

CHAPTER VI

PHYSICS AND CHEMISTRY OF AN IONIC LIQUID IN SOME INDUSTRIALLY IMPORTANT SOLVENT MEDIA PROBED BY PHYSICOCHEMICAL TECHNIQUES

6.1. INTRODUCTION

An ionic liquid (IL) is an electrolyte in the liquid state or phase, whose melting point is below some arbitrary temperature, such as 100°C. In general, Ionic Liquids (ILs) are liquid electrolytes that consist of combinations of organic-organic or organic-inorganic cation/anions. Because of their unique physicochemical properties, such as the favorable solubility of organic and inorganic compounds, low vapor pressures, low melting points, high thermal stability, good solvent characteristics for organic, inorganic and polymeric materials, adjustable polarity, selective catalytic effects, chemical and thermal stability, non-flammability and high ionic conductivity, ionic liquids have generated significant interest for a wide range of industrial applications [1]. They are used as recyclable solvents for organic reactions and separation processes [2], lubricating fluids [3], electrolytic media in various electrochemical systems [4], pharmaceuticals, cellulose processing, food and bi-products, waste recycling, batteries among others.

It is well-known that the reaction medium plays an important role in determining reactivity reflected in thermodynamic, transport, and spectral properties [5]. Study of transport properties of electrolytes in different solvent media are of great importance to obtain information as to the solvation and association behavior of ions in solutions. Consequently, a number of conductometric [6] and related studies of electrolytes in non-aqueous solvents have been made for their optimal use in high-energy batteries [7] and for further more understanding organic reaction mechanisms [8]. The thermodynamic properties of solutions are very useful to obtain information on the intermolecular interactions and geometrical effects in the systems. Moreover,

knowledge of the thermodynamic properties is essential for the proper design of industrial processes. Accurate knowledge of thermodynamic properties of solution mixtures has great relevance in theoretical and applied areas of research. Measurements of the bulk properties, such as viscosity and density of liquids, measurements of excess molar enthalpies and measurements of isentropic compressibility provide insight into the molecular interactions prevailing in electrolyte solution systems. In general, the measurements help promote better understanding of the behaviour of the electrolyte with different solvents. Studies on the apparent and partial molar volumes of the electrolyte and the dependence of viscosity on the concentration of electrolyte have been employed as a way to study ion-ion and ion-solvent interactions [9]. The solvents used in this study find wide industrial usage. Dimethylsulfoxide (DMSO), a typical aprotic solvent having both polar and non polar groups, is an important solvent in chemistry, biotechnology, and medicine for the dissolution of various substances and as an antifreeze agent of living cells [10]. It is widely used in pharmaceutical applications, enzyme-catalyzed reactions, veterinary medicine, dermatology, experimental immunology and microbiology [11]. N,N-dimethylacetamide (DMA) is commonly used as a solvent for fibers and in the adhesive industry, in the production of pharmaceuticals and plasticizers as a reaction medium, in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings [12]. N,N-dimethylformamide (DMF), which is a versatile solvent, is used as the separation agent for saturated and unsaturated hydrocarbons, as a solvent for vinyl resins, acid gases, polyacrylic fibres, and as a catalyst in carbonylation reaction, organic electrolyte batteries, photo electrochemical cells, electro-deposition, wet electrolyte capacitors or electro-organic synthesis.

In continuation of our investigation on electrical conductances [13], an attempt has been made in the present study, to ascertain the nature of ion-solvent interactions of the ionic liquid (IL) tetrabutylphosphonium Tetrafluoroborate [Bu₄PBF₄] in dimethyl sulfoxide (DMSO), dimethylacetamide (DMA), dimethylformamide (DMF) at 298.15 K. Thermodynamic parameters are evaluated and discussed.

6.2. EXPERIMENTAL SECTION

6.2.1. Source and purity of samples

The IL [Bu₄PBF₄] of puriss grade was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of [Bu₄PBF₄] was ≥ 0.99 . The solvents DMSO, DMA and DMF were procured from Merck, India. These were further purified by standard methods [14]. The values of their mass fraction purity obtained were ≥ 0.99 . See Table 1.

6.2.2. Apparatus and Procedure

A stock solution of the electrolyte [Bu₄PBF₄] was prepared by mass (Mettler Toledo AG-285 with uncertainty ± 0.0003 g) and the working solutions were obtained by mass dilution at $T = 298.15$ K. The conductance measurements were carried out in a Systronic-308 conductivity bridge (accuracy ± 0.01 %) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 0.001) cm⁻¹. Measurements were made in a water bath maintained within $T = (298.15 \pm 0.01)$ K and the cell was calibrated by the method proposed by Lind et al.[15] The conductance data were reported at a frequency of 1 kHz and were uncertain to ± 0.3 %.

