



Ion association and solvation behaviours of the ionic liquids [Bupy]Cl, [Bupy]Br, [Bupy][BF₄] and [Bupy][PF₆] in some binary mixed solvents at various temperatures

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Abstract

Herein, for the first time, this article provides the transport properties and the association behaviour of pyridinium family-based ionic liquids in dilute solution systems. Investigation of molecular interactions via accurate molar conductance (Λ) measurements are reported for solution systems of various 1-butylpyridinium-based ionic liquids, namely [Bupy]Cl, [Bupy]Br, [Bupy][BF₄] and [Bupy][PF₆], in 10%, 30% and 50% (w/w) DMF–H₂O and MeOH–H₂O mixtures at various temperatures. The conductance data are examined via the Fuoss-Edelson equation in terms of the ionic association constant (K_A) and the limiting molar conductance (Λ_0). It is shown that the type of anion affects the ionic association constants and limiting molar conductance for each of the systems studied. For the [Bupy]⁺cation, the limiting molar conductance of the system was found to decrease in the order Cl⁻ > Br⁻ > [BF₄]⁻ > [PF₆]⁻, with the ionic association constants following the order [BF₄]⁻ > [PF₆]⁻ > Br⁻ > Cl⁻ in the solvents used; limiting molar conductance are also found to increase when the temperature is increased in all instances. All four of these electrolytes were solvated to a different extent by the mixture solvents, and their K_A is influenced significantly by ionic solvation. Furthermore, the transport properties including limiting ionic conductance (λ_0^\pm), the transference numbers (t_\pm), ionic mobility (u_\pm), diffusion coefficient (D_0) for individual ions, Walden product ($\Lambda_0\eta_0$), hydrodynamic radii (R_H) and the activation energy of the transport process (E_a) are also estimated and discussed. Based on the temperature variations, the association constants have been examined to obtain the thermodynamic functions (ΔG_A° , ΔS_A° and ΔH_A° changes) for all systems. The results are discussed in terms of ion–ion and ion–solvent interactions, hydrogen bond formation, structural aspects, and configurational theory. It is anticipated that this information will be beneficial when attempting to modify of the ionic liquids' conductance according to the type of anion, and physical properties of the solvent mixtures.

Keywords: ion association, transport properties, ionic liquids.

1. Introduction

Pyridinium compounds have been recognised for several decades, [1,2] and their spectroscopy, [3,4] and synthesis, [5-8] have been discussed extensively in the literature; nonetheless, very little

is known in terms of their conductances and association behaviors [9-12] in comparison, for instance, with imidazolium and its derivatives [13-17]. In general, pyridinium salts are liquid at room temperature, and are referred to as “pyridinium

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ionic liquids". Owing to their exceptional chemical and physical properties such as low flammability, high electrical conductivity, high thermal stability, negligible vapour pressure, the ability to dissolve several of the existing substances, extra-large liquid temperature range, as well as reusability in chemical applications, [18-23] they are highly suitable for use in various applications. For instance, their high electrical conductivity and chemical reactions in instances where a good charge transporter is needed, and they can also be used in industrial applications such as surfactants, cosmetics, polymerization phase transfer agents, catalysis, dyes, and pharmaceuticals [8,9,18,24-29]. Interestingly, the transport properties and association behaviour of these compounds can be tuned over a wide range according to requirements, either by altering the nature of the anions and/or cation or by modifying the latter through attachment of different length alkyl chains [13,15,27,30-32]. This provides the opportunity to design and develop ionic compounds with quite finely tuned properties for any given application [18,29] such as ionic conductivity, association behaviour, viscosity, polarity, solubility and ease of extraction. These properties are influenced by anion-cation and ion-solvent interactions and thus, arguably at least, the size of the cation and anion play a crucial role in controlling the associated properties [13,15,27,30]. In this context, some experimental techniques such as spectroscopy [33,34] and isothermal titration calorimetry have been utilized to understand the cation-anion and ion-solvent interactions of the ionic system compounds [35,36]. The conductance behaviour and ionic association of many electrolytes in mixed solvent systems can be

affected significantly by factors such as dielectric constant, viscosity, density of the medium, ion-solvent interactions and solvent-solvent interactions. Conductometric investigations in solvent mixtures can provide information about ion-ion and ion-solvent interactions, and can further provide useful information about preferential solvation of ions from a thermodynamics of association perspective [10,14,33,37-45]. Various theoretical and experimental investigations into ionic system compounds in various solvent systems have recently been published that provide useful background information about their behaviours in solution, [9-17,30,33] and we will discuss some of the more notable examples in further detail. Wang *et al.* [13] studied the effects of alkyl chain length on cations and type of anion on limiting molar conductance (Λ_o) and ionic association constant (K_A) of $[C_4mim][BF_4]$, $[C_4mim][PF_6]$, and $[C_nmim]Br$, ($n = 4, 6, 8, 10, 12$) in various solvents such as water (H_2O), methanol (MeOH), acetonitrile (MeCN), and acetone (AcetOH) at ambient temperature. They examined the conductance data by means of the Lee-Wheaton equation in terms of limiting molar conductance and ionic association constant. Their study showed that anion size and alkyl chain length each have an effect on the Λ_o and K_A for a given anion (Br^-), whereby Λ_o decreases with increasing cation alkyl chain length for all pure solvents, whilst K_A decreases in organic solvents but increases in water with increasing alkyl chain length. For the $[C_4mim]^+$ cation, Λ_o decreases in the order $Br^- > [BF_4]^- > [PF_6]^-$, whereas the ionic association constants decreased in the order $[BF_4]^- > [PF_6]^- > Br^-$ in H_2O , AcetOH, and MeCN. Additionally, they observed a linear relationship

between $\ln K_A$ and the reciprocal of the dielectric constants of the pure solvents. The authors found that organic solvents are enhanced by the ionic association of the compounds used, whereas H_2O promotes their dissociation significantly. Another study of the conductivity and association of pyridinium-based [Bumpy][BF_4] and imidazolium-based ([Bumim]Br, [Ethmim][BF_4], [Bumim][BF_4], [Hexmim][BF_4] and [Bumim][Tf] were reported when using a polar solvent as an ionic polar H-bonded at different temperatures [16]. They found that all compounds show moderate ion association in MeOH, with K_A being relatively greater for the BF_4^- anions compared to Br and Tf anions. The dependence of K_A on temperature was found to be negligible for all investigated systems. The study observed that the Λ_o for imidazolium compound solutions in MeOH decreased with increasing alkyl chain length, in this case from ethyl to hexyl. In addition, they demonstrated that the anion contribution to Λ_o was greater than that of the cations or, in other words, large organic cations and anions ([Ethmim]⁺, [Bumim]⁺, [Hexmim]⁺, [Tf]⁻) were slightly solvated in MeOH, because the effective radii of the ions were close to structural ones (structural radii). The Br^- anion was sufficiently solvated in MeOH which led to its hydrodynamic radius being 1.5-2 times larger than its structural radius. In this regard, Zhang *et. al.*, [9] investigated the impact of successive addition of methylene groups and of molecular solvents (MeOH, EtOH, MeCN and propylene carbonate (PC)) on electrical conductance over a temperature range of 283.15 to 313.15 K. The results indicated that the introduction of a methyl group to the pyridinium ring is effective in increasing electrical

conductance. The authors observed that the conductance increased with increasing temperature. They found that an increase in temperature leads to an increase in ion mobility, and hence conductance. Using the conductometric technique, Radhika and Manikyamba demonstrated the effect of ion solvation behaviour of pyridinium dichromate in 0, 20, 40, 40, 60, 80 and 100% (v/v) water-*N,N*-dimethyl formamide (DMF- H_2O) solvent mixtures over a range of temperatures [10]. They observed that both Λ_o and K_A increased with increasing temperature, suggesting that these changes are most likely due to increases in the mobility of the ions with increasing temperature. The authors also demonstrated that Λ_o and K_A at a given temperature are dependent on the solvent system. Increasing the proportion of DMF to water was found to decrease the limiting molar values, which the authors attributed to the associated variation in the dielectric constant, viscosity, and temperature of the medium. They found that these factors have affect the ion-solvent interactions which in turn affects the range of solvation, which means a decrease in conductance is an indication of an increase in the extent of solvation. Furthermore, they indicated that the association constant increased continuously with the addition of DMF to H_2O , in which the highest recorded values were in actually in binary solvent mixtures rather than in the corresponding pure solvents. This was thought to be due to the variation of the dielectric constant and the viscosity of the mixture of solvents. Although the literature is replete with such studies of pyridinium and its derivatives, and indeed many such systems as those mentioned above, it seems there remains a dearth of systematic investigations into the transport

