

Lithium–coronand electrolytes. Thermodynamic and electrochemical aspects

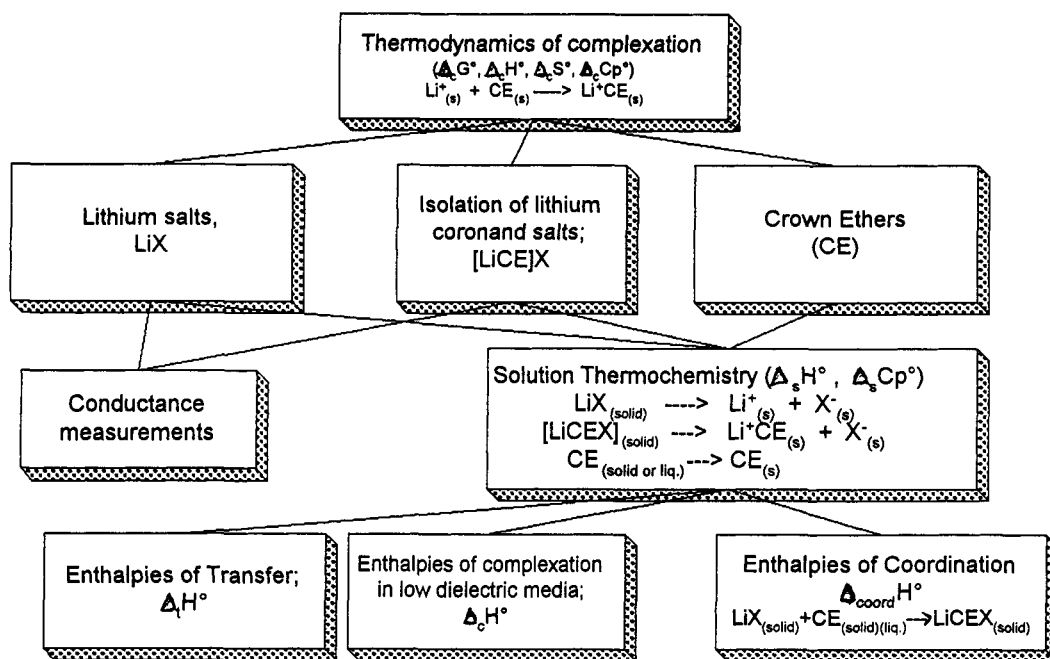
Angela F. Danil de Namor¹, Margot A. Llosa Tanco¹, Joe C.Y. Ng¹ and Mark Salomon²

¹Laboratory of Thermochemistry, Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, UK and ²US Army ARL, Power Sources Division, Fort Monmouth, New Jersey 07703, USA.

Abstract. The research strategy for the selection of lithium coronand electrolytes which may be relevant to battery technology is described. Particular emphasis is placed on the solution thermochemical behaviour of lithium and lithium coronand electrolytes in acetonitrile, propylene carbonate and tetrahydrofuran. Enthalpies of coordination referred to reactants and products in their pure physical state are used in combination with corresponding solution data for the host, the guest and the resulting complex to derive for the first time the enthalpies of complexation of lithium and crown ethers in low permittivity media. The implication of thermodynamic studies on the conductance behaviour of lithium and lithium coronand electrolytes in propylene carbonate is quantitatively demonstrated in the limiting molar conductivities of these electrolytes in this solvent.