The densities of the solvents (ρ) were measured by means of vibrating-tube Anton Paar density-meter (DMA 4500M) with a precision of ± 0.00005 g. cm⁻³ maintained at ± 0.01 K of the desired temperature. It was calibrated by double-distilled water and dry air.

Solution viscosities (η) were measured by means of suspended Ubbelohde type viscometer, calibrated at $T = 298.15$ K with doubly distilled water and purified methanol. A thoroughly cleaned and perfectly dried viscometer filled with experimental solution was placed vertically in a glass-walled thermostat (Bose Panda Instruments Pvt. Ltd.) maintained to 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stop watch. The flow times were accurate to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times with the aim of determining possible dispersion of the results obtained. Adequate

precautions were taken to minimize evaporation losses during the actual measurements.

The precision of density measurements was $\pm 3.10^{-4} \text{ g} \cdot \text{cm}^{-3}$.

The viscosity of the solution is evaluated using the following equation [16]

$$\eta = \left(Kt - \frac{L}{t} \right) \rho \quad (1)$$

where K and L are the viscometer constants, t is the efflux time of flow in seconds and ρ is the density of the experimental liquid. The uncertainty in viscosity measurements is within $\pm 0.003 \text{ mPa} \cdot \text{s}$.

The ultrasonic velocities, u in $\text{m} \cdot \text{s}^{-1}$ were measured using an ultrasonic interferometer (Model M-83) from Mittal enterprises. The interferometer working at 2 MHz is based on the same principle as was used by Freyer et al. [17] and Kiyoharo et al. [18]. The velocities obtained were corrected for diffraction errors as given by Subrahmayan et al. [19]. The maximum uncertainty in the velocity is $\pm 0.5 \text{ m} \cdot \text{s}^{-1}$. The temperature was controlled within $\pm 0.01 \text{ K}$ using a Lauda thermostat for velocity measurements.

6.3. RESULTS AND DISCUSSION

6.3.1. Electrical Conductance

The physical properties of the pure solvent were in good agreement with values found in the literature, as reported in Table 2. The experimental values of equivalent conductances (Λ) of the electrolyte measured at the corresponding molar concentrations (c) in DMSO, DMA and DMF are given in Table 3. The conductance results have been analysed using the Fuoss conductance equation [20]. For a given set of conductivity values ($c_j, \Lambda_j, j=1, \dots, n$) three adjustable parameters, the limiting molar conductivity (Λ_0), the association constant (K_A), and the distance of closest approach of ions (R) are derived from the following set of equations:

$$\Lambda = P\Lambda_o[(1+R_X)+E_L] \quad (2)$$

$$P = 1 - \alpha(1 - \gamma) \quad (3)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (4)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (5)$$

$$\beta = e^2 / (\epsilon k_B T) \quad (6)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (7)$$

where R_X is the relaxation field effect, E_L is the electrophoretic counter current, k is 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. The initial Λ_o values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set $(c_j, \Lambda_j, j=1, \dots, n), n, \epsilon, \eta, T$, initial values of Λ_o , and an instruction to cover a preselected range of R values.

In practice, calculations are performed by finding the values of Λ_o and R that minimize the standard deviation:

$$\delta^2 = \sum [\Lambda_j(cal) - \Lambda_j(obs)]^2 / (n-2) \quad (8)$$

or a sequence of R values and then plotting δ against R ; the best fit R corresponds to the minimum of the δ - R versus R curve. So, approximate runs are made over a fairly wide range of R values using 0.1 increments to locate the minimum, but no significant minima were found in the δ - R curves for $[\text{Bu}_4\text{PBF}_4]$ electrolytes in DMSO, DMA and DMF; thus, R values are assumed to be $R = a + d$, where a is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by

$$d (\text{\AA}) = 1.183(M / \rho)^{1/3} \quad (9)$$

where M is the molar mass of the solvent and ρ is its density. The values of Λ_o , K_A , and R obtained by this procedure are represented in Table 4. Perusal of Table 4 and Figure 1

reveals that the limiting molar conductance Λ_0 of $[\text{Bu}_4\text{PBF}_4]$ in DMF is greater than that in DMA and DMSO, which is in order DMF > DMA > DMSO. Figure 2 and the Table 4 also reveal that the association constant (K_A) of the $[\text{Bu}_4\text{PBF}_4]$ is greater in DMSO than in DMA than in DMF. Hence, this shows that there is more ion-solvent interaction in DMSO than in DMA than in DMF leading to a lower conductance of $[\text{Bu}_4\text{PBF}_4]$ in the former than the latter two. The greater viscosity of DMSO also supports the above fact because with higher viscosity the Λ_0 value should decrease.

