

**Investigation of Diverse Interactions of Lithium Hexafluoroarsenate Prevailing in Pure and Mixed Industrial Solvent Systems by Physicochemical Methodology**Biraj Kumar Barman¹, Deepak Ekka^{1,2}, Rajani Dewan³, Mahendra Nath Roy^{1*}

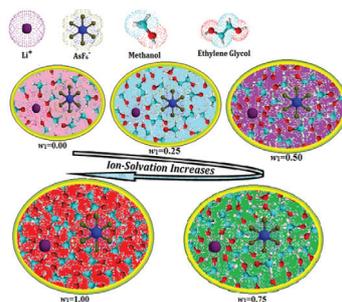
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Received 31st July 2017; Revised 18th August 2017; Accepted 21st August 2017**ABSTRACT**

Precise measurements of electrolytic conductivities, densities, and viscosities of lithium hexafluoroarsenate (LiAsF_6) have been reported in $w_1=0.00, 0.25, 0.50, 0.75, 1.00$ mass fraction of ethylene glycol in methanol at 298.15 K. The limiting molar conductivities (Λ_0), association constants (K_A), and the distance of closest approach of the ions (R) have been evaluated using the Fuoss conductance equation (1978) for ion-pair formation. The Walden products have been obtained and discussed. Apparent molar volumes (ϕ_V) and viscosity B-coefficients have been determined from the density (ρ) and viscosity (η) data, respectively. The limiting apparent molar volumes (ϕ_V^0), and experimental slopes (S_V^*) have been obtained from Masson equation and interpreted in terms of ion-solvent and ion-ion interactions, respectively. The viscosity data have been analyzed using Jones-Dole equation, and the derived parameters A- and B-coefficient have also been interpreted for ion-ion and ion-solvent interactions, respectively, in the solutions.

Graphical abstract

The exploration of ion-association of lithium hexafluoroarsenate in the binary system of ethylene glycol+methanol provides most useful inkling in lithium-ion batteries.



Key words: Lithium hexafluoroarsenate, Ethylene glycol, Methanol, Conductivity, Density, Viscosity.

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 on the concentration of the electrolyte and also on 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 and lithium-ion batteries is 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, the study of the behavior of lithium ion in

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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 deal 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 behavior of the salt with different solvents. Studies on the apparent/partial molar volumes, viscosity coefficient of electrolytes, and the dependence on the 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 and relative permittivity. 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 298.15 K, 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.

2. EXPERIMENTAL

2.1. Materials

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

2.2. Apparatus and Procedure

Binary solvent mixtures were prepared by mixing the required volumes of EG and MeOH using the appropriate conversion of the required mass of each liquid into the 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 ± 0.0003 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 Table 1.

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 $T = 298.15 \pm 0.01$ 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 4500 M) 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 ± 0.01 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 is ± 0.03 K.

Table 1: 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

^aUncertainty in the density values: $\pm 0.00002 \cdot 10^{-3} \text{ kg m}^{-3}$. ^bUncertainty in the viscosity values: $\pm 0.003 \text{ mPa s}$. ^cRef. [10].

^dCalculated using the procedure described in ref. [9]. EG: Ethylene glycol, MeOH: Methanol

3. RESULTS AND DISCUSSION

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 analyzed using the Fuoss conductance equation [12,13].

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 LiAsF₆ 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.

$$\Lambda = P\Lambda_0[(1+R\chi)+E_1] \tag{1}$$

$$P = 1 - \alpha(1 - \gamma) \tag{2}$$

$$\gamma = 1 - K_A c \gamma^2 \tag{3}$$

$$-\ln f = \beta k / 2(1 + kR) \tag{4}$$

$$\beta = e^2 / (\epsilon k_B T) \tag{5}$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \tag{6}$$

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 was 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, ϵ, η, T initial values of Λ_0 and an instruction to cover a preselected range of R values.

