

CHAPTER-IV

Investigation of Diverse Interactions of Lithium Hexafluoroarsenate Prevailing in Pure and Mixed Industrial Solvent Systems by Physicochemical Methodology

IV.1. Introduction

Conductivities of electrolytes in various pure and mixed solvent systems are of much interest to chemists. The electrical conductivity of electrolytes in mixed solvent solutions mainly depends upon the concentration of the electrolyte and also upon the viscosity of the solvent. The use of mixed solvents in high energy[1]batteries has also extended the horizon in the field of mixed solvent systems[2, 3] Considering the latest development in battery industries, lithium-ion batteries are the best available energy source in the market. Lithium-ion rechargeable batteries[4] are widely used in various kinds of portable electric devices because of their high performance with large capacity and high output voltage[5]. The development of electrolyte solutions with high ionic conductivity is needed for high performance lithium ion batteries. The electrolyte solution requires high ionic conductivity, low melting point, high boiling point, and high chemical and electrochemical stabilities for the batteries of high performance as well as in practical usages[6]. Therefore, study of the behavior of lithium ion in different solvent systems helps in the production of more useful and most effective batteries[7].

The study of thermodynamic and transport properties gives a magnificent information about the molecular interactions occurring in solution systems. Volumetric and viscometric studies also deals an idea about the different molecular interactions prevailing in salt solutions containing pure and mixed solvent systems and help in the better understanding of the behaviour of the salt with different solvents. Studies on the apparent/partial molar volumes, viscosity coefficient of electrolytes and the dependence on concentration of solution have been undertaken as a function, for studying the ion-ion and ion-solvent interactions.

The solvents used in this study find wide industrial usage. The mixture of these two solvents provides a wide range of variation of thermodynamic properties as viscosity, relative permittivity etc. The variation in these properties has been taken into consideration, as these properties help in determining the extent of ion-solvent and solvent-solvent interactions occurring in the solution systems.

This work is an attempt to understand the thermodynamics of lithium hexafluoroarsenate (LiAsF_6) in different mass fraction (w_1) of ethylene glycol (EG) in methanol (MeOH) at 298.15K, in order to explore the molecular interactions occurring in the systems. The results are useful for the interpretation of the nature of interactions that occur between the salts and mixed solvent systems. Thermodynamic parameters are evaluated and discussed.

IV.2. Experimental Section

IV.2.1. Materials

Lithium hexafluoroarsenate (LiAsF_6) has been procured form Sigma Aldrich, Germany and used as purchased. The mass fraction purity of LiAsF_6 was 0.98. Methanol (MeOH) and ethylene glycol (EG) were procured from Merck, India and were purified by standard methods[8]. The purity of the solvents was 99%.

IV.2.2. Apparatus and procedure

Binary solvent mixtures were prepared by mixing the required volumes of ethylene glycol and methanol using the appropriate conversion of the required mass of each liquid into volume at 298.15 K using solvent density (Table 1). A stock solution for each salt was prepared by mass (Mettler Toledo AG-285 with uncertainty $\pm 0.0003\text{g}$), and the working solutions were obtained by mass dilution in both pure and mixed solvents. The uncertainty of molarity of different salt solutions was evaluated to be $\pm 0.0001 \text{ mol}\cdot\text{dm}^{-3}$.

The values of relative permittivity (ϵ) of the solvent mixtures were assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald and Moldner[9]. The physical properties of the binary solvent mixtures of different mass fractions at 298.15 K are listed in

Table1. Density (ρ), viscosity (η) and relative permittivity (ε) of solvent mixtures at 298.15 K

Mass fraction of EG (w_1) in MeOH	$^a\rho \cdot 10^{-3} / \text{kg} \cdot \text{m}^{-3}$		$^b\eta / \text{mPa} \cdot \text{s}$		ε
	Expt	Lit	Expt	Lit	
$w_1=0.00$	0.78590	0.78660 ^c	0.54	0.5445 ^c	32.7 ^c
$w_1=0.25$	0.86436	-	2.03	-	34.7 ^d
$w_1=0.50$	0.94433	-	4.17	-	36.7 ^d
$w_1=0.75$	1.02077	-	7.45	-	38.7 ^d
$w_1=1.00$	1.10900	1.10980 ^c	16.88	16.90 ^c	40.7 ^c

^a uncertainty in the density values: $\pm 0.00002 \cdot 10^{-3} \text{ kg m}^{-3}$.

^b uncertainty in the viscosity values: $\pm 0.003 \text{ mPa s}$.

^c ref [10].

^d calculated using the procedure described in ref [9].

