

Characterization of Mixed Solvents of Tetrahydrofuran and Acetonitrile for Magnesium Ion Battery

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ABSTRACT

Mixed organic electrolytes formed by the combination of Tetrahydrofuran (THF)/ and Acetonitrile (AN) solvents with Magnesium Perchlorate salt were prepared and characterized for their physico-chemical properties. These properties include density, viscosity, conductivity, dielectric constant, Critical distance for ion pair formation, . The cells of Mg²⁺ ion containing electrolytic solutions of the binary mixtures of organic solvents 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 25⁰c 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 remain stable even at high temperatures. The mixing ratio of the organic solvents for optimal battery performance is established to be between 15-25%THF for the system studied.

Key words: Battery, Magnesium ions, conductivity, viscosity, density, voltage

Introduction:

Magnesium – based batteries are very attractive alternatives to lithium batteries. Magnesium has electrochemical characteristics similar to lithium (12 grams – per Faraday (g/F), compared to 7 g/F for lithium or 23 g/F for sodium). Magnesium–ion batteries with a Mg-metal negative electrode are expected to combine high energy density and high electromotive force, owing to the divalent careers and its low redox potential. It is capable of storing energy double that stored by Lithium ion cells (Ichitsubo et al, 2011).

Magnesium was discovered by Joseph Black in 1755. It is cheap, safe, light weight and its compounds are usually non-toxic. Metallic lithium costs about 24 times more than metallic magnesium. This is because magnesium is abundant in the earth’s crust. It is the eight most abundant element in the earth’s crust and ninth in the known universe as a whole. Magnesium is safer because it is stable when exposed to the atmosphere. Magnesium provides a theoretical specific capacity of 2,205 ampere – hours/kilogram, making it an attractive high energy density battery system (physorg. com, 2011). Magnesium catalyst that fuels magnesium battery is also much more powerful than that of the lithium batteries currently in use. The power is strong enough to run a car for seven hours, much longer than current battery powered cars. Also, as earlier mentioned, in order to meet the rising demands of consumer electronics such as watches, cameras, computers, mobile phones etc, the developments of rechargeable batteries have been the focus in the recent years. The key atomic properties of magnesium (Mg) are listed in Table 1 below

Table 1: Key properties of Magnesium.

Atomic number	12
Atomic weight	24.305 u
Atomic radius	150pm
Ionic charge	+2
Ionic radius	86pm

Magnesium – air primary batteries exists, while rechargeable magnesium batteries have not yet been commercially successful, due to the low reversibility of the magnesium electrode/electrolyte ion transfer

mechanism because of the passivating oxide layer on the magnesium anode, the lack of suitable high-conductivity Mg^{++} ion conducting electrolytes and the need for a high voltage cathode systems.

In accordance with the basic requirements of an ideal electrolyte which include high dielectric constant (ϵ), low viscosity, low melting point, high boiling point and high flash point, the following solvent properties which are useful and are important parameters of potential organic electrolytes were measured in this work: Density, Viscosity, Conductivity, Dielectric constant and Critical Distance.

This study was carried out to determine the applicability of Tetrahydrofuran/Acetonitrile (THF /AN) binary systems in the development of high energy – density Magnesium ion batteries

Materials and Methods

Materials: The solvents, d Tetrahydrofuran (THF)(99.5%) (BDH chemicals Ltd, Poole, England), Acetonitrile (AN) (99.96%) (Tedia company, Inc. USA) and the salt, Magnesium Perchlorate ($Mg(ClO_4)_2$) dried (99%) (May and Baker Ltd, Dagenham, England) were all obtained commercially.

Methods

sample preparations: Binary mixtures of d THF/AN were prepared in varying proportions of 100%, 85%, 75%,50%, 25%, 15% and 0% of THF, corresponding to mole fractions of 1.000, 0.788, 0.663, 0.397, 0.179, 0.104, and 0 of THF for THF/AN system, The working temperatures were 25, 40, 50, 60, 70°C . 0.1M, 1.0M and 2.0M of $Mg(ClO_4)_2$ solutions of each binary system were prepared. The weightings were done on Adam AAA electronic balance with a precision of $\pm 0.001g$.