Table 2: The concentration (c) and molar conductance (Λ) of LiAsF₆ in different mass fractions 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		

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

LiAsF₆: Lithium hexafluoroarsenate, EG: Ethylene glycol, MeOH: Methanol

In practice, for the minimization of standard deviation, all the calculations are performed by finding the values of A_0 and δ .

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

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 . Hence, 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 using the following Ekka and Roy equation [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 A_0 , K_A , and R attained by this procedure are reported in Table 3.

A perusal of Table 3 and Figure 1 shows that the values of A_0 for LiAsF₆ decrease as the concentration (c) of EG in the binary solvent mixture increases. Figure 2 shows that the values of A_0 both in pure and solvent mixtures are positive and decrease 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 favors 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.

Ion solvation can also be explained with the help of another characteristic property called the Walden

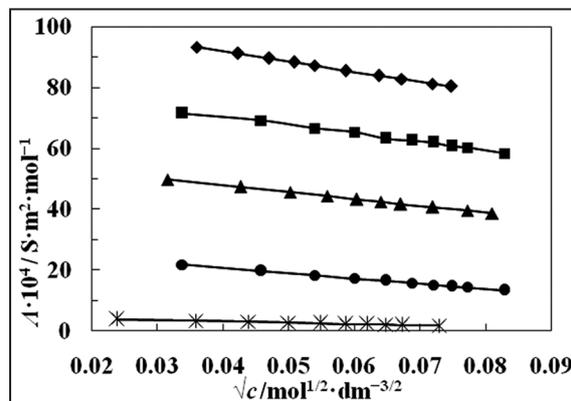


Figure 1: Plot of molar conductance (A) and the square root of concentration (\sqrt{c}) of lithium hexafluoroarsenate in $w_1=0.00$ (-♦-), $w_1=0.25$ (-■-), $w_1=0.50$ (-▲-), $w_1=0.75$ (-●-), and $w_1=1.00$ (-*-) mass fraction of ethylene glycol in methanol at $T=298.15$ K.

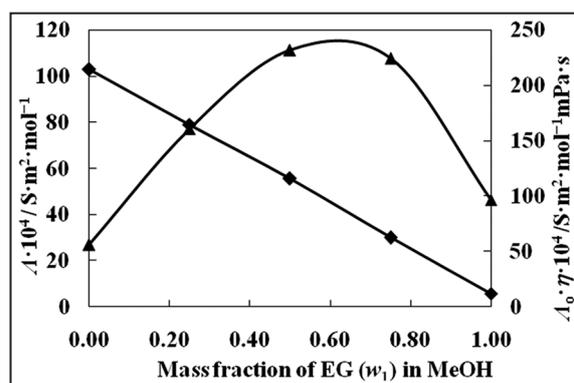


Figure 2: Plot of limiting molar conductance (A_0) (-♦-) and Walden Product ($A_0\eta$) (-▲-) of lithium hexafluoroarsenate in different mass fraction (w_1) of ethylene glycol in methanol at $T=298.15$ K.

Table 3: Limiting molar conductance (A_0), association constant (K_A), co-sphere diameter (R), and standard deviations of experimental A (δ) of LiAsF₆ in different mass fractions of EG (w_1) in MeOH at 298.15 K

Mass fraction of EG (w_1) in MeOH	$A_0 \cdot 10^4 / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$K_A / \text{dm}^3 \cdot \text{mol}^{-1}$	$R / \text{\AA}$	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

LiAsF₆: Lithium hexafluoroarsenate, EG: Ethylene glycol, MeOH: Methanol

product ($A_0\eta$). Walden products of the electrolyte in various binary solvent mixtures have been calculated and given in Table 4.

