

The Effect of Salt Concentration on the Conductivity and Viscosity of Binary Mixed Electrolyte Solutions

Frank U Nwokobia¹, Grace A Cooley² and Augustine A Abia¹.

¹Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria.

²Department of Chemistry, Rivers State University of Science and Technology, Port Harcourt, Nigeria

Abstract: Conductivity, density measurements have been used to study the physical and thermodynamic properties of different molar concentrations of lithium perchlorate salt (LiClO_4) in binary mixed solvents of varying proportions of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) at 25 °C. The variation of conductivity with solvent compositions and salt concentrations has been explained based on the changes in viscosity and dielectric constant of the binary mixed solutions. These changes have been attributed to ion-ion, ion-solvent or solvent-solvent interactions in the mixed solutions. The results also show that the viscosity and conductivity of pure and mixed solvents of PC and DME in the presence and absence of LiClO_4 electrolyte are significantly different. However, those of the mixed PC-DME solutions are intermediate between those of the single pure solvents. The conductivity of the mixed solution increased as the concentration of PC with much larger dielectric constant increased, implying greater dissociation of LiClO_4 ions. The calculated values of A and B parameters from Jones-Dole equation indicate that ion-solvent interactions are much stronger than ion-ion and solvent-solvent interactions in the various solutions of LiClO_4 in the binary mixtures of PC and DME solvents. We also established that the mixing ratio of PC-DME system for optimum battery performance is between 63-68% of DME and of the different salt concentrations studied, 0.1 M LiClO_4 (lowest value) solution had the highest molar conductivity.

Keywords: Viscosity, dielectric constant, conductivity, lithium perchlorate, propylene carbonate.

I. Introduction

Various studies have shown that a sustainable battery technology depends on a robust electrolyte that can support high performance electrodes (Kikuko and Yuichi 2004). For high energy density lithium batteries that have found usefulness in a wide range of applications such as in watches, automated cameras, mobile phones etc. any design of its electrolyte solution must be predicated on the interdependence of the performance characteristics of the active materials and electrolyte properties (Kumar and Shukla 2008). Liquid electrolytes suitable for lithium batteries are mostly solutions of binary mixed aprotic organic solvents in which appropriate lithium salts have been dissolved. The selection of the organic solvents and the lithium salts are important in determining the performance of lithium batteries, and most problems from lithium-ion batteries emanate from the wrong choice of the electrolyte materials.

The high chemical activity of lithium metal with aqueous solvents is the reason for which organic aprotic solvents are employed in lithium batteries (Aurbach et al 2004). Ideally, liquid electrolytes are associated with high dielectric constants (so that ions are easily dissociated) as well as low viscosity to facilitate ion transfer. However, it is practically difficult to find solvents with these properties. High dielectric constant or high solvent polarity is also associated with strong solvent-interactions, resulting in enhanced solubility. Hence, mixtures of a solvent with large dielectric constant and high viscosity and a supplementary solvent with low viscosity but small dielectric constant are used to obtain better ionic conductivity (Kikuko and Yuichi 2004).

In commercial secondary batteries, solutions of lithium hexafluorophosphate (LiPF_6) in diethyl carbonate + ethylene carbonate and dimethyl carbonate + ethylene carbonate mixed solvent systems are common electrolyte solutions (Morita et al 1997). However, in primary lithium batteries the most practical liquid electrolytes employed are solutions of LiClO_4 salt in mixed solvents of propylene carbonate + 1,2-dimethoxyethane, and propylene carbonate + dimethyl carbonate (Saito et al 1976).