Results:

Table 2: Calculated Mole Fractions Of THF/AN System

% THF	X_1	X_2
100	1.000	0.000
85	0.788	0.212
75	0.663	0.337
50	0.397	0.603
25	0.179	0.821
15	0.104	0.896
0	0.000	1.000

Table 3: Densities, ρ ,(g/cm^3) of pure and mixed solvents of THF/AN

Sample THF) (%)	Density at 25 ^o C	Density at 40 ^o C	Density at 50 ^o C	Density at 60 ^o C	Density at 70 ^o C
100	0.891	0.861	0.859	0.855	0.845
85	0.870	0.848	0.837	0.826	0.793
75	0.856	0.839	0.829	0.819	0.801
50	0.836	0.818	0.808	0.797	0.789
25	0.801	0.788	0.780	0.771	0.762
15	0.793	0.775	0.769	0.758	0.723
0	0.771	0.761	0.750	0.741	0.719

Table 4: Viscosity (cP) of pure and mixed solvents of THF / AN at 25⁰C

Sample (% THF)	Viscosity (cP) at 25 ⁰ C
100	0.420
85	0.411
75	0.395
50	0.371
25	0.352
15	0.33
0	0.311

Table 5: Dielectric constant of pure and mixed solvents of THF /AN at 25⁰C

Sample (% THF)	Dielectric Constant
100	7.58
85	12.068
75	14.86
50	22.14
25	29.42
15	33.012
0	36.7

Table 6: Conductivity measurement of mixed solvents of THF/ AN with salt in mS

Sample (% THF)	Conductivity without salt	Conductivity (0.1M salt)	Conductivity (1.0M salt)	Conductivity (2.0M salt)
100	0.005	0.41	9.5	6.9
85	0.0083	2.6	17.7	15.7
75	0.0022	5.0	16.3	15.2
50	0.12	7.9	25.6	24.5
25	0.16	6.5	34.3	37.5
15	0.0138	6.1	15.4	15.5
0	0.0031	4.1	45.8	46.8

Table 7: Conductivity measurement of mixed solvents of THF/AN with salt in Scm² mol⁻¹

Sample (% THF)	Conductivity (0.1M salt)	Conductivity (1.0M salt)	Conductivity (2.0M salt)
100	4.1	9.5	3.45
85	26	17.7	7.85
75	50	16.3	7.6
50	79	25.6	12.25
25	65	34.3	18.75
15	61	15.4	7.75
0	41	45.8	23.8

Table 8: Calculated values of critical Distance and Dielectric constant of THF/AN System

Sample (% THF)	Critical distance (10^{-10} m)	Dielectric constant
100	73.9	7.58
85	46.34	12.068
75	37.7	14.86
50	25.3	22.14
25	19.0	29.42
15	16.94	33.012
0	15.3	36.7

Table 9: Density, ρ , (g/cm^3) of THF/AN with 0.1M salt

(% THF)	25 ⁰ C	40 ⁰ C	50 ⁰ C	60 ⁰ C	70 ⁰ C
100	0.9004	0.8751	0.8658	0.8563	0.8399
85	0.8859	0.8661	0.8545	0.8429	0.8371
75	0.8714	0.8571	0.8433	0.8294	0.8225
50	0.8506	0.8330	0.8201	0.8072	0.8008
25	0.8184	0.8032	0.7943	0.7854	0.7810
15	0.8064	0.7894	0.7797	0.7700	0.7652
0	0.7944	0.7756	0.7651	0.7546	0.7494

Table 10: Density, ρ , (g/cm^3) of THF/AN with 1.0M salt

(% THF)	25 ⁰ C	40 ⁰ C	50 ⁰ C	60 ⁰ C	70 ⁰ C
100	1.0241	1.0048	1.0010	0.9895	0.9778
85	1.0140	0.9945	0.9852	0.9768	0.9685
75	1.0039	0.9814	0.9730	0.9640	0.9580
50	0.9821	0.9588	0.9489	0.9432	0.9402
25	0.9450	0.9224	0.9154	0.9109	0.9001
15	0.9351	0.9147	0.9071	0.8959	0.8883
0	0.9253	0.9069	0.8988	0.8808	0.8765

Table 11: Kinematic Viscosity Measurements of Mixed solvents of 0.1M $\text{Mg}(\text{ClO}_4)_2$, THF/ AN Mixture.

% THF	25 ⁰ C	40 ⁰ C	50 ⁰ C	60 ⁰ C	70 ⁰ C
100	0.762	0.648	0.610	0.574	0.530
85	0.712	0.636	0.590	0.564	0.524
75	0.677	0.591	0.563	0.555	0.519
50	0.610	0.580	0.554	0.545	0.515
25	0.570	0.553	0.536	0.519	0.501
15	0.562	0.540	0.528	0.510	0.498
0	0.553	0.534	0.522	0.502	0.489

Table 12: Kinematic Viscosity Measurements of Mixed solvents of 1M $\text{Mg}(\text{ClO}_4)_2$, THF/AN mixture.

