JOURNAL OF APPLIED ELECTROCHEMISTRY 23 (1993) 151–156

Conductivity and viscosity studies of ethylene carbonate based solutions containing lithium perchlorate

P. V. S. S. PRABHU, T. PREM KUMAR, P. N. N. NAMBOODIRI, R. GANGADHARAN

Lithium Battery Section, Central Electrochemical Research Institute, Karaikudi 623 006 Tamil Nadu, India

Received 30 March 1992; revised 8 July 1992

Specific conductivities and viscosities of lithium perchlorate at four different concentrations (0.5, 1.0, 1.5 and 2.0 M) in ethylene carbonate (EC) based binary mixed solvent systems at 25 °C are reported. The co-solvents chosen were tetrahydrofuran (THF), 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL). Viscosity variations in all the three mixed solvent systems without electrolyte showed negative deviation from ideal behaviour thereby indicating the occurrence of a structure breaking effect in these three different binary systems. The increase in viscosity with increase in concentration of $LiClO_4$ is attributed to the structural enhancement through the formation of a solvated complex which occupies interstitials in the solvent mixtures. 1 M $LiClO_4$ solution shows maximum specific conductivity at 30 vol % EC for EC + DME and EC + DOL mixtures and at 50 vol % EC for EC + THF mixtures. Conductivity variations are explained on the basis of preferential solvation of lithium perchlorate by co-solvents (THF, DME and DOL) in their respective mixtures with ethylene carbonate.

1. Introduction

The study of electrolytic properties of mixed non-aqueous electrolyte solutions is of current interest because of their potential use in lithium batteries [1–4]. The concept of mixing high dielectric ester with low viscous ether to obtain a best conducting electrolyte solution has recently been studied [5–9]. In this context ethylene carbonate (EC) based electrolytes have received much attention. Studies on the electrolytic properties of ethylene carbonate based solutions and the charge–discharge cycling behaviour of lithium in these solutions have been carried out by Tobishima *et al.* [10–14]. From these studies EC has been identified as an important electrolyte solvent with desirable properties for use in lithium secondary batteries.

The structural changes that occur at molecular level by mixing ethylene carbonate with other co-solvents (without electrolyte) have not been discussed in detail. Also the presence of an electrolyte in these binary mixtures influences the molecular arrangements. The structural changes are reflected in the conductivity and viscosity behaviour of these electrolyte solutions. Therefore, we have undertaken viscosity and conductance studies of EC based binary mixtures with tetrahydrofuran (THF), 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL), containing lithium perchlorate. In this paper conductivity and viscosity data are reported for lithium perchlorate at four different concentrations, namely 0.5, 1.0, 1.5 and 2.0 M, in the above mentioned binary mixtures over the entire solvent composition range at 25 °C. An attempt has been made to obtain an insight into the structural changes that occur in these solutions on the basis of conductivity and viscosity variations.

2. Experimental aspects

2.1. *Materials*

Ethylene carbonate (BDH, LR) was distilled over molecular sieves (4A, mesh) under vacuum at 4 torr. The purity of EC was estimated to be around 99.5% using gas chromatography [15].

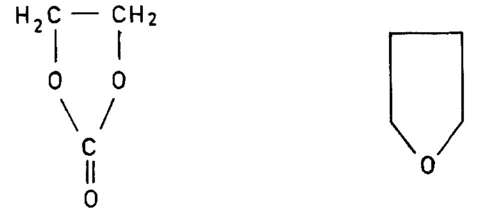
Tetrahydrofuran (Merck) was allowed to stand for 48 h over freshly fused sodium hydroxide and 24 h over sodium wire, over which it was refluxed. It was fractionally distilled in an atmosphere of dry nitrogen and finally vacuum distilled from lithium aluminium hydride [16].

1,2-Dimethoxyethane (Fluka) was treated with lithium aluminium hydride and fractionally distilled and stored over molecular sieves [17].

1,3-Dioxolane (Fluka) was refluxed for 2 h, with lead (IV) oxide, cooled and filtered. Xylene and more lead (IV) oxide were added and the mixture was fractionally distilled. The main fraction collected at 70–71 °C was treated with xylene and sodium wire and then distilled. More sodium was added to the product and, finally, a sample boiling at 74–75 °C was collected [18].