INTRODUCTION

Almost twenty eight years ago Charles Pedersen¹ discovered the crown ethers. Since then, the synthetic developments in the area of macrocyclic chemistry have expanded explosively as reflected by the large variety of new ligands available at the present time. A particularly important but rather unexplored aspect of macrocyclic chemistry is that related to the solution properties of electrolytes resulting from the interaction of neutral macrocycles with metal and organic cations. In a recent publication² we have discussed thermodynamic, structural and conductance studies of lithium coronand electrolytes relevant to battery technology, using, 15 crown 5 (15C5) and 1-aza-12 crown 4 (1-A-12C4) as the crown ethers (CE) constituents of these electrolytes and highly polarisable anions such as hexafluoroarsenate; AsF_6^- ; tetrafluoroborate; BF_4^- ; and trifluoromethanesulphonate; CF_3SO_3^- . These studies were carried out in acetonitrile (MeCN) and in propylene carbonate (PC), solvents currently used in battery technology. The strategy adopted for this research summarised in Scheme 1, uses a thermodynamic approach a) to determine the strength of complexation of lithium and crown ethers in the appropriate solvent in order to proceed with the isolation of lithium coronand electrolytes and b) to study the solvation properties of the host, the guest and the resulting complexes in these solvents from interpretation of solution data. These results were used to explain the enhancement in conductivity observed by the addition of crown ethers to lithium salts, an important aspect to consider in battery technology. Scheme 1 is now followed to gain information regarding interactions between various crown ethers (Fig.1) and lithium in acetonitrile and in propylene carbonate. Thus, the implications of these results on the properties of lithium coronand electrolytes are discussed on the basis of representative data on these systems.



Scheme 1. Research Strategy for the Selection of Lithium coronand electrolytes.

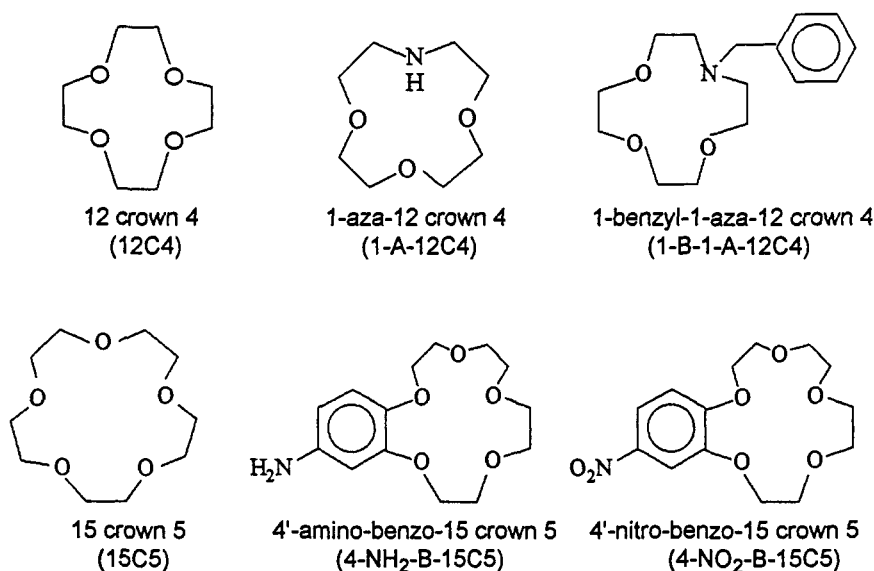


Fig. 1. Structure of Crown Ethers

THERMODYNAMICS OF COMPLEXATION

Table 1 lists stability constants and derived standard Gibbs energies, $\Delta_c G^\circ$, enthalpies, $\Delta_c H^\circ$ and entropies, $\Delta_c S^\circ$, for the complexation of crown ethers and lithium in acetonitrile and in propylene carbonate at 298.15 K.

The data shown in table 1 reflect that the favourable Gibbs energies observed in these processes are enthalpy controlled where in most cases $\Delta_c H^\circ < 0 < T\Delta_c S^\circ$. Interesting enough, replacement of one of the oxygen donor atoms in 12 crown 4 by NH (1-A-12C4) leads to a slight increase in stability. It must be noted that there are large discrepancies between the data reported in the

Table 1. Thermodynamics of complexation of lithium and crown ethers in acetonitrile and in propylene carbonate at 298.15 K

