Raman Spectra and Transport Properties of Lithium Perchlorate in Ethylene Carbonate Based Binary Solvent Systems for Lithium Batteries

B. Klassen and R. Aroca*

Materials and Surface Science Group, University of Windsor, Windsor, Ontario, N9B 3P4 Canada

M. Nazri and G. A. Nazri

Physics and Physical Chemistry Department, General Motors Research and Development Centre, Warren, Michigan 48090

Electrolyte solutions formed by the addition of lithium perchlorate to a binary solvent mixture obtained by mixing ethylene carbonate (EC) with propylene carbonate (PC), diethyl carbonate (DEC), or dimethyl carbonate (DMC) were studied. The Raman spectra, conductivity, and viscosity of the EC based binary solvent electrolytes were measured. The salt concentration was optimized for maximum conductivity. Conductivity increases with increasing lithium perchlorate concentration in the $EC/PC/LiClO_4$ electrolyte until a maximum of 6.1 $k\Omega^{-1}$ cm^{-1} is reached at 0.82 M $LiClO_4$ ($EC/PC/LiClO_4$ = 8/8/1). For the optimized salt concentration, the conductivity and viscosity dependence on the percent EC content of each electrolyte was measured at 25 °C. The maximum conductivity is observed for the $EC/DMC/LiClO_4$ electrolyte at about 60% EC. The temperature dependence of conductivity and viscosity in the −30 ° to 60 °C range was also examined. The spectroscopic evidence for specific Li^+ coordination is supported by quantum chemical calculations.

Introduction

In a lithium ion battery, the anode is commonly made up of carbonaceous material, which is well-known for its good ionic lithium insertion−disinsertion properties.[1,4] One "ideal" anode is produced by the insertion of one lithium atom for every six atoms of carbon, LiC_6. Candidates for the makeup of the cathode are transition metal oxides, chalcogenides, $LiMO_2$ (M = Co, Ni, Mn, Fe), or 3-D spinel $LiMn_2O_4$ which show a good aptitude for lithium insertion−desinsertion and have relatively high discharge potential (3−4 V). Electrolytes are composed of a lithium salt ($LiClO_4$, $LiPF_6$, $LiCF_3SO_3$, etc.) dissolved in an organic solvent or more commonly a mixture of organic solvents such as ethylene carbonate, propylene carbonate, 2-methyltetrahydrofuran, etc. There are also examples of ternary solvent blends which have been used in an attempt to improve low-temperature performance. Although progress has been made in enhancing the conductivity of solid electrolytes, liquid electrolytes are still used the most in electrochemical systems. The basic requirements of a suitable electrolyte for electrochemical devices include high ionic conductivity, low melting and high boiling points, and chemical and electrochemical stability. The composition of nonaqueous electrolyte solutions for secondary lithium batteries plays an important role in determining cycle life, cell performance, operating temperature range, and storage temperature range. There have been numerous studies and reviews concerning the conductivity and properties of nonaqueous electrolyte solutions.[5−9] Since a battery is an interactive system, many of the problems encountered in lithium batteries concerning the solution phase actually involve interactions between the components of the electrolyte solution. The characterization of these interactions that determine the performance of binary-solvent electrolyte solution will be the focus of this study. The high degree of ionic conductivity shown by nonaqueous electrolytic solutions made up of organic solvents, such as propylene carbonate or ethylene carbonate, fully justifies the research effort for their use in high-energy density batteries.

Experimental Section

High-purity cyclic ester solvents and linear carbonates PC, EC, DMC, and DEC were purchased from Fluka. To reduce the residual moisture, the solvents were stored over molecular sieves for at least 24 h. Electrolytes were prepared in a drybox filled with 99.999% argon. The atmosphere of the box was continuously circulated over Cu shaving catalyst and over titanium sponge at 700 °C to remove residual oxygen, moisture, and nitrogen. The drybox was a vacuum atmosphere model MO-40-2H/DRI, equipped with Nitrian and catalyst recirculating unit. A 40 W tungsten light bulb was cracked and installed in the box to monitor the purity of the box atmosphere. Usually each lamp last over 2 months before burning out. Conductivity measurements were performed using dip cells (model A-01 with cell constant 0.1) from Rosemount Analytical Inc. This cell uses two platinized parallel plates fixed in a cylindrical glass cavity. The electrode is dipped in the electrolyte and remained there for at least 5 min before measurements were taken. The cell was connected to a Genrad model GR1689/1689M precision RLC Digibridge. During conductivity and viscosity measurements, it is important to maintain the electrolyte at a constant temperature. We have used a constant temperature circulating bath with an accuracy of 0.1 °C. The conductivity was measured from −30 to 60 °C. This temperature range is acceptable for testing conductivity of practical electrolytes for battery applications. The viscosity of electrolytes was measured using a Brookfield viscometer model M/85-150E accurate to 1% of the stated values. The measured value on a Brookfield

**TABLE 1: Optimized Geometry of Ethylene Carbonate Using Various Basis Sets (Distances in Å, Angles in deg)**

	measured	6-311G	6-311G**	6-311++G**
O1−C2	1.15	1.175	1.191	1.168
C2−O3	1.33	1.330	1.359	1.327
O3−C5	1.40	1.412	1.455	1.410
O1−C2−O3	124.08	124.887	125.631	124.831
C2−O3−C5	109	111.677	112.566	111.621

viscometer is translated to centipoise according to the following equation: dial reading × speed factor = viscosity in centipoise (mPa·S).

