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RESEARCH ARTICLE

PHYSICOCHEMICAL STUDIES OF NICOTINIC ACID IN AQUEOUS MEDIUM IN PRESENCE OF IONIC LIQUIDS, 1-BUTYL-2, 3-DIMETHYLIMIDAZOLIUM TETRAFLUOROBORATE AND 1-ETHYL-3-METHYLIMIDAZOLIUM TOSYLATE AT DIFFERENT TEMPERATURES

[1]Kalipada Sarkar and *[2]Mahendra Nath Roy

[1]Assistant Professor, Islampur College, Islampur, Uttar Dinajpur, 733202, India
[2]Professor and Corresponding Author, Department of Chemistry, University of North Bengal, Darjeeling 734013, India

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ABSTRACT

The apparent molar volume (ϕ_V) and viscosity B-coefficient have been estimated of 0.01 m, 0.03 m and 0.05 m aqueous nicotinic acid solutions in presence of the ionic liquids (IL), 1-butyl-2, 3 – dimethylimidazolium tetrafluoroborate (BdmimBF$_4$) and 1-ethyl-3-methylimidazolium tosylate (EmimOTs) at 298 K, 303 K and 308 K from densities (ρ) and viscosities (η) measurements. The limiting apparent molar volumes (ϕ_V^0) and experimental slopes (S_V*) obtained from the Masson equation have been explained in terms of solute–solvent and solute–solute interactions respectively. The limiting apparent molar volumes of transfer ($\Delta\phi_V^0$) have been used to interpret various hydrophobic–hydrophilic and hydrophobic–hydrophobic group interactions between the solute and co-solute in aqueous medium. The viscosity data were examined using the Jones–Dole equation and the resulting parameter *B* has also been interpreted in terms of solute–solvent interactions in the solutions. Molar free energy of activation of viscous flow of the solvent, $\Delta\mu_1^0$ and solute, $\Delta\mu_2^\circ$ has been deduced to understand the stability of ground state over transition state.

INTRODUCTION

A vitamin is an organic compound requisite by an organism as a vital nutrient in restricted amounts. Vitamins are necessary precursors for various coenzymes. These coenzymes are therefore required in almost all metabolic pathways (Robinson, 1951). Nicotinic acid has gained huge attention over the years since it was synthesized in 1867 by Huber (Elvehjem, 1943). This is because of its versatility in terms of chemical, biochemical, and therapeutic applications (Elvehjem, 1943). This derivative of pyridine has the molecular formula $C_6H_5NO_2$ with a carboxyl group (−COOH) at the 3-position. The molecular structure of nicotinic acid is presented in Scheme-I. It is sometimes called niacin or vitamin B3 in combination with nicotinamide (Nesmeyanov, 1981 and Fauci, 1998). It is a colorless, water-soluble compound, and it can be converted to nicotinamide adenine dinucleotide (NAD+) and NAD phosphate (NADP+) *in-vivo* in pharmacological doses. It reverses atherosclerosis by reducing the total cholesterol, triglycerides and lipoproteins. It also plays a crucial role in both repairing DNA and in the production of steroid hormones in the adrenal gland. Hence, it finds widespread application as an additive in food, forage and cosmetics (Block, 1996 and Carlson, 2005). Ionic liquids are very attractive because of their unique properties, such as large liquid range, high thermal stability, negligible vapor pressure, ability of dissolving a variety of chemicals, miscibility with common molecular liquids, large electrochemical window and their potential as “designer solvents” and “green” replacements, i.e. alternative solvents to volatile organic solvents (Ekka, 2014; Welton, 1999 and Earle, 2000) used in reactions involving inorganic compounds as well as biocatalysts. They are also used as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells) (Dupont, 2002; Plechkova, 2008 and Endres, 2006). The molecular structure of the studied IL is represented in Scheme-I. The volumetric and viscometric behavior of solutes is very much useful in elucidating the various interactions occurring in solutions. Studies on the effect of concentration (molality), the apparent molar volumes of solutes have been extensively used to obtain information on solute-solute, solute-solvent and solvent-solvent interactions (Wang, 2003; McDowall, 1974; Deck,