Macrocycle	log K_s	Acetonitrile		
		$\Delta_c G^\circ$ kJ.mol ⁻¹	$\Delta_c H^\circ$ kJ.mol ⁻¹	$\Delta_c S^\circ$ J.K ⁻¹ .mol ⁻¹
12C4	3.91±0.02	-22.32	-21.16	3.9
1-A-12C4	4.23 ^a	-24.15 ^a	-18.69 ^a	18.3
1-B-A-12C4	4.31±0.02	-24.50±0.05	-27.44±0.33	-2.0
15C5	4.40 ^a	-25.12 ^a	-24.15 ^a	3.0
4-NH ₂ -B-15C5	4.02±0.16	-23.02±0.90	-21.29±1.76	5.8
4-NO ₂ -B-15C5	3.66±0.13	-20.89±0.72	-20.89±1.07	0.2

Propylene Carbonate				
Macrocycle	log K_s	$\Delta_c G^\circ$ kJ.mol ⁻¹	$\Delta_c H^\circ$ kJ.mol ⁻¹	$\Delta_c S^\circ$ J.K ⁻¹ .mol ⁻¹
12C4	2.84±0.34	-16.21±1.95	-17.05±0.45	-2.8
1-A-12C4	3.87 ^a	-22.09 ^a	-15.08 ^a	23.5 ^a
1-B-A-12C4	4.59±0.03	-26.20±0.20	-24.70±0.03	5.1
15C5	4.23	-24.15	-23.11	3.5

^aRef.2

literature for 12 crown 4 and lithium in acetonitrile at 298.15 K. Thus log K_s values of 4.25³, 3.40⁴, and 3.14⁵ have been reported. Our value agree reasonably well with the former data³. However, being oxygen more electronegative than N, a greater stability is expected for 12 crown 4 relative to 1-aza-12 crown 4. In fact, this is reflected in the enthalpy. The stability increase observed for 1-aza-12 crown 4 in its complexation with lithium, is the result of a more favourable entropy observed for this ligand and this cation relative to 12 crown 4.

Positive entropies are either observed in processes where extensive cation desolvation takes place upon complexation⁶⁻⁸ or when the ligand undergoes conformational changes. The latter could be the case for 1-A-12C4 when interacting with this cation as reflected in the ¹H and ¹³C NMR data previously discussed². A greater enhancement in stability is found for the N-substituted crown relative to 12 crown 4 in complexation with lithium. It should be pointed out that the methylene (-CH₂-) group between 12 crown 4 and the benzene ring confers flexibility to the side arm of this ligand to the extent that its presence may contribute to the stabilisation of the complex.

As far as thermodynamic data for the complexation of 15 crown 5 and its derivatives with lithium are concerned, the results are indicative that the stability of this cation with 15 crown 5 is greater than that for the benzo-substituted derivatives and lithium in these solvents. For useful comparison, thermodynamic data for benzo-15 crown 5 and lithium in acetonitrile at 298.15 K (log K_s = 3.20; $\Delta_c G^\circ$ =-18.26 kJ.mol⁻¹; $\Delta_c H^\circ$ = -17.50 kJ.mol⁻¹; $\Delta_c S^\circ$ =2.5 J.K⁻¹.mol⁻¹)⁹ are considered. As expected the presence of a benzo group in 15C5 lowers the electronic density of the oxygen atoms close to the ring and consequently a decrease in stability for lithium is observed in its complexation with the aromatic crown relative to 15 crown 5.

The effect of substituents in the benzene ring are reflected in the data for 4'-amino benzo 15 crown 5 and 4'-nitro benzo 15 crown 5. Thus, the increase in electronic density of the oxygen in *para* position relative to the amino group appears to make a significant contribution to the stability enhancement of 4-NH₂-15 crown 5 relative to B15C5. On the other hand, the introduction of a NO₂ group (electron withdrawing) does not alter significantly the stability of the complex relative to the unsubstituted benzo derivative.

Based on the stability of lithium coronand complexes, we proceeded with their isolation. In the following section, solution enthalpies of crown ethers, lithium and lithium coronand electrolytes in acetonitrile and in propylene carbonate at 298.15 K are discussed.

