International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 10 Issue 3 ǁ 2022 ǁ PP. 62-67

Conductivity and Viscosities Studies of Mixed Organic Electrolyte Solvents of Propylene Carbonate, Diethyl Carbonate and Dimethylformamide for High Energy Density Lithium-ion and Magnesium -ion Batteries at 298.15K.

Edimeh A. I.[1]*
EkpeteO. A.[1]
Kpee F.[1]
1Department of Chemistry
Ignatius Ajuru University of Eduction.
**Corresponence Author Edimeh Agatha*

Abstract.
Conductivity determinations of pure solvents of propylene carbonate, diethyl carbonate and dimethylformamide with their various salt solutions comprising 0.01M,0.1M,0.5M and 1M lithium perchlorate ($LiClO_4$) and magnesium perchlorate was carried out at 298.15K to ascertain the appropriateness of the systems for high energy density lithium-ion and magnesium-ion batteries. Densities, viscosities, dielectric constants critical distance for ion-association were also determined. The obtained values of these physical parameters space-between those of the component pure solvents. Variations in dielectric constants and viscosities were used to account for the observed changes in conductivities of pure solvents and the solutions of the salts in the corresponding binary mixtures. Results obtained showed that the conductivities of the mixtures increased with increasing composition of dimethylformamide (DMF) anddiethyl carbonate (DEC) which both have lower viscosities thanpropylene carbonate(PC) thus improving ionic mobility which in turn resulted in higher conductivities. However, the molar conductivity of the mixed solutions decreased with increasing concentration of $LiClO_4$ and $Mg(ClO_4)_2$ This was attributed to probably increased solvation of ions with salt concentration and greater ion- ion interactions which may result in ion-pair formation. Hence 0.1M $LiClO_4$ and$Mg(ClO_4)_2$ gave the highest molar conductivities. The ideal mixing ratio of PC/DEC and PC/DMF mixed organic systems for optimum battery performance has been established at 40-55% PC for PC/DEC and 65-70%PCfor PC/DMF. It is recommended that PC/DEC and PC/DMF could be employed as potential electrolytic solvents for lithium-ion and magnesium -ion batteries. Apart from conductivity performance, interaction of electrolytes with electrodes is crucial for good battery performance. So, more studies can be carried out to determine the compatibility of the organic electrolytes with battery electrodes.

Key Words: *Conductivity, Viscosity, Density,Dielectric constant,Solvents, dimethylformamide Propylene carbonate, diethyl carbonate, Electrolyte.*

Date of Submission: 28-02-2022 Date of acceptance: 09-03-2022

I. Introduction.

Lithium-ion battery (LIB) is a secondary or rechargeable battery, widely used in household and portable electronics e.g. laptops, notebooks, mobile phones etc. and it is fast gaining popularity in military electric vehicles, golf cars, and aerospace application(Ballon, 2008). Magnesium-ion batteries are next in line attractive alternatives to lithium-ion batteries as the current advanced lithium-ion batteries may not be able to meet the future needs or demands in terms of electronics, hybrid electric vehicles (HEV) and plug in hybrid electric vehicles. The role of the electrolyte is very crucial in any battery system. It can be said to be the “soul” of the battery as they act as passages for ionic charges (Bertrand et al., 2014). In the course of high energy density battery development, mixed organic solvents have been used as electrolyte solutions. Recent studies on high energy density batteries have focused on the properties of mixed organic electrolytes and their interactions with ionic solutes. Such properties include; conductivity, viscosity, diffusion, electrochemical stability, solvation, operation temperature range, safety features and thermodynamic properties. Some variables such as dielectric constant, donor and acceptor numbers have become functional tools in the study of battery electrolyte systems.

Mixed organic solvents data have become useful tools inmany industrial applications and are exceedingly pertinent to high energy density evolution and technology. Many impediments to progress in advancements of the next generation high energy density batteries can be overcome with smart electrolytic designs. These coupled with good electrode configuration that power chemical interaction and electrolyte can help to achieve rechargeable batteries with higher safety, energy and cycling performance (Jennifer et al,2012). Researchers are so much interested in the chemistry of mixed solvents including ionic liquids and organic solvents, aimed at obtaining the best electrolyte systems for the next generation high energy density batteries (Prem-Kumar& Shukla, 2008).