As all these solvents are highly hygroscopic they were stored over molecular sieves after purification and kept in a glove box containing an argon atmosphere. The water content in the pure solvents was estimated to be around 50 ppm as measured by Aquatest 8 (USA). After addition of electrolyte the water content was found to increase up to 100 ppm. Lithium perchlorate (Fluka, A. G., Purum 99%) was dried at 160 °C under vacuum for 24 h. All the solutions were prepared inside a glove box.

0021-891X



(a) Ethylene Carbonate (b) Tetrahydrofuran

(c) 1,2- Dimethoxyethane (d) 1,3- Dioxolane

Fig. 1. The molecular structures of the solvents.

2.2. *Apparatus and procedure*

A Cannon–Fenske direct flow viscometer was used for viscosity measurements. It was standardised by measuring the times of flow for conductivity water, acetone, propylene carbonate and acetonitrile whose viscosity values are available in the literature [19]. The viscometer constant determined through this procedure is 0.008 74 kg m^{-1} s^{-1}. The kinetic energy term for the viscometer is well within the experimental error and was therefore neglected. At least three determinations were made for each solution to check the reproducibility of the time of flow within ±0.2 s. This led to an error of ±0.04–0.08. Therefore, the overall uncertainty in the viscosity was estimated to be within 0.1%.

Conductivity measurements were carried out using a Wayne Kerr autobalance precision bridge type B 331/MK 11 having a frequency of 1592 Hz. A conductance cell, similar in design to that reported by Shedlovsky [20], was used, with electrodes made up of bright platinum discs soldered in glass. The electrode compartment was sealed to the side of a 250 cm^3 conical flask closed by a ground glass cap. The cell was calibrated following the method of Fuoss and coworkers [21] using aqueous potassium chloride solutions in the concentration range (3–50) × 10^{-4} M. The cell constant was determined to be 0.3354 cm^{-1}. All experiments were performed inside a glove box in which argon gas was circulated. The temperature inside the glove box was maintained at 25 ± 0.1 °C. Taking account of the purity of the electrolyte and solvents and also the method of measurements employed the overall accuracy of the conductance measurements was ±0.1%.

3. Results and discussion

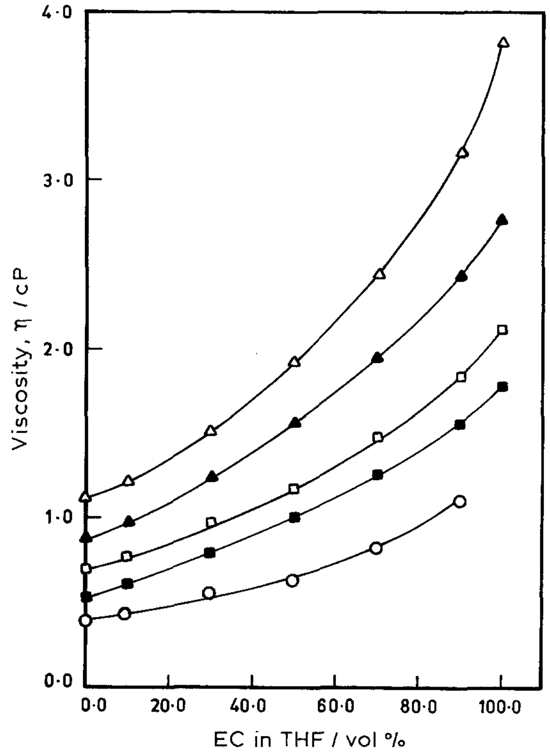


Fig. 2. Viscosity variations of EC + THF mixtures containing LiClO$_4$ at 25 °C. Concentrations: (△) 2.0, (▲) 1.5, (□) 1.0, and (■) 0.5 M; (○) without electrolyte.