properties and association behaviour of pyridinium in aqueous-organic solvents. To gain further understanding and extend the range of data in this regard, the limiting molar conductances and the ion association behaviour of four protic pyridinium family species in aqueous-organic solvents have been investigated via the conductometric technique. For the first time, this article highlights the molar conductance, Λ , of four species of the ionic pyridinium family: 1-butylpyridinium chloride, [Bupy]Cl; 1-butylpyridinium bromide, [Bupy]Br; 1-butylpyridinium tetrafluoroborate, [Bupy][BF₄]; and 1-butylpyridinium hexafluorophosphate, [Bupy][PF₆], (Scheme 1) in 10%, 30% and 50% (w/w) *N,N*-dimethylformamide-water (DMF-H₂O) and methanol-water (MeOH-H₂O) solvent mixtures at temperatures of 298.15, 303.15, 308.15, and 313.15 K. The molar conductance data are analysed by means of the Fuoss-Edelson equation in terms of the limiting molar conductance (Λ_o) and the ionic association constant (K_A). At the same time, pyridinium, with a fixed cation [Bupy]⁺ but different anions, Cl⁻, Br⁻, [BF₄]⁻ and [PF₆]⁻, are examined to understand the effects of anion size on the transport properties and the association behaviour of these systems. Moreover, different proportions of solvents covering the dielectric constant (ϵ), viscosity (η_o), and density (ρ) ranges of were utilized to understand the potential influence of the solvent on the ionic association of the associated compounds. Further, the transport properties of cations and anions are investigated, such as limiting ionic conductance (λ_{\pm}^o), transfer numbers (t_{\pm}), the diffusion coefficient (D_o), ionic mobility (μ_{\pm}), Walden product ($\Lambda_o \eta_o$), and hydrodynamic radii ($(1/rs^+ + 1/rs^-)^{-1}$). The activation

energy of the transport process [12] and the standard thermodynamic parameters of association (ΔG_A^o , ΔH_A^o and ΔS_A^o) were also calculated and discussed for the species under study. The results provide novel insights into their association behaviours, allowing for a further understanding of the peculiarities of species of the pyridinium family in binary alcoholic-aqueous mixtures, about which almost nothing is currently known.

2. Experimental

Chemicals and materials

1-butylpyridinium chloride (99.0%), 1-butylpyridinium bromide, ($\geq 99.0\%$), 1-butylpyridinium tetrafluoroborate ($> 94.0\%$) and 1-butylpyridinium hexafluorophosphate ($> 98.0\%$), *N,N*-dimethylformamide, HPLC Grade (DMF $\geq 99.9\%$) and methanol, spectrophotometric grade, (MeOH $\geq 99.9\%$) were supplied by Sigma-Aldrich and/or Tokyo Chemistry Industry and used without further purification. Milli-Q water (with a specific conductance of $0.06 \mu\text{S cm}^{-1}$ at 298.15 K) was utilized during the experiments.

Apparatus

The specific conductances (K_s , $\mu\text{S cm}^{-1}$) of the prepared solutions were determined using a Jenway Conductivity Bridge with a cell constant of 1.15 cm^{-1} and a deviation of $\pm 0.1 \mu\text{S cm}^{-1}$. The cell constant was determined using potassium chloride solutions [46]. The conductivity bridge was connected to a MLW 3230 ultrathermostate to maintain a constant temperature with an error of $\pm 0.005^\circ\text{C}$.

Solutions

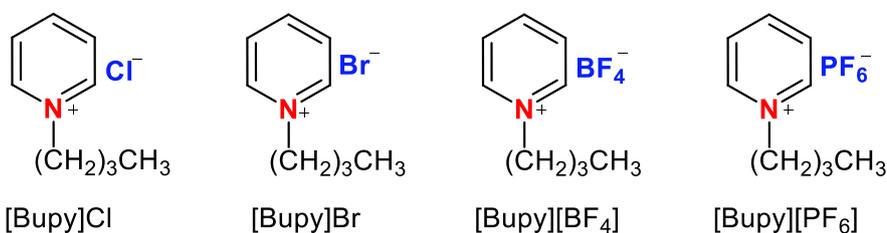
Twelve solutions of the species under investigation with concentration ranges of 0.18954×10^{-3} –

$5.714 \times 10^{-3} \text{ mol dm}^{-3}$, were prepared by taking appropriate volumes of the associated standard solutions and diluting to the required volume for measurements by the previously prepared mixed solvents. Binary mixed solvents at 10%, 30%, and 50% (w/w) of DMF-H₂O and MeOH-H₂O were prepared by mixing the required volume of methanol and dimethyl formamide with water (with error $\pm 0.01\%$) by applying the following equation:

$$\text{Alcohol percentage} = [(v_1 d_1)100/(v_1 d_1 + v_2 d_2)] \dots\dots\dots (1)$$

where d_1 and d_2 are the densities of alcohol and water, respectively, v_1 is the volume of alcohol to

be added to the volume v_2 of water to achieve a mixture of the required proportions. Physical properties, namely relative permittivities (ϵ), densities (ρ), and viscosities (η_o) for DMF-H₂O and MeOH-H₂O were taken from the literature [41-45] and are reported in Table 1. Unknown values of these properties were evaluated by applying the empirical relations of these properties at the available temperatures taken from the referred references.



Scheme 1. Structures and nomenclature adopted herein for 1-butylpyridinium cations with the various anions under study.

Table 1. Relative permittivities (ϵ), densities (ρ , $g \text{ cm}^{-3}$), and viscosities (η_o , cP) of the mixed solvents at various temperatures.

Solvent	property	T/K			
		298.15	303.15	308.15	313.15
10% DMF-H ₂ O	ϵ	76.10	74.12	72.21	70.31
	ρ	1.0129	1.0118	1.0102	1.0012
	η_o	0.7899	0.7451	0.691	0.6512
30% DMF-H ₂ O	ϵ	67.05	65.11	63.65	61.13
	ρ	0.9668	0.9659	0.9601	0.959
	η_o	0.8436	0.8036	0.7562	0.7123
50% DMF-H ₂ O	ϵ	58.34	56.76	54.78	52.56
	ρ	0.9231	0.9193	0.9142	0.9034
	η_o	0.8765	0.8621	0.8214	0.7734
10% MeOH-H ₂ O	ϵ	74.31	72.34	70.44	68.23
	ρ	1.0110	1.009	1.0081	1.0009
	η_o	0.7459	0.7018	0.6508	0.6107
30% MeOH-H ₂ O	ϵ	65.40	63.75	61.79	59.67
	ρ	0.9643	0.9600	0.9590	0.9540
	η_o	0.7982	0.7528	0.6924	0.6541
50% MeOH-H ₂ O	ϵ	55.32	53.56	51.54	49.76
	ρ	0.9145	0.9114	0.9034	0.9002
	η_o	0.8410	0.8321	0.8278	0.8115

3. Results and discussion

Conductances and transport properties

The molar conductances (Λ) for all studied systems were calculated using Eq. (2).

$$\Lambda = 103K_s/c \dots \dots \dots (2)$$

where C is the molarity (mol l^{-1}), K_s is the measured specific conductance of the solution of interest, from which the specific conductance of the solvent being used was subtracted. The molar conductance, Λ , for all the systems investigated are illustrated in Figures S1-S8 in the supplementary information, as a function of concentration, temperature and solvent mixtures. The uncertainty of the molar conductance Λ was estimated to be about $0.05 \text{ S mol}^{-1} \text{ cm}^2$. The limiting molar conductances (Λ_o) of the investigated systems were evaluated using the Onsager relation (3): [47].