The most important parameter used to access the performance of any battery is conductivity. Usually, the conductivity of an electrolyte solution is improved by employing binary mixed solvents rather than the single components. For a moderately concentrated solution (for example, 1 mol dm⁻³ LiClO_4), the synergistic effect of mixing two solvents on the conductivity of an electrolyte solution seems to be enhanced mainly by an appropriate combination of a solvent of high dielectric constant and that of low viscous flow (Matsuda et al, 1983). However, solvation of lithium ions in mixed organic electrolyte solutions has been an important problem in the development of advanced batteries. The formation of ion-permeable film at the interface between the negative electrodes and electrolyte solutions of secondary lithium batteries has been reported (Iris, Odziemkowski 1993). Safety has also been reported (Balakrishnan et al. 2006) to be a major concern despite the

plethora of safety standards associated with lithium-ion batteries. There is also a low tolerance level of present-day lithium ion batteries, which is a direct fallout of the inherent chemistry of a system that combines highly reactive substances such as lithiated metal oxides in contact with combustible electrolytes in restricted volume.

Most studies reported on batteries are mainly in isolated areas of interest (Kikuko and Yuichi 2004), (Matsuada et al 1983) with limited investigation on the effect of salt concentration on the conductive properties of binary mixed solvents. Thus this study, embraces the effect of LiClO_4 salt on the electrolytic conductivity, viscosity and dielectric constant of binary mixtures of PC and DME solvents at different volume percent of DME. The combination of high dielectric constant of PC and low viscous flow of DME will hopefully result in synergistic effect that will enhance the performance of lithium ion batteries.

II. Materials And Methods

DME (99.5% pure) and dry LiClO_4 salt were products of BDH Chemicals Ltd., Poole, England. Propylene carbonate (99.5% pure) was from Riedel-DeHaen AG Seelze, Hannover. These samples were used without further purification. The purity of the solvents was assessed by comparing the experimentally determined densities with those reported in the literature at 25⁰C. The experimental and literature density values were in good agreement (Vogel et al 1996). Different mixtures of DME and PC in varying volume proportions; 100%, 75%, 50%, 25% and 0% of DME were prepared. The viscosities, densities and conductivities of these mixtures were measured. The viscosities of the binary mixtures were measured at 25, 40 and 60 ⁰C using a Ubbelohde viscometer while the conductivities were measured at 25⁰C with Orion Thermo conductivity meter. The densities were measured with a density bottle at 25 ⁰C. 0.1, 1.0 and 2.0M solutions of LiClO_4 were prepared in binary mixtures of the solvents in the same volume ratios as above. The conductivity and viscosity of each solution was measured at 25 ⁰C.

III. Results And Discussion

Table 1: Experimental and literature values of some Physical Properties of the organic solvents used in this work at 25⁰C.

Solvent	Density (g/ml) (this work)	Density (g/ml) (literature)	Viscosity (cP) (this work)	Viscosity (cP) (literature)	Dielectric Constant (literature)
DME	0.87	0.86	0.46	0.46	7.20 ^a
PC	1.21	1.20	2.40	2.50	65.00 ^a

a:Vogel et al, 1996.

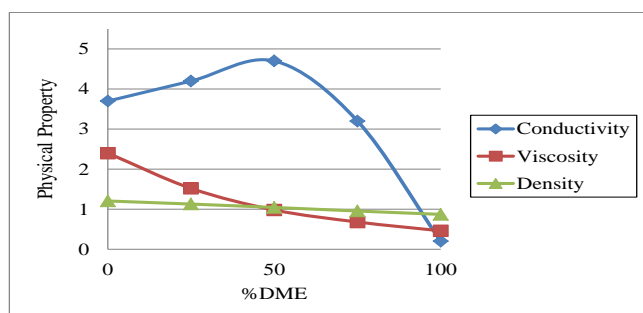


Figure 1: Physical properties of the different volume percent of DME in DME/PC mixtures at 25 ⁰C

Figure 1 shows the dependence of conductivity, viscosity and density on the percentage by volumes of the binary mixed solvents.

