + \sqrt{\alpha c}} \tag{3}$$

Table 3. Limiting molar conductivities as a function of temperature of tetraethylammonium bromide in different solvents (P = 1 atm).

T / K	Systems			
	Et_4NBr + DMF	Et_4NBr + GBL	Et_4NBr + AN	Et_4NBr + PC
243.15	36.44 ± 1.01	15.29 ± 0.25	126.72 ± 7.04	6.69 ± 0.07
253.15	45.12 ± 1.23	20.06 ± 0.37	143.23 ± 7.31	10.15 ± 0.13
263.15	54.55 ± 1.50	25.42 ± 0.47	159.46 ± 8.05	14.30 ± 0.21
268.15	59.55 ± 1.62	28.32 ± 0.52	167.53 ± 8.61	16.64 ± 0.27
273.15	64.43 ± 1.78	31.35 ± 0.58	175.72 ± 9.33	19.11 ± 0.33
278.15	69.44 ± 1.92	34.43 ± 0.65	183.52 ± 10.2	21.72 ± 0.39
283.15	74.44 ± 2.07	37.64 ± 0.73	191.36 ± 11.2	24.46 ± 0.46

The obtained limiting molar conductivities for each solution are shown in Tables 2 and 3 and they always increase with temperature. At 25 ºC our results published elsewhere [5, 15, 24, 25] are comparable with others already published as it can be seen in Table 4.

The thermodynamic association constants were evaluated as a function of the degree of dissociation according to the relationship (4), as well as Fuoss and Hsia's equation [21]

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

where K_A is the association constant, c the molar concentration and $f_\pm$ the activity coefficient obtained by eq. (5)

$$\log f_\pm = - A|Z_+Z_-|\sqrt{\mu} \tag{5}$$

being A the Debye-Hückel coefficient, Z_+ and Z_-, the ionic charges and μ the ionic strength. So the association constants were calculated from the curve gradient Λ *versus* $\Lambda^2 c f_\pm^2$. The obtained data are presented in Fig. 1 to 3 and they show that K_A always increases with temperature, certainly as a consequence of endoenergetic behavior.

Table 4. Values of limiting molar conductivity of $LiClO_4$ and Et_4NBr salts in different solvents at 25 ºC.

System	Λ_0 / S cm^2 mol^{-1}	
	This study	Literature
$LiClO_4$ + PC	29.4445	26.4010[a]
«		26.7500[b]
$LiClO_4$ + GBL	46.6163	40.3037[a]
$LiClO_4$ + AN	173.196	173.290[b]
$LiClO_4$ + DMF	77.9229	77.400[d]
Et_4NBr + AN	185.581	185.300[c]

[a]data from ref. 5; [b]data from ref. 24; [c]data from ref. 15;
[d]data from ref. 25

Table 5. Coefficients a_i of the fitted temperature dependences of Gibbs energy.

System	Coefficients		
	a_0	a_1	a_2
$LiClO_4$ + GBL	6524.44	−62.8592	0.05198
Et_4NBr + GBL	−6314.52	38.5313	−0.14756
$LiClO_4$ + PC	−19936.2	134.705	−0.31044
Et_4NBr + PC	1141.83	−9.05434	−0.06885
$LiClO_4$ + AN	−20897.1	137.165	−0.35065
Et_4NBr + AN	33807.8	−303.475	−0.49302
$LiClO_4$ + DMF	−2164.30	−9.39931	−0.05466
Et_4NBr + DMF	2334.78	−30.8288	0.03585
$LiClO_4$ + NMP	3460.27	−47.3008	0.02343
$LiClO_4$ + DMA	19061.7	−142.839	0.18358