A lot of studies have been carried out on mixed organic electrolyte properties and suitability.Nwokobia et al. (2010) determined the densities and conductivities of different molar concentrations of Lithuim Perchlorate salt ($LiClO_4$) in binary mixed solvents of propylene carbonate (PC) and I, 2-dimethoxyethane (DME) at 25 °C. The variation of conductivity with solvent composition and salt concentration was explained based on the changes in viscosity and dielectric constants of the mixed solvents. These changes were attributed to ion-ion, ion –solvent or solvent-solvent interactions. They observed that the viscosity and conductivity of pure and mixed solvents of PC and DME in the presence and absence of $LiClO_4$ were significantly different. It was reported that the observed mixing ratio of PC-DME for optimum battery performance lies between 63 and 68%. Macaet al. (2013), compared specific conductivity and dielectric constants in different mixtures of Propylene carbonate (PC), ethylene carbonate (EC) and dimethylsulphoxide . The mixture of EC and DMSO gave the highest conductivity. Maduelosi et al. (2014) carried out studies on mixed binary organic solvents of tetrahydrofuran (THF) and acetonitrile (AN) with magnesium perchlorate. Densities, viscosities, dielectric constants and conductivities of the mixtures were determined at room temperature. The results of the conductivity measurements indicated that the mixed solvents exhibited a wider electrochemical stability than the pure solvents. The properties of the mixed solvents were said to be affected by ion-solvent and solvent-solvent interactions. From results obtained, it was established that the ideal mixing ratio of the mixed solvents was between 15-25% volume of THF.Commercial liquid electrolytes for lithium-ion batteries were prepared by Sivaraja and Hirankuma (2014). They dissolved 0.1M lithuimnanofluoro-1-butane sulfonate in mixed organic solvents of propylene carbonate and 1,2-dimethoxyethane respectively. The effect of the mixing ratio of the binary solvents on the conductivity and dielectric properties of the liquid electrolytes was studied. They used 1:1, 1:2 and 2:1 V% with constant salt concentration of 0.1M for all solvent ratios. A maximum conductivity of 2.52 $mScm\text{-}^{1}$ was obtained for 1:1 V% PC-DME mixture than other solvent ratios. For the 1:2 V% of PC-DME, the dielectric constant value was reduced by increasing the amount of DME, leading to reduction in ionic dissociation. In the 2:1v% PC-DME, the mobility of the ions was decreased due to high viscous nature of PC compared to DME. In this work conductivities of different mixtures of propylene carbonate-diethyl carbonate (PC-DEC), propylene-carbonate-dimethylformamide (PC-DMF) with different salt concentrations of $Mg(ClO_4)_2$ and $LiClO_4$ are studied. Conductivity is an important characteristic of an electrolyte and it is crucial for the improved life of high energy density batteries. PC, DEC, and DMF are polar aprotic organic solvents often employed in industrial and laboratory practices.

Magnesium perchlorate is a popular electrolyte used in magnesium ion batteries. It has high conductivity and solubility in water and most other solvents. Magnesium perchlorate is a white crystalline solid with the formula $Mg(ClO_4)_2$ and a powerful oxidizing agent. It is also a deliquescent salt with a high melting point of 251^0 C and density of $2.21gcm^{-3}$.

Lithium perchlorate is an inorganic compound with formula $LiClO_4$, it is a white or sometimes colourless salt. It has a remarkable solubility in many solvents. It has a melting point of 236^0 C, boiling point of 430^0 C and density of $2.42g/cm^{-3}$.

II. Materials and Methods.

Analytical grade Propylene carbonate (PC), diethyl carbonate (DEC) and dimethylformamide (DMF), lithium perchlorate ($LiClO_4$) and magnesium perchlorate [$Mg(ClO_4)_2$] products of Sigma Aldrich, United Kingdom were obtained commercially. These reagents were used without further purification. The purity of the solvents was checked by measuring the densities at 25 ^{0} C and comparing them with what is reported in literature at the same temperature. The experimental and literature values were in good agreement.

Binary mixed solvents of propylene carbonate-diethyl carbonate (PC-DEC), and (PC-DMF) was prepared with PC as the principal solvent while DEC and DMF are co-solvents. Various sample mixtures of different volume percent of propylene carbonate (100,75,65,55,35,15and 0%) with the co-solvents was prepared.0.01 ,0.1 ,0.5 and 1M solutions of lithium perchlorate and magnesium perchlorate were also prepared in the mixtures with the same volume ratios. The various solutions were prepared by weighing the calculated weight of the salt samples dissolving it in the appropriate volume of the mixed solvents and shaken thoroughly. Sample preparations was done in a fume cupboard. The mass equivalents of the four concentrations are

0.01064g,0.1064g,0.533g and 1.064g of $LiClO_4$ respectively while the mass of Mg $(ClO_4)_2$ are 0.0223g,0.223g,1.116g and 2.332g. the weighing was done on Ohaus Analytical weighing balance with a precision of±0.001g. All samples were stored in air tight glass sample bottles at ambient temperature. The bottles were washed, rinsed with distilled water and dried in an oven before use.In each set of measurements, measurement for the pure solvents before mixing were taken and values were compared with literature values. All values for all parameters compared well.

