

Research Article

Conductivity and Viscosity Studies of Binary Mixtures of Dimethyl Carbonate and Dimethyl Sulphoxide Based Electrolyte for Li-Ion Battery at 298.15k

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Abstract

Conductivity Measurement of Pure solvents of Dimethyl-Carbonate (DMC) and Dimethyl-Sulphoxide (DMSO) and their salt solutions containing 0.1M, 0.5M and 1M Lithium Perchlorate(LiClO₄) were determined with varying percentage solvent compositions (by volume) at 298.15K to determine the applicability of the electrolyte system for Li-ion battery. Densities, viscosities of the different solvent mixtures and their dielectric constant were also determined. The observed variations in conductivity of different solvent composition with LiClO₄ were explained on the basis of changes in viscosities and the dielectric constants. These changes have been said to be due to ion-ion, ion-solvent and solvent-solvent interactions within the mixed binary solutions. The values for viscosities and conductivities of the pure solvents and mixed solvents with LiClO₄ are different. The values for the mixed solvents fall in-between those of the pure solvents. With the addition of DMC, the viscosity of the mixture is lowered. This invariably increases ionic mobility and conductivity is improved. The conductivity decreases at higher concentration due to decrease in solvation. Hence 0.1M LiClO₄ solutions gave the highest molar conductivity.

The ideal mixing ratio of DMC-DMSO binary mixed electrolyte system for best conductivity and invariably battery performance has been established at 50-55% DMC. Since conductivity is higher at lower concentration, it is recommended that more work could be carried out at lower concentrations than 0.1M LiClO₄.

Keywords: Conductivity, Density, viscosity, dielectric constant, battery, solvents, dimethyl-Sulphoxide, electrolyte, ion-solvent interactions

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Introduction

A battery is a source of electrical energy; it converts stored chemical energy to electrical energy [1]. Lithium ion battery (sometimes written as Li-ion battery or LIB) is a rechargeable battery (secondary battery). It is widely used in portable electronics and fast gaining popularity for military electric vehicles, aerospace applications [2], and fast becoming a common replacement for lead acid batteries. Li-ion battery has two electrodes and an electrolyte as basic components. A critical parameter for lithium ion battery is the role of the electrolyte as they act as passage for ionic charges. A good electrolyte should be environmentally friendly, inert to other cells components, good electrical insulator, have a wide electrochemical, mechanical and thermal stability. Above all it should be a good conductor. Recently it has been found that mixtures of cyclic and non-cyclic carbonates are very suitable as solvents for lithium ion-battery as optimum properties desired in an electrolyte is not exclusive in a single material [3]. Binary, ternary and quaternary systems are the primary focus. Nwokobia *et al.* [4], studied properties of binary mixtures of propylene carbonate (PC), and 1, 2-dimethoxyethane (DME) in LiClO₄ for Li-ion battery. Viscosity, density and conductivity measurements were taken by varying solvent ratio. They established the mixing ratio to be between 63-68% DME. Maca *et al.* [5], compared specific conductivity and dielectric constants in different mixtures: Propylene carbonate (PC), ethylene carbonate (EC) and dimethylsulphoxide (DMSO) in different mixing ratios. The mixture of EC and DMSO gave the highest conductivity. Sirvaranja *et al.* [6], prepared electrolyte solution for Li-ion batteries by varying ratios of PC+DMC mixtures in a constant 0.1M salt solution. A maximum conductivity was obtained for 1:1V% PC:DMC. In this work conductivities of different mixtures of DMC-DMSO with different salt concentrations are studied. Conductivity is an important characteristic of an electrolyte and it is crucial for the improved life of the Li-ion battery. The choice of LiClO₄ stems from its property to completely dissociate in solutions and good solvation of its ions. It is used especially in organic solvents and often employed as battery electrolyte [7]. Hence its use in this

study with high dielectric constant of DMSO and low viscosity of DMC is expected to produce good conductivity for improved lithium-ion battery performance.