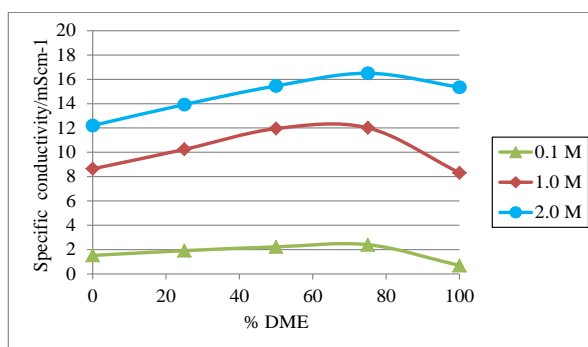


Figure 2; Specific conductivity versus percentage compositions of DME at different concentrations of LiClO_4 and at 25°C .

Figure 2 shows the variation of specific conductivity with solvent compositions and concentrations of LiClO_4 salt. Conductivity is observed to increase as the composition of DME increased with a maximum occurring at approximately 75% composition for all the three concentrations of LiClO_4 after which a sharp decrease is observed. Table 1 shows that the viscosity of PC is approximately five times that of DME. Increasing the composition of DME is therefore expected to reduce the viscosity of PC in a DME/PC binary mixture. Hence, lowering the solvent viscosity should reduce any drag forces associated with ionic mobility thus increasing the conductivity of the solution. However, the maxima at high composition of DME may be suggestive of some complex formation between the binary solvent mixtures and LiClO_4 ions. It is not surprising that the conductivity of the solution increased with increasing concentration of LiClO_4 salt as the number of ions in solution inadvertently increased with increasing concentration of LiClO_4 . Contrarily, Figure 3 shows that the molar conductivity of LiClO_4 in the binary mixed solvents is inversely proportional to the concentration of the salt. Similar observations have also been reported (Matsuda et.al.2000) and were explained on the basis of viscosities and dielectric constants of the individual solvents as well as ion-ion, ion-solvent and solvent-solvent interactions. The molar conductivity of an ion, λ is directly related to its mobility by equation 1;

	$\lambda = z\mu F$	(1)
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where μ is the ionic mobility, z , the ionic charge and F , the Faraday's constant.

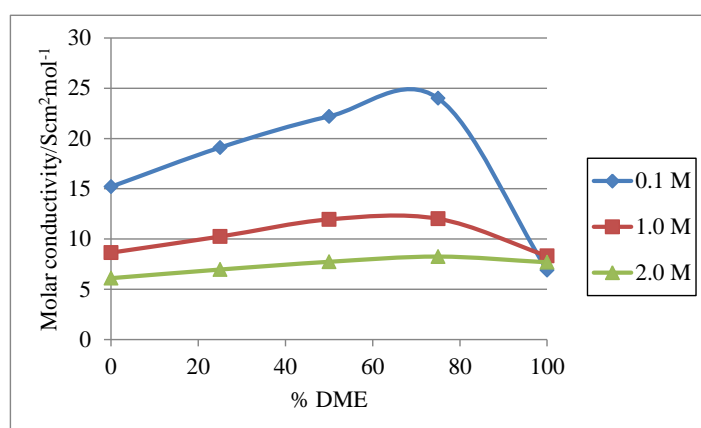


Figure 3: Molar conductivity versus percentage composition of DME at different concentrations of LiClO_4

So, it is imperative from Figure 3 that the more concentrated the solution is, the lower the ionic mobility and the lower the molar conductivity of the electrolyte solution. Overall results show that conductivity is not linear with % DME indicating that there is no monotonous rise in the molar conductivity with mixture composition. However, the measured molar conductivity in each of the different salt concentrations has a maximum value, which indicates that the deviation from the monotonous rise is as a result of the actual lowering of the dielectric constant by the addition of DME, which probably gives rise to ion-pair formation (Gans et.al. 1989).