The densities of pure and mixed solvents (with and without salt) were measured with a 10ml densitybottleweighing11.09gat298.5K

The densities were determined from the weights taken using the relationship in equation 1

$$\text{Density} = \frac{mass}{volume} \qquad 1$$

Threedensityreadingsweretaken in each measurement and the average valuerecorded.

The viscosity measurements were carried out using an Ubbelhode kinematic viscometer.The viscometer was calibrated with distilled water and the viscometer constant was 0.0447. The viscosities of mixtures without lithium perchlorate and magnesium perchlorate salts were measured at the different solvent compositions. The viscosities of the mixed solvents containing different concentrations of lithium perchlorate and that of mixed solvents with different concentration of magnesium perchlorate was also measured. A minimum of three flow times for each solvent composition and salt concentration was taken and the average of the readings was used in each case to calculate the kinematic viscosity of the solution using relationship in equation 2.

$$\nu = kt \qquad 2$$

where ν is the kinematic viscosity, k is the viscometer constant while t is the flow time through the viscometer capillary. The dynamic viscosities were calculated from the kinematic viscosities and densities obtained from experiment measurements using equation 3.

$$\eta = \nu\rho 3$$

where, η is dynamic viscosity (absolute viscosity), ν is the kinematic viscosity and ρ is the density of the mixture.

Specific conductivity measurements of mixtures were done with Hanna conductivity meter, E-214. The conductivity meter was calibrated by first rinsing the probe with distilled water, then inserting it in a calibration standard (KCl solution) and living in in the solution for some time to enable full interaction with the probe. The probe was rinsed in distilled water after each measurement and recalibrated at intervals for more accurate measurements.

III. Results and Discussions.

Table 1: Mole Fractions (X) , Densities and Viscosities(cP) of Mixed Solvents of PC/DEC and PC/DMF at 298.15K

	PC/DEC				PC/DMF			
Vol% PC	**X_{PC}**	**X_{DEC}**	**Density(g/cm^3)**	**Viscosity(cP)**	**X_{PC}**	**X_{DMF}**	**Density(g/cm^3)**	**Viscosity(cP)**
100	**1**	**0**	**1.202**	**2.451**	**1**	**0**	**1.202**	**2.451**
75	**0.786**	**0.214**	**1.131**	**1.909**	**0.791**	**0.209**	**1.109**	**1.923**
65	**0.690**	**0.310**	**1.092**	**1.636**	**0.701**	**0.299**	**1.060**	**1.647**
55	**0.599**	**0.401**	**1.044**	**1.386**	**0.607**	**0.393**	**1.023**	**1.433**
35	**0.397**	**0.603**	**1.019**	**1.149**	**0.405**	**0.595**	**0.998**	**1.213**
15	**0.177**	**0.823**	**0.999**	**0.947**	**0.223**	**0.777**	**0.968**	**0.991**
0	**0**	**1**	**0.977**	**0.749**	**0**	**1**	**0.946**	**0.778**

Table 2: Dynamic Viscosities (cP) of Pure and Mixed Solvents of PC/DEC and PC/DMF withDifferent Concentration of $LiClO_4$ at 298.15K

	PC/DEC				PC/DMF			
Vol % PC	**0.01M**	**0.1M**	**0.5M**	**1M**	**0.01M**	**0.1M**	**0.5M**	**1M**
100	2.865	3.381	4.152	4.660	2.865	3.381	4.152	4.660
75	1.931	2.230	3.100	3.918	1.951	2.349	3.180	4.050

65	1.723	1.912	2.925	3.631	1.750	2.029	3.001	3.784
55	1.550	1.838	2.804	3.352	1.622	1.842	2.841	3.586
35	1.409	1.522	2.478	3.022	1.431	1.615	2.712	3.161
15	1.142	1.295	2.314	2.796	1.220	1.378	2.471	2.911
0	0.894	1.177	2.042	2.622	0.961	1.215	2.162	2.647