The conductance measurements were performed in a Systronics-308 conductivity bridge (accuracy $\pm 0.01 \%$) using a dip-type immersion conductivity cell, CD-10, having a cell constant of $0.1 \pm 0.001 \text{ cm}^{-1}$. A water bath maintained within $T = (298.15 \pm 0.01) \text{ K}$ was used and the cell was calibrated by the method proposed by Lind et al[11]. The conductance data were reported at a frequency of 1 kHz and were uncertain to $\pm 0.3\%$.

The measurement of density (ρ) was done by vibrating-tube Anton Paar density-meter (DMA 4500M) with a precision of $\pm 0.0005 \text{ g} \cdot \text{cm}^{-3}$. It was calibrated by double-distilled water and dry air. The temperature was automatically kept constant within $\pm 0.01 \text{ K}$.

The viscosity was also measured with the help of Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 fitted to a Brookfield Digital Bath TC-500. The temperature was controlled by the Brookfield Digital Bath TC-500. The uncertainty of the viscosity values are $\pm 0.03 \text{ K}$.

IV.3. Results and Discussion

IV.3.1 Conductance Measurement

The experimental values of equivalent conductances (Λ) of the electrolyte measured at the corresponding molar concentrations(c) are given in Table 2. The conductance results have been analysed using the Fuoss conductance equation[12, 13].

Table2. The concentration (c) and molar conductance (Λ) of LiAsF₆ in different mass fraction of EG (w_1) in MeOH at 298.15 K

${}^d c \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	${}^e \Lambda \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	${}^d c \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	${}^e \Lambda \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	${}^d c \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	${}^e \Lambda \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$
$w_1=0.00$		$w_1=0.25$		$w_1=0.50$	
12.91	93.35	11.45	71.55	9.93	49.85
17.87	91.22	20.99	69.22	18.21	47.39
22.13	89.64	29.06	66.64	25.21	45.64
25.81	88.38	35.98	65.38	31.22	44.38
29.04	87.25	41.98	63.25	36.42	43.25
34.42	85.65	47.22	62.65	40.97	42.45
40.56	84.02	51.85	62.02	44.99	41.72
45.17	82.82	55.97	60.82	51.75	40.72
51.63	81.32	59.65	60.32	59.60	39.62
55.93	80.45	68.69	58.45	65.56	38.65
$w_1=0.75$		$w_1=1.00$			
11.45	21.85	5.68	3.85		
20.99	19.79	12.83	3.39		
29.06	18.34	19.28	3.04		
35.98	17.28	24.98	2.78		
41.98	16.55	30.02	2.55		
47.22	15.75	34.48	2.35		
51.85	15.22	38.45	2.22		
55.97	14.72	42.01	2.12		
59.65	14.42	45.20	2.02		
68.69	13.45	53.11	1.82		

^d Uncertainty in the molarity: $\pm 0.0002 \text{ mol dm}^{-3}$.^e Uncertainty in the molar conductance: $\pm 0.01 \text{ S m}^2 \text{ mol}^{-1}$

Three adjustable parameters namely the limiting molar conductivity (Λ_0), the association constant (K_A , A association constant describing the bonding affinity of two molecules at equilibrium, especially the bonding affinity of lithium hexafluoroarsenate

and solvent molecule.) and the distance of closest approach of ions (R) are derived for a given set of conductivity values ($c_j, \Lambda_j, j = 1, \dots, n$) from the following set of equations.

$$\Lambda = P \Lambda_0 [(1 + R_X) + E_L] \quad (1)$$

$$P = 1 - \alpha(1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_A c \gamma^2 / 2 \quad (3)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (4)$$

$$\beta = e^2 / (\varepsilon k_B T) \quad (5)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (6)$$

here the relaxation field effect is denoted by R_X , E_L represents the electrophoretic counter current, k denotes the radius of the ion atmosphere, ε is the relative permittivity of the solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_S is the association constant of the contact-pairs, K_R is the association constant of the solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance. The computations were performed using a program suggested by Fuoss[12] [13] and Shedlovsky extrapolation[14] of the data were employed to obtain the initial Λ_0 values for the iteration procedure. Input for the program is the set $(c_j, \Lambda_j, j = 1, \dots, n), n, \varepsilon, \eta, T$, initial values of Λ_0 , and an instruction to cover a preselected range of R values.

In practice, for the minimization of standard deviation all the calculations are performed by finding the values of Λ_0 and δ

$$\delta^2 = \sum [\Lambda_j (\text{calcd}) - \Lambda_j (\text{obsd})]^2 / (n-2) \quad (7)$$

For a sequence of R values and then plotting δ against R , the minimum of the δ - R versus R curve represents best-fit R . So, approximate runs are made over a fairly wide range of R values using 0.1 increment to locate the minimum, but no significant minima were found in the δ - R curves for all the salts studied here; thus, R values are assumed to be $R = a+d$, where the sum of the crystallographic radii of the ions is represented by a and the average distance corresponding to the side of a cell occupied by a solvent molecule is denoted by d . The distance d is given by[15]

$$d (\text{\AA}) = 1.183 (M / \rho)^{1/3} \quad (8)$$

Where, M is the molar mass of the solvent and ρ is its density. For mixed solvents, M is replaced by the mole fraction average molar mass (M_{av}) which is given by

$$M_{av} = M_1 M_2 / (w_1 M_2 + w_2 M_1) \quad (9)$$

Where, w_1 is the mass fraction of the first component of molar mass M_1 . The values of Λ_0 , K_A and R attained by this procedure are reported in Table 3.