The evaluation of the thermodynamic functions resulting from ion pair (IP) equilibrium was based on the well-known relationship

$$\Delta G^0 = -RT \ln K_A = \Delta H^0 - T\Delta S^0 \tag{6}$$

According to the results the standard association Gibbs energy variations ΔG^0 fit a quadratic dependence on the temperature,

$$\Delta G^0 = a_0 + a_1 T + a_2 T^2 \tag{7}$$

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

$$\Delta S^0 = -a_1 - 2a_2 T \tag{8}$$

$$\Delta H^0 = a_0 - a_2 T^2 \tag{9}$$

where a_0, a_1 and a_2 were obtained through *least squares method* being them shown in Table 5.
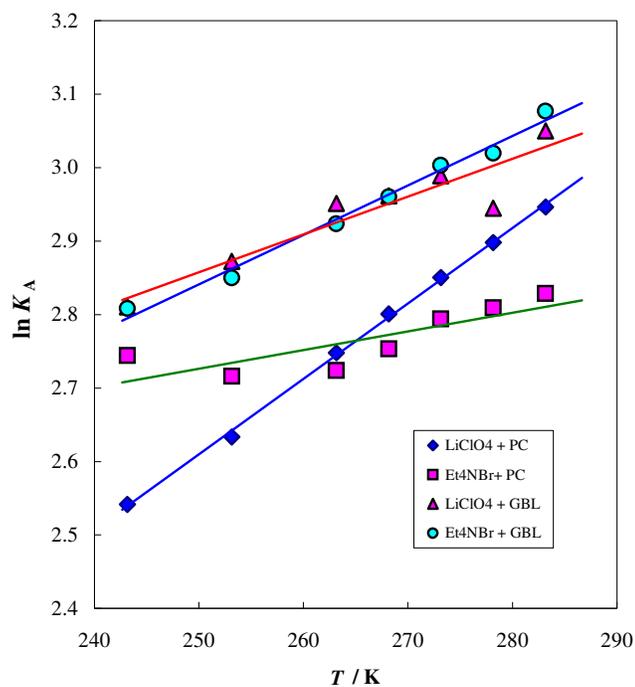
Figure 1. Variation of ln K_A as a function of temperature of LiClO$_4$ and Et$_4$NBr in GBL and PC at 1 atm.

Conclusions

Determinations of limiting conductivities of electrolytes in aprotic solvents at temperatures below 0 ºC are very scarce. However other results we obtained at 25 ºC are comparable to those published by other authors (Table 4).
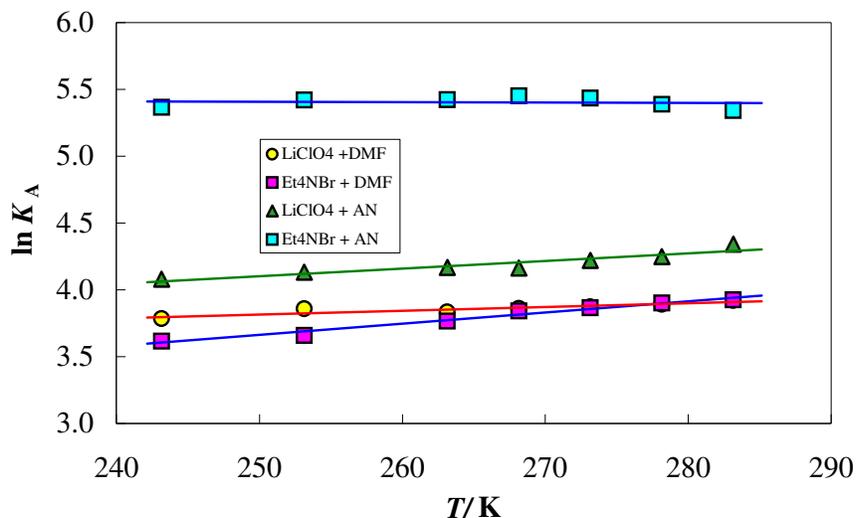
Figure 2. Variation of ln K_A as a function of temperature of $LiClO_4$ and Et_4NBr in DMF and AN at 1 atm.