% THF	25 ⁰ C	40 ⁰ C	50 ⁰ C	60 ⁰ C	70 ⁰ C
100	1.670	1.302	1.005	0.968	0.720
85	1.624	1.300	1.003	0.914	0.711
75	1.508	1.232	0.990	0.869	0.681
50	1.326	1.149	0.908	0.803	0.645
25	1.117	1.087	0.753	0.701	0.604
15	0.952	0.881	0.701	0.654	0.588
0	0.687	0.648	0.620	0.591	0.573

Table 13: Jones-Dole A and B Coefficients for the system THF/AN with the various Salt Concentrations.

Sample(%THF)	A	B
100	5.066	14.63
85	5.204	14.41
75	4.122	11.98
50	2.714	8.577
25	2.205	6.954
15	1.276	5.095
0	0.535	4.057

Table 14: Cell voltages for Mg(ClO₄)₂, (THF-AN) Concentration Cell.

(% THF)	E _{cell} Volts
100	0.30
85	0.23
75	0.25
50	0.27
25	0.23
15	0.32
0	0.27

Discussions

Density and Viscosity: The density values decreased with decrease in the mole fraction of THF for the binary system (tables 3,4,9,10). Density is a measure of solvent- solvent and ion- solvent interactions (Thirumaran et al, 2011). The decrease indicates formation of less dense products. The densities and viscosities of the systems with Mg(ClO₄)₂ increased with concentration which suggests a moderate strong associative nature in which the solute Mg(ClO₄)₂ tends to attract the solvent molecules, which indicates an increase in solvent- solvent and solute- solvent interactions which leads to volume shrinkage. Thirumaran and Satish, 2011 have also made such observations.

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. Rodriguez et al, 2003, Nageshewar et al, 2010 and Motin, 2007, have reported such.

Conductivity

The conductivity of an electrolyte solution depends on the concentration of the ionic species. The results of the conductivity measurements in tables 6 and 7, show an increase in molar conductivities with increase in %THF in the system. This increase is attributed to both the high dielectric constant of AN and the low viscosity of THF. , Tobishima et al 1989, have made such observation .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 by Matsuda and Satake 1980, and Saito et al, 1976. The decrease in conductivity observed with mole fractions with lower %THF is attributed to (1) Increase in viscosity. (2) Relaxation effect. (3) Electrophoretic effect. Such observation has also been made by Corkum et al, 1978).

Maximum conductivity is obtained in the 15% THF in the system. The results show that ion-solvent and solvent-solvent interactions contribute to the improvement of conductance. Matsuda et al, 1983 have reported such. A net increase in ion conductivity is achieved when solvents of varying properties are mixed. Increase in THF content (or low AN content) result in a very low dielectric medium where the effect of ion pair formation outweighs that of low viscosity; thus, ion conductivity drops with the increase in THF content. Therefore, the maximum in ion conductivity versus solvent composition is actually the result of the compromise between the effects of the dielectric constant and viscosity. Such a compromise illustrates the superiority of mixed solvent over single solvent electrolytes. The trend in conductance can be described by the viscosity behavior of the electrolytic media.

Jones- Doles A and B Coefficients:

The results of Jones- Doles plots for the binary systems shown in table 13 show that the A coefficient which is a function of solvent properties and the limiting conductivities of ions(Kaminsky, 1957) describes the ion-ion

interactions in the system which is minimal in the 15-25% THF in the system. The B coefficients for the system were positive for the entire fractions, indicating strong ion interactions with the solvent molecules.

Electrochemical Cell Voltage:

The measured electrochemical cell voltage values of the system shown in table 14 shows that the voltage is highest at the 15% THF fraction. The difference in concentrations is the only factor that produces cell potential in the concentration cells (Anusiem, 2000). This shows the dependence of cell potential on concentration. The low voltage also suggests the influence of low reversibility of the magnesium electrode/electrolyte ion transfer mechanism because of the passivating oxide layer on the magnesium anode.

CONCLUSION

The results of experimental measurements of the parameters on the mixed solvents provide some significant information regarding the state of affairs in a solution. The results of the physico-chemical parameters show that the values are intermediate between those of the pure solvents. The mixing ratio of the mixed system for optimum battery performance has been established to be between 15%-25% of the THF. This work shows that the mixing of organic solvents improves the physico properties of the pure solvents, thereby making them suitable for use as electrolytes in Magnesium ion batteries.

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