Table 4 and Figure 2 have shown that the value of Walden product ($A_0\eta$) 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 $A_0\eta$ decreases [16]. This trend suggests the predominance of the A_0 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 A_0 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 ($\lambda_0^\pm\eta$), (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, it is a constant. The values of the ionic conductances (λ_0^\pm) (Table 5 and Figure 3) for the Li^+ and AsF_6^- ion in different mass fractions of EG in

Table 4: Walden product ($A_0\eta$) and Gibbs energy change (ΔG_0) of LiAsF_6 in different mass fractions of ethylene glycol (w_1) in methanol at 298.15 K

Mass fraction of EG (w_1) in MeOH	$A_0\eta \cdot 10^4 / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \text{ mPa} \cdot \text{s}$	$\Delta G_0 \cdot 10^{-3} / \text{kJ} \cdot \text{mol}^{-1}$
$w_1=0.00$	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 5: Ionic limiting molar conductance (λ_0^\pm), ionic Walden product ($\lambda_0^\pm\eta$), crystallographic radii (r_c), l 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	$\lambda_0^\pm \cdot 10^4 / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$		$\lambda_0^\pm\eta \cdot 10^4 / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \text{ mPa} \cdot \text{s}$		$r_c / \text{\AA}$		$r_s / \text{\AA}$	
	Li^+	AsF_6^-	Li^+	AsF_6^-	Li^+	AsF_6^-	Li^+	AsF_6^-
$w_1=0.00$	61.22	41.76	33.34	22.74	1.33	1.95	2.46	3.60
$w_1=0.25$	47.06	32.10	95.53	65.16	1.33	1.95	0.86	1.26
$w_1=0.50$	33.04	22.54	137.79	93.98	1.33	1.95	0.59	0.87
$w_1=0.75$	17.90	12.21	133.32	90.93	1.33	1.95	0.61	0.90
$w_1=1.00$	3.40	2.32	57.45	39.18	1.33	1.95	1.43	2.09

LiAsF_6 : Lithium hexafluoroarsenate, EG: Ethylene glycol, MeOH: Methanol

MeOH were calculated using tetrabutylammonium tetraphenylborate as a "reference electrolyte" following the scheme as suggested by Das *et al.* [17].

The λ_0^\pm values were in turn utilized for the calculation of Stokes' radii (r_s) according to the following classical expression [16]:

$$r_s = \frac{F^2}{6\pi N_A \lambda_0^\pm r_c} \tag{10}$$

There are marked characteristic behaviors 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 EG in the solvent mixture. Such behavior in the solvent mixture is also observed in other alcohols [18].

The Gibbs energy change, ΔG^0 for association, is calculated from the following relation [19] and is reported in Table 4.

$$\Delta G^0 = -RT \ln K_A \tag{11}$$

The negative values ΔG^0 can be explained by considering the participation of specific interaction

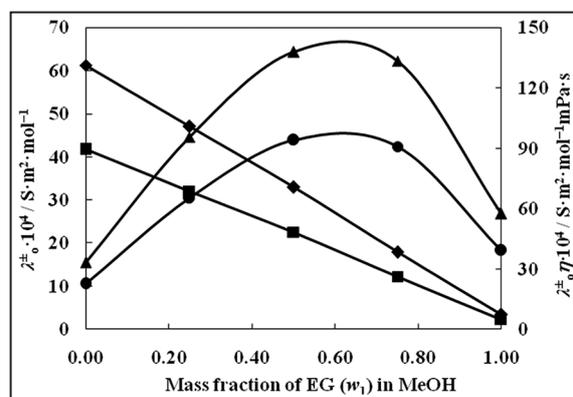


Figure 3: Plot of limiting ionic conductance (λ_0^\pm) of Li^+ (\blacklozenge), AsF_6^- (\blacksquare) and ionic Walden Product ($\lambda_0^\pm\eta$) of Li^+ (\blacktriangle), AsF_6^- (\bullet) in different mass fraction (w_1) of ethylene glycol in methanol at $T=298.15$.

in the ion-association process for ion-pair formation of $\text{Li}^+/\text{AsF}_6^-$ with the solvents in binary mixture of EG and MeOH. From Table 4, it can be seen that the ΔG^0 values decrease with increasing mass fraction (w_1) of EG in solvent mixtures indicating greater degree of ion association. The ΔG^0 in Table 4 along with the other parameters mentioned above is in good agreement with the results observed by Barthel [20] and Hazra [21].