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 the tetraethylammonium ion due to its large volume and low charge density over it.
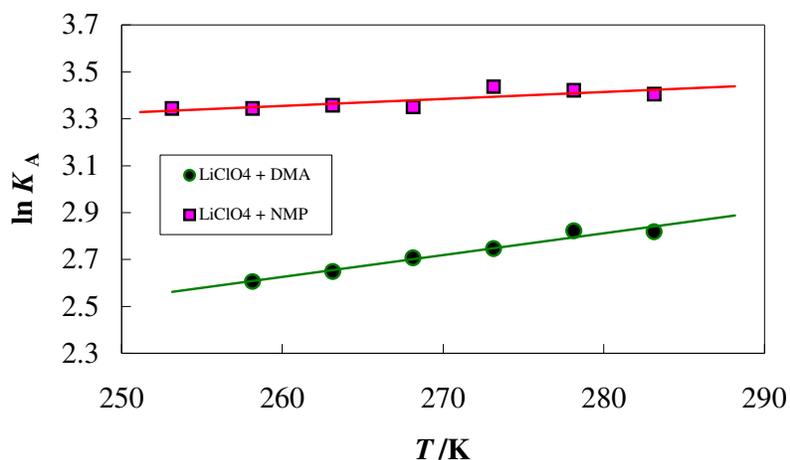
Figure 3. Variation of ln K_A as a function of temperature of LiClO$_4$ in DMA and NMP at 1 atm.
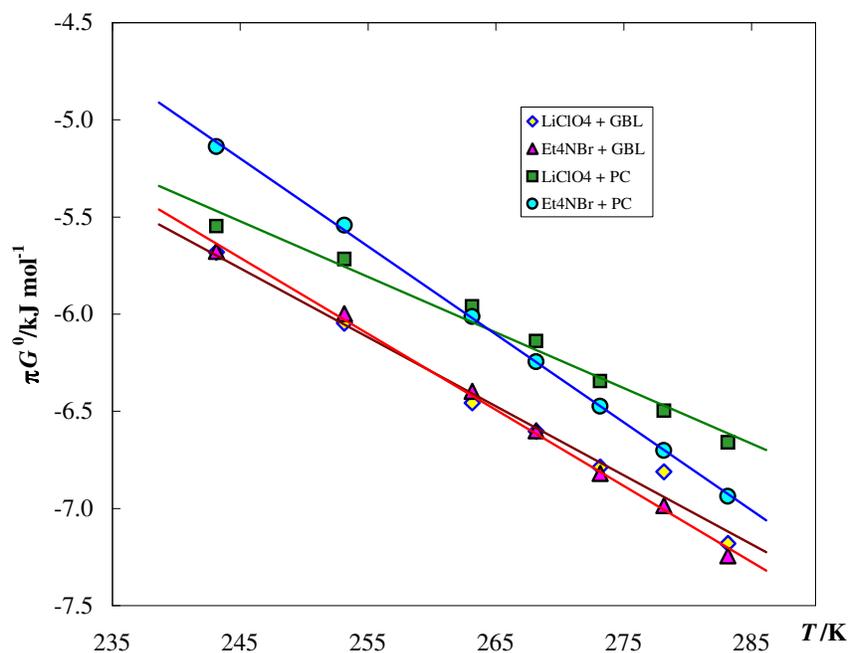
Figure 4. Variation of Gibbs energy as a function of temperature of LiClO$_4$ and Et$_4$NBr in GBL and PC at 1 atm.
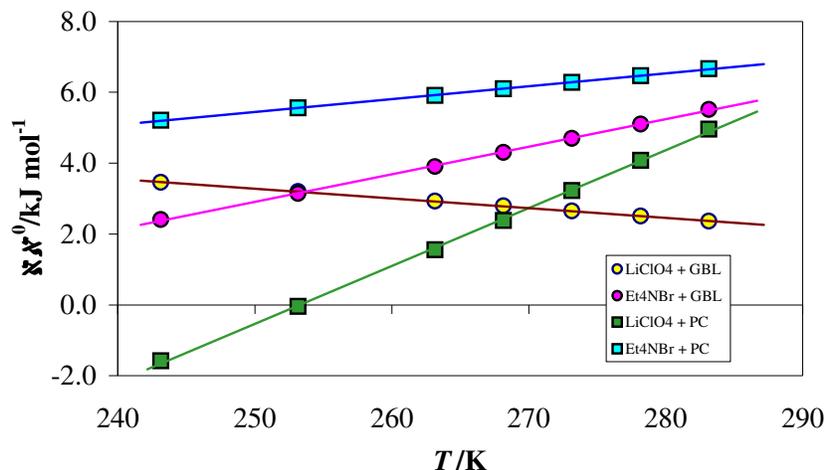
Figure 5. Variation of enthalpies as a function of temperature of $LiClO_4$ and Et_4NBr in GBL and PC at 1 atm.