Nonetheless, dielectric constants also play significant role in the conductivity of a solvent. The relative permittivity, ϵ , gives an indication of the ability of a solvent to separate or dissociate molecules of the electrolyte

salt into its individual ions, and in this case, Li^+ and ClO_4^- ions. From earlier studies, the dielectric constant of binary solvent mixtures was found to vary almost linearly with the solvent composition (Matsuda et.al. 1983). For the present study, the dielectric constant of the mixtures was calculated using the equation developed by Rohdewald and Moldner, 1973(Eq. 2)

	$\epsilon_{\text{mix}} = [(\% \text{DME})\epsilon_{\text{DME}} + (\% \text{PC})\epsilon_{\text{PC}}] / 100$	(2)
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where ϵ_{DME} and ϵ_{PC} are the dielectric constants of pure DME and PC respectively taken from literature. The values of the dielectric constant, viscosity and density of the pure solvents together with their corresponding literature values at 25 °C are shown in Table 1. Figure 4 shows the plot of the calculated dielectric constants of PC-DME mixtures versus the percentage compositions of DME. It is observed that the dielectric constant of the mixtures decreased with increasing composition of DME. This behaviour may be attributed to the overall contributions of the pure solvents based on their individual dielectric constants. From Table 1, the dielectric constant of PC is 65.0 while that of DME is 7.2. It then means that if the composition of DME with smaller dielectric constant increases in its mixture with PC of higher dielectric constant, the overall dielectric constant will decrease.

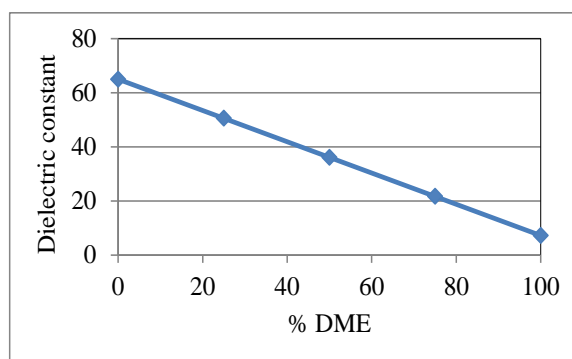


Figure4: Dielectric constant of PC-DME binary mixture versus percentage composition of DME

The viscosities of solutions of different concentrations of LiClO_4 in the binary mixtures of PC and DME at different percentage compositions of DME and various temperatures are plotted and shown in Figure 5. Viscosity is observed to vary directly with concentration of the LiClO_4 ions suggesting that ion-ion interactions greatly enhance the viscosity of ionic solutions. Conversely, viscosity of the mixtures decreases with increasing temperature and composition of DME. It appears then that solvent-solvent interactions are weaker than the interactions between the molecules of the individual solvents leading to an easier flow of solvent mixtures than the single solvents. The decrease in viscosity with temperature is as expected since thermal agitation of molecules will lead to decrease in the viscosity of a solution. As illustrated in Figures 1 and 4 respectively, the densities and dielectric constants of the mixtures vary linearly with the solvent compositions. By implication, the densities and dielectric constants of the mixtures change at a constant rate with composition. In other words, for some fixed change in the composition of the mixture, there is a corresponding fixed change in density and dielectric constant. Studies have shown that lowering the viscosity of electrolyte solutions can improve conductivity (Kikuko and Yuichi 2004). Figure 5 shows that increasing the volume of DME in the mixed solvents reduces the viscosity of the solution; thus retarding any opposition to the movement of the ions in solution. Consequently, ionic mobility is increased leading to increased conductivity as can be seen from the conductivity plot (Figure 2).