$$\Lambda = \Lambda_o - s\sqrt{c} \dots \dots \dots (3)$$

where a plot of Λ versus \sqrt{C} gives a straight line with a y -intercept of Λ_o and a gradient equal to the Onsager constant. The values obtained for Λ_o are reported in Table 2. The uncertainty of the Λ_o was estimated to be about $0.01 \text{ S mol}^{-1} \text{ cm}^2$. To investigate the role of the individual IL ions in the ion solvation, one must split the limiting molar conductances into their constituent ionic contributions. It is known that the limiting ionic conductances (λ_o^-) of Cl^- , Br^- , $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$ are 76.4, 78.1, 75.1 and $65.5 \text{ S mol}^{-1} \text{ cm}^2$ in water at 298.15 K, respectively. [13,48] Since there is no accessible data for λ_o^- in 10, 30 and 50% (w/w) DMF-H₂O and MeOH-H₂O mixtures, they were calculated, with the Λ_o of [Bupy]Cl, [Bupy]Br, [Bupy][BF₄] and [Bupy][PF₆] being determined as 282.94, 249.93, 235.85 and $222.22 \text{ S mol}^{-1} \text{ cm}^2$, respectively in water at 298.15 K (see Table S1 and Figure S9 in the supplementary information). This was based on the above data for the λ_o^- of the anions for each solvent mixture by applying an empirical

equation by multiplying (the ratio of Λ_o in the solvent at 298.15 K to that in water at 298.15 K) by the appropriate λ_o^- under the same conditions. Since $\Lambda_o = \nu_+ \lambda_o^+ + \nu_- \lambda_o^-$, the limiting ionic conductance of [Bupy]⁺ can be calculated from the observed Λ_o above by using appropriate values of λ_o^- from the literature [13,48]. The values so obtained for λ_o^\pm at different temperatures, in all mixtures of solvents, are summarized in Table 2, and indicate that the Λ_o and λ_o^\pm were observed to be inversely proportional to the proportions of the organic-aqueous solvents at the same temperature as follows: 30% < 20% < 10%. This behaviour may be due to the formation of hydrogen bonds, which leads to the association of alcohol and H₂O molecules and so reduces the ion mobility and decreases Λ_o and λ_o^\pm to a greater extent than otherwise observed for the organic solvent. In studying the effect of the solvent nature on the Λ_o and λ_o^\pm as a function of concentration and comparing the percentage of DMF-H₂O and percentage of MeOH-H₂O, it was observed that both Λ_o and λ_o^\pm in the case of MeOH-H₂O is greater than for DMF-H₂O, which is due to higher intermolecular hydrogen bonding in DMF and possibly also related to the higher polarity of DMF-H₂O.

This behaviour has also been reported by other authors [13,39,40,49-56]. Both Λ_o and λ_o^\pm decreased when the viscosity of the solvent mixtures was increased at all the temperatures investigated, which was expected due to ionic mobility being reduced by the more viscous media. Interestingly, there was a regular increase in the limiting molar conductance for each of the compounds and the reciprocal of the viscosity ($1/\eta_o$) for the solvent mixtures (see Figure 1 as an example). This suggests that the viscosity of the solvents plays a prevailing role determining the magnitudes of

Λ_o and λ_o^\pm of compounds. An examination of the values of Λ_o and λ_o^\pm determined at different temperatures indicates that these increased when the temperature was increased, which suggests that the mobility of the ions increases with increasing temperature. The λ_o^+ calculated for the [Bupy]⁺ cation for each compound decreases from Cl⁻ to [PF₆]⁻ (Table 2) This is due to an increase in ionic association of the cations with the anions of the compounds studied and also because the anions (Cl⁻, Br⁻, [BF₄]⁻, [PF₆]⁻) are responsible for a greater share of ionic association than the common

pyridinium cation [Bupy]⁺. The data in Table 2 might also potentially allow for an understanding of the effect of anion size on the limiting molar conductances. In all the mixtures, the limiting molar conductances (Table 2) over all composition ranges follow the order [Bupy]Cl > [Bupy]Br > [Bupy][BF₄] > [Bupy][PF₆].

The same trend was observed in the case of the limiting ionic conductances of the cation [Bupy]⁺ under the same conditions.

Table 2. Limiting molar conductance (Λ_o , S.mol⁻¹ cm²) and limiting ionic conductance (λ_o^\pm , S.mol⁻¹ cm²) for the system investigated in the various solvents used, as determined at various temperatures.

Solvent	T/K ±0.15	Λ_o	λ_o^+	λ_o^-	Λ_o	λ_o^+	λ_o^-	Λ_o	λ_o^+	λ_o^-	Λ_o	λ_o^+	λ_o^-	
		[Bupy]Cl	[Bupy] ⁺	Cl ⁻	[Bupy]Br	[Bupy] ⁺	Br ⁻	[Bupy][BF ₄]	[Bupy] ⁺	[BF ₄] ⁻	[Bupy][PF ₆]	[Bupy] ⁺	[PF ₆] ⁻	
DMF-H ₂ O	10%	298	201.46	147.06	54.40	176.01	121.01	55.00	170.45	116.17	54.28	162.43	114.55	47.88
		303	210.63	153.75	56.87	187.47	128.89	58.58	180.80	123.23	57.57	171.75	121.13	50.62
		308	227.43	166.02	61.41	199.57	137.21	62.36	191.65	130.62	61.03	181.57	128.05	53.52
		313	241.70	176.44	65.26	211.47	145.39	66.08	202.90	138.29	64.61	191.89	135.33	56.56
	30%	298	196.42	143.39	53.04	169.19	116.32	52.87	161.63	110.16	51.47	155.71	109.81	45.90
		303	206.87	151.01	55.86	179.98	123.74	56.24	171.50	116.89	54.61	164.82	116.24	48.58
		308	221.30	161.54	59.76	191.33	131.54	59.79	181.90	123.98	57.92	174.30	122.92	51.38
		313	236.35	172.53	63.82	203.02	139.58	63.44	192.78	131.39	61.39	184.23	129.93	54.30
	50%	298	185.24	135.22	50.02	163.67	112.53	51.14	153.81	104.83	48.98	150.57	106.19	44.38
		303	198.99	145.26	53.73	174.75	120.14	54.61	163.34	111.33	52.01	159.57	112.54	47.03
		308	212.48	155.11	57.37	185.85	127.77	58.08	173.32	118.13	55.19	169.09	119.25	49.84
		313	223.38	163.06	60.32	197.38	135.70	61.68	183.68	125.19	58.49	178.94	126.20	52.74
MeOH-H ₂ O	10%	298	244.69	178.62	66.07	224.43	154.30	70.13	214.56	146.24	68.32	202.45	142.78	59.67
		303	256.17	187.00	69.17	237.76	163.46	74.30	226.63	154.47	72.16	213.44	150.53	62.91
		308	270.08	197.15	72.93	251.31	172.78	78.53	239.07	162.94	76.13	224.59	158.39	66.20
		313	288.96	210.93	78.03	264.42	181.79	82.63	251.85	171.66	80.19	236.07	166.49	69.58
	30%	298	232.76	169.91	62.85	215.22	147.97	67.25	203.90	138.97	64.93	195.44	137.83	57.61
		303	248.64	181.50	67.14	227.63	156.50	71.13	215.54	146.91	68.63	206.24	145.45	60.79
		308	264.50	193.08	71.42	240.39	165.27	75.12	227.52	155.07	72.45	217.31	153.26	64.05
		313	274.38	200.29	74.09	253.91	174.57	79.35	239.93	163.53	76.40	228.52	161.16	67.36
	50%	298	223.98	163.50	60.48	209.21	143.83	65.38	194.44	132.53	61.91	189.24	133.46	55.78
		303	239.31	174.69	64.62	221.62	152.37	69.25	205.61	140.14	65.47	199.94	141.01	58.93
		308	251.52	183.60	67.92	234.30	161.08	73.22	217.13	147.99	69.14	210.91	148.74	62.17
		313	268.37	195.91	72.47	249.06	171.23	77.83	228.96	156.05	72.91	222.23	156.73	65.50

Uncertainties are [0.01 and 0.05 S mol⁻¹ cm² for Λ_o and λ_o^\pm , respectively]