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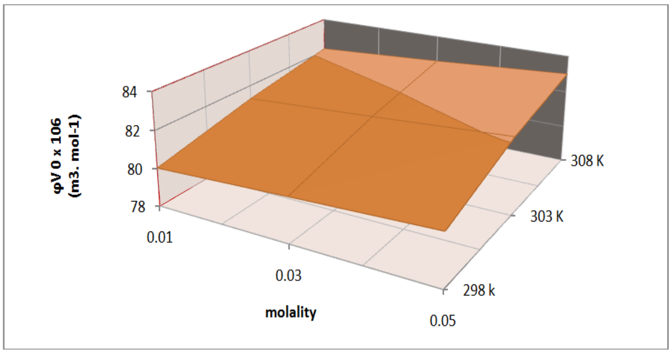
Corresponding author: Kalipada Sarkar
Assistant Professor, Islampur College, Islampur, Uttar Dinajpur: 733202, India

1975; Roy, 2005 and Roy, 2010). In continuance of our earlier study (Bhattacharjee, 2010; Ekka, 2012; Ekka, 2013; Roy, 2014 and Roy, 2014), we have attempted to establish the nature of solute-solvent/cosolute interactions of aqueous nicotinic acid solutions in presence of the ionic liquids (IL), 1-butyl-2, 3 – dimethylimidazolium tetrafluoroborate (Bdmim BF_4) and 1-ethyl-3-methylimidazolium tosylate (EmimOTs) at 298 K, 303 K and 308 K.



Graph 1.Variation of ϕ_V^0 with malality of nicotinic acid and temperature in K

The densities and viscosities of 0.01, 0.03 and 0.05 m aqueous nicotinic acid solutions at 298 K, 303 K and 308 K are reported in Table 1 and densities and viscosities of aqueous nicotinic acid solutions in presence of the ionic liquids (IL), 1-butyl-2, 3 – dimethylimidazolium tetrafluoroborate ($BdmimBF_4$) and 1-ethyl-3-methylimidazo lium tosylate (EmimOTs) at 298 K, 303 K and 308 K are reported in Table 2 and 3 respectively. We have attempted to report the limiting apparent molar volume (ϕ_V^0), experimental slopes (S_V*) and viscosity *B*-coefficients in terms of solute-solvent/co-solute interactions aqueous nicotinic acid solutions in presence of the cited ionic liquids.

EXPERIMENTAL METHODS

Source and purity of samples: The studied ILs, 1-butyl-2, 3 – dimethylimidazolium tetrafluoroborate ($BdmimBF_4$) and 1-ethyl-3-methylimidazolium to sylate (EmimOTs) and co-solute nicotinic acid of puriss grade was purchased from Sigma-Aldrich, Germany and was used as purchased. The mass purity of salts was ≥0.99.

Table 1. Experimental values of density (ρ), viscosity (η) of different molality of aqueous nicotinic acid solution at 298 K, 303 K and 308 K

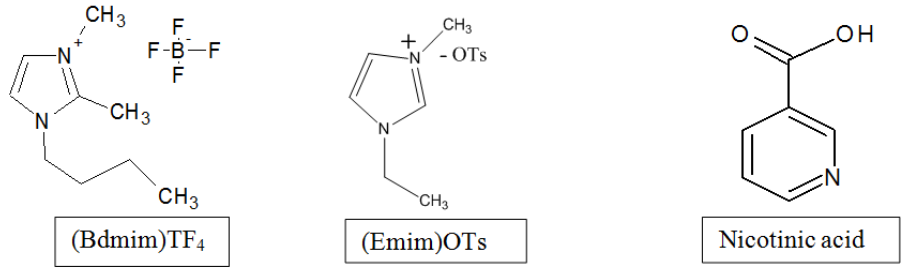
Aqueous solvent molality	$\rho\times10^{-3}$/kg.m^{-3}			η/mP.s		
	298 K	303 K	308 K	298 K	303 K	308 K
0.01 m	0.99853	0.99641	0.99562	0.8988	0.8127	0.8167
0.03 m	0.99891	0.99588	0.99675	0.912	0.8234	0.7512
0.05 m	0.99975	0.99826	0.99702	0.9193	0.8356	0.7612