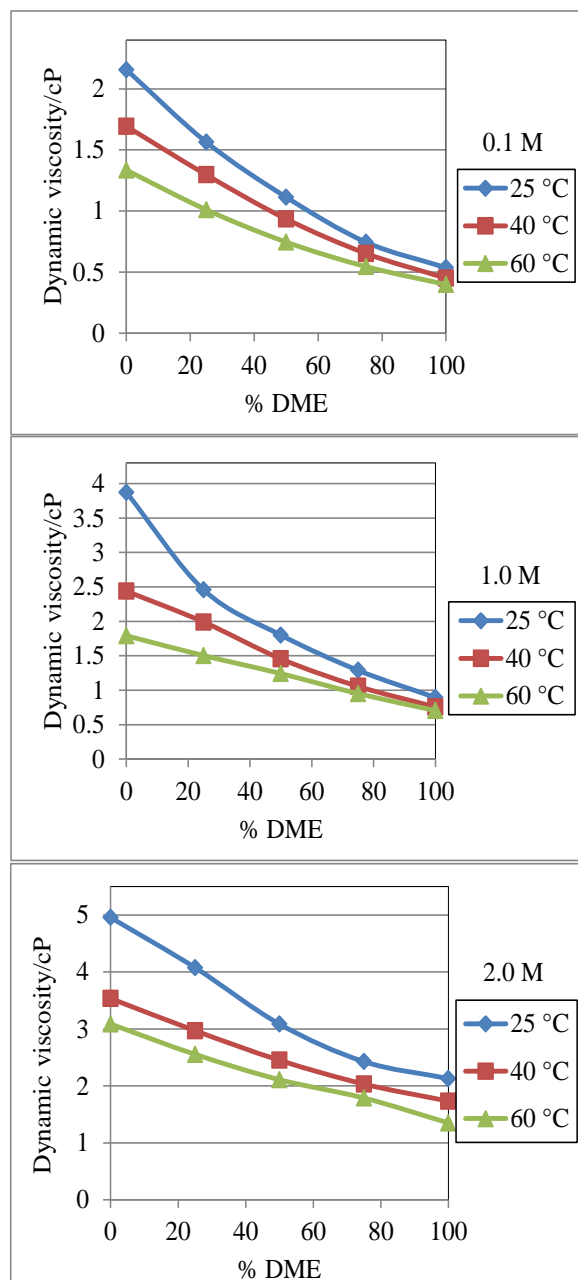


Figure 5: Plot of the viscosity of 0.1, 1.0 and 2.0 M PC-DME binary mixtures versus percentage composition of DME at different temperatures.

The magnitudes of the viscosity values obtained for the three different molar concentrations of LiClO_4 in binary mixtures of PC and DME at a given temperature are in the order 0.1 < 1 < 2 M. This shows that the viscosity of electrolyte solutions in mixed solvent systems is influenced by not only the composition of the solvents but also by the concentration of the electrolyte. In systems with strong ion association, viscosity is affected by the concentration of ions, ion-pairs, solvent and ion-pair-solvent interactions (Matsuda et al. 1983). In 0.1 M solution, the curve is almost linear indicating that the decrease in viscosity is mainly as a result of the increasing volume of DME. As the concentration of the salt increases, the deviation from straight line becomes very significant indicating the existence of other complex interactions.

The conductivity of an ionic solution depends on the concentration of the ions. At very low salt concentration, the salt is completely dissociated and ions solvated and there are strong ion-solvent interactions. Strong electrolytes like LiClO_4 are believed to dissociate completely in solution too. However, the concentration dependence of conductivity is usually linear for dilute solutions but in some highly concentrated solutions, ionic interactions can alter the linear relationship between conductivity and concentration (Penfold et al., 1999). The conductivity of a solution of a strong electrolyte at low concentration follows Kohlrausch's law given as

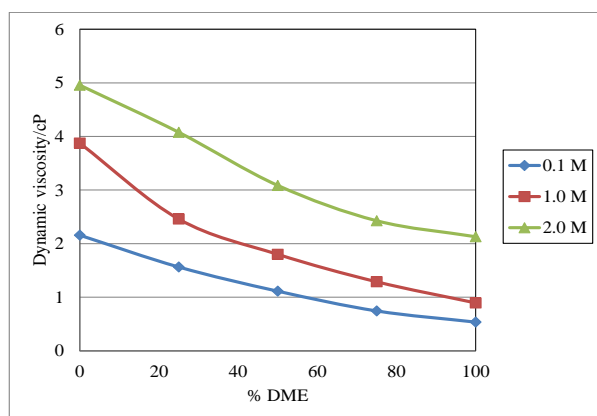


Figure6: Plots of the viscosity of PC-DME binary mixtures versus percentage composition of DME at 25°C and different concentrations of LiClO₄.