The physical properties of the solvents used in the present study are given in Table 1. The molecular structures of the four solvents are also shown in Fig. 1. Viscosity variations for the three types of solvent mixtures with (and without) electrolyte compound at four different concentrations are shown in Figs 2, 3 and 4. The viscosity variations appear to be similar in all the three cases. It can be seen from Fig. 2 (for example EC + THF mixtures) that the viscosity variation shows a continuous increase with increase in EC content in THF (viscosity of pure EC could not be measured as it is solid at room temperature). The viscosity composition curve (without electrolyte) is

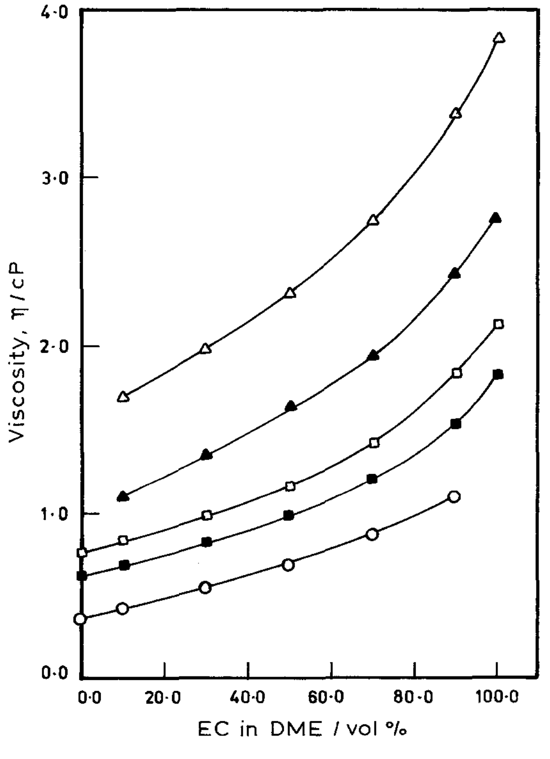


Fig. 3. Viscosity variations of EC + DME mixtures containing LiClO$_4$ at 25 °C. Concentrations: as Fig. 2. (○) without electrolyte.

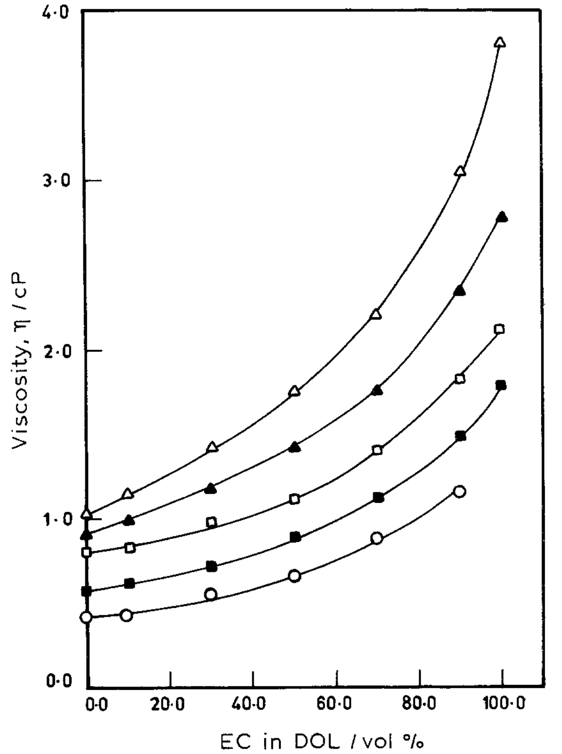


Fig. 4. Viscosity variations of EC + DOL mixtures containing $LiClO_4$ at 25 °C. Concentrations: as Fig. 2. (○) without electrolyte.

concave upward, this showing a slight negative deviation from ideal behaviour. This indicates the existence of interaction between the two components of these mixtures. The negative deviation from ideal behaviour is generally attributed to the structure breaking influence of one component on the other.

Pure ethylene carbonate possesses intermolecular association, as observed through dielectric constant measurements [22]. The interaction between EC and THF is such that the basic network of intermolecular association in EC is disrupted and the individual EC and THF molecules are loosely bound together to give rise to a less structured solution. This loose association of molecules gives rise to an apparent slight negative deviation in viscosity variation. This explanation is also valid for the other two systems because of the similar viscosity variations observed. These viscosity variations are analogous to those of ethylene glycol + water mixtures [23] and formamide + water mixtures [24]. It can also be observed from Figs 2, 3, and 4 that the viscosity increases with the addition of electrolyte in all the solvent mixtures at each composition.