Table3. Limiting molar conductance (Λ_0), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental Λ (δ) of LiAsF₆ in different mass fraction of EG (w_1) in MeOH at 298.15 K.

Mass fraction of EG (w_1) in MeOH	$\Lambda_0 \cdot 10^4 / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$K_A / \text{dm}^3 \cdot \text{mol}^{-1}$	$R/\text{\AA}$	δ
$w_1=0.00$	102.98	76.06	8.37	0.06
$w_1=0.25$	79.16	82.47	8.42	0.43
$w_1=0.50$	55.58	115.73	8.50	0.16
$w_1=0.75$	30.10	447.75	8.64	0.34
$w_1=1.00$	5.72	1160.25	8.83	0.14

A perusal of Table 3 and Figure 1, shows that the values of Λ_0 for LiAsF₆ decrease as the concentration (c) of EG in the binary solvent mixture increases. Figure 2 shows that the values of Λ_0 both in pure and solvent mixtures are positive and decreases as mass fraction of EG in MeOH increases. This can be explained in view of the relative permittivity and viscosity of the solvent mixtures. The viscosity of the solvent mixture increases with increasing mass fraction (w_1) of the EG in MeOH rendering to greater solvation of LiAsF₆. This can also be interpreted on the basis of preferential solvation. The salt prefers EG than MeOH in binary mixtures. The structure of EG also favours the observation. Due to the presence of two -OH groups in the molecule the ions are more solvated by EG than MeOH. The greater interaction has been seen by the interaction of charged ion and adjacent solvent molecules, which leads to reduction in mobility of ions, and thus increases the solvation. With the increasing mass fraction of EG in the solvent mixture the conductance of the solution decreases and ion-solvent interaction increases.

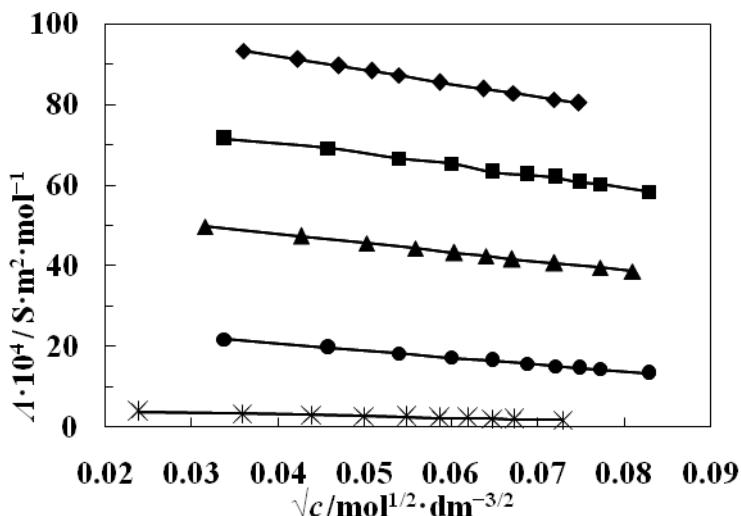


Fig.1. Plot of molar conductance (Λ) and the square root of concentration (\sqrt{c}) of LiAsF₆ in $w_1=0.00$ (-◆-), $w_1=0.25$ (-■-), $w_1=0.50$ (-▲-), $w_1=0.75$ (-●-), and $w_1=1.00$ (-*-*) mass fraction of EG in MeOH at $T = 298.15\text{ K}$