Table 2. Density (ρ) and viscosity (η) of different molality ($BdmimBF_4$) aqueous in aqueous nicotinic acid solution at 298 K, 303 K and 308 K

Molality Mol.kg-1	$\rho\times10^{-3}$ kg.m^{-3}			Ƞ mP.s		
	298 K	303 K	308 K	298 K	303 K	308 K
0.01m NA solution						
0.013	0.99893	0.99679	0.99599	0.9078	0.8215	0.8264
0.025	0.99926	0.99711	0.99631	0.9150	0.8293	0.8349
0.050	0.99978	0.99763	0.99685	0.9286	0.8442	0.8525
0.03m NA solution						
0.013	0.99928	0.99623	0.99708	0.9219	0.8326	0.7602
0.025	0.99959	0.99653	0.99737	0.9306	0.8410	0.7686
0.050	1.0001	0.99703	0.99786	0.9470	0.8575	0.7855
0.05m NA solution						
0.013	1.00009	0.99858	0.99732	0.9291	0.8448	0.7705
0.025	1.00039	0.99887	0.99759	0.9381	0.8538	0.7796
0.050	1.00093	0.99939	0.99808	0.9555	0.871	0.7975

Table 3. Density (ρ) and viscosity (η) of different molality of (EmimOTs) aqueous in aqueous nicotinic acid solution at 298 K, 303 K and 308 K

Molality Mol.kg-1	$\rho\times10^{-3}$ kg.m^{-3}			η mP.s		
	298 K	303 K	308 K	298 K	303 K	308 K
0.01m NA solution						
0.013	0.9989	0.99676	0.99596	0.9071	0.8207	0.8257
0.025	0.99921	0.99706	0.99626	0.9143	0.8285	0.8342
0.050	0.99971	0.99756	0.99678	0.9279	0.8434	0.8518
0.03m NA solution						
0.013	0.99925	0.99620	0.99705	0.9211	0.8319	0.7595
0.025	0.999537	0.99648	0.99732	0.9298	0.8403	0.7679
0.050	1.00003	0.99696	0.99779	0.9462	0.8568	0.7848
0.05m NA solution						
0.013	1.00006	0.99855	0.99729	0.9283	0.8441	0.7697
0.025	1.00034	0.99882	0.99754	0.9373	0.8531	0.7789
0.050	1.00086	0.99932	0.99801	0.9547	0.8703	0.7967



Scheme I. Molecular structures of the ionic liquids and nicotinic acid

Table 4. Apparent molar volume, (ϕ_V) and $(\eta/\eta_0-1)/\sqrt{m}$ of 0.01 m, 0.03 m and 0.05 m nicotinic acid *in aqueous* (BdmimBF$_4$) solution at different temperatures