$$\Lambda_m = \Lambda_m^o - KC^{1/2} \quad (3)$$

where Λ_m , is the molar conductivity, Λ_m^o , is the limiting molar conductivity, C, is concentration and K, is a constant. To account for other factors affecting the molar conductivity of a strong electrolyte at low concentration, a theoretical interpretation is provided by the Debye-Hückel-Onsager equation (Wright, 2007),

$$\Lambda_m = \Lambda_m^o - (A + B\Lambda_m^o)\sqrt{C} \quad (4)$$

A and B are constants that depend only on known quantities such as temperature, the charges on the ions and the dielectric constant and viscosity of the solvent. As the concentration increases the average distance between the cation and anion decreases and the more the inter-ionic interaction (cation and anion interact) to form an ion-pair thereby retarding the mobility of ions in the solution and leading to decrease in the conductivity of the solution as observed at higher compositions of DME.

Similarly, the Jones-Dole equation is used to explain the effect of salt concentration on the viscosity of mixed solvent systems (Abdulagatov et.al, 2005).

$$\eta_r = \eta/\eta^o = 1 + AC^{1/2} + BC \quad (5)$$

In equation 5, C is the concentration of the solute, η^o is the dynamic viscosity of solvent, η is the dynamic viscosity of solution, η_r is the relative viscosity of solution, A is the Falkenhagen coefficient which describes the impact of charge-charge interactions while B is the Jones-Dole coefficient that gives information on ion-solvent interactions (Ali et.al 2002).

Using the Jones-Dole equation and plotting

$$\frac{\eta}{\eta^o} - 1 \text{ vs. } \sqrt{C}$$

gives the following values of A and B coefficients in the mixed solvents containing 0.1M LiClO₄.

Table 2: Calculated values of A and B from Jones-Dole Equation for 0.1 M solution of DME-PC solvent mixtures at 25 °C.

%DME	A	B
100	0.34	0.60
75	0.05	0.85
50	0.18	0.75
25	-0.14	0.74
0	-0.023	0.98

Table 2 lists the values of A and B calculated from Jones Dole equation. The values of A-coefficient are small and decrease as the composition of DME increase. This suggests that ion-ion interactions are relatively weak and become weaker with increasing composition of DME and have no significant effect on the viscosity of the solutions. The small and decreasing values of A as composition of DME increase also accounts for the same trend in the molar conductivities of the solutions (Figure 3). Though the values of B-coefficients are small too, they are larger than those of A, which implies that ion-solvent interactions are stronger than ion-ion interactions in all the solutions.

IV. Conclusion

Results of the viscosity and conductivity measurements of pure and mixed solvents of PC and DME in the presence and absence of LiClO_4 electrolyte are significantly different. The viscosities, conductivities and dielectric constants of the mixed PC-DME solutions are intermediate between those of the pure solvents. The conductivity of the mixed solution increased at higher concentrations of PC which has large dielectric constant, implying greater dissociation of LiClO_4 ions. The dielectric constant of DME is very low (7.2) compared to that of PC (65.0) and as its concentration increases and that of PC decreases, the dissociation of the salt becomes more difficult leading to a decrease in conductivity. The viscosity of the individual solvents also influence the conductivity of their electrolyte solutions as the easier a solvent mixture flows, the faster it transports the ions in solution.

We have established that the mixing ratio of mixed PC-DME system for optimum battery performance is between 63-68% of DME and the salt concentration with the highest molar conductivity is 0.1M LiClO_4 . This goes to show that though high salt concentration generally indicates increase in the number of ion. It does not however, translate to increase in conductivity.