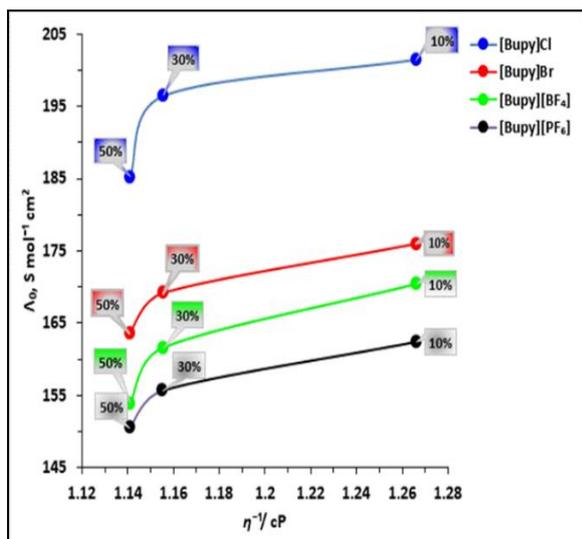


Fig. 1. Plot of Λ_0 vs. η_o^{-1} for the species investigated in DMF-H₂O mixtures at T = 298.15 K. The findings are as expected, in that the larger the size of the bare ion, the smaller its ionic mobility which hence limits the molar conductance. This observed order for Λ_o and λ_o^\pm , at least for the last three anions, is in agreement with those reported in the literature [13]. From the Λ_o and λ_o^\pm data for the ionic mobilities (u_\pm), transfer number (t_\pm) and mobility of the all ions under consideration in the experimental conditions could be determined, and the following set of equations was applied:

$$u_\pm = \lambda_o^\pm / z_\pm F \dots\dots\dots (4)$$

$$t_\pm = \lambda_o^\pm / \Lambda_o \dots\dots\dots (5)$$

where, z_\pm and F , are the charges of the cations and anions and the Faraday constant (96485.3365 coulombs/mole), respectively. The t_\pm of the cations and/or anions studied can be calculated, where $t_+ + t_- = 1$. The transfer number remained almost unchanged to four significant figures in the solvent mixtures used, though there is no obvious reason why it should not change, and are further given in Table S2 in the supplementary information. The values of u_+ and u_- for all ions studied in 10%, 30% and 50% (w/w) DMF-H₂O and MeOH-H₂O mixtures at different temperatures are presented in Table 3. The changes in the values

of u_+ and u_- are analogous to that observed for λ_o^\pm , where u_+ and u_- were found to increase with increasing temperature and decrease with increasing proportion of organic solvent. This might well be related to the increase in the kinetic energy of the ions as the temperature increases and the increases in viscosity as the proportion of organic solvent increased, respectively.

The λ_o^\pm for the cations and anions were therefore utilized for the estimation of limiting diffusion coefficients D_o of the IL by employing the Nernst-Haskell equation (6) [57,58]. The values of D_o determined at different temperatures are summarized in Table 3.

$$D_o = 17.872 \times 10^{-10} \left(\frac{\lambda_o^+ \lambda_o^-}{\Lambda_o} \right) \dots\dots\dots (6)$$

The results indicate that the D_o values for all the systems studied show an analogous trend of change to that of the limiting molar conductance, with some minor exceptions, and whose uncertainty was estimated to be about $\pm 0.004\%$. The values of D_o were found to increase as the temperature increased as a result of the increase in kinetic energy and ionic mobilities of the ions studied. These same values were also found to decrease as the proportions of the organic solvents increased at a given temperature as follows: 10% > 30% > 50%. The D_o values observed for MeOH-H₂O were comparatively larger than those observed for DMF-H₂O; this is probably due to the special pathway of D_o by structured solvents such as MeOH for the field-induced diffusion of charged species, and which can also be interpreted on the basis of the hydrogen-bonding effect. Where the limiting diffusion coefficient of the system studied in MeOH-H₂O is slightly greater than that in DMF-H₂O, and where this ordering was observed at all temperatures.

Table 3. Ionic mobilities ($u_{\pm} \times 10^{-4}$, cm² Sec⁻¹V⁻¹) and diffusion coefficients ($D_o \times 10^{-5}$, cm² sec⁻¹) for the system investigated in the various solvents used, as determined at various temperatures.

Solvent	T/K ±0.15	u_+	u_-	D_o	u_+	u_-	D_o	u_+	u_-	D_o	u_+	u_-	D_o	
		[Bupy] ⁺	[Cl] ⁻	[Bupy][Cl]	[Bupy] ⁺	[Br] ⁻	[Bupy][Br]	[Bupy] ⁺	[BF ₄] ⁻	[Bupy][BF ₄]	[Bupy] ⁺	[PF ₆] ⁻	[Bupy][PF ₆]	
DMF-H ₂ O	10%	298	0.1524	5.64	2.120	0.1254	5.70	2.010	0.1204	5.630	1.970	0.1187	4.96	1.800
		303	0.1594	5.89	2.250	0.1336	6.07	2.180	0.1277	5.970	2.130	0.1255	5.25	1.930
		308	0.1721	6.360	2.470	0.1422	6.46	2.360	0.1354	6.320	2.290	0.1327	5.55	2.080
		313	0.1829	6.760	2.670	0.1507	6.85	2.540	0.1433	6.700	2.460	0.1403	5.86	2.230
	30%	298	0.1486	5.500	2.060	0.1206	5.480	1.940	0.1142	5.330	1.870	0.1138	4.76	1.720
		303	0.1565	5.790	2.210	0.1282	5.830	2.090	0.1211	5.660	2.020	0.1205	5.03	1.860
		308	0.1674	6.190	2.400	0.1363	6.20	2.260	0.1285	6.000	2.170	0.1274	5.33	2.000
		313	0.1788	6.610	2.610	0.1447	6.580	2.440	0.1362	6.360	2.340	0.1347	5.63	2.140
	50%	298	0.1401	5.180	1.950	0.1166	5.30	1.870	0.1374	6.420	2.250	0.1101	4.60	1.670
		303	0.1506	5.570	2.130	0.1245	5.660	2.030	0.1452	6.790	2.420	0.1166	4.87	1.800
		308	0.1608	5.950	2.310	0.1324	6.020	2.200	0.1534	7.170	2.600	0.1236	5.17	1.940
		313	0.1690	6.250	2.460	0.1406	6.390	2.370	0.1617	7.560	2.780	0.1308	5.47	2.080
MeOH-H ₂ O	10%	298	0.1851	6.850	2.570	0.1599	7.270	2.570	0.1516	7.080	2.480	0.148	6.18	2.240
		303	0.1938	7.170	2.740	0.1694	7.70	2.770	0.1601	7.480	2.660	0.156	6.52	2.400
		308	0.2043	7.560	2.930	0.1791	8.140	2.970	0.1689	7.890	2.860	0.1642	6.86	2.570
		313	0.2186	8.090	3.190	0.1884	8.560	3.180	0.1779	8.310	3.060	0.1726	7.21	2.750
	30%	298	0.1761	6.510	2.440	0.1534	6.970	2.460	0.1440	6.730	2.360	0.1429	5.97	2.160
		303	0.1881	6.960	2.660	0.1622	7.370	2.650	0.1523	7.110	2.530	0.1507	6.30	2.320
		308	0.2001	7.400	2.870	0.1713	7.790	2.840	0.1607	7.510	2.720	0.1588	6.64	2.490
		313	0.2076	7.680	3.030	0.1809	8.220	3.050	0.1695	7.920	2.910	0.167	6.98	2.660
	50%	298	0.1695	6.270	2.350	0.1491	6.780	2.400	0.1087	5.080	1.780	0.1383	5.78	2.100
		303	0.1811	6.700	2.560	0.1579	7.180	2.580	0.1154	5.390	1.920	0.1461	6.11	2.250
		308	0.1903	7.040	2.730	0.1669	7.590	2.770	0.1224	5.720	2.070	0.1542	6.44	2.410
		313	0.2030	7.510	2.960	0.1775	8.070	2.990	0.1298	6.06	2.230	0.1624	6.79	2.590

Uncertainties are [0.0002 and 0.001 cm² Sec⁻¹V⁻¹ for u_+ and u_- , respectively and 0.004 cm² sec⁻¹ for D_o]

This may be the result of the greater temperature sensitivity to viscosity of IL solutions. The observed trend of D_o suggests that both the co-solvent properties and ion structure of the electrolyte have an exceptional influence on the D_o of the electrolytes. The lower values of D_o for [Bupy][PF₆] could be ascribed to the bulky size of the species'. In comparison, the D_o values for the DMF-H₂O system have the following [Bupy]Cl > [Bupy]Br > [Bupy][BF₄] > [Bupy][PF₆] in 10% and 30% DMF-H₂O and [Bupy][BF₄] > [Bupy]Cl > [Bupy]Br > [Bupy][PF₆] in 50% and 30% DMF-H₂O whereas, the D_o values in the MeOH-H₂O system follow the order [Bupy]Br > [Bupy]Cl > [Bupy][BF₄] > [Bupy][PF₆] in 10% and 30% MeOH-H₂O and [Bupy]Br > [Bupy]Cl > [Bupy][PF₆] [Bupy][BF₄] in 50% MeOH-H₂O. This order of the limiting diffusion coefficient behaviour is difficult to understand and the reason for the above is currently unknown and requires further study in the future.