Polar aprotic solvents, (e.g.; DMF, DMA, and DMSO) dissolve ionic compounds and solvate cations very well. They do not solvate anions to any appreciable extent because they cannot form H-bonds and having positive centers are well shielded from any interaction with anions. When the ionic compound $[\text{Bu}_4\text{PBF}_4]$ is dissolved in the above mentioned polar aprotic solvents, following interaction may be observed.

The schematic representation of ion-solvation, for the particular ion in the studied solvent is depicted in **Scheme 1**.

In case of solvent DMF, the only interaction present is between negatively charged oxygen atom of DMF and positively charged P atom of $[\text{Bu}_4\text{P}]^+$, shown in (I). Same type of interaction is present in case of solvent DMA (II). Here the interaction is more intense due to the presence of methyl ($-\text{CH}_3$) group which pushes electrons towards oxygen, making it more negative for stronger interaction. In case of DMSO as solvent, two types of interaction shown in (III) possibly occur

a) between the negatively charged oxygen atom of DMSO and positively charged P atom of $[\text{Bu}_4\text{P}]^+$ and

b) between the positively charged S atom of DMSO and negatively charged B atom of $[\text{BF}_4]$. The interaction (b) is only possible because S atom is larger than N atom and is less shielded by two methyl group compared to N atom in case of DMF and DMA. For these reason, conductance of $[\text{Bu}_4\text{PBF}_4]$ is greater in DMF than DMA and DMSO, hence, lower is the conductance, greater the interaction/association, which is in the following order



The trend in Λ_0 can be discussed through another characteristic function called the Walden product, $\Lambda_0\eta_0$. From Table 4 and Figure 1 the decreasing trend of Walden products is mainly in agreement with the concomitant decrease of solvent viscosity and increase of limiting molar conductance for the electrolyte in the solvents. This is also justified as the Walden product of an ion or solute is inversely proportional to the radius of the ion or solute in a particular solvent [21].

The starting point for most evaluations of ionic conductance is Stokes' law which states that the limiting Walden product ($\lambda_0^\pm\eta_0$), (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_0^\pm (for the $[\text{Bu}_4\text{P}]^+$ cation and $[\text{BF}_4]^-$ anion) in different solvents DMSO, DMA and DMF were calculated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as a 'reference electrolyte' following the scheme as suggested by B. Das et al. [22]. The λ_0^\pm values were in turn utilized for the calculation of Stokes' radii (r_s) according to the classical expression [23]

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

Ionic Walden products $\lambda_0^\pm\eta_0$, Stokes' radii r_s , and crystallographic radii r_c are presented in Table 5. The trends in Walden products $\Lambda_0\eta_0$ and ionic Walden products $\lambda_0^\pm\eta_0$ for the electrolytes in the solvent DMSO, DMA, and DMF are shown in Tables 4 and 5 and Figures 1 and 3, respectively. They indicate that both the ionic Walden products $\lambda_0^\pm\eta_0$ and Walden products $\Lambda_0\eta_0$ for the electrolyte are greater in the case of DMSO than DMA and DMF. For the Bu_4P^+ and BF_4^- ions, the Stokes' radii r_s are either lower or comparable to their crystallographic radii r_c . This suggests that the ions are comparatively less solvated than alkali metal ions due to intrinsic low surface charge density. The distance parameter R , shown in Table 4, is the least distance that two free ions can approach together before they merge into an ion pair.

The nature of the curve for the Gibbs free energy changes for ion-pair formation, ΔG° , which clearly predicts the tendency for ion-pair formation, Figure 2. The Gibbs free

energy change ΔG° is calculated by the following relationship [24] and is given in Table 4.

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

where K_A is the association constant. The negative values of ΔG° can be explained by considering the participation of specific covalent interactions in the ion-association process. The lower value of ΔG° for the $[\text{Bu}_4\text{PBF}_4]$ electrolyte in DMSO than DMA and DMF shows that greater degree of association in DMSO.

From the overall study, it is evident that the ion-solvent interaction between the ionic liquid investigated and the solvents is greater in DMSO than in DMA which is, in turn, greater than that in DMF. This is diagrammatically shown in **Scheme 2**.

6.3.2. Density calculation

The measured values of density of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF as a function of concentration at $T = 298.15$ K are listed in Table 6. Partial molar volumes are very important for the analysis of interaction of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF. For this purpose, the apparent molar volumes ϕ_V were determined from the solution densities using the following equation and the values are given in Table 6.

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

where M is the molar mass of the solute, c is the molarity of the solution ρ and ρ_o are the densities of the solution and solvent respectively. The limiting apparent molar volume ϕ_V^0 was calculated using a least-square treatment to the plots of ϕ_V versus \sqrt{c} using the Masson equation [25].