The increase in concentration of electrolyte from 0.5 to 2.0 M gives an increase in viscosity at each composition of the mixtures. This increase in viscosity may be attributed to the association of Li^+ ions and ClO_4^- ions to the solvent molecules resulting in the formation of solvated complexes (solvent separated ion-pair) [25–27]. Evidence for the formation of these solvated complexes is also provided from conductivity results discussed in the following paragraphs. Both the components of the solvent mixtures have the heteroatom 'Oxygen' which acts as the complexing centre.

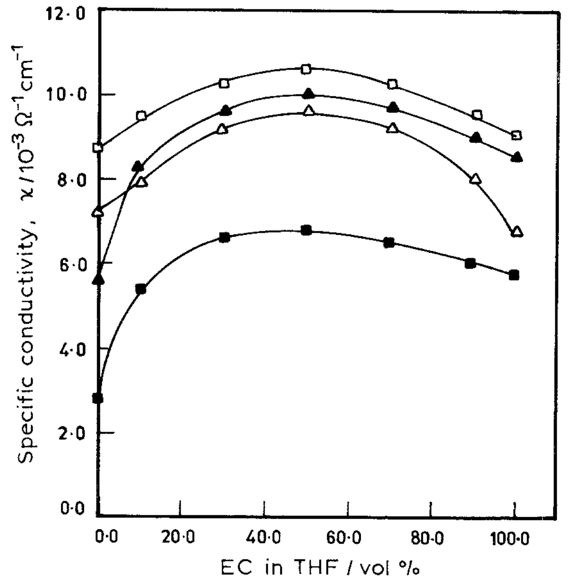


Fig. 5. Specific conductivity variations of $LiClO_4$ in EC + THF mixtures at 25 °C. Concentrations: as Fig. 2.

When the electrolyte $LiClO_4$ is added to the solvent mixtures, the dissociated Li^+ and ClO_4^- ions are associated with the individual solvent molecules. As these associated species form, the ions are accommodated in the interstitials (voids) available in the mixtures. This contributes to the structural enhancement in these solutions, which results in an increase in viscosity with the addition of electrolyte. Further, with the increase in concentration of the electrolyte the viscosity–composition curves become more and more shallow. This indicates that the structure of the electrolyte solution becomes increasingly compact as more and more ions are accommodated in the interstitials. Hence, there is an increase in viscosity with increase in concentration of electrolyte. This argument applies for all the three systems.

The variations of specific conductivity of these three different types of electrolyte solutions with respect to solvent composition and at different concentrations of the electrolyte are shown in Figs 5, 6 and 7. The specific conductivity values obtained for 1 M $LiClO_4$ in pure EC, THF, DME and DOL (the solubility limit of $LiClO_4$ in pure DME is around 1 M) in present investigation are 8.54, 8.71, 10.57 and 8.72 $m\Omega^{-1} cm^{-1}$, respectively. The reported values for 1 M $LiClO_4$ in these solvents in the same sequence are 7.87, 4.0, 7.2 and 1.8 $m\Omega^{-1} cm^{-1}$, respectively [5, 11, 28, 29]. This little difference in the conductivity values is probably because of unaccounted experimental errors and also the different types of purification methods followed. The trend in variations of conductivity with respect to solvent composition is not very different from that observed by Tobishima [11] at 1 M $LiClO_4$ concentration as shown in Fig. 8. The conductivity increases with increase in EC content in the solvent mixtures and passes through a maximum at around 30 vol % EC in EC + DME and EC + DOL mixtures and 50 vol % EC in EC + THF mixtures.

The appearance of conductivity maximum can be qualitatively explained as arising from a favourable

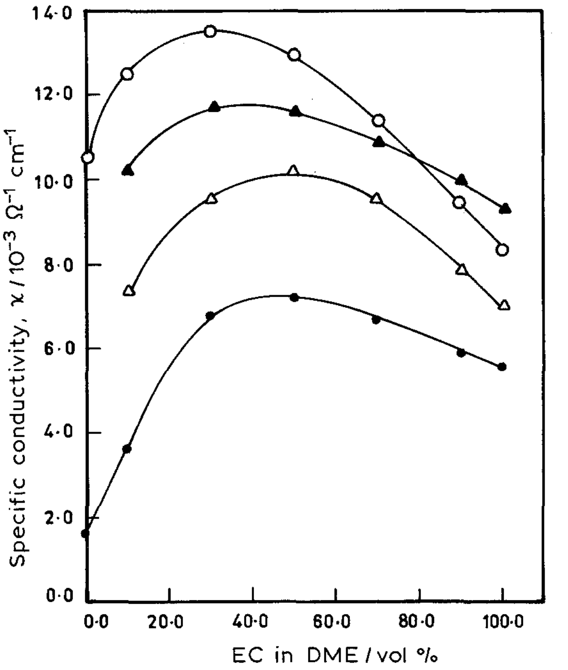


Fig. 6. Specific conductivity variations of $LiClO_4$ in EC + DME mixtures at 25 °C. Concentrations: as Fig. 2.