Ion-pair association behaviour, Walden product and the hydrodynamic radii

Conductometry can provide valuable information about ion-pair association behaviour in solution, we considered the following equilibria. The following equilibria in our solutions; $M^+ + A^- \leftrightarrow MA$. Herein the conductometric data obtained are treated by means of the Fuoss-Edelson equation (7)[59]. Using a computer program, to evaluate the ion-pair association constants of the salts studied and to re-evaluate the limiting molar conductances (Λ_o), where the following equation is proposed:

$$\Delta F = \Lambda_o - XK_A / \Lambda_o \dots \dots \dots (7)$$

Where $X = C\gamma_{\pm}\Delta F(\Delta F - \Lambda_o/2)$

$$F = [(1 - \delta C^{1/2})^{-1} + (\Lambda_o - \lambda_o^- / 2A)] / [1 + (\Lambda_o - \lambda_o^- / 2A_o)]$$

Where λ_o^- is the limiting ionic conductance of the anion, δ is the Onsager's slope divided by Λ_o , C is the molar concentration of the anion and γ_{\pm} is the ion activity coefficient of the cation, which can be estimated by the Debye-Hückel second approximation equation (8).

$$\log \gamma_{\pm} = (-A[Zi]^2\sqrt{u}/1 + Ba\sqrt{u}) \dots \dots \dots (8)$$

where A, B are empirical constants, $A = 1.824 \cdot 10^6 / (\epsilon T)^{3/2}$; $B = 50.29 \cdot 10^8 (\epsilon T)^{-1/2}$, where T is the absolute temperature, a is the ion size parameter or the distance of closet approach ($\approx 3.0, 1.82, 2.27, 2.56 \text{ \AA}$ for Cl^- , Br^- , $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, respectively [13,48,60], u is the ionic strength and Z is the valence of the cation. According to the Fuoss-Edelson, a plot of ΔF versus X , which gave a straight line with an intercept equal to Λ_o and a gradient equal to $-K_A/\Lambda_o$, allowed Λ_o and K_A to be evaluated. Then, we repeated, this processes to find the fixed value of Λ_o for all systems being studied, and thus the corresponding K_A values could be determined. The estimated values of the ion-pair association constant (K_A) for all the systems under study are reported in Table 4.

It is interesting to note that the association constant K_A depends on the temperature, relative permittivity, viscosity of the medium, and the formation of intermolecular hydrogen bonding. In light of Table 4, the K_A values for all electrolytes increased when the temperature increased, which is as expected. This observation can be explained in the context of desolvation and association behaviour; if the temperature increases, desolvation of the ions will take place, or in other words with increasing temperature the number of free ions per unit volume decreases, the tendency for ion-pair formation increases. Accordingly, the association of the ions increases, as represented in Figure 2a. In addition to this effect, increased temperature can result in a decrease in the dielectric constant of the solvent and hence an increase in the association constant. A careful investigation of the data indicates that there is a linear relationship between $\ln K_A$ and the reciprocal of ϵ for the solvent mixtures, as illustrated in Figure 2b, which is qualitatively in agreement with reports in the

literature regarding the typical ionic association theory of electrolytes [52,61].

The most predominant order of K_A for the investigation systems in the solvent used was found to increase as follows: K_A in MeOH-H₂O $>$ K_A in DMF-H₂O at any given temperature, and there is also a progressive increase in association constant with decreasing proportion, i.e., 10% $<$ 30% $<$ 50% in both solvent mixtures used. The overall schematic representation of the interaction or ion-solvation that occurs in the solution systems studied is represented in Scheme 2a. showing the steps in the formation of a contact ion pair (CIP) from solvated "free" ions in the solution are as follows: the cation approaches the anion, solvent molecules surrounding the ions were displaced to form the solvent-separated ion pair (SSIP) and the solvent-shared ion pair (SShIP) before the CIP through a series of stepwise equilibria in which one or two shared water shells separated the ions. Generic cations, anions and solvent molecules are indicated by the red, green, and blue circles, respectively, in the summary in Scheme 2a.

Table 4. Ionic association constant (K_A , mol. dm⁻³), Walden product ($\Lambda_o\eta_o$, S mol⁻¹ cm² cP) and hydrodynamic radii (R_H , Å × 10⁻³) for the investigated systems in the various solvents used at various temperatures.

Solvent	T/K ±0.15	[Bupy][Cl]			[Bupy][Br]			[Bupy][BF ₄]			[Bupy][PF ₆]			
		K_A	$\Lambda_o\eta_o$	R_H	K_A	$\Lambda_o\eta_o$	R_H	K_A	$\Lambda_o\eta_o$	R_H	K_A	$\Lambda_o\eta_o$	R_H	
DMF-H ₂ O	10%	298	421.32	159.14	5.15	425.71	139.0	5.90	456.34	134.6	6.09	443.84	128.3	6.39
		303	424.09	156.9	5.22	430.52	139.8	5.87	457.01	134.7	6.09	444.51	127.9	6.41
		308	426.15	157.2	5.220	437.65	137.9	5.95	457.62	132.4	6.19	445.12	125.5	6.54
		313	427.64	157.4	5.210	439.24	137.7	5.95	458.04	132.1	6.21	445.53	124.9	6.56
	30%	298	429.92	165.7	4.950	435.07	142.7	5.75	457.91	136.3	6.01	445.40	131.3	6.24
		303	432.59	166.2	4.930	436.47	144.6	5.67	458.28	137.8	5.95	445.76	132.4	6.19
		308	434.5	167.3	4.900	439.72	144.7	5.67	458.72	137.5	5.96	446.21	131.8	6.22
		313	437.28	168.3	4.870	440.11	144.61	5.67	459.92	137.3	5.97	447.43	131.23	6.25
	50%	298	430.35	162.4	5.050	440.70	143.5	5.72	458.93	134.8	6.08	446.41	132.0	6.21
		303	433.45	171.5	4.780	443.21	150.6	5.44	459.57	140.8	5.82	447.06	137.6	5.96
		308	435.10	174.5	4.700	445.39	152.7	5.37	460.15	142.4	5.76	447.65	138.9	5.90
		313	438.12	172.8	4.750	445.64	152.6	5.37	460.90	142.1	5.77	448.40	138.4	5.93
MeOH-H ₂ O	10%	298	407.01	182.5	4.490	414.68	167.4	4.90	451.61	160.0	5.12	444.41	151.0	5.43
		303	421.71	179.8	4.560	425.45	166.8	4.91	452.26	159.1	5.16	445.06	149.8	5.47
		308	422.10	175.77	4.670	431.81	163.5	5.01	453.01	155.6	5.27	445.80	146.1	5.61
		313	426.52	176.5	4.650	436.21	161.4	5.08	453.61	153.8	5.33	446.41	144.2	5.69
	30%	298	418.57	185.8	4.410	432.02	171.8	4.77	451.11	162.7	5.04	443.92	156.0	5.26
		303	422.96	187.2	4.380	432.59	171.3	4.79	451.79	162.3	5.05	444.60	155.	5.28
		308	423.56	183.1	4.480	435.22	166.4	4.93	452.21	157.5	5.21	445.01	150.4	5.450
		313	427.29	179.5	4.570	439.08	166.1	4.94	452.41	156.9	5.22	445.2	149.5	5.49
	50%	298	423.75	188.4	4.350	435.24	175.9	4.66	453.09	163.5	5.01	445.89	159.1	5.15
		303	424.89	199.1	4.120	437.77	184.4	4.45	453.55	171.1	4.79	446.36	166.4	4.93
		308	426.59	208.2	3.940	438.33	193.9	4.23	454.53	179.7	4.56	447.33	174.6	4.70
		313	430.67	217.8	3.770	438.95	202.1	4.06	454.86	185.8	4.41	447.66	180.3	4.55

Uncertainties are [K_A , 0.01 mol. dm⁻³; $\Lambda_o\eta_o$, 0.1 S mol⁻¹ cm² cP and R_H , 0.02 Å × 10⁻³].