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

where ϕ_V^0 is the limiting apparent molar volume at infinite dilution and S_V^* is the experimental slope. The plots of ϕ_V against square root of molar concentration (\sqrt{c}) were found to be linear with negative slopes. The values of ϕ_V^0 and S_V^* are reported in Table 6. The ϕ_V^0 value indicates the extent of ion-solvent interaction. A perusal of Table

6 reveals that the ϕ_V^0 values are positive and is highest in case of [Bu₄PBF₄] in DMSO indicating that the ion-solvent interaction is more in DMSO than in DMA than in DMF. On the other hand, S_V^* values indicate the extent of ion-ion interaction. From Table 6, the values of S_V^* is greater in the case of the DMF than DMA and DMSO. A quantitative comparison of the magnitude of ϕ_V^0 values is much greater than S_V^* values for the solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions. The values of ϕ_V^0 also support the fact that lower ion-solvent interaction in DMF leads to higher conductance of [Bu₄PBF₄] in it than DMA and DMSO obtained from the conductometric measurement.

6.3.3. Viscosity calculation

The viscosity results have been analysed using the Jones-Dole equation [26]

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

where $\eta_r = \eta/\eta_0$, η_0 and η are the viscosities of the solvent and solution respectively, c is the molar concentration of the solution, A and B are the viscosity coefficient estimated by a least-squares method. The values of A and B coefficients are obtained from the straight line by plotting $(\eta_r - 1)/\sqrt{c}$ against \sqrt{c} reported in Table 7. A perusal of Table 7 shows that the values of the A -coefficient are lower than the value of B -coefficient for all of the solutions under investigation. The results indicate the presence of very weak ion-ion interactions. These results are in excellent agreement with those obtained from S_V^* values discussed earlier.

The effects of ion-solvent interactions on the solution viscosity can be inferred from the B -coefficient [27]. The viscosity B -coefficient is a valuable tool to provide information concerning the solvation of the ions and their effects on the structure of the solvent. From Table 7, it is evident that the values of the B -coefficient are positive and much higher than the A -coefficient, thereby suggesting the presence of strong ion-solvent interactions. The viscosity B coefficient value is lowest for [Bu₄PBF₄] in DMF supporting the fact that the conductance of [Bu₄PBF₄] in DMF is highest.

The B -coefficients as determined experimentally using the Jones-Dole equation does not give any impression regarding ion-solvent interactions unless there is some way to identify the separate contribution of cations and anions to the total ion-solvent interaction. For the division of B -values in the ionic components, Sacco *et al.* proposed the “reference electrolytic” method for the division of B -values.

The values obtained are in good agreement with those obtained by other methods. The viscosity B -coefficients for ions are given in Table 5. The criteria adopted for the separation of B -coefficients in non-aqueous solvents differ from those generally used in water. However, the methods are based on the equality of equivalent conductances of counter ions at infinite dilutions. According to Krumgalz [28] any method of resolution based on the equality of equivalent conductance, the equality of B -coefficients of these ions is likely to be solvent and ion-structure dependent. Since the electrolyte ion-structure effect is same, so the B -coefficients are dependent on the solvent. The viscosity B -value as well as the B -ionic value in DMSO is greater than DMA and DMF, which indicates ions are more solvated in DMSO.

The B -ion values can also be judged from the equations:

$$B_{Bu_4PBF_4} = B_{Bu_4P^+} + B_{BF_4^-} \quad (15)$$

The method requires knowledge of the B -values for $[Bu_4PBF_4]$ and is equally applicable to non-aqueous solvents. The B -ion values obtained by this method agree well with those reported by Sacco *et al.* in different organic solvents.

6.3.4. Ultrasonic speed calculation

The adiabatic compressibility (β) was evaluated from the following equation:

$$\beta = 1 / u^2 \rho \quad (16)$$

where ρ is the density of solution and u is the speed of sound in the solution. The apparent molar adiabatic compressibility (ϕ_K) of the solutions was determined from the relation,

$$\phi_K = M \beta / \rho + 1000(\beta \rho_o - \beta_o \rho) / c \rho \rho_o \quad (17)$$

Where β_0, β are the adiabatic compressibility of the solvent and solution respectively and c is the molarity of the solution. The values of β and ϕ_K are reported in Table 8. The limiting partial molar adiabatic compressibility (ϕ_K^0) and experimental slope (S_K^*) were obtained by fitting ϕ_K against the square root of concentration of the electrolyte (\sqrt{c}) using the least squares method.

$$\phi_K = \phi_K^0 + S_K^* \cdot \sqrt{c} \quad (18)$$

The values of ϕ_K^0 and S_K^* are also presented in Table 8. The values of ϕ_K^0 and S_K^* are measures of ion-solvent and ion-ion interactions respectively. A perusal of Table 8 shows that the ϕ_K^0 value is highest in the case of $[\text{Bu}_4\text{PBF}_4]$ in DMSO indicating that the ion-solvent interaction is greater in DMSO than in DMA than in DMF.

