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## **INVENTING A GOOD ELECTROLYTE SYSTEM FOR A SECONDARY CELL**

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### **ABSTRACT**

The development of a magnesium ion battery system is primarily based on the interactions of mixed organic electrolytes solutions formed by the combination of dimethylformamide(DMF) and Propylene carbonate (PC) solvents with Magnesium perchlorate  $Mg(ClO_4)_2$  salt. The binary mixtures were prepared for their physico-chemical properties in order to establish their suitability for magnesium ion battery. These properties include density, viscosity, conductivity and dielectric constant. The cells of  $Mg^{2+}$  ion containing electrolytic solutions of the binary mixtures were also studied. Molar conductivity measurements investigated at 25°C demonstrated that the mixed systems exhibit a wide electrochemical stability and improved property than the pure solvents. The properties of the mixed electrolytes were affected by ion-solvent and solvent-solvent interactions. The results have been interpreted on the basis of the intermolecular interactions among the component molecules of the systems. The temperatures studied 25,40,50,60 and 70°C show that the battery system remains stable even at high temperatures. The mixing ratio of the organic solvents for optimal battery performance is

established to be between 50-70% PC for the battery system because it is at this range that the system gave the highest conductivity and electromotive force (EMF).

**Keywords: Development, Battery system, viscosity, binary mixture.**



## INTRODUCTION

Increasing depletion of fossil resources, high industrial pollution and ecological destruction are some of the major reasons for the high demand of low-cost and high energy density batteries for electric vehicles and storage of energy from renewable sources (Armand and Tarascon, 2008). Magnesium ion battery is one of the improved forms of battery innovation but has not been commonly established compared to work which has been previously done on Nickel-Iron battery (NiFe) and lithium ion-battery. Batteries are technically, the combination of two or more cells, electrically connected to transform chemical energy to electrical energy. The cell is made up of two electrodes, the positive electrode (cathode) and negative electrode (anode) which are immersed in an electrolyte. Batteries are of varied sizes, shapes, voltages and configurations (Bin *et al.*; 2013). Batteries are broadly divided into two which includes; Non-rechargeable and rechargeable cells. These are designed to produce current immediately on assembly and will continue until the active materials are depleted and voltage too low to

operate a given device. Thereafter, they are discarded. Examples include Alkaline batteries and Carbon-Zinc (LeClanche) batteries. Rechargeable or Secondary batteries can be recharged after discharging. They are recharged by direct current to the original state. Examples include Lead-acid batteries, Lithium batteries, magnesium batteries, silver batteries and thermal batteries. Magnesium-based batteries have high attractive property which makes an alternative to lithium batteries; the electrochemical characteristic of magnesium is similar to that of lithium (12g-per faraday g/f compared to 7g/f for lithium or 23g/f for sodium). Magnesium-ion batteries with a Mg-metal negative electrode are expected to combine high energy density and a high electromotive force due to its divalency and its low redox potential. (Ichistubo *et al*, 2011), reported that it is capable of storing energy double than that stored by lithium ion cells. Secondary magnesium cells have not yet been made in large quantities because of low recharging of magnesium cell ion transfer process and also the passivating oxide layer on the magnesium anode, the shortage of appropriate great conductivity Mg<sup>++</sup> ion conducting mixtures and the necessity for an increase in power output. The intermolecular interactions of mixed organic solvents has been an area of interest for any research work involving battery systems as mixed solvents may have properties which are more useful than those of the pure component solvents. The suitability of a solvent or solvent mixture for such battery requires the possession of high dielectric constant and low viscosity which are rarely integrated into a single solvent. In the past, greater attention was given to lithium ion batteries than any other rechargeable battery because of its high energy density. In recent times, the battery market is rapidly shifting towards other new generation batteries such as battery electric vehicles (BEV) and plug-in hybrid electric vehicles (PHEV). As part of the global automakers efforts to improve ways of powering electric cars, researchers are developing a magnesium based battery capable of storing double the energy stored by lithium ions cells that would transfer to a higher mileage on a single charge. Example includes the Toyota Motor Corporation led by Jeffrey Makarewicz (David, 2011). This research was carried out to determine the development and applicability of dimethylformamide (DMF) and Propylene Carbonate (PC) binary system in the development of high energy-density Magnesium ion battery.

### Material and Method

**Materials** :The solvents, Propylene Carbonate (99.5%), Dimethylformamide (99.5%) and the salt, Magnesium Perchlorate (Mg(ClO<sub>4</sub>)<sub>2</sub> dried (99%) were all obtained commercially.