3.2. Density Measurement

The measured value of densities (ρ) and viscosities (η) of LiAsF_6 in different mass fraction (w_1) of EG

in MeOH, as a function of concentration at 298.15 K, is reported in Table 6. For the analysis of interaction of LiAsF_6 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 from the solution density values using the following equation [22]:

$$\phi_V = M/\rho_0 - 1000(\rho - \rho_0)/c\rho\rho_0 \quad (12)$$

Where M is the molar mass of the solute, c is the molarity of the solution, and 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), and viscosities (η), $(\eta/\eta_0 - 1)\sqrt{c}$ of LiAsF_6 in different mass fraction of EG (w_1) in MeOH at T=298.15 K

f Molarity (c)/ $\text{mol}\cdot\text{dm}^{-3}$	$^g \cdot 10^{-3}/\text{kg}\cdot\text{cm}^{-3}$	$\phi_V \cdot 10^6/\text{m}^3\cdot\text{mol}^{-1}$	$^h \eta/\text{mPa}\cdot\text{s}$	$(\eta/\eta_0 - 1)\sqrt{c}/\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$
$w_1=0.00$				
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

(Contd...)

Table 6: (Continue)

^f Molarity (<i>c</i>)/mol·dm ⁻³	^g $\rho \cdot 10^{-3}$ /kg·cm ⁻³	$\phi_V \cdot 10^6$ /m ³ ·mol ⁻¹	^h η /mPa·s	$(\eta/\eta_0 - 1)\sqrt{c/\text{kg}^{1/2} \cdot \text{mol}^{-1/2}}$
0.089	1.03034	87.70	8.68	0.554
<i>w</i> 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

^fUncertainty in the molarity: ± 0.0002 mol dm⁻³. ^gUncertainty in the density values: $\pm 0.00002 \cdot 10^{-3}$ kg m⁻³. ^hUncertainty in the viscosity values: ± 0.003 mPa s. LiAsF₆: Lithium hexafluoroarsenate, EG: Ethylene glycol, MeOH: Methanol

Table 7: Limiting apparent molar volume (ϕ_V^0), experimental slopes (S_V^*), *A*- and *B*- coefficients of LiAsF₆ in different mass fraction of EG (*w*₁) in MeOH at 298.15 K

Mass fraction of EG (<i>w</i> 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}	<i>A</i> /kg ^{1/2} ·mol ^{-1/2}	<i>B</i> /kg·mol ⁻¹
<i>w</i> ₁ =0.00	72.62	-72.95	1.329	1.785
<i>w</i> ₁ =0.25	85.74	-96.03	0.659	1.830
<i>w</i> ₁ =0.50	105.88	-129.12	0.067	2.190
<i>w</i> ₁ =0.75	132.73	-150.63	-0.193	2.499
<i>w</i> ₁ =1.00	168.63	-182.52	-0.291	2.546

LiAsF₆: Lithium hexafluoroarsenate, EG: Ethylene glycol, MeOH: Methanol

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.

The variation of ϕ_V^0 with the increase in the mass fraction of EG 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.

The Scheme 1 suggested that the more number of electrolytes (LiAsF₆) interact with EG (have two plausible side for interaction) than MeOH (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

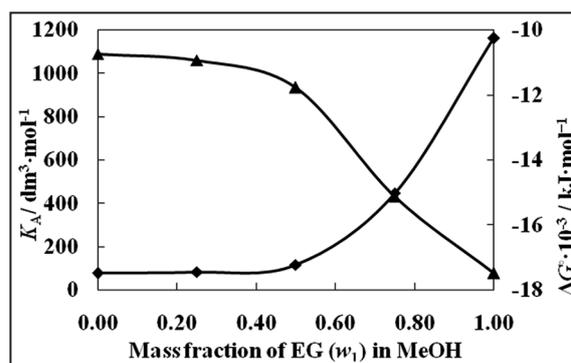


Figure 4: Plot of association constant (K_A) (◆), and Gibbs energy change (ΔG^0) (▲) of LiAsF₆ in different mass fraction (*w*₁) of ethylene glycol in methanol at 298.15 K.