On the other hand, the S_K^* values indicate the extent of ion-ion interaction. From Table 8 the values of S_K^* are greater in the case of the DMF than for DMA and DMSO. A quantitative comparison of the magnitude of ϕ_K^0 values is much greater than S_K^* values, for the solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions and the values are in agreement with results drawn from the values of ϕ_V^0 and S_V^* discussed earlier.

6.4. CONCLUSIONS

The extensive conductometric study of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF leads to the conclusion that the electrolyte more associated in DMSO than in the other two solvents. The reliable value of volumetric, viscometric and interferometric studies also suggests that in solution there is more ion-solvent interaction than the ion-ion interaction.

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TABLES

Table 1.

Sample provenance and purity

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity
[Bu ₄ PBF ₄]	Sigma-Aldrich, Germany	0.99	Used as procured	0.99
DMSO	Merck, India	0.98	Purified by standard methods [14]	0.99
DMA	Merck, India	0.98	Purified by standard methods [14]	0.99
DMF	Merck, India	0.98	Purified by standard methods [14]	0.99

Table 2. Values of density (ρ), viscosity (η), refractive index (n_D), Speed of sound (u), and relative permittivity (ϵ_r) of the pure solvents studied at T = 298.15 K.

Solvent	$10^{-3}\rho^a$ (kg m ⁻³)		η^b /(mPa . s)		u^c / (m . s ⁻¹)		ϵ_r
	Expt	Lit	Expt	Lit	Expt	Lit	
DMSO	1.09602	1.09600[29]	1.946	1.948[29]	1490.8	1490.0[29]	46.70[30]
DMA	0.93680	0.93660[29]	0.923	0.920[29]	1458.5	1458.0[29]	37.78[30]
DMF	0.94450	0.94450[29]	0.794	0.796[29]	1451.7	1451.0[29]	36.71[30]

^a uncertainty in the density values: ± 0.00002 g cm⁻³.

^b uncertainty in the viscosity values: ± 0.003 mPa s.

^c uncertainty in the ultrasonic speed: ± 0.5 m s⁻¹.

Table 3. The molar conductance (Λ) and corresponding concentration (c) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K

$c^d \times 10^4$ (mol dm ⁻³)	$\Lambda^e \times 10^4$ (S m ² mol ⁻¹)	$c^d \times 10^4$ (mol dm ⁻³)	$\Lambda^e \times 10^4$ (S m ² mol ⁻¹)	$c^d \times 10^4$ (mol dm ⁻³)	$\Lambda^e \times 10^4$ (S m ² mol ⁻¹)
DMSO		DMA		DMF	
20.4903	21.28	19.8974	39.77	18.55961	55.50
37.5655	20.00	27.5503	38.47	25.69792	54.86
52.0138	19.00	34.1099	37.97	31.81648	54.37
64.3981	18.60	39.7949	37.45	37.11922	53.96
75.1311	17.97	44.7692	36.77	45.85316	53.40
84.5224	17.65	53.0598	36.35	52.74837	52.99
100.1748	17.10	59.6923	35.73	62.94129	52.46
112.6966	16.82	69.6411	34.80	70.11409	52.11
131.4794	16.28	79.5898	34.10	75.43584	51.83
150.2621	15.58	86.2223	33.72	82.05302	51.47
171.7281	15.01	92.2518	33.25	87.14948	51.19
185.1444	14.62	97.6784	32.90	92.15807	50.98

^d Uncertainty in the molarity: ± 0.0002 mol dm⁻³.^e Uncertainty in the molar conductance: ± 0.01 S m² mol⁻¹.**Table 4. Limiting molar conductivity (Λ_0), the association constant (K_A), the distance of closest approach of ions (R), Standard Deviations δ , Walden Product ($\Lambda_0 \eta_0$) and Gibbs free energy change (ΔG°) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K**

Solvents	$\Lambda_0 \times 10^4$ (S m ² mol ⁻¹)	$K_A \times 10^{-4}$ (dm ² mol ⁻¹)	R (Å)	δ	$\Lambda_0 \eta_0 \times 10^4$ (S m ² mol ⁻¹ mPa s)	ΔG° (kJ mol ⁻¹)
DMSO	35.74	23.60	12.10	0.32	69.55	-3.06
DMA	53.09	9.76	12.96	0.26	49.00	-2.84
DMF	60.84	2.37	12.64	0.08	48.31	-2.49

Table 5. Limiting Ionic Conductance (λ_o^\pm), Ionic Walden Product ($\lambda_o^\pm \eta_o$), Stokes' Radii (r_s), Crystallographic Radii (r_c), ionic viscosity B -coefficients (B_\pm) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K

