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Study of the intermolecular interactions of mixed solvents of tetrahydofuran and propylene carbonate for magnesium ion battery

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ABSTRACT

Intermolecular interactions of Mixed organic electrolytes formed by the combination of Tetrahydrofuran (THF) and Propylene carbonate (PC) solvents with Magnesium Perchlorate salt were studied. The mixtures were prepared and characterized for their physical and thermodynamic properties. These properties include density, viscosity, conductivity, dielectric constant, Grunberg and Nissan d parameter and Critical distance for ion pair formation, . The cells of Mg^{2+} ion containing electrolytic solutions of the binary mixtures were also studied. Jones –Dole viscosity/concentration dependence plots were made, and the ion-ion interaction coefficient (A) and the ion-solvent interaction coefficient (B) were determined. Molar conductivity measurements investigated at 25^0c demonstrated that the mixed systems exhibit a wide electrochemical stability window 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 show that the battery remains stable even at high temperatures. The mixing ratio of the organic solvents for optimal battery performance is established to be between 75-85%THF for the system.

Key words: Battery, ions, conductivity, viscosity, density, intermolecular interactions.
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INTRODUCTION

Before now, lithium ion batteries have been in the forefront of the rechargeable batteries being studied because of its high energy density. The battery market is rapidly growing and a s battery electric vehicles (BEV) and plug-in hybrid electric vehicles (PHEV) continue to increase in usability, their market share is rapidly increasing, pulling the battery market up together with it. The battery market has been growing steadily for the past 20 years and is expected to continue to grow with years. William Tahil (2005), points out in his report, The Trouble with Lithium, that if all the BEV and PHEV of the future would be powered by lithium-ion batteries there would not be enough lithium in the world to sustain even one year of production. This calls for the need of new types of batteries.

Magnesium is a very good choice since it offers a good trade-off between the mentioned factors above. Magnesium-based batteries have also been subjected to some research since the last 20 years and the worldwide magnesium industry is already producing over 700,000 tonnes a year, thereby benefiting the research and production of this technology 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 [3]. This study was carried to determine the applicability of Tetrahydrofuran (THF) and Propylene Carbonate(PC) binary system in the development of high energy – density Magnesium ion batteries

The parameters studied include, Density, Viscosity, Conductivity, Dielectric constant, Critical Distance, D – parameter, and Electrochemical Cell Voltage

EXPERIMENTAL SECTION

Materials : The solvents, Propylene Carbonate(PC) (99.5%) and Tetrahydrofuran (THF)(99.5%) (BDH chemicals Ltd, Poole, England), and the salt, Magnesium Perchlorate $(Mg(ClO_4)_2)$ dried (99%) (May and Baker Ltd, Dagenham, England) were all obtained commercially.

Sample preparations: Binary mixtures of THF/PC were prepared in varying proportions of 100%, 85%, 75%,50%, 25%, 15% and 0% of THF, corresponding to mole fractions of 1, 0.856, 0.759, 0.513, 0.259, 0.157 and 0 of THF.The working temperatures were 25, 40, 50, 60, 70°C . 0.1M, 1.0M and 2.0M of $Mg(ClO_4)_2$ solutions of the binary system were also prepared. The weightings were done on Adam AAA electronic balance with a precision of ±0.001g.

RESULTS

Table 1:Calculated Mole Fractions Of THF/PC System

%THF	X_1 (THF)	X_2(PC)
100	1.000	0.000
85	0.856	0.144
75	0.759	0.241
50	0.513	0.487
25	0.259	0.741
15	0.157	0.843
0	0.000	1.000

Table 2: Densities, ρ,(g/cm³) of pure and mixed solvents of THF & PC

% THF	Density at 25°C	Density at 40°C	Density at 50°C	Density at 60°C	Density at 70°C
100	0.891	0.861	0.859	0.855	0.845
85	0.899	0.881	0.873	0.865	0.849
75	0.926	0.900	0.894	0.887	0.870
50	0.954	0.940	0.933	0.927	0.911
25	0.991	0.980	0.976	0.974	0.960
15	1.005	0.986	0.983	0.980	0.970
0	1.198	1.022	1.016	1.009	1.001