Raman spectra were collected using a Spex 1403 spectrometer interfaced to an IBM computer. The double monochromator is equipped with two holographic gratings (1800 grooves/mm). The inelastically scattered light was detected by a thermoelectrical and water-cooled Hamamatsu R928 multi-alkali photomultiplier tube followed by conventional photon counting electronics. The 514.5 nm laser line from a Spectra-Physics model 164 Ar$^+$ laser was used for Raman excitation. Interference filters supplied by Spectra-Physics were used to remove plasma lines. The incident laser light was plane polarized and could be rotated by a Spectra-Physics model 310-21 polarization rotator. All spectra were collected using 90° geometry. The liquid samples were contained in high-quality glass capillaries having a 2 mm inside diameter.

Results and Discussion

Ethylene Carbonate Structure and Vibrational Assignment. The structure of EC optimized geometry is

Ethylene carbonate
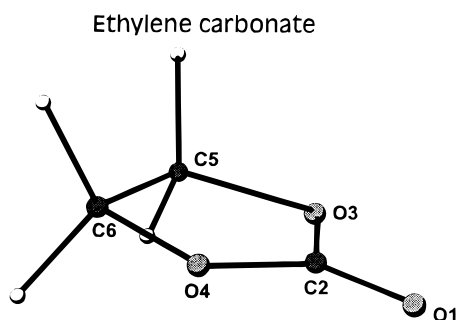
a five-member ring containing two oxygen atoms with a carbonyl group located at the apex. The results of the geometry optimization using several levels of theory in HF are listed Table 1. The calculations compare very well with the published crystal structure,[10] where it was determined that the structure of EC is not planar. However, the structure has been shown to be planar in a gaseous or liquid phase.[11] Recent calculations using HF/D95V** basis set agrees with the conclusion that EC has a planar ring structure in the gas phase.[12]

There have been several studies of EC including FTIR and Raman spectroscopy.[13,14] However, a complete vibrational assignment of infrared and Raman vibrational modes is not available. The symmetry of EC is assumed to be C_{2v} with the ring being planar. EC has 24 fundamental vibrational modes. According to group theory, the number of vibrations of each irreducible representation is

$$\Gamma = 8a_1 + 4a_2 + 5b_1 + 7b_2$$

All of the vibrational modes are Raman-active while only a_1, b_1, and b_2 are infrared-active. The calculated harmonic vibrational wavenumbers at the highest level of theory, 6-311++G**, and their corresponding Raman intensities (given in parentheses) are listed in Table 2. Calculated harmonic frequencies were uniformly scaled by a factor of 0.9 to compensate for the well-known overestimation of the wavenumbers obtained by the HF-SCF method. Observed Raman and infrared wavenumbers are also given. The carbonyl stretching mode is observed at 1794 cm^{-1} in the experimental Raman spectrum, while the calculated value is 1856 cm^{-1}. The strong band at 891 cm^{-1} is attributed to the symmetric ring breathing mode, and its calculated value is 890 cm^{-1}. The ring breathing mode of EC is an important fundamental vibration for the study of the effects of salt solvation. This fundamental vibration is a key marker for EC and allows one to distinguish the EC molecule in EC/PC mixed solvents, since the strong ring breathing in PC is observed at 849 cm^{-1}.

Raman Spectra of EC/PC/LiClO$_4$ Electrolyte Solution. The Raman spectra of EC/PC solutions containing variable lithium perchlorate concentrations were recorded in the 100−3500 cm^{-1} spectral range. Molar ratios range from 20/20/1 (EC/PC/LiClO$_4$) to 1/1/1 (0.3−6.6 M lithium perchlorate). The recorded Raman spectra are illustrated in Figure 1a,b, where the 250−750$^-$ and 750−1000 cm^{-1} regions are displayed separately. The spectra are presented so that the bands affected by the addition of lithium perchlorate can be viewed in detail. There are several vibrational bands whose wavenumber and bandwidth remain unaffected by the addition of lithium perchlorate. For instance, the C−H bending mode of EC located at 1220 cm^{-1} is such an example, and this vibration has been chosen as internal standard for comparisons. There have been some discussion on the behavior of band shifts in EC/PC binary solvent electrolytes.[14,15] The vibrational assignment of observed frequencies for PC, LiClO$_4$, and EC have been previously discussed,[7,16] so that we can focus only on the changes in the spectra of the electrolytes. The areas of interest in the Raman spectral regions are those that showed changes due to solvent−solute interactions with an increase in lithium perchlorate concentration. From the model of molecular dipoles one would expect that the lithium cation would attach itself to the most electronegative part of the solvent molecules. In the case of EC and PC, the carbonyl oxygen would be the most likely positions for the lithium atom. This should result in vibrational energy shift and/or intensity change in the carbonyl end of the molecules while the hydrogen-related vibrations should remain unaffected.

The first significant change in the observed Raman spectra is an increase in the full width at half-maximum (fwhm) of the band at 457 cm^{-1}, which is attributed to both the ring twisting mode of PC and the perchlorate $\nu_2(e)$ band. The intensity increase of the 629 cm^{-1} band assigned to the perchlorate $\nu_4(f)$ vibration is also observed. At same time the relative intensity of the shoulder at 633 cm^{-1}, a coupled ring bending mode and CH$_2$ twist, is unaffected. The band centered at 714 cm^{-1} shows a significant decrease in intensity as the concentration of lithium perchlorate increases while the opposite trend in intensity is observed for the 724 cm^{-1} band with increasing salt concentration (Figure 1a). According to the assignments, the EC out-of-plane O=C ring bending mode is observed at 714 cm^{-1}, and the PC ring distortion mode is seen at 712 cm^{-1}. The new band at 724 cm^{-1} then can be considered to be one (or both) of the above frequencies undergoing a shift of ca. 10 cm^{-1}. The intense band located at 891 cm^{-1}, shown in Figure 1b, is a characteristic vibrational wavenumber of the EC molecule that belongs to the symmetric ring breathing mode. This EC Raman band is well separated from PC Raman modes, and it provides the most significant evidence of EC perturbation due to the