**Sample preparation**: Binary mixtures of DMF/PC were prepared in varying proportions of 100, 70, 50, 40, 30, 20, 10 and 0% of PC, corresponding to mole fractions of 1.0, 0.680, 0.477, 0.378, 0.280, 0.185, 0.091 and 0.00 of PC. The working temperatures were 25, 40, 50, 60 and 70°C. Different concentrations of 0.1M, 0.5M and 1.0M of Mg(ClO<sub>4</sub>)<sub>2</sub> solutions of the binary system were also prepared. The weighings were done on Adam AAA electronic balance with a precision of ±0.001g. The densities were measured using a 10ml pycnometer bottle, the viscosities were measured using viscometer at different temperatures. The relationship involves  $V=Kt$  where  $V$ =kinematic viscosity,  $t$ =time of flow of liquid through

the capillary and K= viscometer constant. The conductivities were measured at different concentrations with the use of conductivity meter and a multimeter for the cell voltage.

### RESULTS AND DISCUSSION

**Table1.0** Densities ( $\text{g/cm}^3$ ) of pure and binary solvents of PC/DMF at different temperatures ( $^{\circ}\text{C}$ ).

%PC	25	40	50	60	70
100	1.1945	1.1615	1.1524	1.0943	1.0795
70	1.1625	1.1562	1.1241	1.0895	0.0685
50	1.1431	1.264	1.0346	0.9654	0.9571
40	1.1046	1.0561	1.0035	0.9593	0.9468
30	0.9934	0.9741	0.9416	0.9356	0.9216
20	0.9816	0.9536	0.9348	0.9168	0.9085
10	0.9643	0.94218	0.9258	0.9137	0.9023
0	0.9385	0.9368	0.9042	0.8657	0.8516

**Table2.0** viscosities (cP) of pure and binary solvents of PC/DMF at different temperatures ( $^{\circ}\text{C}$ )

%PC	25	40	50	60	70
100	0.1035	0.0982	0.9692	0.0921	0.0897
70	0.0988	0.0964	0.0935	0.0905	0.0861
50	0.9122	0.0883	0.0081	0.0802	0.0723
40	0.0874	0.0793	0.0749	0.0748	0.0703
30	0.0753	0.0713	0.0707	0.0706	0.0655
20	0.0703	0.0611	0.0609	0.0607	0.0600
10	0.0657	0.0610	0.0589	0.0577	0.0568
0	0.0627	0.0604	0.0572	0.0545	0.0535

#### Density and Viscosity

The density values decreased with increase in mole fractions of PC for the PC/DMF system as shown in table1.0 .The density of a solution is a measure of solvent- solvent and ion-solvent interactions (Thirumaran and sathish,2011). The decrease in density with mole fraction may indicate the dominance of dispersive forces which allows less dense products to be formed in the mixture, this could show an improved solvent-solvent and ion-solvent interaction as reported by (Anantaraman,1986 and Zamir, 2004).Similarly,viscosity values decreased with increase in the mole fraction of DMF which can be attributed to a low resistance to intermolecular interactions, formation of less dense products and dominance of dispersion forces as reported by Ali and Nain, 1996. Solvents of low viscosity have always been considered the right choice for a good electrolyte because of very low resistance in ion

mobility(Motin,2007). However, it has to be associated with a high dielectric constant.This is because solvents with low dielectric constant cannot dissociate ions completely or effectively enough to prevent the formation of ion-pairing(Motin,2007).The observed decrease in density and viscosity of the mixtures with increase in temperature is attributed to higher thermal excitation and reduction of attractive forces between the ions. Earlier researchers,(Nageshewar and Anil,2010) made similar reports. This is because increase in temperature breaks the intermolecular bonds thereby, allowing the free movement or interaction of the ions.On the other hand, the densities and viscosities of solutions of  $Mg(ClO_4)_2$  in the binary solvent systems increased with increasing concentration which suggests a moderately strong associative nature in which the solute  $[Mg(ClO_4)_2]$  tends to attract the solvent molecules. This is suggestive increase in solvent- solvent and solute- solvent interactions resulting in volume reduction.(Thirumaran and sathish,2011) made such observations.When solvated ions migrate within an electrolyte solution, the drag force applied by similarly charged surrounding solvent molecules is measured by solvent viscosity. Thus, in a solvent of lower viscosity, the solvated ions would move more easily in response to an applied electric field, as expressed by the Einstein-Stokes relation( Hoyuleos *et al*,1996). Solvents of low viscosity have always been considered the ideal solvents for electrolyte applications.However, their actual use was restricted because most of these solvents have low dielectric constants and cannot dissociate ions effectively enough to prevent ion pairing( Hoyuleos *et al*,1996). The observed decrease in densities and viscosities with increase in temperature is attributed to greater thermal excitation and reduction of attractive forces between the ions. Similar reports have been made by ( Rodriguez *et al* 2003).