Table 3: Viscosity (cP) of pure and mixed solvents of THF and PC at 25°C

% THF	Viscosity (cP) at 25°C
100	0.420
85	0.976
75	1.097
50	1.666
25	1.785
15	2.052
0	2.50

Table 4: Conductivity measurement of mixed solvents of THF and PC with salt in $Scm^2\ mol^{-1}$

% THF	Conductivity($Scm^2\ mol^{-1}$)(0.1M salt)	Conductivity($Scm^2\ mol^{-1}$)(1.0M salt)	Conductivity($Scm^2\ mol^{-1}$)(2.0M salt)
100	4.1	9.5	3.45
85	17.0	9.3	4.75
75	15.0	11.1	4.35
50	13.0	7.0	3.95
25	6.0	3.7	2.60
15	7.0	2.7	3.35
0	3.0	2.6	1.60

Table 5: Calculated values of critical Distance and Dielectric constant of THF – PC System

%THF	Critical distance (10^{-10}m)	Dielectric constant
100	73.9	7.58
85	34.596	16.193
75	25.5	21.94
50	15.2	36.92
25	11.1	50.65
15	9.935	56.387
0	8.6	65

Table 6: Density, ρ, (g/cm^3) of THF/PC with 0.1M salt

% THF	25^0C	40^0C	50^0C	60^0C	70^0C
100	0.9004	0.8751	0.8658	0.8563	0.8399
85	0.9175	0.8977	0.8899	0.8821	0.8712
75	0.9345	0.9202	0.9140	0.9078	0.9025
50	0.9692	0.9584	0.9506	0.9427	0.9402
25	1.0090	1.0007	0.9932	0.9852	0.9833
15	1.0242	1.0157	1.0091	1.0023	1.0004
0	1.0393	1.0306	1.0250	1.0193	1.0175

Table 7: Kinematic Viscosity Measurements of Mixed solvents of 0.1M Mg(ClO$_4$)$_2$, THF and PC mixture

% THF	25^0C	40^0C	50^0C	60^0C	70^0C
100	0.762	0.648	0.610	0.574	0.530
85	1.240	0.989	0.850	0.720	0.610
75	1.514	1.351	1.137	0.923	0.850
50	5.241	3.800	2.770	1.750	1.137
25	8.956	6.800	5.169	4.539	2.770
15	10.204	8.668	7.602	6.005	5.169
0	12.402	10.398	9.705	8.015	7.602

Table 8: Jones-Dole A and B Coefficients for the system THF/PC with the various Salt Concentrations

%THF	A	B
100	5.066	14.63
85	2.792	7.414
75	1.717	7.816
50	5.225	0.859
25	14.18	-4.236
15	14.59	-4.822
0	15.38	-6.093

Table 9: Cell Voltages for Mg(ClO$_4$)$_2$, (THF-PC) Concentration Cell

% THF	E_{cell} (Volts)
100	0.40
85	0.86
75	0.63
50	0.31
25	0.29
15	0.27
0	0.28

DISCUSSION

Density and Viscosity

The density values increased with decrease in mole fractions of THF for the THF/PC system (Table 2) Density is a measure of solvent- solvent and ion- solvent interactions [17]. The increase in density with mole fraction is as a result of increase in molecular chain, indicating that bulky compounds have been formed. This suggests that geometrical factors, allowing the molecular species to form a more dense structure within the mixture were present. [2, 19] have reported such.

The increase in the viscosity values with decrease in the mole fraction of THF in the THF/PC system indicates formation of higher molecular weight product. This causes the hindrance in the flow of solvent mixture. Similar results have been presented by earlier researchers [7,4].