Lithium Perchlorate in Ethylene Carbonate

J. Phys. Chem. B, Vol. 102, No. 24, 1998 **4797**

TABLE 2: Calculated Wavenumbers (cm^{-1}) and Raman Intensities (Å^4/amu) for Ethylene Carbonate and Observed Raman and Infrared Wavenumbers^a

| mode | 6-311++G** | experimental | | assignment |
		Raman	infrared	
$\nu_1(a_1)$	2915 (208)	2931 (s)	2926	C−H stretch
$\nu_2(a_1)$	1855 (12)	1794 (m)	1796	C=O stretch
$\nu_3(a_1)$	1506 (3)	1481 (m)	1486	C5−C6 stretch, H$_2$−C scissors
$\nu_4(a_1)$	1373 (3)		1392	H$_2$C scissor
$\nu_5(a_1)$	1141 (2)	1080 (sh)	1070	C5−C6, O−C stretch
$\nu_6(a_1)$	952 (6)	970 (m)	969	C2−O$_2$, C5−C6 stretch
$\nu_7(a_1)$	890 (18)	891 (vs)	891	ring breathing
$\nu_8(a_1)$	708 (4)	695 (sh)		i.p. ring distortion
$\nu_9(a_2)$	2942 (59)	3003 (s)		C−H stretch
$\nu_{10}(a_2)$	1216 (5)	1232 (sh)		CH$_2$ twist
$\nu_{11}(a_2)$	1134 (0)			H$_2$−C rock, o.p. ring
$\nu_{12}(a_2)$	112 (0)			ring torsion
$\nu_{13}(b_1)$	2964 (64)	3028 (sh)	3040	C−H stretch
$\nu_{14}(b_1)$	1213 (7)	1220 (m)	1218	H$_2$−C twist
$\nu_{15}(b_1)$	825 (0.2)		769	H$_2$−C rocking
$\nu_{16}(b_1)$	789 (1)	714 (s)		o.p. C=O-ring bend
$\nu_{17}(b_1)$	166 (0.2)			o.p. ring bend
$\nu_{18}(b_2)$	2906 (32)	2975 (m)	2960	C−H stretch
$\nu_{19}(b_2)$	1492 (9)		1472	H$_2$−C scissors
$\nu_{20}(b_2)$	1404 (9)		1419	H$_2$−C wag, C2−O stretch
$\nu_{21}(b_2)$	1171 (1)			H$_2$−C wag, C2−O stretch
$\nu_{22}(b_2)$	1075 (0.4)	1097 (m)		O3−C5, O4−C6 stretch
$\nu_{23}(b_2)$	744 (3)	754		i.p. ring distortion
$\nu_{24}(b_2)$	523 (0.4)			i.p. ring-C=O bend

^{a} Abbreviations used: i.p. = in plane, o.p. = out of plane.

addition of lithium perchlorate as can be seen in Figure 1b. The Raman band at 891 cm^{-1} is shifted by 12 cm^{-1} to 903 cm^{-1}. The 891 cm^{-1} band is gradually been replaced by the Raman band at 903 cm^{-1} as the lithium perchlorate concentration increases from 10/10/1 (EC/PC/LiClO$_4$) to 1/1/1. Clearly the 903 cm^{-1} Raman band must be assigned to the associated EC molecule. Correspondingly, the symmetric stretch $\nu_1(a_1)$ of the perchlorate anion, also shown in Figure 1b, is seen at 933 cm^{-1} along with an increasing contribution (as the lithium perchlorate concentration increases) of the vibrational bands that include the solvent-shared ion pairs (938 cm^{-1}) and contact ion pairs (944 cm^{-1}) which appears only in the most concentrated solutions.[7] The broadening due to these contributions is clearly seen in Figure 1b. The region between 1040 and 1100 cm^{-1} contains the ring C−O stretching vibrations of EC and PC, which are also affected by the increase in lithium perchlorate concentration. The vibrations observed between 1200 and 1500 cm^{-1} are various hydrogen−carbon bending modes of both EC and PC which are unaffected by the addition of lithium perchlorate. It is important to point out the change in the band shape of the carbonyl stretches located at 1781 cm^{-1} (PC) and 1794 cm^{-1} (EC) that takes place due to increase concentration of lithium perchlorate as shown in Figure 2. It is well-known that an increase in charge polarization around the carbonyl moieties would decrease the Raman cross section, and the relative intensities of these Raman bands are notably smaller as seen in Figure 2. The spectral data permit to conclude that a specific interaction between the cation and the functional group containing oxygen in both PC and EC takes place. However, the changes observed for the EC band at 891 cm^{-1} provide the most compelling evidence of a strong EC−Li$^+$ interaction.

Raman Spectra of EC/DEC/LiClO$_4$ Electrolyte Solutions. Raman spectra of the EC/DEC/LiClO$_4$ electrolyte solutions with varying molar ratios ranging from 20/20/1 to 1/1/1 (0.3 to 6.6 M lithium perchlorate concentrations) were obtained, and a representative spectral region is shown in Figure 3.