combination of high dielectric solvent EC and the low viscous co-solvent (THF, DME and DOL). The electrolyte solutions of low viscous ethers, which have low dielectric constant (≈ 7.0), contain more contact ion-pairs because of greater degree of ion association. When the solution of high dielectric ester EC is added to the ether solutions, the conductivity increases because of the gradual dissociation of these ion-pairs. Even though, the viscosity increases with increase in EC content (cf. Figs 2, 3 and 4), the high dielectric constant of EC seems to have greater contribution for the increase in ionic mobility in the co-solvent (THF, DME and DOL) rich region. After passing through the maximum, conductivity gradually decreases with further increase in EC content in the mixtures (cf. Figs 5, 6, and 7). This may be due to the predominant influence of viscosity on the mobility of ions in the EC-rich region. Therefore, as a first approximation, these conductivity variations are considered to be a result of compensation of viscosity and dielectric constant of the solvent components of the mixtures.

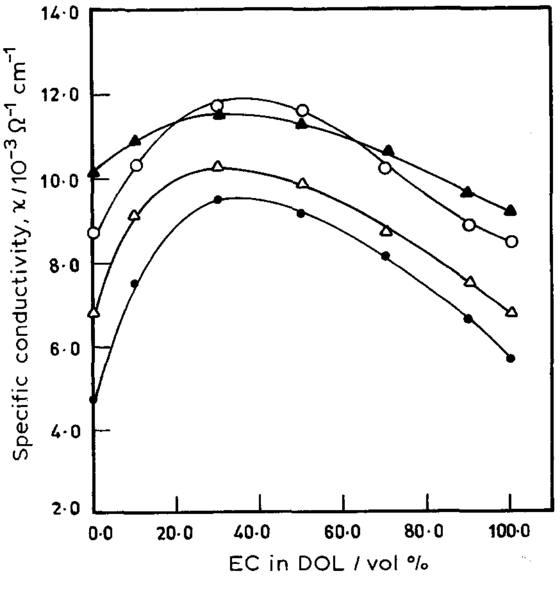


Fig. 7. Specific conductivity variations of $LiClO_4$ in EC + DOL mixtures at 25 °C. Concentrations: as Fig. 2.

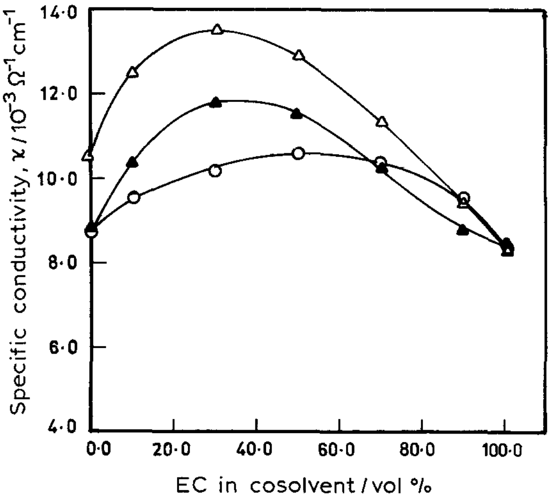


Fig. 8. Variations of specific conductivities at 1 M $LiClO_4$ in each of the solvent mixtures: (○) EC + THF, (△)EC + DME, and (▲) EC + DOL.