Solvents	Ion	λ_o^\pm ($\text{S m}^2 \text{mol}^{-1}$)	$\lambda_o^\pm \eta_o$ ($\text{S m}^2 \text{mol}^{-1} \text{mPa s}$)	r_s (\AA)	r_c (\AA)	B_\pm ($\text{L}^{1/2} \text{mol}^{-1/2}$)
DMSO	Bu_4P^+	13.80	26.85	3.05	4.42	0.85
	BF_4^-	21.94	42.70	1.92	2.78	0.54
DMA	Bu_4P^+	20.50	18.92	4.33	4.42	0.79
	BF_4^-	32.59	30.08	2.72	2.78	0.50
DMF	Bu_4P^+	23.49	18.65	4.39	4.42	0.75
	BF_4^-	37.35	29.66	2.76	2.78	0.47

Table 6. Experimental values of Molarity (c), Densities (ρ), Apparent Molar Volume (ϕ_V), Limiting Apparent Molar Volume (ϕ_V^0) and Experimental Slope (S_V^*) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K

c^f (mol dm^{-3})	$\rho^g \times 10^{-3}$ (kg m^{-3})	ϕ_V ($\text{m}^3 \text{mol}^{-1}$)	$\phi_V^0 \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	S_V^* ($\text{m}^3 \text{mol}^{-3/2} \text{L}^{1/2}$)
DMSO				
0.0046	1.09605	310.4323	324.21	-193.88
0.0184	1.0964	298.5712		
0.0323	1.09702	289.8383		
0.0463	1.09784	282.6956		
0.0604	1.09883	276.4632		
0.0746	1.09998	270.7432		
DMA				
0.0053	0.93722	279.9317	290.34	-146.73
0.0215	0.93869	268.7233		
0.0377	0.94034	261.6323		
0.0541	0.94213	255.8070		
0.0705	0.94401	251.1923		
0.0871	0.94594	247.6409		
DMF				
0.0053	0.94498	264.9444	275.29	-139.97
0.0213	0.94661	254.8862		
0.0374	0.9484	248.6092		
0.0536	0.95034	242.9222		

0.0699	0.9524	237.9053
0.0863	0.9545	234.2403

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

^gUncertainty in the density values: $\pm 0.00002 \text{ g cm}^{-3}$.

Table 7. Experimental values of Molarity (c), Viscosities (η), $(\eta_r - 1)/\sqrt{c}$, Viscosity A, B -coefficients of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K

c^h (mol dm^{-3})	η^i (mPa s)	$(\eta_r - 1)/\sqrt{c}$ ($\text{kg}^{1/2} \text{ mol}^{-1/2}$)	A (L mol^{-1})	B ($\text{L}^{1/2} \text{ mol}^{-1/2}$)
DMSO				
0.0046	1.952	0.042		
0.0184	1.982	0.138		
0.0323	2.015	0.197	-0.05124	1.39
0.0463	2.049	0.247		
0.0604	2.085	0.290		
0.0746	2.120	0.327		
DMA				
0.0053	0.930	0.097		
0.0215	0.949	0.188		
0.0377	0.968	0.249	0.00053	1.29
0.0541	0.987	0.297		
0.0705	1.007	0.342		
0.0871	1.028	0.385		
DMF				
0.0053	0.802	0.133		
0.0213	0.820	0.218		
0.0374	0.837	0.275	0.0403	1.23
0.0536	0.854	0.322		
0.0699	0.871	0.364		
0.0729	0.889	0.406		

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

ⁱ Uncertainty in the viscosity values: $\pm 0.003 \text{ mPa s}$.

Table 8. Experimental Values of Molarity (c), Speed of Sound (u), Adiabatic Compressibility (β) and Apparent Molar Adiabatic Compressibility (ϕ_K), Limiting Apparent Molar Adiabatic Compressibility (ϕ_K^0), and Experimental Slopes (S_K^*) of [Bu₄PBF₄] in DMSO, DMA and DMF at 298.15 K

c^j (mol dm ⁻³)	u^k (m s ⁻¹)	$\beta \times 10^{11}$ (Pa ⁻¹)	$\phi_K \times 10^{11}$ (m ³ mol ⁻¹ Pa ⁻¹)	$\phi_K^0 \times 10^{10}$ (m ³ mol ⁻¹ Pa ⁻¹)	$S_K^* \times 10^{10}$ (m ³ mol ^{-3/2} Pa ⁻¹ kg ^{1/2})
DMSO					
0.0046	1492.7	40.947	-8.369		
0.0184	1501.5	40.456	-17.595		
0.0323	1513.7	39.784	-24.360		
0.0463	1527.9	39.019	-29.080	0.144	-14.257
0.0604	1544.5	38.150	-33.310		
0.0746	1564.6	37.137	-37.831		
DMA					
0.0053	1461.8	49.932	-35.692		
0.0215	1473.5	49.066	-42.288		
0.0377	1486.9	48.101	-46.311		
0.0541	1501.6	47.074	-49.306	-2.958	-8.537
0.0705	1517.8	45.983	-51.986		
0.0871	1536.3	44.790	-54.958		
DMF					
0.0053	1455.6	49.945	-45.536		
0.0213	1468.7	48.974	-50.480		
0.0374	1483.2	47.930	-53.487		
0.0536	1498.6	46.854	-55.497	-4.116	-6.248
0.0699	1515.4	45.722	-57.545		
0.0863	1533.8	44.533	-59.556		

^j Uncertainty in the molarity: ± 0.0002 mol dm⁻³.