Materials and Methods

The solvents DMC (99.05%) and DMSO (99%) were from Loba Chemie, India. The salt lithium Perchlorate (95%) is a product of Sigma Aldrich USA. The purity of the solvents was ascertained by measuring the densities at 298.15K and comparing them to what is reported in literature. The experimental and literature values were in good agreement (table 1) Samples containing DMC and DMSO in different proportions 100%, 70%, 50%, 30%, 20%, 10% and 0% were prepared. 0.1M, 0.5M and 1M solutions with LiClO₄ were also prepared in the same volume ratios as above. 0.11g, 0.523g and 1.064g of salt (LiClO₄) were dissolved in 10ml of each mixed solvent combination to give 0.1M, 0.5M and 1M solutions respectively. The weighing was done on a GulFex FA 2104A electronic weighing balance with a precision at ± 0.001 g. The densities were measured with a density bottle and the viscosity measurements were carried out using an Ubbelohde kinematic viscometer. Conductivity measurement was taken with a KC, model DDS-11A conductivity meter.

Results and Discussions

Table 1 Experimental and literature values of some physical properties of the DMC and DMSO at 298.15k

Solvent	Density(g/cm ³) (experimental)	Density (g/cm ³) (literature)	Viscosity (cP) (experimental)	Viscosity (cP) (literature)	Dielectric constant (literature)
DMC	1.068	1.069	0.644	0.630	3.1 [8]
DMSO	1.094	1.100	2.022	1.998	47 [8]

Table 2 Density, kinematic viscosity (Cs) and dynamic viscosity (cP) of pure and mixed solvents of DMC and DMSO at 298.15k

Sample % DMC	Density	Kinematic viscosity(Cs)	Dynamic viscosity(cP)
0	1.094	1.848	2.022
10	1.089	1.737	1.892
20	1.085	1.579	1.714
30	1.081	1.391	1.504
50	1.078	1.180	1.273
70	1.074	0.858	0.921
100	1.068	0.603	0.644

The kinematic viscosity was calculated using the equation below

$$v = kt \quad (1)$$

Where v is the kinematic viscosity, k is the viscometer constant while t is the flow time through the viscometer capillary. The dynamic viscosity is estimated from the kinematic viscosity and density measurements using the equation:

$$\eta = v\rho \quad (2)$$

η is dynamic viscosity and ρ is the density of the mixture.

Table 3 Specific Conductivity (mS/cm) measurement of mixed solvents of DMC and DMSO at 298.15K

Sample %DMC	0.1M LiClO ₄	0.5M LiClO ₄	1M LiClO ₄
0	2.16	7.90	9.44
10	2.17	9.10	10.91
20	2.68	9.77	11.38
30	3.26	9.88	12.13
50	3.62	10.37	12.47
70	3.17	9.40	9.75
100	0.20	3.04	9.44

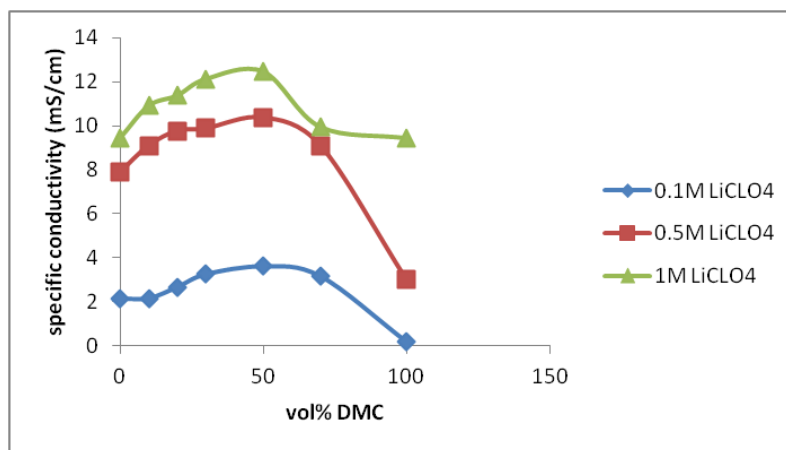


Figure 1 plot of specific conductivity versus volume% DMC at 298.15K

Figure 1 shows the variation of specific conductivity with distinct solvent composition and concentrations of LiClO_4 . As the percentage composition of DMC is increased, conductivity increases. A maximum value is observed at 50% DMC. With the addition of DMC which has a lower viscosity, the viscosity of the solution reduces and ionic mobility expectedly increases thus, conductivity of the mixture increases. At higher concentration of LiClO_4 , there is increase in specific conductivity, this is due to the fact that more ions are present in solution at higher concentrations.