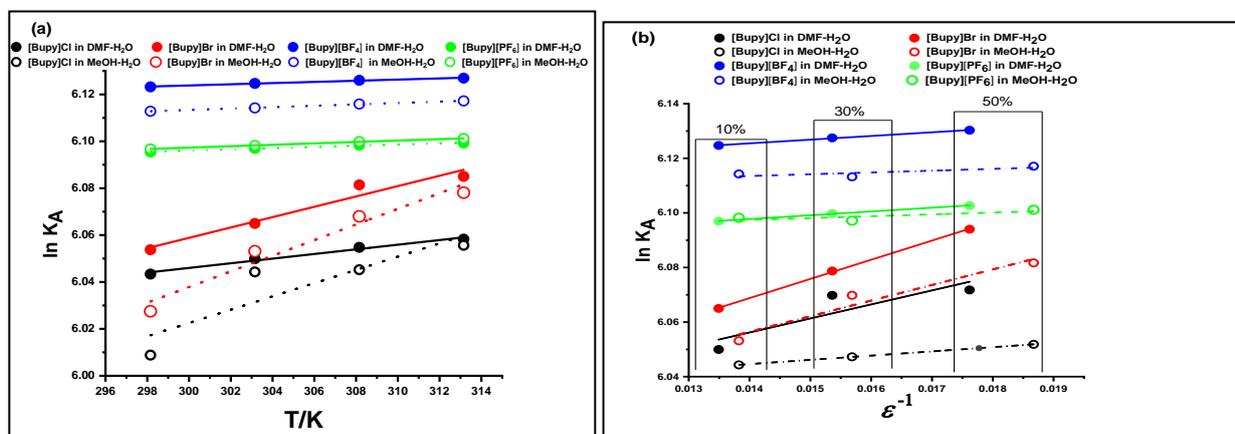


Fig. 2 (a): The temperature dependence of $\ln K_A$ in 10% solvent mixtures at different temperatures. **(b):** relation of $\ln K_A$ vs. ϵ^{-1} for the compounds investigated at 303.15 K in the solvents used.

Furthermore, interaction in the solution can occur as ion-solvent interactions and/or the formation of a dimer by hydrogen bonding, or the formation of dimer such as cation-anion-cation or anion-cation-anion and the charge of the respective ions in the

solvent mixture as proposed in Scheme 2b. In spite of this, the various types of anions can link via various hydrogen bonds, but it is difficult to consider the hydrogen-bonding interactions in isolation whilst excluding the electrostatics in

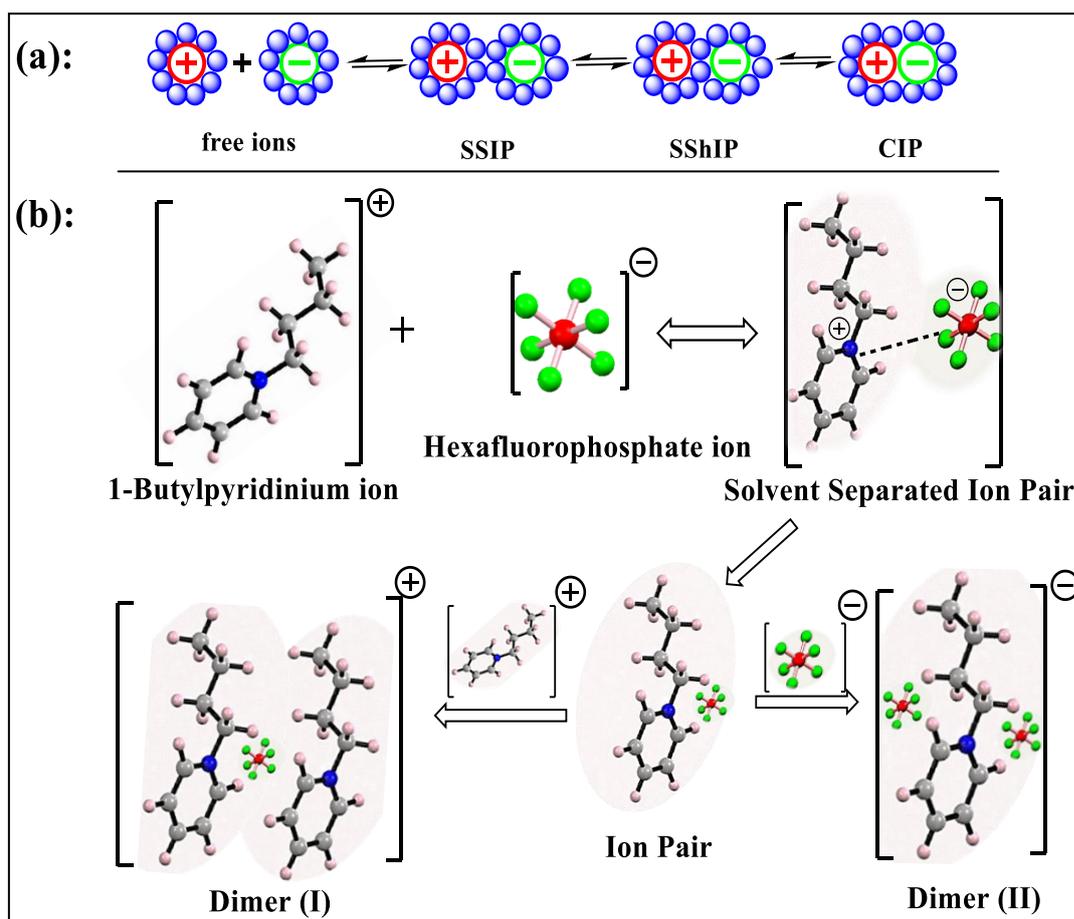
principle, the main criteria for forming a hydrogen bond is the distance between the basic acceptor atom and proton on a donor group, or in other words $R_{XH} \cdots Y$ is smaller than the sum of the relevant van der Waals radii. For the systems under investigation, the high electronic delocalization on the butylpyridinium ring and the contribution of the two resonance forms may have caused the larger positive charges on the C-H of the pyridine ring, which became the prime interaction site with the anion [62-65]. For anions with monatomic ions such as [Bupy]Cl, as per Figure 3a, only one C-H \cdots Cl hydrogen bond forms between the anion and cation, while for polyatomic anions like [Bupy][PF₆] in Figure 3b, it is more likely that there is more than one C-H \cdots F hydrogen bond between the anion and cation [65-68].