^k Uncertainty in the ultrasonic speed: ± 0.5 m s⁻¹.

FIGURES

Figure 1. Plots of values of limiting molar conductivity (Λ_0) and Walden Product ($\Lambda_0 \eta_0$) of the salt $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA, DMF at 298.15 K

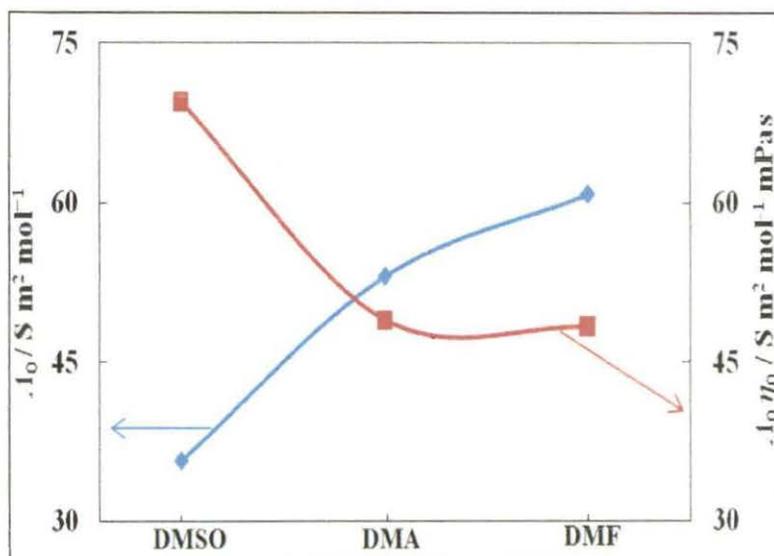


Figure 2. Plots of values of Association constant (K_A) and Gibbs free energy change (ΔG°) of the salt $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K

