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CONDUCTIVITY AND DIELECTRIC CONSTANT OF SOME ORGANIC SOLVENTS AS ALTERNATIVE ENERGY SOURCES

ENYINDAH, LAWRENCE AND OKAH, REMINUS,

SCIENCE LABORATORY TECHNOLOGY

SCHOOL OF SCIENCE AND TECHNOLOGY

CAPTAIN ELECHI AMADI POLYTECHNIC RUMUOLA, PORT-HARCOURT. RIVERS-STATE, NIGERIA.

E-MAIL- ogweru12345@gmail.com

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ABSTRACT

Intermolecular 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 were studied.The mixtures were prepared and characterized for their physical and thermodynamic properties. These properties include conductivity, dielectric constant and cell voltage. The cells of Mg^{2+} ion containing electrolytic solutions of the binary mixtures were also studied. Molar conductivity measurements investigated at 25^0C 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 system. 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 .

Keywords: Conductivity, dielectric system, cell voltage, binary mixture

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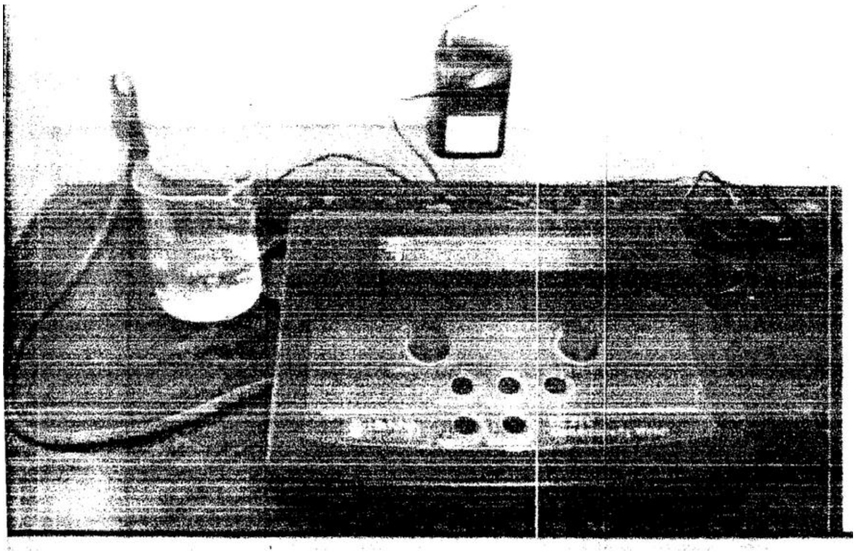
INTRODUCTION

The chemistry of mixed organic solvents has been an area of interest for many research works as these solvents have properties which could be more useful than those of pure solvents in other to reduce or eliminate high industrial pollution and ecological destruction. Since a high dielectric constant and low viscosity cannot be integrated into a single solvent. Binary mixtures, with one of the components selected for its high dielectric constant and the other for its low viscosity are usually used to formulate electrolytes of high conductivity for batteries in other to get a balance between these two properties. Carbonates are usually selected for high dielectric constant and others for low viscosity (Thirumaran and Sathish 2011). Since the inception of non-aqueous electrolytes, a wide spectrum of polar solvents has been investigated, and the majority of them fall into either organic esters or ether families. The magnesium salt used as electrolyte solutes is mainly magnesium chlorate $Mg(C10_4)_2$.Magnesium is a metallic element with a symbol Mg and atomic number 12. It is an alkaline earth metal which belongs to group two of the periodic table. It has an oxidation number (+2) and has the lowest melting and boiling points, It is a highly flammable metal especially when powdered or shared into strips at certain temperatures. Magnesium can be used as a source of light, for example use of magnesium ribbon to electrically ignite flash bulbs and manufacture of fireworks. Because of its low weight and good mechanical and electrical properties, magnesium is widely used for batteries, laptops, mobile phones. Some of these properties that can be used to characterize organic solvents are conductivities,melting points, boiling points, dielectric constant, density, flash point, resistivity, transport number, solubility. Batteries are devices made up of two or more cellls that are connected together to convert chemical energy to electrical energy. The cells consist of positive electrode (cathode) and negative electrode (anode) which are immersed in an electrolyte. Batteries are of different configuration, sizes and voltages which determine their rate of performances. (Armand and Tarascon,2008). Magnesium ion battery is one of the improved form 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^{++} 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 (Motin,2007). 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 $(Mg(ClO_4)_2$ 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 70^0C . Different concentrations of 0.1M, 0.5M and 1.0M of $Mg(ClO4)_2$ solutions of the binary system were also prepared. The weighings were done on Adam AAA electronic balance with a precision of ±0.001g the cappliary 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

Table 1.0 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 2.0 MOLAR CONDUCTIVIES OF SOLUTIONS OF $Mg(ClO_4)_2$ in BINARY MIXTURES OF PC/DMF AT VARIUOS CONCENTRATIONS.

%PC	without salt	0.1M (Scm^2mol^{-1})	0.5M Salt (Scm^2mol^{-1})	1.0M (Scm^2mol^{-1})
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 (maduelosi *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 3.0 DIELECTRIC CONSTANT OF PURE AND VARIOUS MIXTURES OF PC/DMF AT 25^0C

PC	DIELECTRIC CONSTANT
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 (ε): table3.0 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 (Obunwo and Izuonfo 1999.). 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 $Mg(ClO_4)_2$ 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 $Mg(ClO4)_2$.

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The research has provided data on the physico-chemical and performance parameters of the PC-DMF system studied which were not previously known,from the research new electrolyte system of PC-DMF has been established which has indicated good conductivity as an energy source for wealth creation.

Conductivity graph with different concentrations.

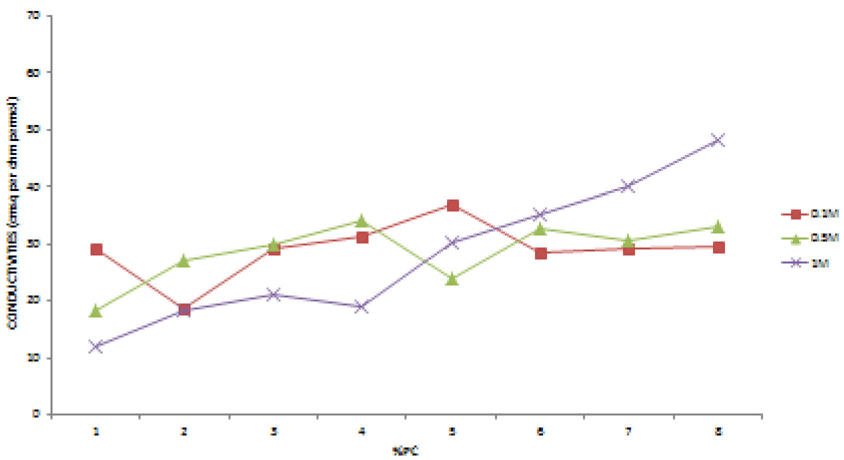

Fig.1