STANDARD ENTHALPIES OF SOLUTION

Table 2 lists standard enthalpies of solution of crown ethers (12 crown 4 and 1-benzyl 1-aza-12 crown 4) in acetonitrile and in propylene carbonate at 298.15 K. Also included in this table are corresponding data for 1-aza-12 crown 4 and 15 crown 5 previously reported². The endothermic character of the dissolution process for 1-aza-12 crown 4 in these solvents reflected in the data given in table 2 is indicative of the different physical state of this ligand (solid) relative to the others (liquid).

As far as the electrolytes are concerned the data for lithium coronand salts containing 12 crown 4 and 1-benzyl-1-aza-12 crown 4 lend further support to previous studies² which demonstrated that lithium in common salts is much more solvated than coronand electrolytes in these solvents. The implications of these results on the conductance of electrolytes are discussed below on the basis of quantitative data for molar conductances, Δ° of lithium and lithium coronand electrolytes in propylene carbonate at 298.15 K.

In order to assess the difference in solvation of cations and anions in these solvents, single-ion values based on the Parker convention¹⁰ are calculated and the results are reported in table 3. Since a wider range of electrolytes have been considered for the derivation of single-ion values, these slightly differ from $\Delta_t H^\circ$ data previously reported² for AsF_6^- , BF_4^- , CF_3SO_3^- , Li^+ -A-12C4 and Li^+ ions.

Table 2. Standard enthalpies of solution of crown ethers, lithium and lithium coronand electrolytes in acetonitrile and in propylene carbonate at 298.15 K in $\text{kJ}\cdot\text{mol}^{-1}$. Derived enthalpies of transfer from propylene carbonate (reference solvent)

Compound	$\Delta_s H^\circ$ MeCN	$\Delta_s H^\circ$ PC	$\Delta_t H^\circ(\text{obs.})$ PC \rightarrow MeCN	$\Delta_t H^\circ(\text{calc.})$ PC \rightarrow MeCN
12 crown 4	-3.64 \pm 0.07	-3.06 \pm 0.06	-0.58	
1-A-12C4	20.50 ^a	20.57 ^a	-0.07	
1-B-A-12C4	1.73 \pm 0.06	-3.32 \pm 0.24	5.05	
15 crown 5	-3.67 ^a	-3.13 ^a	-0.54	
LiAsF_6	-18.45 \pm 1.85	-15.14 ^a	-3.31	-1.78
LiBF_4	-14.57 ^a	-15.55 ^a	0.98	-1.45
LiCF_3SO_3	-15.59 ^a	-12.50 ^a	-3.09	-3.04
$[\text{Li}1\text{A}12\text{C}4]\text{AsF}_6$	3.72 ^a	4.84 ^a	-1.12	-2.38
$[\text{Li}15\text{C}5]\text{AsF}_6$	10.62 ^a	13.19 ^a	-2.57	-2.91
$[\text{Li}12\text{C}4]\text{BF}_4$	6.26 \pm 0.26	9.69 \pm 0.50	-3.43	
$[\text{Li}1\text{A}12\text{C}4]\text{BF}_4$	0.85 ^a	3.73 ^a	-2.88	-2.05
$[\text{Li}15\text{C}5]\text{BF}_4$	4.18 ^a	7.29	-3.11	-2.64
$[\text{Li}1\text{A}12\text{C}4]\text{CF}_3\text{SO}_3$	14.66 ^a	18.74 ^a	-4.08	-3.64
$[\text{Li}15\text{C}5]\text{CF}_3\text{SO}_3$	9.17 ^a	13.34	-4.17	-4.23

^aRef 2.

Single-ion values for lithium and lithium coronand cations show that these are enthalpically more stable in acetonitrile than in propylene carbonate. Therefore, on the assumption that enthalpies of transfer are suitable reporters of solvation effects, it should be expected that as far as conductance measurements are concerned, propylene carbonate offers a more suitable medium than acetonitrile. The implication of this statement is that any enhancement in the electrolyte conductance of lithium coronands relative to common lithium electrolytes is likely to be more pronounced in propylene carbonate than in acetonitrile.