Table 3: Dynamic Viscosities (cP) of Pure and Mixed Solvents of PC/DEC and PC/DMF with Different Concentrations of $Mg(ClO_4)_2$ at 298.15K

	PC/DEC				**PC/DMF**			
Vol % PC	**0.01M**	**0.1M**	**0.5M**	**1M**	**0.01M**	**0.1M**	**0.5M**	**1M**
100	3.162	3.787	4.595	5.145	3.162	3.787	4.595	5.145
75	2.603	3.167	4.152	4.633	2.644	3.268	4.202	4.667
65	2.114	2.874	3.899	4.408	2.244	2.953	3.931	4.666
55	1.845	2.718	3.684	4.201	1.991	2.780	3.747	4.276
35	1.740	2.510	3.404	3.929	1.781	2.581	3.494	3.982
15	1.501	2.256	3.117	3.670	1.610	2.337	3.228	3.733
0	1.333	2.061	2.833	3.440	1.433	2.114	2.965	3.508

Table 4: Molar Conductivity ($Scm^2 \, mol^{-1}$) Values for Mixed Solvents of PC/DEC and PC/DMF With LiClO4

PC/DEC PC/DMF

Vol%PC	**0.01M**	**0.1M**	**0.5M**	**1M**	**0.01M**	**0.1M**	**0.5M**	**1M**
100	0.30	2.40	6.62	8.99	0.30	2.40	6.62	8.99
75	0.80	22.30	11.13	9.01	1.58	35.81	19.76	13.50
65	1.16	25.80	11.89	9.52	1.62	39.20	21.34	13.97
55	1.49	34.60	13.68	10.74	1.50	36.13	20.52	13.09
35	1.37	32.24	12.63	10.21	1.44	33.60	18.20	12.72
15	0.46	19.41	5.18	5.78	1.37	31.76	15.78	9.83
0	0.12	0.67	2.21	2.00	0.18	0.92	4.36	3.79

Table 5: Molar Conductivity (Scm^2 mol^{-1}) Values for Mixed Solvents of PC/DEC and PC/DMF With Mg(ClO4)2

	PC/DEC				PC/DMF			
Vol%PC	**0.01M**	**0.1M**	**0.5M**	**1M**	**0.01M**	**0.1M**	**0.5M**	**1M**
100	1.20	3.60	9.07	6.16	1.20	3.60	8.00	8.29
75	1.60	42.10	14.01	8.20	3.90	54.70	22.00	13.27
65	1.76	48.91	15.71	8.46	3.14	59.21	25.91	12.77
55	1.99	56.68	19.44	10.00	2.56	53.70	22.25	12.42
35	1.92	53.13	18.62	9.42	2.14	50.11	21.82	11.82
15	1.10	26.06	8.04	5.04	1.80	41.88	18.45	8.10
0	0.35	2.16	4.03	1.67	0.54	2.46	6.45	3.02

Viscosity

The dynamic viscosities of the mixtures are observed to decrease with increasing volume percent of the cosolvents (DEC, DMF) which both have lower viscosities than PC and increase with increasing salt concentrations as clearly seen in tables1 and 2. So, the decrease in the viscosities is mainly as a result of the increasing volume percentage of the lower viscous cosolvents. Viscosity is also observed to vary directly with the different concentrations of the salts. Viscosity which is the measure of a fluid's resistance to flow depends on the intermolecular forces of attraction between molecules present in the fluid. It can be deduced from this that the salt ions interactions with solvent molecules impacts electrolyte viscosity, Correlative results have been reported by earlier researchers, Izonfuo&Kemeakegha (2009) and Nageshewar et al (2010). The tables1 and 2 show that viscosity decreased in the order order 0.01<0.1<0.5<1.0M. for both Mg $(ClO_4)_2$ and $LiClO_4$ salts, although viscosities of the molar solutions of solvents with different concentrations of $Mg(ClO_4)_2$ are higher indicating higher solute -solvent interaction or increased number of ions in solution which retarded the smooth flow of solvent mixtures

Conductivity.

The molar conductivity was calculated from the specific conductivity using the relationship;

$$\Lambda = k/C \qquad 4$$

where Λ is the molar conductivity, C is the molar concentration and k is the specific conductivity determined from the experiment.