A detailed experimental and theoretical study of the Raman spectra of pure DEC has also been carried out.[16] Considering
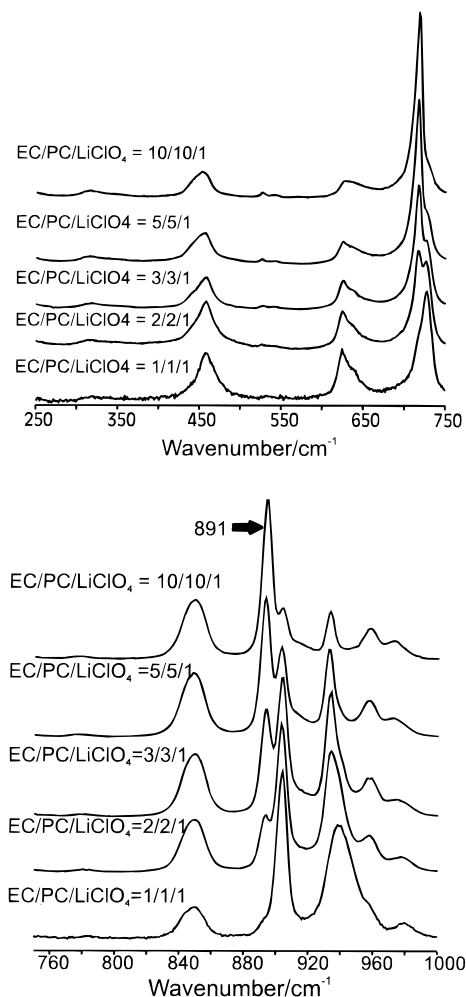

Figure 1. Raman spectra of EC/PC/LiClO$_4$ electrolyte with varying concentrations of salt: (a, top) 250−750 cm^{-1} and (b, bottom) 750−1000 cm^{-1}. The free (891 cm^{-1}) and the associated $\nu_7(a_1)$ mode at 903 cm^{-1} are shown in this spectral region.
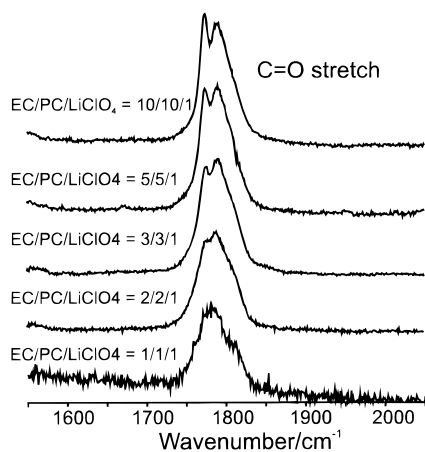
Figure 2. Carbonyl stretching region in the Raman spectra of EC/PC/LiClO$_4$ electrolyte solutions.
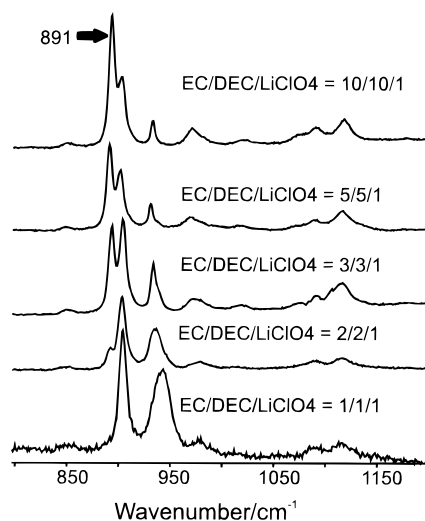

Figure 3. Salt concentration dependence of the Raman spectra of EC/DEC/LiClO$_4$ electrolyte.

the electrolyte solution contains EC, the vibrational band shifts due to EC should occur in EC/DEC/LiClO$_4$ as in the electrolyte solution EC/PC/LiClO$_4$. For instance, the 714 cm^{-1} (C=O ring bending) EC vibrational band undergoes changes due to the increase in lithium perchlorate concentration. This band is solely associated with EC since there are no bands belonging to DEC in this region. The band at 714 cm^{-1} shows a significant decrease in intensity as the concentration of lithium perchlorate increases while at the same time a band at 724 cm^{-1} becomes more intense with increasing salt concentration. However, the 724 cm^{-1} band in the EC/DEC/LiClO$_4$ does not achieve the high relative intensity of the 724 cm^{-1} band in the EC/PC/LiClO$_4$ spectra, confirming the partial contribution from the PC band to the total intensity. It can be seen in Figure 3 that same trend observed for the intense EC band at 891 cm^{-1} (EC ring breathing) in EC/PC/LiClO$_4$ solutions is also seen for EC/DEC/LiClO$_4$ electrolyte solution, where the 891 cm^{-1} band is again shifted to 903 cm^{-1} with increase salt concentration. Similarly, the symmetric stretch $\nu_1(a_1)$ of the perchlorate anion is as expected at 933 cm^{-1} broadened due to the contribution of bands that include the solvent-shared ion pairs (938 cm^{-1}) and contact ion pairs (944 cm^{-1}) at higher electrolyte concentrations. The changes of the carbonyl stretches, with wavenumbers at 1746 cm^{-1} (DEC) and 1794 cm^{-1} (EC), that occur in the Raman spectra with increasing lithium perchlorate concentration are in the band shapes. In fact, the carbonyl bands almost
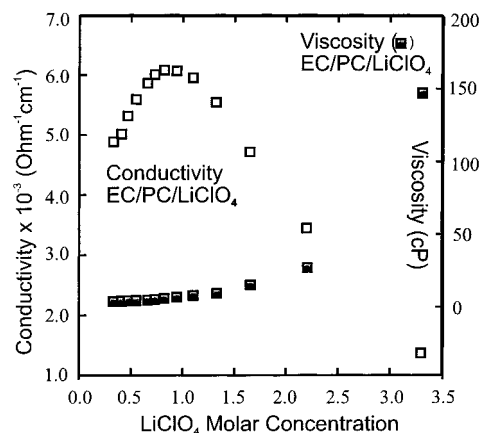

Figure 4. Viscosity and conductivity of EC/PC/LiClO$_4$ as a function of salt concentration.

completely disappear at the highest concentration of lithium perchlorate salt. The observed vibrational wavenumbers in the 2850−3100 cm^{-1} region correspond to the C−H stretching modes are unaffected by the addition of lithium perchlorate.