**Table 3.0** Cell Voltages (Volts) of solution of binary mixtures of PC/DMF and salt.

%PC	$E_{cell}$ (Volts)
100	0.56
70	1.02
50	0.98
40	0.62
30	0.58
20	0.49
10	0.51
0	0.48

### Electrochemical Cell Voltage (volts).

Cell potentials depend on concentration of the solution and shows the output of the battery system. The values of the measured electrochemical cell voltage values are shown in table 3 and indicates an improved system due to the mixing. The values obtained are also attributed to the combined influence of low viscosity of DMF and high dielectric constant of PC and ionic mobility. The voltage was highest at 70% of PC showing the highest output of the battery system with value of 1.02volts.

**Table 4.0 MOLAR CONDUCTIVITIES OF SOLUTIONS OF  $Mg(ClO_4)_2$  in BINARY MIXTURES OF PC/DMF AT VARIOUS CONCENTRATIONS.**

<b>%PC</b>	<b>without salt</b>	<b>0.1M (<math>Scm^2mol^{-1}</math>)</b>	<b>0.5M Salt (<math>Scm^2mol^{-1}</math>)</b>	<b>1.0M (<math>Scm^2mol^{-1}</math>)</b>
100	0.025	2.93	9.23	12.06
70	0.081	3.88	17.64	38.44
50	0.078	3.71	16.90	36.70
40	0.054	3.14	16.99	36.58
30	0.011	3.68	11.91	30.16
20	0.023	2.86	16.31	35.13
10	0.033	2.92	15.30	34.96
0	0.012	2.95	16.49	35.11

### Conductivity

The conductivity of an electrolyte solution depends on the concentration of the ionic species. The results of the conductivity measurements of solutions  $Mg(ClO_4)_2$  in binary mixtures of PC and DMF of different %PC (table 5.0) show an increase in molar conductivities with decrease in %PC. This increase could be attributed to both the high dielectric constant of PC and the low viscosity of DMF. Thus, it may be inferred that the combination of the dielectric constant and viscosity in a solvent results in conductivity of its solution. Such observations have been reported earlier by (mauelosi *et al*, 2014). Maximum conductivity was observed between the 50-70%PC. These results show that ion-solvent and solvent-solvent interactions contribute to the improvement of conductance. This was also observed by (Obunwo and Izonfuo, 1999). It can thus be suggested that increase in ionic conductivity is achievable in binary mixtures of solvents where one of the components has high dielectric constant and the other solvent a low viscosity. The highest conductivity values were seen at the maximum concentration of the salt (1.0M). This also explains that increase in the concentration of the salt increases the conductivity of the system to an extent that is,

as long as the ionic mobility is not hindered. According to Nwokobia *etal*,2013 a net increase in ion conductivity is achieved when solvents of varying properties are mixed. This is basically described by the viscosity of the electrolytic media.

**Table 5.0** DIELECTRIC CONSTANT OF PURE AND VARIOUS MIXTURES OF PC/DMF AT 25°C

<b>PC</b>	<b>DIELECTRIC CONSTANT</b>
100	36.7
70	70.65
50	69.85
40	53.68
30	56.51
20	59.34
10	62.17
0	65.00

**Dielectric Constant ( $\epsilon$ ):** table5.0 shows changes in the values of the dielectric constant of the system on mixing. This indicates improvement in properties of a solvent when mixed with another. The increase in the values of the dielectric constant of the mixtures with the mole fraction PC is implied since the dielectric constant of a mixture is just an additive factor. Molecular interactions that affect density and viscosity of a mixture do not necessarily have effect on the dielectric constant this could mean that interactions and dissociation of solute-solvent are high and there is a minimum ion-pair formation. For a solvated ion to migrate by the influence of an electric field, it must not be allowed to form close ion pairs with its counter ions by the solvating solvent(William,2005). The efficiency of the solvent molecule in shielding the inter-ionic columbic attraction is determined by the dielectric constant of the solvent. Obviously, with the higher dielectric constant values obtained in table 5.0, the magnesium ions would have a high probability of staying free at a given concentration and ion association will subsequently be less likely to occur. Studies have shown that solvents with dielectric constant in the range 20-40 show extensive ion-pair formation (Gans and Gill, 1989). The attraction between solute and solvent is essentially that of ion-dipole interaction which depends mainly on ion size and polarity of the solvents. The strength of such interaction also depends on the charge and magnitude of the distance between the ion and dipolar molecule.

### Conclusion

Results of experimental measurements of the properties of the mixed solvents have provided significant information regarding the state of affairs in the mixture. The results obtained for solutions of  $\text{Mg}(\text{ClO}_4)_2$  in binary mixtures of PC and DMF at varying composition of PC show that the values of the properties studied have intermediate between those of the pure solvents. The molar conductivity in the mixed solvents is much higher than that in the pure solvents. The mixing ratio of the mixed PC-DMF system for optimum battery performance has been established to be between 50-70%PC for the system studied. The salt concentration with the highest molar conductivity is 1.0M  $\text{Mg}(\text{ClO}_4)_2$ .

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