Table 3. Single-ion $\Delta_t H^\circ$ values from propylene carbonate to acetonitrile at 298.15 K.

Ion	$\Delta_t H^\circ$ (PC→MeCN) kJ.mol ⁻¹
Li ⁺	-2.42 ^a
Li ⁺ 12C4	-4.40 ^b
Li ⁺ 1-A-12C4	-3.02
Li ⁺ 15C5	-3.61
AsF ₆ ⁻	0.64
BF ₄ ⁻	0.97
CF ₃ SO ₃ ⁻	-0.62

^aFrom L.Ghousseini, PhD thesis; University of Surrey; 1985. ^bDerived from [Li⁺12C4]BF₄ only

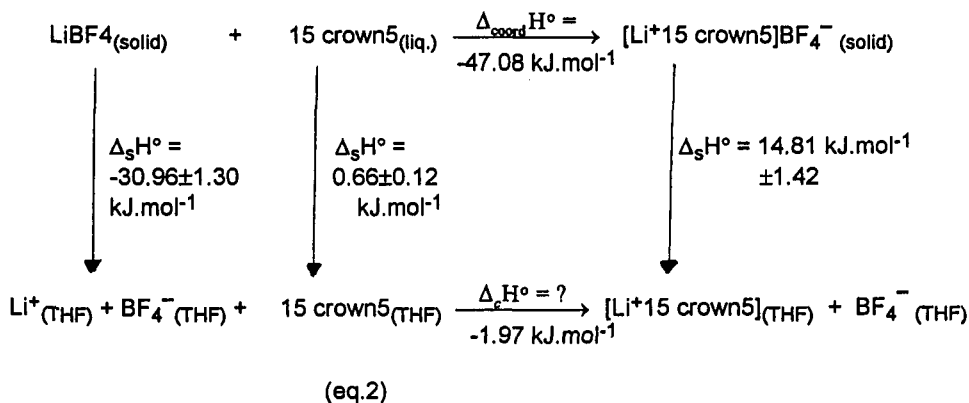
ENTHALPIES OF COMPLEXATION IN LOW DIELECTRIC MEDIA

Enthalpies of coordination, $\Delta_{\text{coord}}H^\circ$ for several lithium salts (LiBF₄, LiCF₃SO₃ and LiAsF₆) and crown ethers (15 crown 5 and 1-aza-12 crown 4) referred to reactants and products in their pure physical state have been recently reported². We have now calculated the enthalpy of coordination for the following process,



Data derived from acetonitrile ($\Delta_{\text{coord}}H^\circ = -45.59 \text{ kJ.mol}^{-1}$) are in excellent agreement with those calculated from propylene carbonate ($\Delta_{\text{coord}}H^\circ = -46.94 \text{ kJ.mol}^{-1}$) and these do not differ from the values reported for the same salt and 15 crown 5 ($\Delta_{\text{coord}}H^\circ = -47.08 \text{ kJ.mol}^{-1}$) reported in the literature. It must be strongly emphasised that in low dielectric medium, ion-pair formation between the single and the complexed lithium cations and the anion takes place and as a result direct calorimetric measurements involves not only the heat due to the complexation process but also to ion-pair formation and therefore, complexation data reported in the literature in solvents of low permittivity are misleading⁹.

A representative example for the calculation of enthalpies of complexation of crown ethers and metal cations in low permittivity media is given by inserting the appropriate values for the processes indicated in the following thermodynamic cycle. Solution data are referred to tetrahydrofuran (THF) as the solvent.