In conclusion, the Raman studies show that the vibrational band shape of the hydrogen−carbon stretching modes in the region 2800−3200 cm^{-1} do not change even at the highest concentration of lithium perchlorate, indicating that the solvent−ion interaction is highly localized on the oxygen atoms. It can also be said that there is no hydrogen bonding between the perchlorate anion oxygens and hydrogens of the solvent molecules. This is supported by the fact that hydrogen−carbon bending modes, in the region 1200−1300 cm^{-1}, remain unaffected by increase in lithium perchlorate concentration. The lithium oxygen coordination is clearly illustrated by the O=C ring bending mode of EC located at 714 cm^{-1}, which clearly decreases in intensity with increasing salt concentration as the new band of the associated solvent molecule at 724 cm^{-1} gains in intensity. Therefore, as the salt concentration increases, the bands attributed to the coordinated solvent−cation species gain relative intensity in the Raman spectrum of the electrolyte. This effect is particularly well-defined in solutions containing the EC solvent where the band at 891 cm^{-1} (EC ring breathing) is replaced by a band at 903 cm^{-1} at high salt concentrations.

Lithium Perchlorate Concentration Dependence of Viscosity and Conductivity in Binary-Solvent Electrolyte Solutions. Electrolyte conductivity is the key parameter in selecting an electrolyte for electrochemical devices such as batteries, fuel cells, capacitors, sensors, and electrochromic displays. The conductivity and viscosity were optimized for the binary-solvent electrolyte solutions EC/PC/LiClO$_4$. The results for a 1:1 molar ratio of EC and PC as a function of lithium perchlorate concentration are presented in Figure 4. Similar results were obtained for the electrolyte solution EC/DEC/LiClO$_4$ with a 1:1 EC−DEC molar ratio and are shown in Figure 5. Viscosity for the EC/PC/LiClO$_4$ electrolyte is observed to increase with increase in lithium perchlorate concentration. For lithium perchlorate concentrations from 0.33 M (EC/PC/LiClO$_4$ = 20/20/1) to 3.3 M (EC/PC/LiClO$_4$ = 2/2/1), viscosity changes from 3.82 to 147 cP. The electrolyte having EC/PC/LiClO$_4$ = 1/1/1 molar ratio (6.6 M) was a solid at room temperature; thus, viscosity data could not be collected at this high concentration. The viscosity data for the EC/DEC/LiClO$_4$ electrolyte behaved in the same manner as the EC/PC/LiClO$_4$ electrolyte, where the viscosity increased with increased lithium perchlorate concentration. However, for lithium perchlorate concentrations
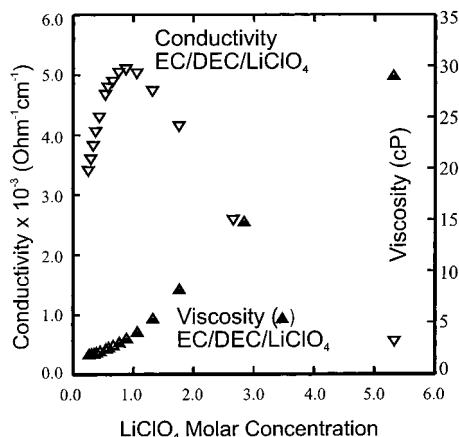
Lithium Perchlorate in Ethylene Carbonate

J. Phys. Chem. B, Vol. 102, No. 24, 1998 **4799**

Figure 5. Viscosity and conductivity of EC/DEC/LiClO$_4$ as a function of salt concentration.

from 0.26 M (EC/DEC/LiClO$_4$ = 20/20/1) to 5.3 M (EC/DEC/ LiClO$_4$ = 1/1/1), viscosity only changes from 1.84 to 29.0 cP.

Conductivity (Figure 4) increases with increasing lithium perchlorate concentration in the EC/PC/LiClO$_4$ electrolyte until a maximum of 6.1 kΩ^{-1} cm^{-1} is reached at 0.82 M LiClO$_4$ (EC/PC/LiClO$_4$ = 8/8/1), after which the conductivity decreases rapidly between 0.82 and 3.3 M to a minimum of 1.4 kΩ^{-1} cm^{-1}. In a similar fashion, the conductivity of EC/DEC/LiClO$_4$ (Figure 5) increases with increasing lithium perchlorate concentration until a maximum of 5.1 kΩ^{-1} cm^{-1} is obtained at a lithium perchlorate concentration of 0.88 M (EC/DEC/LiClO$_4$ = 6/6/1). Once again the conductivity drops off rapidly between the lithium perchlorate concentrations of 0.88 and 5.32 M, reaching a minimum conductivity of 0.57 kΩ^{-1} cm^{-1}.