The decrease in K_A may be attributed to an increased contribution from the hydrogen-bonding forms, [Bupy][PF₄] and [Bupy][PF₆]. Certainly, an anion can take possession of many stable conformers around the cation, and despite the energetic variation being very small, the hydrogen bond direction can differ considerably. On the other hand, it should be pointed out that the K_A values for the systems studied follow the order [Bupy][BF₄] > [Bupy][PF₆] > [Bupy]Br > [Bupy]Cl in any given solvent mixture (Table 4). The reason for this trend is difficult to understand however, the fact that Cl⁻ anion has a much smaller size, higher surface charge density and thus stronger electrostatic interaction than [Bupy]⁺ indicates that the high solvation of the Cl⁻ anion will considerably reduce its K_A with the cation in the solvent mixtures, leading to the trend observed in the experiment. The weaker solvation of the anion enhances the ionic association, whilst the stronger ionic solvation weakens the ionic association of the ILs in solvent

mixtures, as has previously been reported [13]. The Walden product ($\Lambda_o \eta_o$), which is informative from the point of view of ion-solvent interactions, [69] has a constant value because the Λ_o of an ion at infinite dilution relies purely upon its rapidity and, therefore, the ion conductance product by means of viscosity of the medium should be independent of the nature of the solvent. Thus, $\Lambda_o \eta_o$ is more likely to be constant in a particular electrolyte in a set of solvent mixtures in which the ion-solvent interactions are regular. Walden presented the associated rule for a 1:1 electrolyte, as expressed in Eq (9).

$$\Lambda_o \eta_o = 0.82 [1/r_s^+ + 1/r_s^-] \dots\dots\dots (9)$$

The expression $[1/r_s^+ + 1/r_s^-]^{-1}$ is defined as a measure of the hydrodynamic radii (R_H) of the ions which can be used to understand ion-solvent interactions assuming the applicability of $\Lambda_o \eta_o$ and R_H are calculated for [Bupy]Cl, [Bupy]Br, [Bupy][BF₄] and [Bupy][PF₆] in 10%, 20% and 30% (w/w) DMF-H₂O and MeOH-H₂O mixtures at different temperatures with the associated values are presented in Tables 4. $\Lambda_o \eta_o$ and R_H for all the systems under study was found to decrease as the proportion of organic solvent increased, and which decreased in the following order: DMF-H₂O > MeOH-H₂O, with few exceptions, suggesting the system under study and its cations and anions were solvated by weight ratios of solvent mixtures to a certain extent and that the solvation of the Cl⁻ anion is much greater than that of the Br, [BF₄] and [PF₆] anions. In addition, it was noticed that the Walden product decreased when the temperature increased. The negative temperature coefficients of $\Lambda_o \eta_o$ may be due to the increase in the volume of solvated ions in the mixtures with increasing temperature.



Scheme 2 (a): The formation stages of a contact ion pair from solvated “free” ions in solution. **(b):** The proposed mechanism for ion-ion and ion-solvent interactions for [Bupy][PF₆].

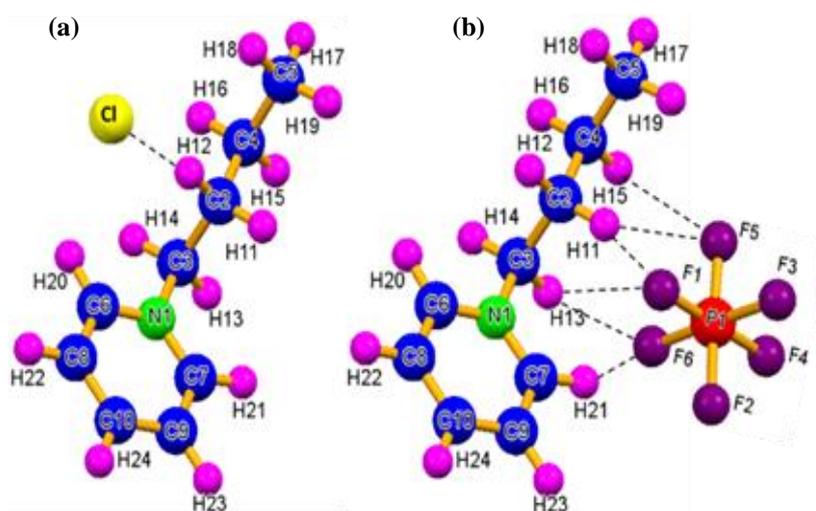


Fig.3. Possible sites for hydrogen bonds in 1-Butylpyridinium-based ion-pairs denoted by dashed lines. **(a)** For [Bupy]Cl ion-pair and **(b)** for [Bupy][PF₆], as represented by the different colours.

This may be the result of the alteration of the ratio of the alcohol and water molecules in the solvation shell with temperature[70]. The main factors that can have an effect on the Walden product are those of η and Λ_o , in which η is inversely proportional to T , and Λ_o is directly proportional to T . Therefore, it can be concluded that viscosity plays a key role in the inversely proportional behaviour of $\Lambda_o\eta_o$ with T .

Activation energy of the transfer process.

According to the theory of transport properties in ionic liquids, an Arrhenius-type expression for the temperature dependence of the conductances is anticipated[43,71]. As the conductances of an ion can be dependent on its movability, it is more sensible to treat the conductances data in a similar manner to that utilized for the rate processes occurring with the alteration of T , as based on Eq. (10):

$\Lambda_o = Ae^{-Ea/RT}$ OR $\ln \Lambda_o = \ln A - Ea/RT$ (10)
where A , R and Ea are the frequency factor, the gas constant and the Arrhenius activation energy for the transfer process, respectively. The Ea values were computed from the gradient of the plot of $\ln \Lambda_o$ vs. $(1/T)$, as represented in Figure. 4 as an example, and with their associated data summarised in Table 5.

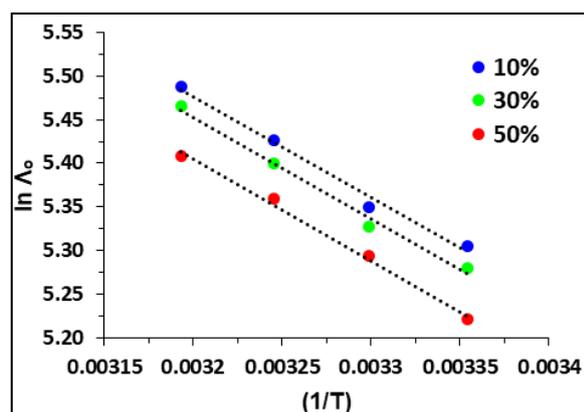


Fig. 4. Plot of $\ln \Lambda_o$ versus $(1/T)$ for [Bupy]Cl in various DMF-H₂O mixtures.

The Ea values were observed to increase with the ratio of the alcohol-aqueous solvents at a fixed same temperature in the order 10% < 30% < 50%, and

indeed increased more for the DMF-H₂O mixture than for the MeOH-H₂O. The results obtained also show that the impact of the anions on the activation energy of transport process behaviour of the compounds studied followed the order $Cl^- < Br^- < [BF_4]^- < [PF_6]^-$ at all the temperatures investigated. The increase in Ea indicates that more energy was used for the transfer process. Furthermore, an increase in Ea was always accompanied by an increase in viscosity, dielectric constant and association behaviour of the system (as a consequence of hydrogen bond formation such as in [Bupy][PF₆]).

Thermodynamic quantities of association

The conventional association constant, K_A as obtained at different temperatures and solvent compositions was used to evaluate thermodynamic quantities such as change in free energy (ΔG_A^o), change in entropy (ΔS_A^o) and change in heat content (ΔH_A^o) of ion association. The ΔG_A^o values for the ion-association process were obtained utilizing the following expression:

$$\Delta G_A^o = -RT \ln K_A \dots \dots \dots (11)$$

ΔH_A^o and ΔS_A^o can be calculated in each instance by utilizing Eq. (12), where a plot of ΔG_A^o vs. T gives a straight line with a gradient of ΔS_A^o and an intercept of ΔH_A^o . The values of ΔG_A^o , ΔS_A^o and ΔH_A^o are reported in Tables 5 and 6.

$$\Delta G_A^o = \Delta H_A^o - T \Delta S_A^o \dots \dots \dots (12)$$

The effect of temperature on entropy was almost negligible for the various DMF-H₂O mixtures for these species, a result which was surprisingly somewhat similar to that for MeOH-H₂O mixtures. As can be observed from Table 5, the ΔS_A^o for all the systems studied are similar to each other as they are all positive values. The entropy of association is positive, suggesting that the specific interaction might be restricted due to ion association. As for the

ΔS_A^o data, the ΔH_A^o showed no significant variations with the solvents used over the temperature range considered, i.e., 298.15 to 313.15 K, in steps of 5 K. The most predominant order of the ΔH_A^o for the systems studied (Table 5) and also varied in the order $\text{Cl}^- > \text{Br}^- > [\text{BF}_4]^- > [\text{PF}_6]^-$ at all temperatures with some exceptions. These values are so small that they would only play a negligible role in the association behaviour, which is mainly established by means of the positive entropy term [45,72,73]. The positive ΔH_A^o calculated are ascribed to the existence of the endothermic nature of the interactions between the ions (association process).