However, there exists appreciable difference in the conductivity variations of these three different electrolyte solutions. For example, the differences in conductivity variations at 1M $LiClO_4$ concentration in the three binary mixtures are clearly shown in Fig. 8. They may be explained as follows. At higher electrolyte concentration and also in solutions of low dielectric constant essentially two types of ion-pairs exist [25, 26]: solvent separated ion pairs and solvated contact ion pairs. These are represented by the following equilibria,

$$(Li^+)S_n + A^- \rightleftharpoons (Li^+)S_n \cdot A^-$$

$$(Li^+)S_n + A^- \rightleftharpoons (Li^+ \cdot A^-)S_{n-m} + mS$$

Where S represents a solvent molecule and A^- an anion. It is possible that redissociation of solvent separated ion-pairs occurs because of the long-range nature of coulomb force and that the resulting free ions contribute to ionic conductance. In other words, the difference in the types of ion pairs would result in the difference of the ionic behaviour. This implies that the degree of differences in the short-range ion-solvent interactions would be responsible for the differences in the ionic behaviour in these three electrolyte solutions. It can also be observed from Figs 5, 6 and 7 that at different concentrations of the electrolyte, particularly at 2.0, 1.5 and 1.0 M, the conductivity curves intersect. At higher concentrations, the presence of different types of ionic species and the competitive interactions between them may possibly lead to such erratic variations.

The conductivity variations are, therefore, explained on the basis of differences in short range ion-solvent interactions. It can be seen from Fig. 8 that the specific conductivity maximum does not correspond

Table 1. The physical properties of the solvents

Solvent	*Dielectric constant (25 °C)*	*Viscosity $\eta \times 10^{-3}$ (20 °C) /kg m^{-1} s^{-1}*	*Molecular volume /nm*	*Donor number (DN)*
Ethylene carbonate	91.2*	1.9*	11.04	16.4
Tetrahydrofuran	7.6	0.55	13.48	20
1,2-dimethoxyethane	7.2	0.48	17.24	24
1,3-dioxolane	7.0	0.57	11.61	24

* Values taken at 40 °C.

to the same composition in these three different solvent mixtures. This suggests the occurrence of preferential solvation of $LiClO_4$ by either one of the solvent components. The shift in conductivity maximum towards co-solvent (DME and DOL) rich region indicates the preferential solvation of $LiClO_4$ by DME and DOL in their respective binary mixtures with EC. In the case of EC + THF mixtures the conductivity maximum is observed around 50 vol % EC. From this observation it is not clear that preferential solvation occurs in this case. However, it is possible to verify these observations on preferential solvation following the donor–acceptor approach [30, 31]. The magnitude of the donor number (DN) of a solvent molecule is a measure of the solvation power of the solvent toward electrolyte ions (Li^+ and ClO_4^-). DN values are useful in determining the solvent environment around lithium ions. The donor number values of the solvents used in the present study are given in Table 1. It can be seen that the DN values of THF, DME and DOL are considerably higher (20, 24 and 24, respectively) than that of EC (16.4). Therefore, preferential solvation of Li^+ ions by THF, DME and DOL can be expected in their respective mixtures with EC. This supports the conclusions derived from conductivity results regarding preferential solvation.

The maximum specific conductivity observed (cf. Fig. 8) at 1 M $LiClO_4$ in the three different mixtures varies in the following order:

$$\mathrm{EC + DME\ (1:3) > EC + DOL\ (1:3) > EC + THF\ (1:1)}$$

The possible way to explain this order of variation is to take into account the parameters such as solvation number (number of ether molecules in the primary solvation sheath in the vicinity of lithium ions) and molecular volume of the solvent. It was shown in the foregoing discussion that Li^+ is preferentially solvated by ether molecules in their respective mixtures with EC. This means that the primary solvation sheath contains more ether molecules. However, the data on solvation numbers in any of the three solvent mixtures under study in present investigation i.e. EC + THF, EC + DME and EC + DOL, are not available in the literature. Such data are found to exist in PC + DME and PC + THF mixtures [32, 33]. The primary solvation numbers of DME and THF for a Li^+ ion are 2 and 4, respectively, in PC + DME and PC + THF mixtures. In addition to this, the data on stokes radius [11, 12] of Li^+ ion in the mixtures (1 : 1) of PC + THF, EC + THF, PC + DME and EC + DME are 0.42, 0.41, 0.39 and 0.39 nm, respectively, suggest that similar type of solvation mechanism is operative in these systems. EC can be considered as an analogous solvent like PC. Therefore, the ionic radius of the solvated Li^+ ion would be larger in EC + THF than in EC + DME as there is no great difference in molecular volumes of THF (13.48 nm) and DME (17.24 nm). Thus, the relatively larger size of the Li^+–THF solvate would be responsible for the lower conductance of EC + THF than in EC + DME. The DN values of DME and DOL are approximately the same. The solvation power of DOL to Li^+ is reported [34] to be similar to that of DME. However, in view of the difference in the molecular volumes of DME (17.24 nm) and DOL (11.61 nm), it is considered that the solvated Li^+ ion with DOL will be bigger in size than that in DME. More DOL molecules are accommodated in the vicinity of the Li^+ ion compared to DME. This results in a slight decrease of conductivity of the EC + DOL solutions compared to that of EC + DME solutions. Therefore, the conductivity curve of EC + DOL solutions falls between that of EC + DME and EC + THF solutions.