It is informative to take a close look at the curve from the EC/PC/LiClO$_4$ viscosity data shown in Figure 4. Notably, the viscosity remains relatively constant from 0.33 M (EC/PC/ LiClO$_4$ = 20/20/1) to 0.82 M (EC/PC/LiClO$_4$ = 8/8/1). The change in viscosity over this range is approximately 2 cP. For lithium perchlorate concentration range between 0.82 and 3.3 M the viscosity increases form 5.9 to 147 cP, giving a total change in viscosity of approximately 141 cP. This rapid increase in viscosity may be attributed to the association of Li$^+$ cations with ClO$_4^-$ anions, resulting in the formation of solvated complexes.[7,17] Evidence for the formation of these solvated complexes is complementary provided by the conductivity measurements and Raman spectroscopy. When lithium perchlorate is added to the solvent mixtures, the dissociated Li$^+$ are associated with individual EC and PC molecules. As these associated species form, the ions are accommodated in the voids available in the solvent, which contributes to the overall conductivity enhancement.[18-20] As mentioned, the conductivity increases with increased lithium perchlorate concentration until a maximum is obtained at 0.82 M (EC/PC/LiClO$_4$ = 8/8/1) lithium perchlorate. This can be qualitatively explained as resulting from a favorable combination of the high dielectric constant binary solvent along with the small change in viscosity in this binary system. With the high dielectric binary solvent, lithium perchlorate will have a large degree of ion dissociation. Increase of lithium perchlorate concentration beyond 0.82 M causes the conductivity to drop off quickly. This decrease in ionic conductivity is due to the influence of viscosity on the mobility of Li$^+$ which reduces the mobility and the number of Li$^+$ charge carriers. An increase in viscosity is also attributed to the formation of ion pairs and ion aggregates, evidence of which is supported by the Raman spectroscopic data. The viscosity data from the EC/DEC/LiClO$_4$ tells a different story
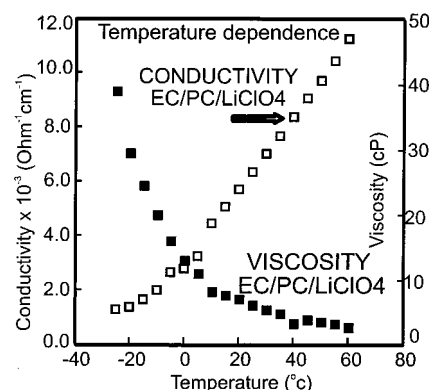

Figure 6. Temperature dependence of viscosity and conductivity for the EC/PC/LiClO$_4$ electrolyte.

from that of the EC/PC/LiClO$_4$ electrolyte. The viscosity remains relatively constant over a greater range than EC/PC/ LiClO$_4$; from 0.26 M (EC/DEC/LiClO$_4$ = 20/20/1) to 1.32 M (EC/DEC/LiClO$_4$ = 4/4/1) the change in viscosity over this range is approximately 3.5 cP. For lithium perchlorate concentration range between 1.32 and 5.32 M the viscosity increases from 5.30 to 29.0 cP, giving a total change in viscosity of approximately 23.7 cP.

Temperature Dependence of Viscosity and Conductivity in Binary-Solvent Electrolyte Solutions. In general, electrolyte conductivity increases as the temperature of the electrolyte is raised. This behavior is mainly due to increase in fluidity of the system at higher temperatures and to an increase in the number of mobile ions. The performance of the electrolytes over a large temperature range is of interest in practical applications. Results for the temperature dependence of conductivity and viscosity of the EC/PC system are presented in Figure 6. Data were collected over the temperature range −30 to 60 °C, which is the expected temperature range that would be useful in practical cells. The concentrations of lithium perchlorate in all measurements are at maximum conductivity for the particular binary-solvent electrolyte solution.

For the electrolyte solutions EC/PC/LiClO$_4$ and EC/DEC/ LiClO$_4$ the maximum conductivity decreases rather rapidly with decreasing temperature. The effect has been explained as being predominantly due to the viscosity increase with decreasing temperature. This expected behavior is due to decrease in fluidity of the system at lower temperatures and to the decrease in the number of mobile ions.

When the temperature was lowered to −22 °C during the viscosity and conductivity measurements of the EC/DEC/LiClO$_4$ solution, a solid formed around the cylinder walls in the viscometer cell and the conductivity sample cell. The formation of the solid prevented further viscosity measurements, and the conductivity dropped off dramatically. The liquid component was separated from the solid component; the solid was then rinsed with DEC solvent. Raman spectroscopy was performed on each of the components to determine the composition. The solid phase is comprised predominantly of EC but also contains a small amount perchlorate anion. On the other hand, the liquid phase contains mainly the DEC solvent along with dissolved perchlorate anion as indicated by the corresponding bands associated with the perchlorate anion shown in Figure 7. This is a clear indication of phase separation of EC at the lowest temperatures. The fact that EC retains a fair amount of the salt, even after rinsing with DEC solvent, is another indication of stronger solvation of the cation by the EC solvent. This question was further investigated by theoretical methods, and the results are discussed in the last section.
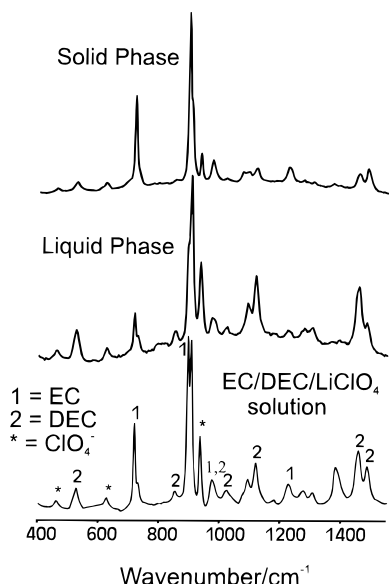
Figure 7. Raman spectra of the EC/DEC/LiClO$_4$ electrolyte (lower trace) and that of the phase-separated solid and liquid.

Ethylene Carbonate Concentration Dependence of Viscosity and Conductivity in Binary-Solvent Electrolyte Solutions. From the lithium perchlorate concentration dependence of viscosity and conductivity, it was found that a lithium perchlorate concentration of approximately 0.8 M gave the highest conductivity for the solutions EC/PC/LiClO$_4$ and EC/DEC/LiClO$_4$. Considering that ethylene carbonate was chosen for its positive influence on the conductivity of the electrolyte solutions, the ethylene carbonate concentration dependence of conductivity and viscosity of three binary solvent solutions EC/PC/LiClO$_4$, EC/DEC/LiClO$_4$, and EC/DMC/LiClO$_4$ were studied. The addition of dialkyl carbonate solvents with high fluidity to ethylene carbonate solutions enhances the ionic motion and lowers the viscosity of the electrolyte.