As can be seen from Table 6, the values of ΔG_A^o for [Bupy][X]; X = Cl^- , Br^- , $[\text{BF}_4]^-$, $[\text{PF}_6]^-$) decreased (more negative) with an increase in temperature in all the media used (see Figure 5 as an example). For [Bupy][X], increasing the temperature might favour the transport of the released solvent molecules into the bulk solvent, thus yielding the reduction in ΔG_A^o observed to more negative values, as well as indicating a spontaneous processes[45,72].

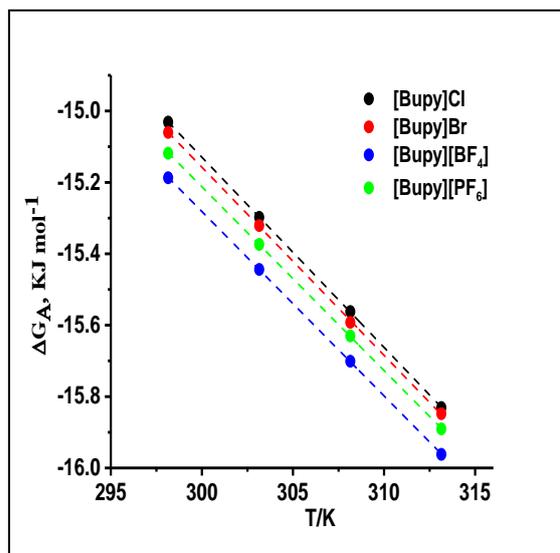


Fig. 5. Plot of (ΔG_A^o) versus (T) for the compounds studied in 30% DMF-H₂O mixtures at different temperatures.

Conclusions

Conductimetric measurements were performed to obtain information on the ion association and solvation phenomena in model 1-butylpyridinium-based ionic liquids ([Bupy][X], X = Cl^- , Br^- , $[\text{BF}_4]^-$, $[\text{PF}_6]^-$) in various binary mixed solvent over the temperature range 298.15 to 313.15 K in steps of 5 K. The results demonstrated that limiting molar conductances varied in the order $[\text{Bupy}]\text{Cl}^- > [\text{Bupy}]\text{Br}^- > [\text{Bupy}][\text{BF}_4]^- > [\text{Bupy}][\text{PF}_6]^-$ in DMF-H₂O whereas

Table 5. The activation energy of transfer, (E_a , kJ mol⁻¹), the entropy (ΔS_A^o , kJ mol⁻¹K⁻¹) and the enthalpy (ΔH_A^o , kJ mol⁻¹) of association for the investigated systems at various temperatures and in the various solvents used

Solvent		[Bupy]Cl			[Bupy]Br			[Bupy][BF ₄]			[Bupy][PF ₆]		
Mixture	Vol.%	E_a	ΔS_A^o	ΔH_A^o	E_a	ΔS_A^o	ΔH_A^o	E_a	ΔS_A^o	ΔH_A^o	E_a	ΔS_A^o	ΔH_A^o
DMF-H ₂ O	10%	8.625	0.053	0.778	9.021	0.056	1.718	9.520	0.051	0.206	9.661	0.051	0.197
	20%	8.701	0.053	0.854	9.121	0.053	0.653	9.438	0.052	0.210	9.729	0.051	0.228
	30%	8.938	0.053	0.893	9.186	0.053	0.588	9.670	0.052	0.228	9.747	0.051	0.226
MeOH-H ₂ O	10%	7.946	0.051	0.166	8.293	0.059	2.592	8.499	0.051	0.220	8.552	0.051	0.234
	20%	8.095	0.057	2.180	8.418	0.053	0.854	8.546	0.051	0.132	8.634	0.051	0.148
	30%	8.313	0.053	0.996	8.458	0.052	0.416	8.982	0.051	0.218	9.194	0.051	0.217

Uncertainties are [E_a , 0.011 kJ mol⁻¹; ΔS_A^o , 0.0002 kJ mol⁻¹K⁻¹ and ΔH_A^o , 0.002 kJ mol⁻¹].

Table 6. The free energy (ΔG_A^o , kJ mol⁻¹) of association for the investigated systems at various temperatures and in the various solvents used

Solvent		T/K ±0.15	[Bupy]Cl	[Bupy]Br	[Bupy][BF ₄]	[Bupy][PF ₆]
Mixture	Vol.%					
DMF-H ₂ O	10%	298	14.98	15.01	15.18	15.11
		303	15.25	15.29	15.44	15.37
		308	15.51	15.58	15.70	15.62
		313	15.77	15.84	15.95	15.88
	20%	298	15.03	15.06	15.19	15.12
		303	15.30	15.32	15.44	15.37
		308	15.56	15.59	15.70	15.63
		313	15.83	15.85	15.96	15.89
	30%	298	15.03	15.09	15.19	15.12
		303	15.30	15.36	15.45	15.38
		308	15.57	15.63	15.71	15.64
		313	15.84	15.88	15.97	15.90
MeOH-H ₂ O	10%	298	14.90	14.94	15.15	15.11
		303	15.23	15.25	15.41	15.37
		308	15.49	15.54	15.67	15.63
		313	15.77	15.82	15.93	15.88
	20%	298	14.96	15.04	15.15	15.11
		303	15.24	15.29	15.41	15.37
		308	15.50	15.56	15.66	15.62
		313	15.77	15.84	15.92	15.88
	30%	298	14.99	15.06	15.16	15.12
		303	15.25	15.32	15.42	15.38
		308	15.51	15.58	15.68	15.64
		313	15.79	15.84	15.93	15.89

Uncertainties in ΔG_A^o , is 0.01 kJ mol⁻¹;

the conductances become significant in MeOH-H₂O over the temperature range investigated. This means that the liquidity factor of the solvents played the predominant role in limiting the molar conductances of the studied systems. The transport properties, including limiting ionic conductance (λ_o^\pm), ionic mobility (u_\pm) and diffusion coefficient (D_o), exhibited a declining trend going from MeOH-H₂O to DMF-H₂O for all ions, suggesting a greater extent of ion-solvent interactions in DMF-H₂O than in MeOH-H₂O. From an examination of the association constant (K_A), shows that the species are solvated to

different extents by the solvent mixtures, and their K_A heavily influenced by ionic solvation, and a priority of solvation of DMF-H₂O > MeOH-H₂O, and for all proportions of organic solvent and at all given temperatures for each of the ILs. The type of anion can clearly have an effect on the ionic association constant and, in all the chosen solvents, the order of ion-association of the anions for the common [Bupy]⁺ cation is [BF₄]⁻ > [PF₆]⁻ > Br⁻ > Cl⁻, which also increases when the temperature is increased. A weaker ionic anion and/or cation solvation enhances the ionic association, whilst a stronger solvation weakens the ionic association of the [Bupy]X in

solvent mixtures. The results are discussed in terms of ion–ion, ion–solvent and hydrogen-bonding interactions. This observation leads us to conclude that the association behaviour of ILs can be modified by means of their anionic species, and the dielectric constants of the solvent mixtures. The Walden product decreased from MeOH-H₂O to DMF-H₂O with an increase in solvent viscosity and a decrease in limiting molar conductance of the [Bupy]X. This is warranted as the contribution of viscosity has the most effect on the inverse proportional behaviour of the Walden product with temperature. Thermodynamic parameters in the chosen solvents were determined according to the temperature reliance of K_A . Given the values of ΔG_A° for [Bupy][X] enhancing the temperature might favour the transport of the solvent molecules released into the bulk solvent, thus the observed reduction in ΔG_A° to more negative values and indicating a spontaneous process. The ΔS_A° of association was positive, suggesting that the specific interaction could be restricted due to ion association. The positive ΔH_A° indicates the endothermic nature of the association processes. Finally, it is worth noting that the ionic association investigated herein can be attributed to the formation of a solvent-separated ion pair (via hydrogen bonding) which can be of various forms from super-ion clusters, contact ion pairs, and/or ion triplets. A further study is currently being conducted to gain a better understanding of the ion triplets and super-ion clusters, that may occur when the dielectric constants of the solvents decrease and/or the IL concentrations increase.

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Supplementary data

Electronic Supplementary Information (ESI) associated for this work are available and have been submitted in the separate file. Information available should be included here]. See DOI:

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