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 AsF₆⁻) 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 AsF₆⁻) 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

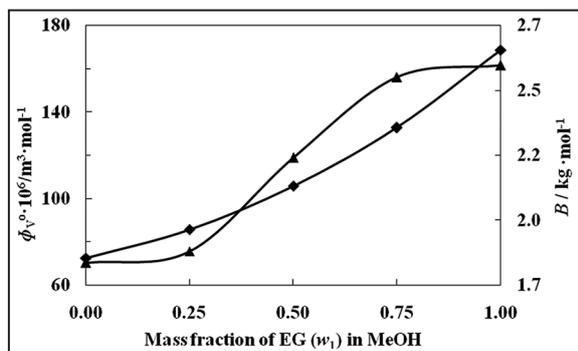


Figure 5: Plot of limiting apparent molar volume (ϕ_v^0) (\blacklozenge) and viscosity B -coefficient (\blacktriangle) versus mass fraction (w) of ethylene glycol in methanol for lithium hexafluoroarsenate at $T=298.15$ K.

are negative and decrease 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 in EG mono methyl ether+methyl alcohol [23].

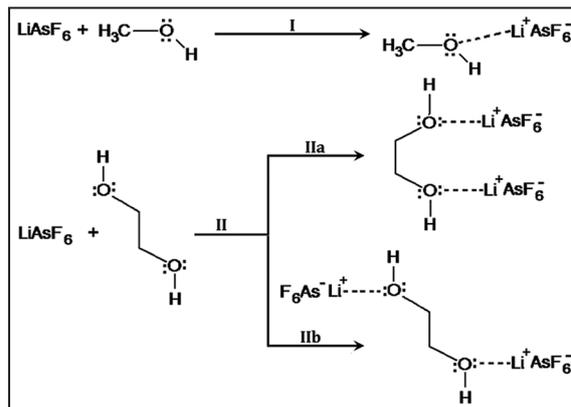
3.3. Viscosity Measurement

These viscosity data were utilized to calculate the viscosity B -coefficient using following Jones-Dole equation [24]:

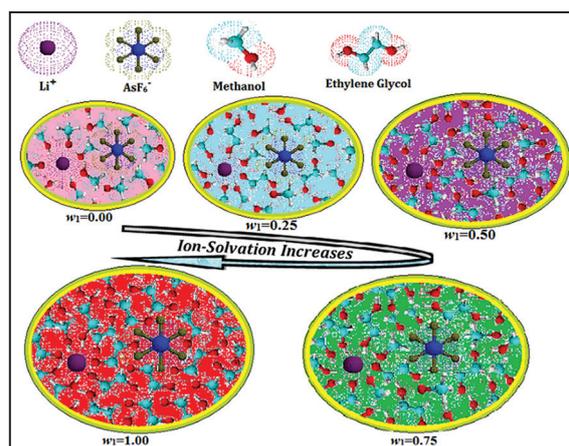
$$\eta/\eta_0 = \eta_r = 1 + Bc + A\sqrt{c} \quad (14)$$

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

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 analyzed by the Jones-Dole equation. A and B are viscosity coefficient and indicate 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 decrease with increasing amount of EG in the mixtures. The viscosity B -coefficient [25] reflects the effects of ion-solvent interactions in the solution. Table 7 and Figure 5 illustrate that the values of the viscosity B -coefficient for the salt in the studied mixed solvent systems are positive, thereby suggesting the presence



Scheme 1: The plausible mechanism of interaction between lithium hexafluoroarsenate and solvents (ethylene glycol and methanol).



Scheme 2: The plausible diagrams of molecular interaction and solvation of the ions in solvent mixtures.

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 Scheme 2.

4. CONCLUSION

The extensive study of LiAsF_6 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 LiAsF_6 in different mass fraction of EG in MeOH. Limiting apparent molar volume and viscosity B -coefficient values for LiAsF_6 in the binary mixtures indicate the presence of strong ion-solvent interactions, and these interactions are further strengthened with increasing mass fraction of EG in MeOH.

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