On the other hand, the densities and viscosities of the systems with $Mg(ClO_4)_2$ increased with concentration which suggests a moderate strong associative nature in which the solute $Mg(CLO_4)_2$ tends to attract the solvent molecules, which indicates an increase in solvent- solvent and solute- solvent interactions which leads to volume shrinkage[17]. When solvated ions migrate within the electrolyte, the drag force applied by the 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 . Solvents of low viscosity have always been considered the ideal candidate for electrolyte application; 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. The observed decrease in densities and viscosities in tables 2 and 3 with increase in temperature is attributed to greater thermal excitation and reduction of attractive forces between the ions. Similar reports have been made by earlier researchers[12,14].

Dielectric Constant (ε) and Critical Distant (r):
The increase in the value of the dielectric constant as the mole fraction is changed is because the dielectric constant of a mixture is just an additive factor. Molecular interactions that affect density and viscosity of a mixture do not have effect on the dielectric constant. The calculated critical distance and dielectric constant values for the 2:1 electrolyte in the systems are shown in table 5. The Critical distance increased in the systems with increase in volume concentration of THF indicating possible ion pair formation.

In order for a solvated ion to migrate under an electric field, it must be prevented from forming close ion pairs with its counter ions by the solvating solvent. The effectiveness of the solvent molecule in shielding the inter-ionic Coulombic attraction is closely related with its dielectric constant. The critical distance for the ion pair formation r is given by the equation according to Bjerrum's treatment given below, with the hypothesis that ion-pair formation occurs if the inter-ionic distance is smaller than r.

$$r = \frac{/z_i\ z_i/e^2}{8\varepsilon_0\ \varepsilon_r\ kT}$$

Where z, ε_0 ε_r, k, and T are the valence orders of ions, the dielectric constant of vacuum and medium, Boltzmann's constant, and temperature, respectively. Apparently, in a solvent with a higher dielectric constant, ions would have a higher probability of staying free at a given salt concentration and ion association would be less likely to occur. Studies have shown that solvents with dielectric constant in the range 20-40 show extensive ion- pair formation [5]. 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.

CONDUCTIVITY
The conductivity of an electrolyte solution depends on the concentration of the ionic species. The results of the conductivity measurements in table 4 .show an increase in molar conductivities with decrease in %THF in the systems. This increase is attributed to both the high dielectric constant of PC a and the low viscosity of THF. The higher the dielectric constant and the lower the viscosity of a solvent, the higher the conductivity of the solution. Such observations have been reported earlier [10,15]. Maximum conductivity is obtained between the 75-85% THF. The results show that ion-solvent and solvent-solvent interactions contribute to the improvement of conductance. Earlier researchers have made such observation [11]. A net increase in ion conductivity is achieved when solvents of varying properties are mixed.

Electrochemical Cell Voltage:
Cell potentials depend on concentration of the solution. The measured electrochemical cell voltage values are shown on table 8. Values suggest the influence of low reversibility of the magnesium electrode/electrolyte ion transfer mechanism because of the passivating oxide layer on the magnesium anode. The values obtained are also attributed to the combined influence of low viscosity of THF and higher dielectric constant of PC. The voltage was highest at 85% of THF.

Jones- Doles A and B Coefficients:
The results of Jones- Doles plots for the binary systems shown in tables show that the A coefficients for the THF/PC system with 0.1M salt were positive for the entire THF fractions (indicating strong electrostatic interaction). The A co-efficient which is a function of solvent properties and the limiting conductivities of ions[8] describes the ion-ion interactions in the system which is minimal in the 25-15%THF .

The B coefficients which relates the interaction between solvent and solutes in a solution were negative for 0-25%THF for the THF/PC system thereby indicating weak interaction.

CONCLUSION

The results of experimental measurements of the parameters on the mixed solvents provide some significant information regarding the state of affairs in the solution.

The results show that the values are 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 THF-PC system for optimum battery performance has been established to be between 75-85%THF for the system studied. .The salt concentration with the highest molar conductivity is 0.1M $Mg(ClO_4)_2$.

Recommendations
All investigations should be carried out at much lower concentrations of the solution and all the organic solutions that are to be investigated should include non-flammable, non- volatile and high thermal stable ionic liquids.

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