It is believed that the Walden product variations will give an insight into the short-range ion-solvent interactions. Generally, for electrolyte solutions of lower concentration only ($\approx 10^{-3}$ M) Walden product variations are interpreted meaningfully. At infinite dilution condition long-range ion–ion interactions will be completely absent and ion–solvent interactions alone are taken into consideration. Therefore, Walden product variations are effectively interpreted on the basis of short-range ion-solvent interactions.

However, in the present study Walden product values are determined at higher electrolyte concentration (≈ 1 M). The three solvent mixtures contain 1 M $LiClO_4$ where the ion–ion and ion–solvent interactions exist. Consequently, these solutions have solvent-separated ion pairs, solvated contact pairs, contact pairs and also free ions that contribute to the conductance current. The difference in the Walden product variations represent the degree of difference in the ionic behaviour arising from the presence of different types of ionic species in these three kinds of solutions.

Walden product variations with respect to the solvent composition are shown in Fig. 9. In the three cases Walden product values increase as the EC content increase in the solvent mixtures. The trend of variation in walden product for the three systems is not very different. At any particular composition of these mixtures the order of variation of Walden product values is as follows (up to 70 vol % EC),

$$\mathrm{EC + DOL > EC + DME > EC + THF}$$

This difference in the magnitude of Walden product can be attributed to the extent of availability of free ions which contribute to the increase in conductivity.

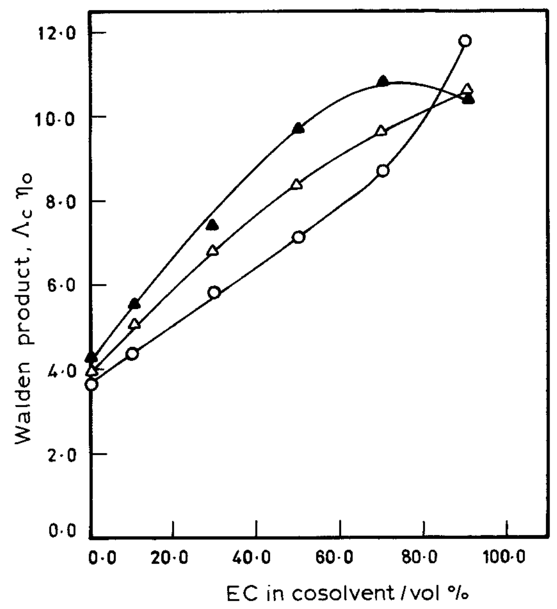


Fig. 9. Walden product variations at 1 M $LiClO_4$ in each of the different types of solvent mixtures: (○) EC + THF, (△) EC + DME, and (▲) EC + DOL.

The above order indicates that the polarizability of EC + DOL solutions is higher and gives rise to relatively more free ions compared to other two systems. Apparently EC + THF solutions have lower conductivity due to the relatively poor polarizability in these solutions. The Walden product variations of EC + DME solutions fall between those of EC + DOL and EC + THF, showing thereby the relative differences in polarizability of EC + DME solution from the other two systems. In the EC-rich region ($\sim$90 vol% EC) overlapping of Walden product variations can be observed. This suggests that in solutions of excess EC content the mobility of the ions is influenced by the complex ion–solvent interactions.

Acknowledgements

The authors are grateful to Prof. S. K. Rangarajan, Director, CECRI for his kind encouragement. The authors also wish to thank Mr. K. Gopala Krishnan for his help in drawing the figures.

References

[1] G. E. Blomgren, 'Lithium Batteries', (edited by J. P. Gabano), Academic Press, New York (1983) Chap. 2.