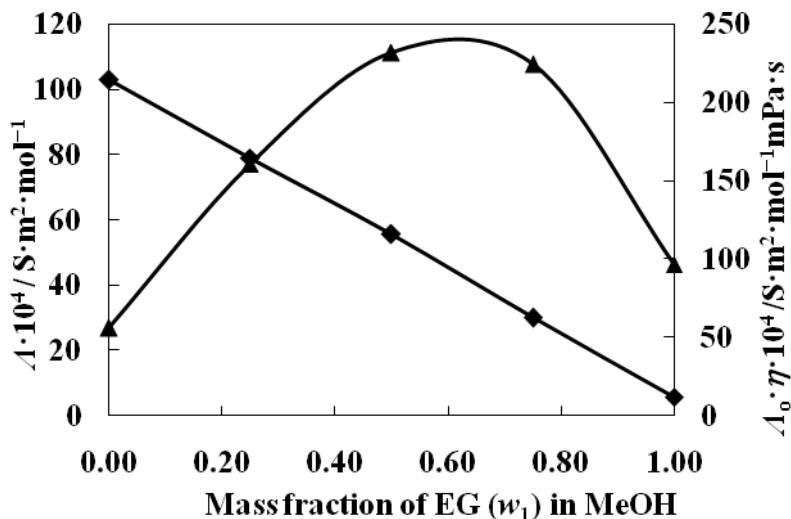


Fig.2. Plot of limiting molar conductance (Λ_o) (-◆-) and Walden Product ($\Lambda_o \cdot \eta$) (-▲-) of LiAsF₆ in different mass fraction (w_1) of EG in MeOH at $T = 298.15\text{ K}$

Ion-solvation can also be explained with the help of another characteristic property called the Walden product ($\Lambda_o \cdot \eta$). Walden products of the electrolyte in various binary solvent mixtures have been calculated and given in Table 4.

Table4. Walden product ($\Lambda_o \cdot \eta$) and Gibb's energy change (ΔG°) of LiAsF₆ in different mass fraction of ethylene glycol (w_1) in methanol at 298.15 K

Mass fraction of EG (w_1) in MeOH	$\Lambda_o \cdot \eta \cdot 10^4 / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \text{mPa} \cdot \text{s}$	$\Delta G^\circ \cdot 10^{-3} / \text{kJ} \cdot \text{mol}^{-1}$
$w_1=0.00$	56.07	-10.74
$w_1=0.25$	160.68	-10.94
$w_1=0.50$	231.77	-11.78
$w_1=0.75$	224.26	-15.13
$w_1=1.00$	96.630	-17.49

Table 4 and Figure 2 have shown that the value of Walden product ($\Lambda_o \eta$) increases as the content of EG (w_1) increases in the binary mixture but in pure EG with the concomitant increase of the solvent viscosity, the $\Lambda_o \eta$ decreases[16]. This trend suggests, the predominance of the Λ_o over solvent viscosity (η) in pure MeOH and solvent mixtures containing 0.00-0.75 mass fraction of EG whereas in case of pure EG the value of Walden product suggests the fact that η predominate Λ_o in pure EG solution. The results of molar conductance and the Walden product reflect strong electrostatic ion-solvent interactions. Changes in the Walden product with concentration are common and they can be attributed to changes in ion-solvation i.e., ion-solvent interactions.

The starting point for most evaluations of ionic conductance is Stokes' law which states that the limiting Walden product ($\lambda_o^\pm \eta$), (product of the limiting ionic conductance and solvent viscosity) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions is a constant. The values of the ionic conductances (λ_o^\pm) (Table 5 and Figure 3) for the Li^+ and AsF_6^- ion in different mass fraction of EG in MeOH were calculated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as a 'reference electrolyte' following the scheme as suggested by B. Das et al[17].

Table5. Ionic limiting molar conductance (λ_o^\pm), ionic Walden product ($\lambda_o^\pm \eta$), crystallographic radii (r_c) and Stoke's radii (r_s) of Li^+ and AsF_6^- ion in different mass fraction of EG (w_1) in MeOH at 298.15 K.

Mass fraction of EG (w_1) in MeOH	$\lambda_o^{\pm} \cdot 10^4 /$	$\lambda_o^{\pm} \eta \cdot 10^4 /$	$r_c / \text{\AA}$	$r_s / \text{\AA}$	
	$\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \text{mPa} \cdot \text{s}$		Li^+	AsF_6^-
$w_1=0.00$	61.22	41.76	33.34	22.74	1.33
$w_1=0.25$	47.06	32.10	95.53	65.16	1.33
$w_1=0.50$	33.04	22.54	137.79	93.98	1.33
$w_1=0.75$	17.90	12.21	133.32	90.93	1.33
$w_1=1.00$	3.40	2.32	57.45	39.18	1.33