The calculated values of A and B parameters from Jones-Dole equation indicate that in the solution of the mixed solvent systems and LiClO_4 studied, ion-solvent and ion-ion interactions are weak but that of ion-solvent is strong.

The development of a single, ideal solvent is desirable, but the mixing of several solvents to achieve the desired properties is a more practical solution. It is noteworthy that since electrolytes react with active materials in lithium batteries, the surface chemistry at the anode and cathode is also central to cell performance. Therefore, the design of new electrolyte systems should also consider the properties of the solid electrolyte interphase at the electrodes.

References

- [1]. Ali, A., Nain, A. K., Kumar, N and Ibrahim M (2002): Density and Viscosity of Magnesium Sulphate in Formamide + Ethylene Glycol Mixed Solvents. Proc. Indian Academy of Science, 114 (3): 495-500.
- [2]. Aurbach, D. Talyosef, Y. Markovsky, B. Markevich, E. Zinigrad, E. Asraf, L. Gnanaraj, S.J and Kim, H (2004): Design of Electrolyte Solutions for Li and Li-ion batteries: a review. Electrochimica Acta, 50 (2): 247-254.
- [3]. Balakrishnan, P., Ramesh, R. and Kumar, T. (2006): 'Safety Mechanisms in Lithium-ion Batteries. Journal of Power sources, 155 (5): 401-414.
- [4]. Gans, P. Gill, J. and Longdon, P.J. (1989): Spectrochemistry of Solutions. Part 21- Inner and Outer-sphere complexes of Lithium with thiocyanate in acetonitrile solutions. Journal of the Chemical Society, Faraday Transactions, 85 (7): 1835-1839.
- [5]. Irish, D.E. and Odziemkowski, M. (1993): An Electrochemical Study of the Reactivity at the Lithium Electrolyte/ Bare Lithium Metal Surface. Journal of Electrochemical Society, 140 (6): 1546-1555.
- [6]. Kikuko, H. and Yuichi, A. (2004): Ion and Solvent Diffusion and Ion Conduction Of PC-DEC and PC-DME binary Solvent Electrolytes of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$. Electrochimica Acta, 49 (4): 3397-3402.
- [7]. Kumar, P. T. and Shukla, A. K. (2008): Materials for next-generation lithium batteries. Current Science, 94 (3): 318-325
- [8]. Matsuda, Y., Morita, M. and Kosaka, K. (1983): Conductivity of Mixed Organic Electrolyte Containing Propylene Carbonate and 1,2-Dimethoxyethane. Journal of the Electrochemical Society, 130 (9): 101-104
- [9]. Matsuda, Y., Fukushima, T., Hashimoto, H. and Arakawa, R. (2000): In Proceedings of the 41st Battery Symposium, (Abstract) Japan.
- [10]. Penfold, J., Staples, E., Thompson, L., Tucker, I., Hines, J., Thomas, R. K., Lu J.R. and Warren N. (1999): Structure and Composition of Mixed Surfactant Micelles of Sodium Dodecyl Sulfate and Hexaethylene Glycol Monododecyl Ether and of Hexadecyltrimethylammonium Bromide and Hexaethylene Glycol Monododecyl Ether. Journal of Physical Chemistry, B 103 (25): 5204-5211.
- [11]. Rohdewald, P. and Moldner, M. (1973): Dielectric constant of amide-water systems. Journal of Physical Chemistry, 77 (3): 373-377.
- [12]. Vogel, A.I., Tatchell, A.R., Furnis, B.S., Hannaford, A.J. and Smith, P.W.G. (1996): Textbook of Practical Organic Chemistry, Vogel, 5th Edition, Prentice Hall, NJ.
- [13]. Wright, M.R. (2007): An Introduction to Aqueous Electrolyte Solution. 84293-84295 Wiley, NJ.