[2] J. Barthel, H. J. Gores, G. Schmeer and R. Wachter, Non-aqueous electrolyte solutions in chemistry and modern technology, in 'Topics in Current Chemistry', Vol. III, (edited by F. L. Boschke), Springer-Verlag, Heidelberg (1983).

[3] J. Barthel and H. J. Gores, *J. Pure Appl. Chem.* **57** (1985) 1071.

[4] R. Janakiraman, P. N. N. Namboodiri and R. Gangadharan, *Portugaliae Electrochimica Acta* **8** (1990) 107.

[5] Y. Matsuda, M. Morita and F. Tachihara, *Bull Chem. Soc. Japan* **59** (1986) 1967.

[6] M. Morita, F. Tachihara and Y. Matsuda, *Electrochim. Acta* **32** (1987) 299.

[7] S. Tobishima, M. Arakawa and J. Yamaki, *ibid.* **33** (1988) 239.

[8] S. Tobishima and T. Okada, *J. Appl. Electrochem.* **15** (1985) 317.

[9] Gopu Kumar, Janakiraman, *et al.*, *J. Chem. Eng. Data* **36** (1961) 467.

[10] S. Tobishima and A. Yamaji, *Electrochim. Acta* **29** (1984) 267.

[11] S. Tobishima, J. Yamaki and T. Okada, *ibid.* **29** (1984) 1471.

[12] S. Tobishima and T. Okada, *ibid.* **30** (1985) 1715.

[13] S. Tobishima, M. Arakawa, T. Hirai and J. Yamaki, *J. Power Sources* **20** (1987) 293.

[14] M. Arakawa, S. Tobishima, T. Hirai and J. Yamaki, *J. Electrochem. Soc.* **133** (1986) 1527.

[15] R. Payne and I. E. Theodorou, *J. Phys. Chem.* **76** (1972) 2892.

[16] D. C. H. Cheng, J. C. McCoubrey, *et al.*, *Trans. Farad. Soc.* **58** (1962) 224.

[17] W. J. Wallace and A. L. Mathews, *J. Chem. Eng. Data* **8** (1963) 496.

[18] S. A. Barker, E. J. Bourne, *et al.*, *J. Chem. Soc.* (1959) 802.

[19] J. A. Riddick, W. B. Bunger and Theodore K. Sakano, 'Organic Solvents – Physical Properties and Methods of Purification', John Wiley & Sons, New York (1986).

[20] T. Shedlovsky, *J. Am. Chem. Soc.* **54** (1932) 1411.

[21] J. E. Lind, Jr., J. J. Zwolenik and R. M. Fuoss, *J. Am. Chem. Soc.* **81** (1959) 1557.

[22] R. Kempa and W. H. Lee, *J. Chem. Soc.* (1958) 1936.

[23] M. V. Ramanamurti, P. V. S. S. Prabhu and Lal Bahadur, *Bull. Chem. Soc. Japan* **59** (1986) 2341.

[24] Lal Bahadur and M. V. Ramanamurti, *J. Electrochem. Soc.* **128** (1981) 339.

[25] R. Fernandez-Prini, 'Physical Chemistry of Organic Solvent Systems', (edited by A. K. Covington and T. Dickinson), Plenum Press, London (1973) Chapter 5.

[26] I. R. Lantzke, 'Physical Chemistry of Organic Solvent Systems', (edited by A. K. Covington and T. Dickinson), Plenum Press, London (1973), Chapter 4.

[27] B. S. Krumgalz, *J. Soln. Chem.* **11** (1982) 283.

[28] G. Pistoia, M. De Ross and B. Scrosati, *J. Electrochem. Soc.* **117** (1970) 500.

[29] G. Pistoia, *ibid.* **118** (1971) 153.

[30] V. Gutmann, *Electrochim. Acta* **21** (1976) 661.

[31] V. Gutmann, 'The Donor-Acceptor Approach to Molecular Interactions', Plenum Press, New York (1978) Chapter 2.

[32] Y. Matsuda, H. Nakashima, M. Morita and Y. Takasu, *J. Electrochem. Soc.* **128** (1981) 2552.

[33] S. Tobishima and A. Yamaji, *Electrochim. Acta* **28** (1983) 1067.

[34] Y. Matsuda, M. Morita and T. Yamashita, 24th Battery Symposium (Japan) **1B08** (1983) 201.