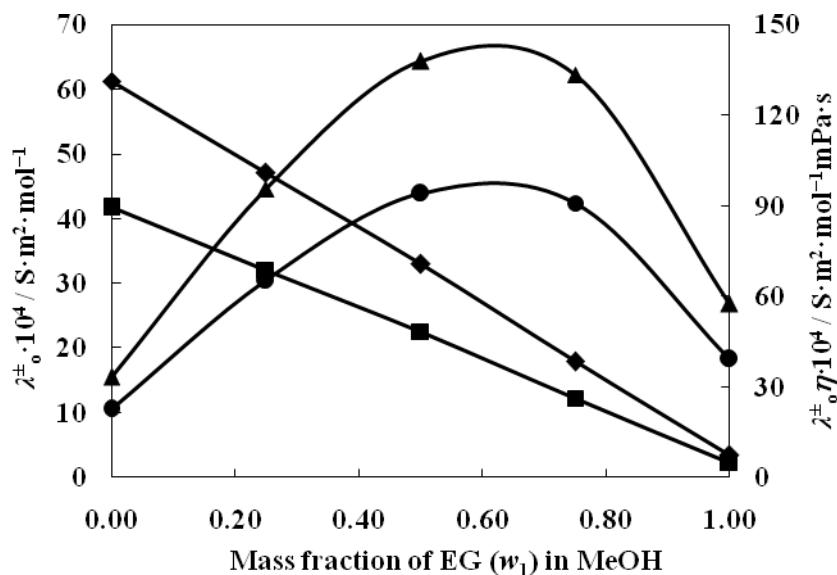


Fig.3. Plot of limiting ionic conductance (λ_o^{\pm}) of Li^+ (-◆-), AsF_6^- (-■-) and ionic Walden Product ($\lambda_o^{\pm} \eta$) of Li^+ (-▲-) , AsF_6^- (-●-) in different mass fraction (w_1) of EG in MeOH at $T = 298.15 \text{ K}$

The λ_o^{\pm} values were in turn utilized for the calculation of Stokes' radii (r_s) according to the classical expression[16]

$$r_s = \frac{F^2}{6\pi N_A \lambda_o^{\pm} r_c} \quad (10)$$

There are marked characteristic behaviours in the association constant (K_A) values. Inspection of Table 3 and Figure 4 shows that K_A value of the electrolyte increases with an increase in the mass fraction of ethylene glycol in the solvent mixture. Such behaviour in the solvent mixture is also observed in other alcohols[18].

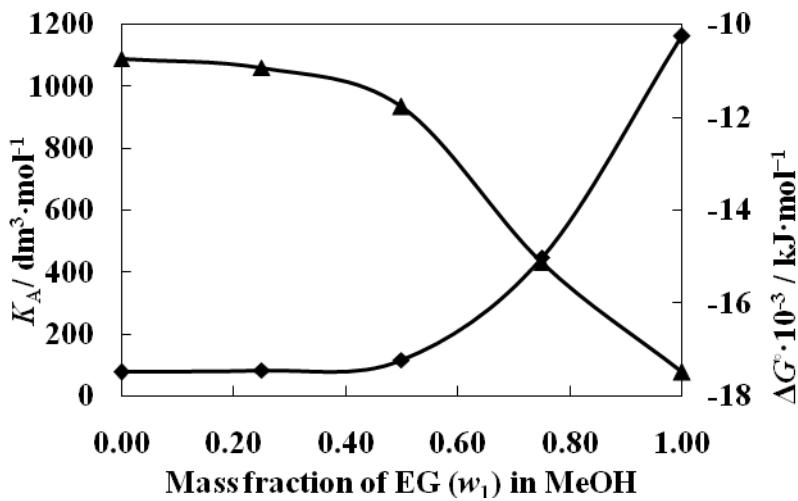


Fig.4. Plot of association constant (K_a) (-♦-), and Gibb's energy change (ΔG°) (-▲-) of LiAsF₆ in different mass fraction (w_1) of EG in MeOH at 298.15 K

The Gibbs energy change, ΔG° for association is calculated from the following relation[19] and is reported in Table 4.

$$\Delta G^\circ = -RT \ln K_a \quad (11)$$

The negative values ΔG° can be explained by considering the participation of specific interaction in the ion-association process for ion-pair formation of Li⁺/AsF₆⁻ with the solvents in binary mixture of EG and MeOH. From Table 4, it can be seen that the ΔG° values decrease with increasing mass fraction (w_1) of EG in solvent mixtures indicating greater degree of ion-association. The ΔG° in Table 4 along with the other parameters mentioned above is in good agreement with the results observed by Barthel[20] and Hazra[21].

IV.3.2 Density Measurement

The measured value of densities (ρ) and viscosities (η) of LiAsF₆ in different mass fraction (w_1) of EG in MeOH, as a function of concentration at 298.15 K are reported in Table 6. For the analysis of interaction of LiAsF₆ in different mass of EG in MeOH, limiting apparent molar volume is important. For this purpose, the apparent molar volumes, ϕ_V , given in Table 6 were found out from the solution density values using the following equation[22]

$$\phi_V = M / \rho_o - 1000(\rho - \rho_o) / c \rho \rho_o \quad (12)$$

where M is the molar mass of the solute, c is the molarity of the solution, ρ and ρ_0 are the densities of the solution and solvent, respectively.

Table 6. Experimental values of densities (ρ), apparent molar volume (ϕ_v), viscosities (η), $(\eta/\eta_0 - 1)/\sqrt{c}$ of LiAsF₆ in different mass fraction of EG (w_1) in MeOH at $T = 298.15$ K.