Conductivity and viscosity measurements for all three types of binary-solvent electrolyte solutions with a lithium perchlorate concentration of 0.8 M (EC/PC/LiClO$_4$, EC/DEC/LiClO$_4$, EC/DMC/LiClO$_4$) and with varying percent EC content at 25 °C were carried out. The viscosity measurements show that there is small change in the EC/PC/LiClO$_4$ electrolytes (remains constant at around 6 cP), while the binary solvents of EC/DEC/LiClO$_4$ and EC/DMC/LiClO$_4$ show a continuous increase in viscosity with increasing EC content. (The viscosity of pure EC could not be measured since it is a solid at room temperature.)

Pure EC possesses intermolecular association, as observed through dielectric constant measurements.[19] The behavior of the EC/PC electrolyte solution viscosity suggests that the interaction between EC and PC is such that the basic network of intermolecular association resembles that of pure PC or EC and remains relatively unaffected; the similarity in the structure of PC and EC allows the viscosity to remain constant even at 90% EC content. Results from the viscosity measurements of the binary-solvent mixtures of EC/DEC and EC/DMC suggest that the intermolecular association in EC is disrupted, and the individual EC and DEC (or DMC) molecules are loosely bound together to give rise to a less structured solution. Similar behavior has been observed in binary-solvent electrolytes made up of EC and tetrahydrofuran (THF) and also systems comprised of water and formamide.[21]

The conductivity results for the three binary-solvent electrolytes with varying EC content are presented in Figure 8. The
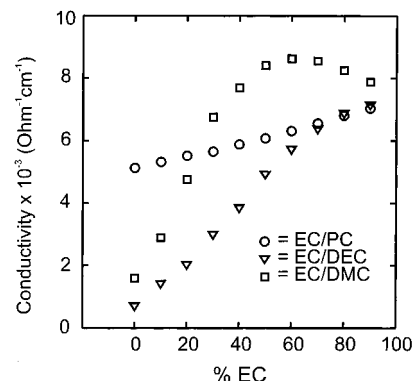

Figure 8. EC concentration dependence of conductivity for the binary solutions: EC/PC/LiClO$_4$, EC/DEC/LiClO$_4$, and EC/DMC/LiClO$_4$.

TABLE 3: Ground-State Energies (kJ mol^{-1}) ab Initio Calculations Using the HF/6-311++G Basis Set[a]**

solvent	pure solvent	solvent + Li$^+$	solvation energy
EC	−894 337.96	−913 560.79	−224.6
PC	−996 901.25	−1 016 098.89	−199.4
DEC	−110 2467.81	−1 121 667.57	−201.5
DMC	−897 413.44	−916 602.03	−190.4

[a] The Li$^+$ energy (HF/6-311+G*) was calculated to be −18 998.16 kJ mol^{-1}.

conductivity increases with increasing EC content in the solvent mixtures. Conductivity passes through a maximum at around 60 vol % EC in EC/DMC, while the conductivity increases at a relatively constant rate for EC/DEC where the maximum appears to occur upon reaching pure EC. The appearance of the conductivity maximum in the EC/DMC solvent mixture can be qualitatively explained as arising from a favorable combination of high dielectric solvent EC and the low viscosity of DMC.

Selective Solvation in Binary Solvent Electrolyte Solutions. The problem of the local structure around the lithium cation in mixed solvent electrolyte solutions is an important issue here. When dealing with electrolyte solutions comprised of two solvents, selective solvation of the lithium cation may occur. The study performed by Hyodo and Okabayashi[21] concluded that selective solvation was not confirmed in the EC/PC/LiClO$_4$ binary solvent solution. The experimental results on transport properties suggest selective solvation to EC. To help the physical interpretation, we have carried out the quantum chemical calculations of vibrations for all the solvents EC, PC, DMC, and DEC studied in this work, and the selective solvation problem was also approached using ab initio quantum chemical calculations. The program Gaussian92 was used for ab initio SCF molecular orbital computations. The starting geometry was taken from the geometry optimization attained with the HF/6-311++G** basis set.[16] The lithium cation was positioned in a 180° geometry with respect to the carbonyl group of each solvent molecule. Upon performing a full optimization, the lithium cation was allowed to move; in other words, the parameters for the bond length, angle, and dihedral angle were set as variables. Binding energies were calculated by subtracting the ground-state energies of free solvent and free lithium cation from the singly coordinated Li$^+$−solvent. Results from the calculations are presented in Table 3.

Experimentally, the binding of Li$^+$ to water has been studied by high-pressure mass spectroscopy[22] and to O(CH$_3$)$_2$ and formaldehyde by ion cyclotron resonance.[23] Blint[12] found that the experimental results agreed closely to the calculated results with the HF/D95V** basis set for the binding energies of Li$^+$ to water and O(CH$_3$)$_2$ and at the most disagreed by 2 kcal/mol

TABLE 4: Calculated Heats of Formation for the Coordination of EC to Li$^+$ Using the HF/6-31G Basis Set

reaction	ΔH (kJ/mol)	Li$^+$$-$O distance (Å)
Li$^+$ + (EC) → Li$^+$(EC)	−247.9	1.74
Li$^+$(EC) + (EC) → Li$^+$(EC)$_2$	−190.1	1.78
Li$^+$(EC)$_2$ + (EC) → Li$^+$(EC)$_3$	−112.2	1.85
Li$^+$(EC)$_3$ + (EC) → Li$^+$(EC)$_4$	−62.0	1.93
Li$^+$(EC)$_4$ + (EC) → Li$^+$(EC)$_5$	7.9	2.07
Li$^+$(EC)$_5$ + (EC) → Li$^+$(EC)$_6$	2.5	2.16

(8 kJ/mol). Using the HF/D95V** basis set, the binding energy of Li$^+$ to EC was calculated to be −52.0 kcal (−217.7 kJ/mol), while the calculation using the basis set HF/6-311++G** resulted in a binding energy of −53.6 kcal/mol (−224.6 kJ/mol). The application of HF/6-311++G** should give satisfactory results for the relative binding energies of the solvents in this study. Results from the HF/6-311++G** calculations show that the single coordination of EC to Li$^+$ is favored over that of Li$^+$ coordinating to PC by the amount of about 26 kJ/mol.