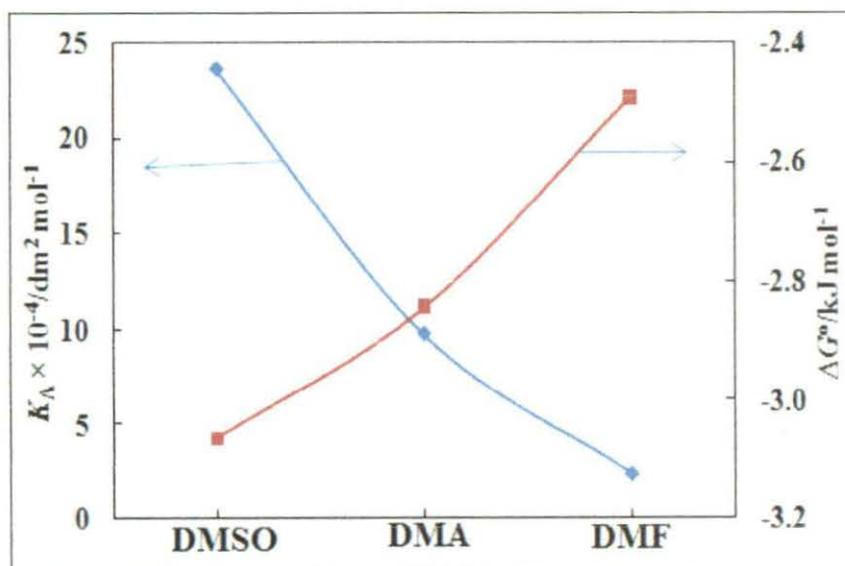
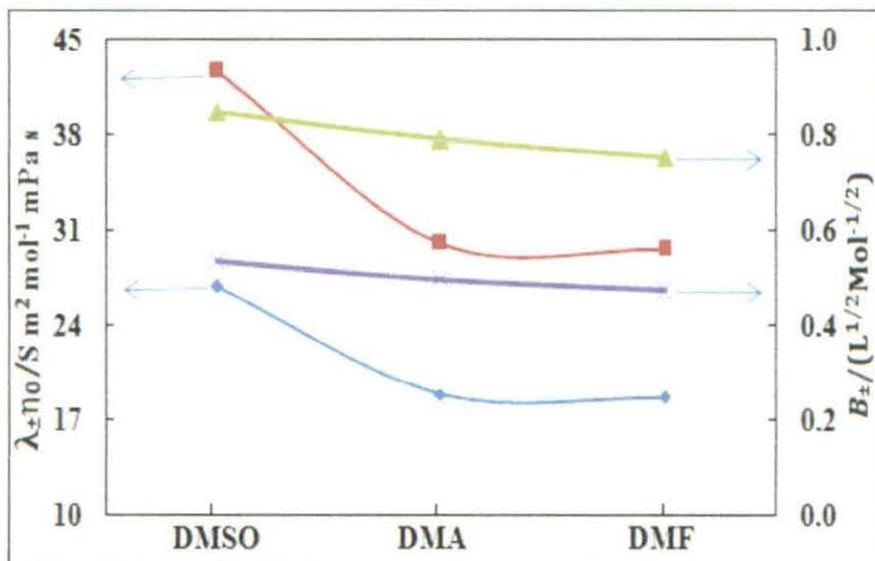
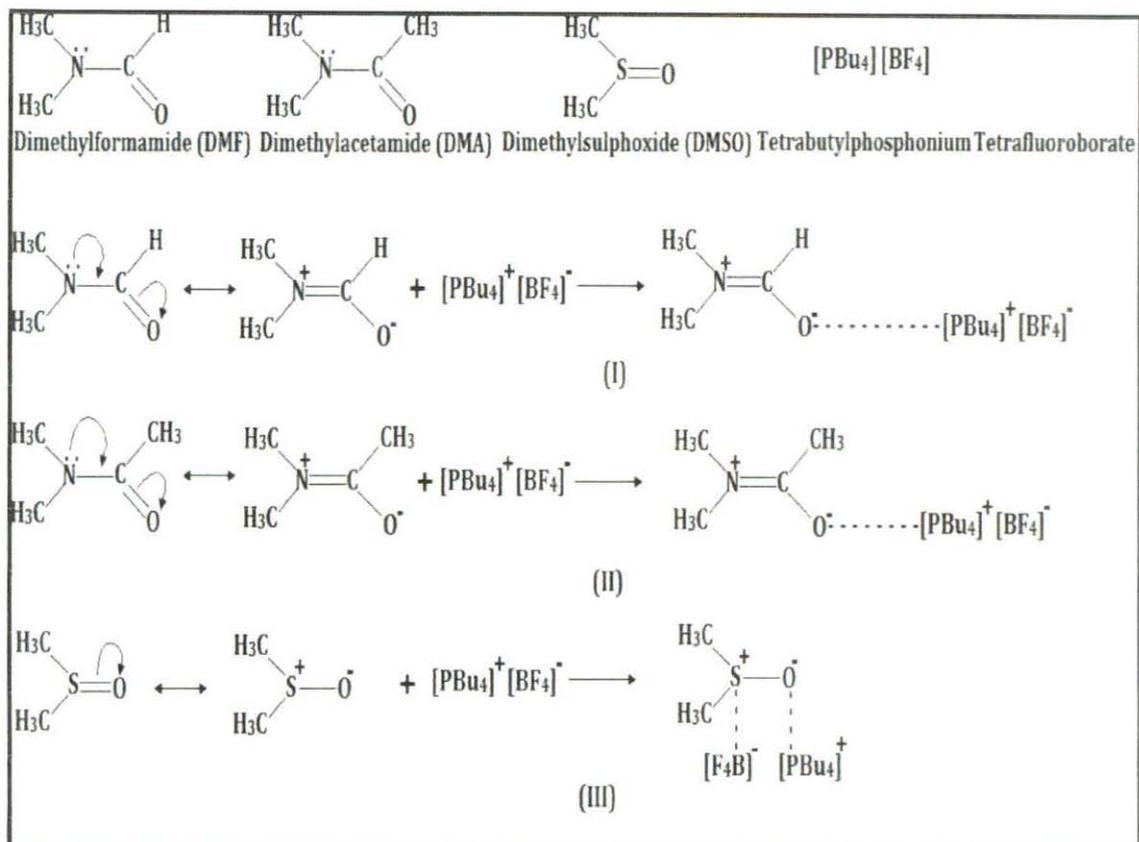


Figure 3. Plots of values of ionic Walden product ($\lambda_{\pm}^{\circ} \eta_0$) for $[\text{Bu}_4\text{P}]^+$ (\blacksquare), for $[\text{BF}_4]^-$ (\blacklozenge), and ionic viscosity B -coefficients (B_{\pm}) for $[\text{Bu}_4\text{P}]^+$ (\blacktriangle), for $[\text{BF}_4]^-$ (\times) in DMSO, DMA, DMF at 298.15 K respectively.



SCHEMES

Scheme 1.



Scheme 2.