^f Molarity (c) / mol·dm ⁻³	^g $\rho \cdot 10^{-3}$ /kg·cm ⁻³	$\phi_v \cdot 10^6$ /m ³ ·mol ⁻¹	^h η /mPa·s	$(\eta/\eta_0 - 1)/\sqrt{c}$ /kg ^{1/2} ·mol ^{-1/2}
$w_1 = 0.00$				
0.000	0.78590	-	0.54	-
0.019	0.78810	62.58	0.67	1.579
0.038	0.79040	58.34	0.73	1.674
0.057	0.79276	55.23	0.78	1.745
0.077	0.79519	52.19	0.83	1.840
0.096	0.79764	50.03	0.87	1.880
0.115	0.80013	48.02	0.91	1.930
$w_1 = 0.25$				
0.000	0.86436	-	2.03	-
0.017	0.86635	73.10	2.27	0.897
0.035	0.86848	67.70	2.41	1.004
0.052	0.87069	63.84	2.53	1.078
0.070	0.87297	60.57	2.64	1.138
0.087	0.87533	57.36	2.75	1.201
0.105	0.87774	54.59	2.85	1.249
$w_1 = 0.50$				
0.000	0.94433	-	4.17	-
0.016	0.946	89.50	4.35	0.342
0.032	0.94785	83.15	4.51	0.457
0.048	0.94985	77.50	4.67	0.548
0.064	0.95194	73.09	4.82	0.617
0.080	0.9541	69.45	4.98	0.687
0.096	0.95635	65.97	5.13	0.744

$w_1 = 0.75$				
0.000	1.02077	-	7.45	-
0.015	1.02196	114.15	7.55	0.111
0.029	1.02336	107.29	7.75	0.235
0.044	1.02494	101.08	7.97	0.332
0.059	1.02664	96.02	8.2	0.414
0.074	1.02843	91.81	8.43	0.484
0.089	1.03034	87.70	8.68	0.554
$w_1 = 1.00$				
0.000	1.10900	-	16.88	-
0.014	1.10949	147.14	16.92	0.010
0.027	1.11026	138.73	17.25	0.126
0.041	1.11124	131.72	17.65	0.220
0.055	1.11234	126.41	18.09	0.302
0.068	1.11362	121.06	18.54	0.371
0.082	1.11505	115.99	19.05	0.444

^f uncertainty in the molarity: $\pm 0.0002 \text{ mol dm}^{-3}$.

^g uncertainty in the density values: $\pm 0.00002 \cdot 10^{-3} \text{ kg m}^{-3}$.

^h uncertainty in the viscosity values: $\pm 0.003 \text{ mPa s}$.

The limiting apparent molar volume ϕ_V^0 was calculated in accordance with a least-squares treatment to the plots of ϕ_V versus \sqrt{c} using the following Masson equation[19]

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{c} \quad (13)$$

where ϕ_V^0 is the apparent molar volume at infinite dilution and S_V^* is the experimental slope. The values of ϕ_V^0 and S_V^* are reported in Table 7.

Table 7. Limiting apparent molar volume (ϕ_V^0), experimental slopes (S_V^*), A-, B-coefficients of LiAsF₆ in different mass fraction of EG (w_1) in MeOH at 298.15 K

Mass fraction of EG (w_1) in MeOH	$\phi_V^0 \cdot 10^6$ /m ³ ·mol ⁻¹	$S_V^* \cdot 10^6$ /m ³ ·mol ^{-3/2} ·kg ^{1/2}	A /kg ^{1/2} ·mol ^{-1/2}	B /kg·mol ⁻¹

$w_1=0.00$	72.62	-72.95	1.329	1.785
$w_1=0.25$	85.74	-96.03	0.659	1.830
$w_1=0.50$	105.88	-129.12	0.067	2.190
$w_1=0.75$	132.73	-150.63	-0.193	2.499
$w_1=1.00$	168.63	-182.52	-0.291	2.546

The variation of ϕ_V^0 with the increase in the mass fraction of ethylene glycol in the solvent mixture is shown in Figure 5. The extent of ion-solvent interaction can be examined by taking the ϕ_V^0 values. The plausible mechanism of interaction between LiAsF₆ and Solvents (EG and MeOH) has been given in the **Scheme 1**. A perusal of Table 7 indicates that the ϕ_V^0 values are generally positive and increase with the increasing amount of EG in the binary mixtures.