By combining coordination and solution data, a value of $-1.97 \text{ kJ.mol}^{-1}$ is calculated for the enthalpy of complexing, $\Delta_c H^\circ$ of 15 crown 5 and lithium in this solvent at 298.15 K. Note that the standard enthalpies of solution of lithium tetrafluoroborate and its derived lithium coronand complex in tetrahydrofuran are the values at $c=0$ (infinite dilution) from a plot of $\Delta_s H$ against $c^{1/2}$; where c are the final concentrations in the calorimetric vessel. The $\Delta_c H^\circ$ value for Li^+ and 15C5 in THF obtained via the cycle has been checked by using coordination and solution data for lithium salts containing different anions (CF_3SO_3^- and AsF_6^-) and good agreement between these data are found with values which do not differ by more than 3 kJ.mol^{-1} . However, $\Delta_c H^\circ$ values derived via the cycle differ significantly from the value obtained from direct calorimetric measurements in which besides complexation, ion-pair formation is involved. In fact, depending on the electrolyte concentrations, the latter values varied from -16 to -20 kJ.mol^{-1} for LiBF_4 and 15 crown 5 in tetrahydrofuran at 298.15 K.

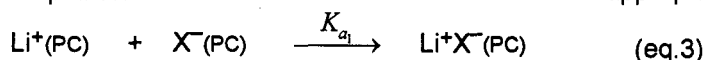
Among the various processes shown in the cycle, the dramatic change observed in the enthalpy associated with the dissolution of the lithium salt (exothermic) relative to that of the lithium coronand salt (endothermic) is striking. In fact, the results in tetrahydrofuran unambiguously demonstrate that in moving from LiBF_4 to $[\text{Li}15\text{C}5]\text{BF}_4$, the enthalpic stability of the process decreases by $\sim 45 \text{ kJ.mol}^{-1}$. This decrease is much more pronounced than that observed for the same system in either propylene carbonate or acetonitrile ($\sim 19 \text{ kJ.mol}^{-1}$). In fact, calculation of transfer enthalpies for these electrolytes from propylene carbonate to tetrahydrofuran show two opposite effects. Thus, for LiBF_4 [$\Delta_t H^\circ(\text{PC} \rightarrow \text{THF}) = -16.40 \text{ kJ.mol}^{-1}$], the solvation enthalpy is more favoured in tetrahydrofuran than in propylene carbonate; while the converse is true for $[\text{Li}15\text{C}5]\text{BF}_4$ [$\Delta_t H^\circ(\text{PC} \rightarrow \text{THF}) = 7.52 \text{ kJ.mol}^{-1}$]. These findings are most encouraging since these may suggest a higher enhancement in conductivity of lithium salts by the addition of 15 crown 5 than that already reported for the same system in propylene carbonate. It should also be noted that as the anion constituent of the electrolyte is the same; therefore, the enthalpy change observed in going from LiBF_4 to $[\text{Li}15\text{C}5]\text{BF}_4$ is entirely dependent on the cation.

Another important aspect to emphasise is that the exothermic character of the complexation reaction observed in acetonitrile and in propylene carbonate (see table 1) is greatly reduced when the reaction medium is tetrahydrofuran. This result is in accord with previous findings suggesting that in the binding of crown ethers or cryptands with metal cations, the stronger is the cation-solvent interaction⁶, the weakest is the interaction between cation and macrocyclic ligand or the more comfortable is the environment provided by the solvent to the cation, the less suitable is this medium for cation-ligand complexation.

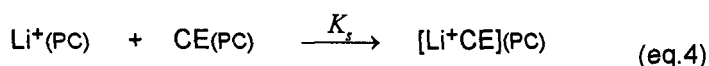
CONDUCTANCE MEASUREMENTS

It has been shown that the addition of crown ethers to lithium salts in propylene carbonate increases the conductance of the solution as a result of complex formation. Thus, conductance data in propylene carbonate at 298.15 K have been used for the derivation of equilibria data for the following processes;

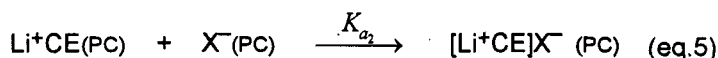
- i) Ion-pair formation between Li^+ and the anion in the appropriate solvent;