Table 4 Molar conductivity ($\text{Scm}^2\text{mol}^{-1}$) measurement of mixed DMC and DMSO at 298.15K

Sample %DMC	0.1M LiClO_4	0.5M LiClO_4	1M LiClO_4
0	20.70	15.80	9.45
10	21.60	18.20	10.91
20	26.80	19.54	11.38
30	32.26	19.76	12.13
50	36.20	20.74	12.47
70	31.70	18.80	9.75
100	2.00	6.03	9.44

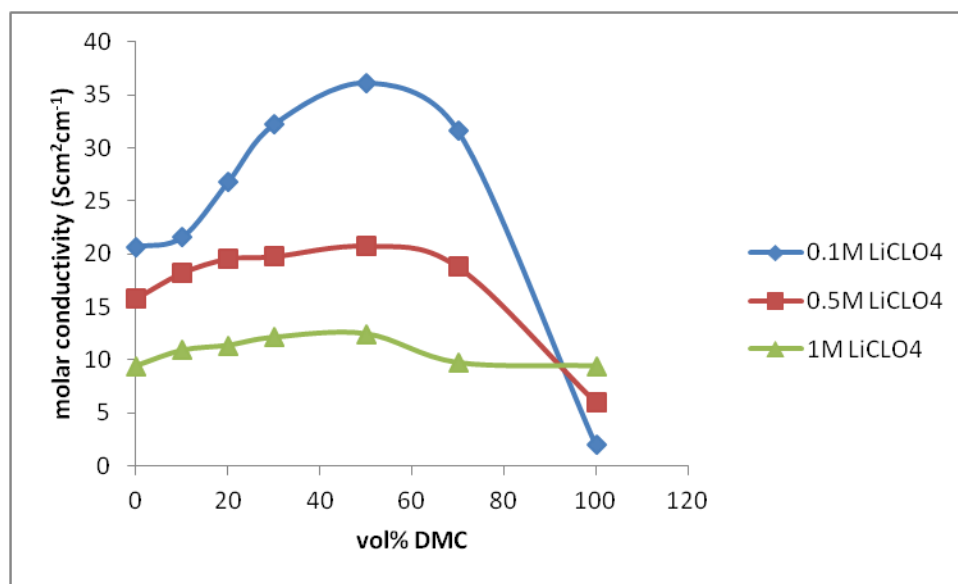


Figure 2 Plot of molar conductivity versus volume % DMC at 298.15K

Figure 2 shows that molar conductivity of the mixtures is inversely proportional to the concentration of the salt. Matsuda *et al.* [9], made same observations which they founded on changes in viscosities and dielectric constants and also ion-ion, ion-solvent and solvent-solvent interactions. Figure 2 shows that the highest molar conductivity values were obtained with 0.1M LiClO₄. Concentration of ions influences the conductivity of an ionic solution. At very low concentration, the salt is completely dissociated and its ions solvated which give rise to strong ion-solvent interactions. LiClO₄ is a strong electrolyte [7]. At higher concentration, there are more inter-ionic interactions as the average distance between ions decreases and there is possibility of ion-pair formation which will retard the mobility of ions thus, conductivity is decreased [10]. The conductivity of a solution of strong electrolyte at low concentration follows Kohlraush's law given below as

$$\Lambda_m = \Lambda_m^0 - Kc^{1/2} \quad (3)$$

Where Λ_m is the molar conductivity, c is the concentration Λ_m^0 is the limiting molar conductivity and K is a constant.

Table 5 Dielectric constant of pure and mixed solvents at 2298.15K

Sample% DMC	Dielectric constant
0	47.00
10	42.61
20	38.22
30	33.83
50	25.05
70	16.27
100	3.1