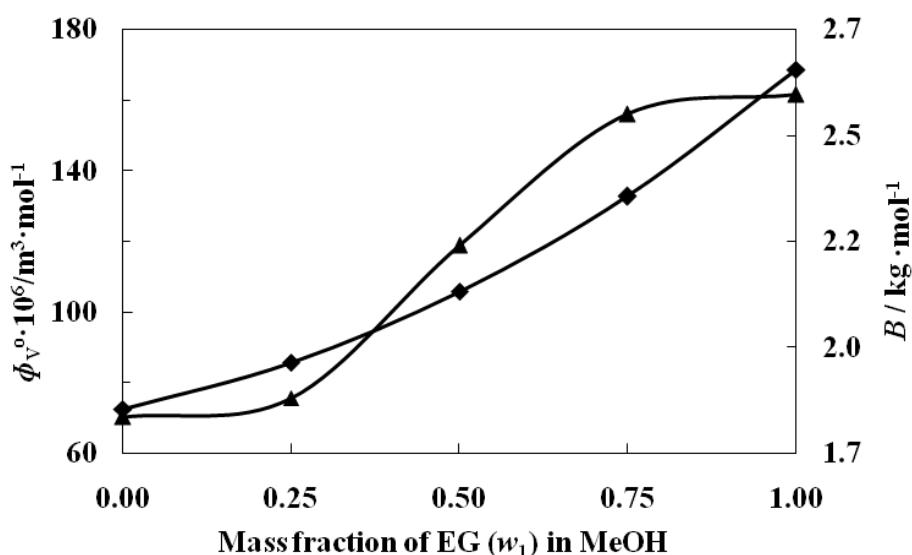


Fig.5. Plot of limiting apparent molar volume (ϕ_V^0) (-◆-) and viscosity B -coefficient (-▲-) vs. mass fraction (w_1) of EG in MeOH for LiAsF₆ at $T = 298.15$ K

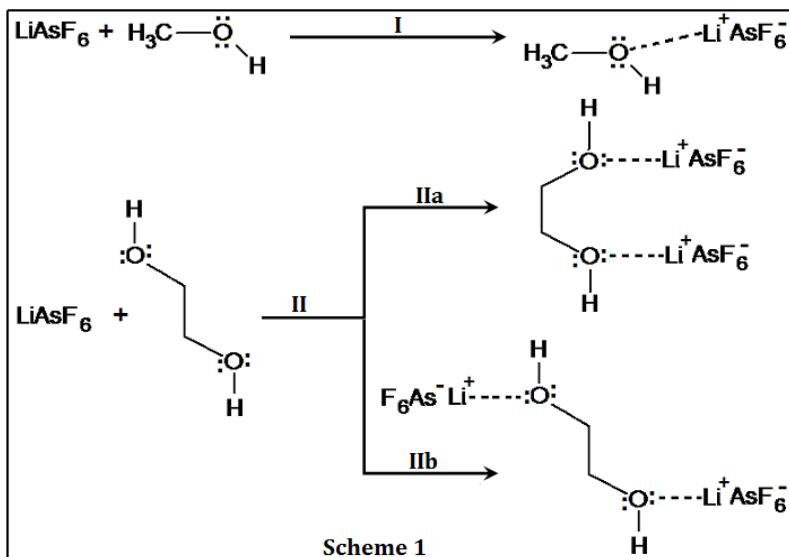


Fig.6: The plausible mechanism of interaction between LiAsF_6 and Solvents (ethylene glycol and methanol)

The Scheme 1 suggested that the more number of electrolytes (LiAsF_6) interact with ethylene glycol (have two plausible side for interaction) than methanol (have only single plausible side for interaction as per the nucleophilic group of the molecules). This indicates the presence of strong ion-solvent interactions and these interactions increase with an increase in the mass fraction of EG in MeOH, suggesting a larger electrostriction at higher amounts of EG in the mixture. The higher the electrostriction of the central (Li^+ and AsF_6^-) ion, greater the pulling effect on the solvent molecules (present in the bulk solution) toward itself. More solvent molecules are associated, which results in higher ϕ_V^0 value. Thus, both the ion (Li^+ and AsF_6^-) strongly associates with the solvents.

On the other hand, S_V^* indicates the extent of ion-ion interactions. Table 7 shows that S_V^* values are negative and decreases with increasing mass fraction of EG in MeOH, which attributes very weak or negligible ion-ion interaction. From the same Table 7 it can be seen that the ϕ_V^0 values are comparatively higher than S_V^* , suggesting the fact that the ion-solvent interaction dominates over the ion-ion interaction. This is in excellent agreement with the results drawn from the conductance data discussed earlier. Similar results were also observed in some 1:1 electrolytes i ethylene glycol mono methyl ether+ methyl alcohol[22].