Finally, the question of the number of EC molecules in the primary solvation shell of the cation is outstanding. The number of EC molecules that can coordinate the lithium cation may be determined using an approximate enthalpy of reaction for coordination:

$$\Delta H_r = E[\text{Li}^+(\text{EC})_n] - E[\text{Li}^+(\text{EC})_{n-1}] - E(\text{EC})$$

where E represents the ground-state calculated energies, n is the number of solvent molecules, and ΔH_r is the enthalpy of the coordination reaction. The coordination reaction that corresponds to the enthalpy of reaction can be written as

$$\text{Li}^+(\text{EC})_{n-1} + \text{EC} \rightarrow \text{Li}^+(\text{EC})_n$$

For the coordination calculations, specific symmetries were imposed. For Li$^+$(EC)$_2$ the EC ligands were positioned 180° from each other. For Li$^+$(EC)$_3$ the EC molecules are trigonal planar, tetrahedral for Li$^+$(EC)$_4$, trigonal bipyramidal for Li$^+$(EC)$_5$, and octahedral for Li$^+$(EC)$_6$. The orientation of the molecules in each of the coordinated systems was selected to give the highest symmetry. Results for the calculated heats of formation for complexes of EC with Li$^+$ are presented in Table 4.

The heats of formation of the first four complexes result in exothermic reactions, suggesting that the formation of Li$^+$(EC)$_4$ is favorable. These results are in full agreement with the conclusions derived from Raman intensity data.[19,20]

Conclusions

The transport properties of binary-solvent solutions formed by dissolving lithium perchlorate in EC combined with one of PC, DEC, or DMC have been measured. The addition of high fluidity solvents enhances the ionic motion, and lower viscosity and maximum conductivity are achieved for the EC/DMC/LiClO$_4$ system. At low temperature the EC selective solvation of lithium ion in a solution of mixed solvents become evident. A theoretical calculation supports a more selective solvation for the EC solvent within the group. In the Raman spectrum the ring breathing vibration observed at 891 cm^{-1} in the EC solvent is gradually been replaced by a Raman band at 903 cm^{-1} as the lithium perchlorate concentration increases from 10/10/1 (EC/PC/LiClO$_4$) to 1/1/1. The 903 cm^{-1} Raman band is assigned to the associated EC molecule. Shifts observed in characteristic vibrational probes observed in the Raman spectra confirm that the Li$^+$ interacts with the solvents through the C=O bonds. Conductivity was found to increase with the increase in electrolyte concentration for all solutions until a maximum was reached at approximately 0.8 M. At higher salt concentrations the conductivity decreased dramatically, a behavior that may be explained by the increased occurrence of contact ion pairs and ion aggregate formation in solution.

References and Notes

(1) Batteries for portable applications and electric vehicles: Holmes C. F., Landgrebe, A. R., Eds. The Electrochemical Society, Proceedings, Vol. 97−18, **1997**.

(2) Ohzuku, T.; Ueda, A. J. *Electrochem. Soc.* **1997**, *144* (8), 2780.

(3) Novack, P.; Müller, K.; Santhanam, K. S. V.; Heas, O. *Chem. Rev.* **1997**, *97*, 207.

(4) Bicke, P.; Chu, W. F.; Weppner, W. *Solid State Ionics* **1997**, *93*, 1.

(5) Zaghib, K. The Prospects for Lithium-Ion Batteries in Japan: Workshop for Li-Ion Batteries and Supercapacitors, Reno, NV, USA, 1995.

(6) Rahner, D.; Machill, S.; Ludwig, G., of Power Sources, J.; **1995**, *54*, 378.

(7) Battisti, D.; Klassen, B.; Nazri, G. A.; Aroca, R. *J. Phys. Chem.* **1993**, *97*, 5826.

(8) Abraham, K. M.; Alamgir, M. *J. Electrochem. Soc.* **1990**, *137*, 1657.

(9) Klassen, B.; Aroca, R.; Nazri, G. A. *J. Phys. Chem.* **1996**, *100*, 9334.

(10) Brown, C. J. *Acta Crystallogr.* **1954**, *7*, 92.

(11) Angell, C. L. *Trans. Faraday Soc.* **1956**, *52*, 1178.

(12) Blint, R. J. *J. Electrochem. Soc.* **1995**, *142*, 696.

(13) Pethrick, R. A.; Wilson, A. D. *Spectrochim. Acta* **1974**, *30A*, 1073.

(14) Hydodo, S.; Okabayashi, K. *Electrochim. Acta* **1989**, *34*, 1551.

(15) Tobishima, S.; Arakawa, M.; Yamaki, J. *Electrochim. Acta* **1988**, *33*, 239.

(16) Klassen, B. Ph.D. Thesis, University of Windsor, 1996.

(17) Salomon, M.; Uchiyama, M.; Xu, M.; Petrucci, S. *J. Phys. Chem.* **1989**, *93*, 4374.

(18) Barthel, J.; Gores, H. J. *Pure Appl. Chem.* **1985**, *57*, 1071.

(19) Deng, Z.; Irish, D. E. *Can. J. Chem.* **1991**, *69*, 1766.

(20) Deng, Z.; Irish, D. E. *Faraday Trans.* **1992**, *88*, 2891.

(21) Hyodo, S.; Okabayashi, K. *Electrochim. Acta* **1989**, *34*, 1557.

(22) Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466.

(23) Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501.