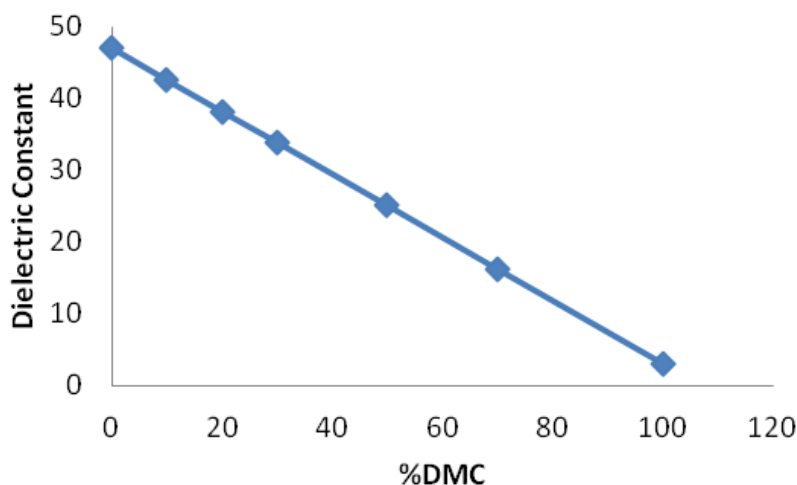


Figure 3 Plot of dielectric constant versus concentration vol% DMC at 298.15K

In **Figure 3**, the dielectric constant varies directly with solvent composition. Such observations in a binary mixture have been made by earlier studies [11]. The dielectric constant was estimated in this study by using equation 4 developed by Rohdewald *et al.* [12].

$$\epsilon_{\text{mix}} = [(\% \text{DMC})\epsilon_{\text{DMC}} + (\% \text{DMSO})\epsilon_{\text{DMSO}}]/100 \quad (4)$$

Where ϵ_{DMC} and ϵ_{DMSO} are the literature values at 298.15K of the dielectric constants of pure DMC and DMSO respectively as can be seen in **Table 3**. The dielectric constant of the mixtures decreased with increasing composition of DMC which has a low dielectric constant of 3.1 as against DMSO's dielectric constant of 47. This implies that dielectric constant is an additive property of the solvents. Dielectric constant however affects the conductivity of an ionic or electrolytic solution. A high dielectric constant indicates that a solvent is highly capable to dissociate molecules of an electrolyte. From Figure 2, the molar conductivity is on a steady rise and reaches a peak at 50% DMC after which, there is a decline. The deviation from the steady rise may be attributed to the lowering of the dielectric

constant by the increasing composition of DMC which may have given rise to ion-pair formation. According to Gans *et al* [13], solvents with dielectric constant in the region of 20-40 have the tendency for ion pair formation. This is not a desirable factor as it can result in decrease in conductivity.

Table 6 Dynamic viscosity (cP) of pure and mixed solvents of DMC/DMSO with different LiClO₄ concentration at 298.15k

%DMC	0.1M	0.5M	1M
0	2.410	2.499	3.815
10	2.022	2.433	3.469
20	2.159	2.262	3.415
30	1.565	1.711	2.901
50	1.321	1.366	2.361
70	1.102	1.255	1.927
100	0.687	0.906	1.747

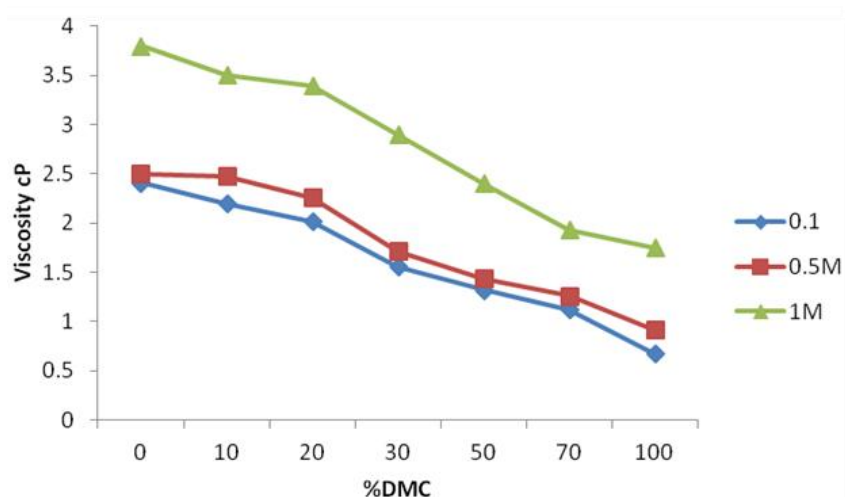


Figure 4 Plot of viscosity of different concentration of salt solution versus %DMC at 298.15K

In **Figure 4**, it can be seen that the addition of the lower viscous DMC reduces the viscosity of the solution as was the case with the pure mixed solvents (Table 2). Viscosity varies directly with concentration of LiCO₄ suggesting that viscosity of the mixture is not only affected by composition of solvents, but interactions between ion and solvent molecules influence electrolyte viscosity. This has been observed from previous studies. Matsuda *et al* (1983) stated that apart from solvent composition, other factors which include concentration of ions, solvent-solvent and solvent-ion interactions affect the viscosity of a bulk solution. From Figure 4, the viscosity of the solution is lowest in the order of 0.1M < 0.5M < 1M. The lowest viscosity observed with 0.1M salt is associated with its best molar conductivity as seen in Figure 2. This is as a result of increased ionic mobility. At higher concentrations, ionic mobility is retarded as more complex interaction between the larger number of ions present in solution may occur and this is due to the reduction in average distance between ions.