As it is shown above linear variations of $\ln K_A$ *versus T* for Et_4NBr in GBL, PC and for $LiClO_4$ in GBL solutions while non-linear for $LiClO_4$ in PC, GBL, AN, DMA and NMP solutions and for Et_4NBr in DMF and AN solutions certainly due to some specific interactions in the latter cases are observed in Fig. 1 to 3. A similar situation was observed by Côté and co-workers [7].

A deeper analysis can be obtained through other thermodynamic functions. The correspondent results were determined through equations (6 – 9) and their variations with *T* are shown in Fig. 4 to 6. Positive enthalpy and entropy variations result from there and always negative Gibbs energies are linked to it.

ΔS^0 is generally higher for Et_4NBr than for $LiClO_4$, which results from smaller ionic association for the former salt than for the latter. A large ion freedom should be observed for that one. Such situation was also demonstrated by Gilkerson and co-workers [13, 14] using U.V. and visible spectroscopies as well as NMR methods.
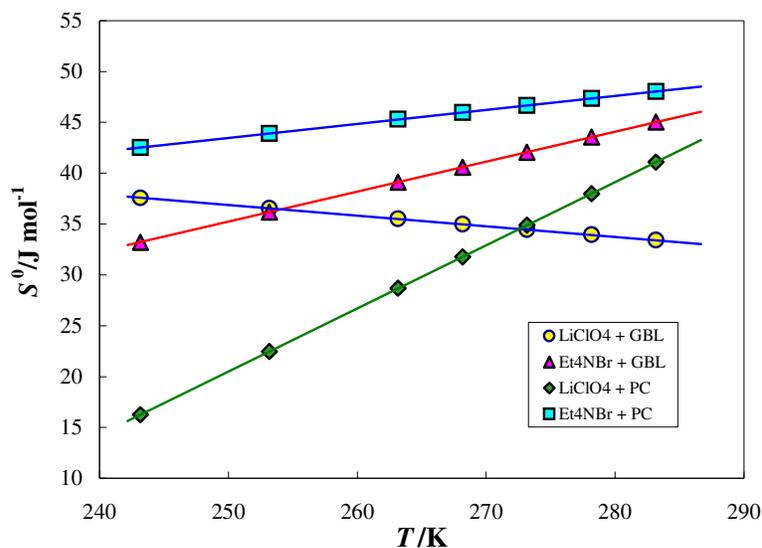
Figure 6. Variation of association entropies as a function of temperature of LiClO$_4$ and Et$_4$NBr in GBL and PC at 1 atm.

The delocalized small charge over a large anion as it is ClO$_4^-$ certainly provokes small solvation on it. However lithium ion is small, therefore creating a high electric field and also a large solvation over it as well as significantly ion association can result. According to the entropy variations it slightly decreases as temperature increases when GBL is used as a solvent: certainly due to some increasing of organization as a result of solvation over the lithium ion.

On the other hand the same salt in PC shows a steep increase of ΔS^0 with temperature certainly due to small ion association and higher ion freedom. As a consequence, it presents a better quality as electrolyte solution than the one in GBL. Complementary ΔH^0 varies from negative to positive as temperature increases. ΔG^0 itself does not give easy interpretation related to the different salts.

Acknowledgments

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