IV.3.3. Viscosity Measurement

These viscosity data were utilized to calculate the viscosity *B*-coefficient using Jones-Dole equation[23]

$$\eta/\eta_0 = \eta_r = 1 + B c + A \sqrt{c} \quad (14)$$

$$(\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \quad (15)$$

where the relative viscosities η_r are expressed by $\eta_r = \eta/\eta_0$, where η and η_0 signify the viscosities of the solution and solvent mixture respectively. The values of $(\eta_r - 1)/\sqrt{c}$ are listed in Table 6. These η_r values have been utilized to calculate the viscosity *B* coefficient analysed by the Jones-Dole equation. *A* and *B* are viscosity coefficient and indicates the ion-ion and ion-solvent interactions respectively. The values of *A* and *B*-coefficient are obtained by plotting $(\eta_r - 1)/\sqrt{c}$ against \sqrt{c} and reported in Table 7. A perusal of Table 7 shows that the values of the *A*-coefficient are generally negative for all the solutions under investigation at all composition ranges and indicate the presence of weak ion-ion interactions, and these interactions further decreases with increasing amount of EG in the mixtures. The viscosity *B*-coefficient[24] reflects the effects of ion-solvent interactions in the solution. Table 7 and Figure 5 illustrates that the values of the viscosity *B*-coefficient for the salt in the studied mixed solvent systems are positive, thereby suggesting the presence of strong ion-solvent interaction in the solution and this interaction is strengthened with increasing amount of EG in the binary mixtures. This is in good agreement with the results of derived parameters obtained from conductance and density measurement, discuss earlier.

In view of various derived parameter obtained and discussed above, the plausible diagrams of molecular interaction and solvation of the ions in solvent mixtures are given in **Schemes 2**.

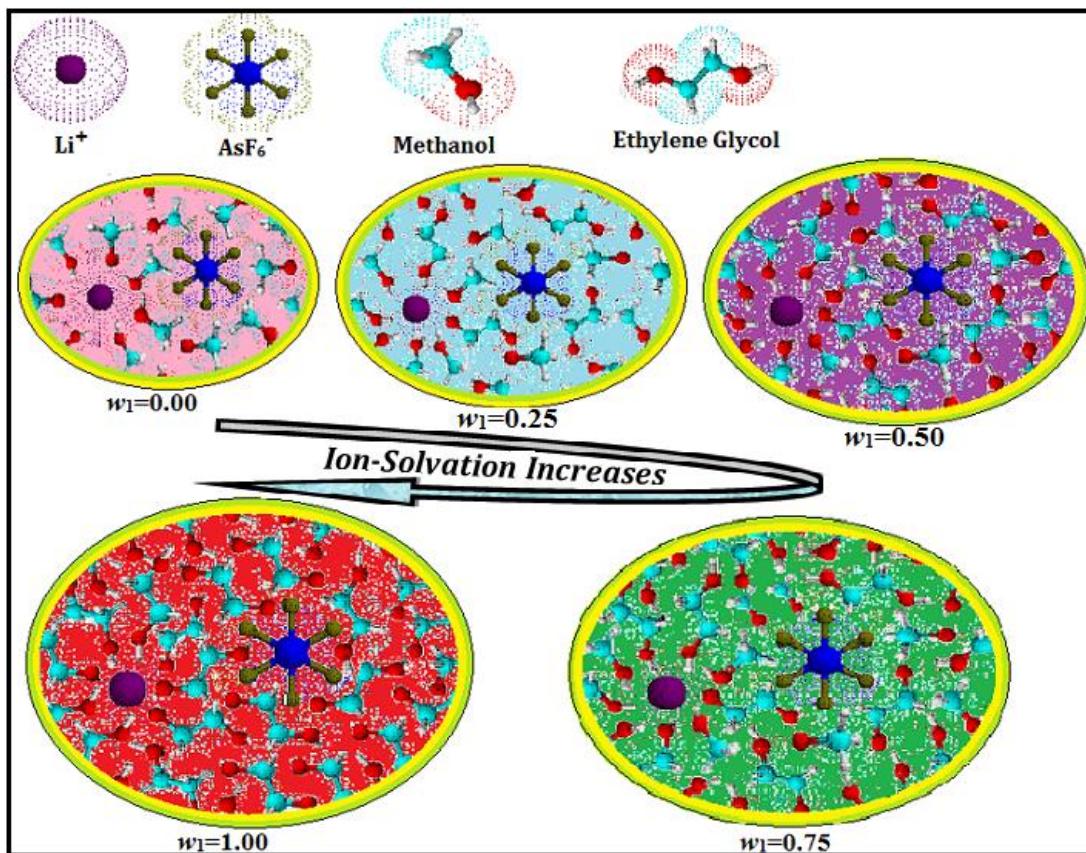


Fig.7. The plausible diagrams of molecular interaction and solvation of the ions in solvent mixtures

IV.4. Conclusion

The extensive study of lithium hexafluoroarsenate in the binary mixture of EG and MeOH suggests the fact that the electrolyte remains largely associated in the mixture which is evident from the conductivity study of LiAsF₆ in different mass fraction of EG in MeOH. Limiting apparent molar volume and viscosity B-coefficient values for LiAsF₆ in the binary mixtures indicates the presence of strong ion-solvent interactions and these interactions are further strengthened with increasing mass fraction of EG in MeOH.