Tables 4 and 5shows that molar conductivity of the solutions of $LiClO_4$ and $Mg(ClO_4)_2$ in the binary mixtures increases as the composition of the cosolvent of DEC and DMF increases with maximum values at 40-55%PC for the PC/DEC mixtures and 65-70% for the PC/DMF mixtures. The lowering of the viscosities of the mixed systems by the cosolvents can be said to reduce opposing and frictionalforcesl that may slow down ionic mobility which invariably leads to increased conductivity. Conductivity is also seen to be inversely proportional to the concentration of the salts. Matsuda et al. (2000) made similar observations which was associated with changes in viscosities, dielectric constants, as well as ion-ion, ion-solvent and solvent-solvent interactions.

.However the highest molar conductivity values were obtained at 0.1M $LiClO_4$;2.40-34.60 ,2.40-39.20Scm^2 mol^{-1}for PC/DEC, PC/DMF respectively and 0.1M $Mg(ClO_4)2$;3.60-56.68,3.60-59.21Scm^2 mol^{-1}for PC/DEC ,PC/DMF respectively . At low concentrations the salts are completely dissociated and ions solvated so the higher conductivity values obtained at 0.1M concentration can be said to be due to ion-solvent interactionsprevailance.

Strong electrolytes like $LiClO_4$ and $Mg(ClO_4)_2$ are believed to dissociate completely in solution. At low concentrations there is a linear relationship between concentration and conductivity for the dilute solutions as can be observed in the 0.01M mixtures but as concentration increases, strong ionic interactions alter this relationship within the binary system (Penfold et al., 1999).Ionic mobility may be slowed down at higher concentrations 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.

IV. Conclusion

The mixing of the solvents produced better electrolytic properties in terms of viscosities and conductivity. Salt concentration also influenced conductivity.The solvents complement each other for better battery performance. The ideal mixing ratio of PC/DEC and PC/DMF mixed organic systems should be at 40-55% PC for PC/DEC and 65-70% PC for PC/DMF.The use of a single electrolyte solvent could be suitable but the mixing of solvents to enhance the desired properties of an electrolyte is a better pragmatic solution.

References

[1]. Aurbach, D., Markovsky, B., Rodkin, A., Levi, C., Cohen, V.S., Kim, H.J. & Schmidt, M.

[2]. (2002). On the capacity fading interactions electrodes:The effect of cycling, Storage, temperature and surface film forming additives. *Electrochemical Acta, 47*(27) 4291-4301.

[3]. Ballon, M., Santos (2008). "Electrovaya, Tata Motors to make electric indica" Viewed 4th November 2021 http://cleantech.com

[4]. Betrand, G., Armand, M. &Marlier, G (2014). Fire behaviour of carbonate-based electrolyte.

[5]. *Journal of Power Sources, 269(*1), 804-811.

[6]. Izonfuo, W.A. &Kemeakegha, A.J. (2009). Intermolecular interactions studies of binary mixtures of a ketoester and carbonyl compounds at 298.15K. *Indian Journal of Chemistry. 48*(A) 1242-1245.

[7]. Jennifer, I., Schaefer, Y., Surya, S. & Lynden, A. (2012). Electrolytes for high energy batteries.

[8]. *Springlerlink.com. Applied Nanoscience 9*(2) 109.

[9]. Maca, J. Frk, M. &Sedlari- Koma, M. (2013). Properties of electrolyte for lithium ion battery for higher fire safety. *Journal of Applied Electrochemistry, 34*(1) ,1120-1125.

[10]. Maduelosi, N., J (2014). Characterization of binary mixed organic electrolytes of tetrahydrofuran and acetonitrile for Magnesium ion Batteries. *Journal of Materials Research*, *6*(12),188- 193.

[11]. Nageshewar, D., Khupse, K. and Anil, K. (2010). Ionic liquids, new materials and wide applications. *Indian Journal of Chemistry, 49*A, 635-648.

[12]. Nwokobia, F.U., Abia, A.A. &Cookey, G.A. (2010). Effect of salt concentration on the conductivity and viscosity of binary mixed electrolyte solutions. *IOSR Journal of Applied Chemistry,8*(2) 1-7.

[13]. Penfold, J., Saples, E., Thomas, J., Hines, J., Thomas, R., Lu, R. & Warren, N. (1999). Structure and composition of mixed surfactant micelles of sodium dodecyl sulphate and hexciethylene glycol monododecylesther and of hexadecyltrimethlammonium bromide and hexaethylene glycol monododecyl ether. *Journal of Physical Chemistry, 103*(25), 5204-5211.

[14]. Prem-Kumar, T.& Shukla, A.K. (2008). Materials for next-generation lithium batteries. *Current Science, 94*(3), 318-325.

[15]. Sivaraja, N. and Hirankumar, 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.