- ii) Complexation of Li^+ and crown ethers in propylene carbonate



- iii) Ion-pair formation between Li^+CE and the anion;



For these purposes, the Fuoss-Hsia equation with the expansion of Fernández-Prini¹¹ was used. Thus, table 4 lists molar conductances at infinite dilution of lithium and lithium coronand electrolytes in propylene carbonate at 298.15 K. Λ_m° for LiClO₄ is that reported in the literature¹¹. Ion-pair formation constants for the process represented by eq. 3 and complexation data eq. 4 are also reported in table 4. Lithium coronand electrolytes were found to be fully dissociated in propylene carbonate.

Table 4. Molar conductances and ion-pair formation constants of lithium and lithium coronand electrolytes in propylene carbonate at 298.15 K. Stability constants of lithium and crown ethers in propylene carbonate at the standard temperature.

System	Λ° (S.cm ² .mol ⁻¹)	K_{a1}	R_2^b nm	σ_λ	log K_s
LiClO ₄	26.75 ^a	1.3	0.55	0.01	-
[Li12C4]ClO ₄	28.91		0.43	0.08	2.90±0.04
LiBF ₄	28.57	0.29	1.06	0.01	-
[Li-1-A-12C4]BF ₄	30.83		1.09	0.01	3.69±0.01
[Li-1-B-1-A12C4]BF ₄	32.70		0.93	0.03	4.33±0.02
[Li15C5]BF ₄	31.06		0.88	0.01	4.31±0.03
LiCF ₃ SO ₃	24.27	1.91	1.19	0.02	-
[Li-1-A-12C4]CF ₃ SO ₃	26.73		0.84	0.03	3.74±0.01
[Li15C5]CF ₃ SO ₃	27.14		0.77	0.01	4.23±0.09

^aRef.11 ^b R_2 fixed at the Bjerrum distance 0.43 nm for propylene carbonate at 298.15 K.

An important aspect to emphasise from the data shown in table 4 is the excellent agreement found between the stability constant values for these systems derived from conductance measurements (see last column table 4) and those obtained calorimetrically (table 1). It must be stressed that the magnitude of the stability constants are well within the scope of these techniques and this is clearly reflected in the agreement found between these two sets of data. As far as Λ° values is concerned, these unambiguously demonstrate that the conductance of lithium coronand electrolytes is higher by approximately 2 S.cm².mol⁻¹ relative to corresponding data for the uncomplexed lithium electrolytes. This is better illustrated in the λ_+° values for lithium¹¹ and lithium coronand cations in propylene carbonate at 298.15 K listed in table 5.

We are now proceeding with heat capacity measurements for these systems.

Table 5. Single-ion molar conductances in propylene carbonate at 298.15 K

Cation	λ_+° /S.cm ² .mol ⁻¹	Anion	λ_-° /S.cm ² .mol ⁻¹
Li ⁺	7.86 ^a	ClO ₄ ⁻	18.89 ^a
[Li ⁺ 12C4]	10.02 ^b	BF ₄ ⁻	20.71
[Li ⁺ 1-A-12C4]	10.17 ^c	CF ₃ ⁻ SO ₃ ⁻	16.41
	10.32		
[Li ⁺ 1-B-1-A-12C4]	11.99 ^d		
[Li ⁺ 15C5]	10.36		
	10.73		

^aRef. 11 ^bCalculated from Λ° [Li⁺12C4]ClO₄⁻ (table 4). ^cCalculated from Λ° [Li⁺1-A-12C4]BF₄⁻ and [Li⁺1-A-12C4]CF₃⁻SO₃⁻ (table 4). ^dCalculated from Λ° [Li⁺1-B-1-A-12C4]BF₄⁻ (table 4). ^eCalculated from data for [Li⁺15C5]BF₄⁻ and [Li⁺15C5]CF₃SO₃⁻

ACKNOWLEDGMENT.

The authors thank the US Army (European Office) for financial support.

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