Conclusion

The results of viscosity and conductivity measurements are in-between those of pure solvents. The conductivity of the mixture with LiClO₄ improved with the complementary factors of the low viscous DMC which results in increased ionic mobility and high dielectric constant of DMSO for increased salt dissociation. Salt concentration also influenced conductivity. Conductivity was in the order of 0.1M > 0.5M > 1M showing that despite that they are more ions in solution at higher salt concentration, it does not necessarily lead to increase in conductivity. The inference here is that the use of mixed solvents electrolyte system is advantageous over use of pure solvents as the properties of electrolyte solutions necessary for improved battery performance are enhanced. The ideal mixing ratio of the DMC-DMSO binary mixed system for optimum battery performance has been established at 50-55% DMC.

References

- [1] Daniel H., Craft, C. and Doughty, C. (2002). Electrical Energy storage systems; Abuse text manual for electric and hybrid vehicle applications, sandia national laboratories. 110(2), 253-480.
- [2] Ballon, M.S. (2008). "Electrovaya, Tata motors to make electric indica" viewed 4th November 2016, <https://cleantech.com>
- [3] Betrand, G., Armand, M. and Marlier, G. (2014). Fire behavior of carbonates- based electrolyte Journal of power sources 269(1), 804-811.
- [4] Nwokobia F. U. (2010). Properties of mixed binary electrolyte of propylene carbonate and 1, 2-Dimethoxy ethane with Lithiumperchlorate for high density batteries 62.
- [5] Maca, J., Frk, M. and Sedlarikoma, M. (2013). Properties of electrolytes for lithium ion battery for higher fire safety Journal of Applied Electrochemistry vol34(1), 1120-1125
- [6] Sivaraja, N., and Hirankamar, H. (2014). Conductivity and dielectric behavior of organic binary solution and electrolyte for lithium-ion battery. International Journal of chemtech Research 6(13), 5280-5285
- [7] Xu, k. (2004). Non-aqueous liquid electrolyte for lithium-ion based rechargeable batteries PDF chemical reviews 14(10) 4303
- [8] Vogel, A.I., Tatchell, A.R., Furnis, B.S., Hannaford, A.J. and Smith, P.W.G. (1996). Vogel Textbook of Practical Organic Chemistry, Vogel, 5th Edition, Prentice Hall, NJ.
- [9] Matsuda, Y., Fukushima, T. Hashimoto, H. and Arakawa, R. (2000) In proceedings of the 41th battery symposium, (abstract), Japan.
- [10] Penfold, J., Saples, E. Thompson, L. Tucker, I. Hines, J. Thomas, R. Lu, J.R. and Warren, N. (1999). Structure and composition of mixed surfactant micelles of sodium dodecyl sulphate and hexaethylene glycol monododecyl esterad of hexadecyltriethylammonium bromide and hexaethylene glycol monododecyl ether. Journal of physical chemistry. B103(25) 5204-5211
- [11] Matsuda, V., Morita, M. and Kosaka, K. (1983). Conductivity of mixed organic electrolyte containing propylene carbonate and 1, 2-Dimethoxyethane, Journal of electrochemical society 130(1) 101-104.
- [12] Rohdewald, P., and Moldner, M. (1973). Dielectric constant of amide-water systems. Journal of physical chemistry. 77(3) 373-377
- [13] Gans, p., gill, J.B. and Longdon, P.J. (1989). Spectrometry of solutions. Part 21- Inner and outer-sphere complexes of lithium with thiocynate in acetonitrile solutions. Journal of chemical society faraday trans. 1, 85(7), 1835-1839

Publication History

Received	19 th July 2017
Revised	11 th Aug 2017
Accepted	14 th Aug 2017
Online	30 th Aug 2017

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