Molality of IL	ϕ_V x 10^6 (m^3. mol^{-1})	$(\eta/\eta_0-1)/\sqrt{m}$ (mol. $kg^{-1})^{-1/2}$	ϕ_V x 10^6 (m^3. mol^{-1})	$(\eta/\eta_0-1)/\sqrt{m}$ (mol. $kg^{-1})^{-1/2}$	ϕ_V x 10^6 (m^3. mol^{-1})	$(\eta/\eta_0-1)/\sqrt{m}$ (mol. $kg^{-1})^{-1/2}$
	298K		303K		308 K	
0.01 m NA						
0.0125	80.4024	0.090	81.5820	0.094	82.4496	0.1029
0.025	80.6807	0.114	81.8616	0.128	82.7306	0.1402
0.05	81.0976	0.148	82.2608	0.173	83.1117	0.1960
0.03 m NA						
0.0125	80.7089	0.099	81.9582	0.092	82.8192	0.105
0.025	80.9872	0.133	82.2389	0.128	83.0599	0.146
0.05	81.3840	0.177	82.6199	0.173	83.4412	0.204
0.05 m NA						
0.0125	80.9971	0.095	82.3402	0.094	83.1968	0.103
0.025	81.2750	0.129	82.5794	0.133	83.4371	0.153
0.05	81.6515	0.176	82.9181	0.187	83.7372	0.213

Table 5. Apparent molar volume, (ϕ_V) and $(\eta/\eta_0-1)/\sqrt{m}$ of 0.01 m, 0.03 m and 0.05 m nicotinic acid *in aqueous* (EmimOTs) solution at different temperatures

Molality of IL	ϕ_V x 10^6 (m^3. mol^{-1})	$(\eta/\eta_0-1)/\sqrt{m}$ (mol. $kg^{-1})^{-1/2}$	ϕ_V x 10^6 (m^3. mol^{-1})	$(\eta/\eta_0-1)/\sqrt{m}$ (mol. $kg^{-1})^{-1/2}$	ϕ_V x 10^6 (m^3. mol^{-1})	$(\eta/\eta_0-1)/\sqrt{m}$ (mol. $kg^{-1})^{-1/2}$
	298K		303K		308 K	
0.01 m NA						
0.0125	80.7235	0.083	81.9040	0.088	82.7726	0.0986
0.025	81.0019	0.109	82.1838	0.123	83.0537	0.1355
0.05	81.3991	0.145	82.5632	0.169	83.4150	0.1922
0.03 m NA						
0.0125	81.0298	0.089	82.2790	0.092	83.1402	0.099
0.025	81.3082	0.123	82.5597	0.130	83.3810	0.141
0.05	81.6853	0.168	82.9206	0.181	83.7422	0.200
0.05 m NA						
0.0125	81.3174	0.088	82.6614	0.091	83.5189	0.100
0.025	81.5955	0.124	82.9009	0.132	83.7593	0.147
0.05	81.9522	0.172	83.2198	0.186	84.0397	0.209

The salts were dried from moisture at 353 K for 48 h, and then they were cooled and store in a desiccator prior to use.

Apparatus and procedure

The density (ρ) was measured by means of vibrating-tube Anton Paar Density-Meter (DMA 4500M) with a precision of 0.00001 x 10^{-3} ($kg \cdot m^{-3}$). It was calibrated by double-distilled water and dry air (Gopal, 1969). The temperature was automatically kept constant within ±0.01 K. The viscosity was determined with the aid of Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 fitted to a Brookfield Digital Bath TC-500 calibrated at 298.15 K with doubly distilled water and purified methanol (Roy, 2004). The uncertainty in viscosity measurements is within ±0.003 mPa·s. The mixtures were prepared by mixing known volume of solutions in airtight-stoppererd bottles. Adequate precautions

Mass measurements for stock solutions were done on a Mettler AG-285 electronic balance with a precision of ±0.0003 x 10^{-3} kg. The conversion of molarity into molality was accomplished using experimental density values. The uncertainty in molality of solution is estimated to be ±0.0001 mol. kg^{-1}

RESULTS AND DISCUSSIONS

Density

Apparent molar volumes (ϕ_V) were estimated from the densities of the solution using the following equation (Ayranci, 1997)

$$\phi_V = M/\rho - 1000\,(\rho - \rho_0)/(m\rho\rho_0) \qquad \ldots\ldots\ldots\ldots..(1)$$

Where *M* is the molar mass of the salt, ρ_0 and ρ is the densities of solvent and solution respectively and m is the molality of the solution. The ϕ_V values of aqueous nicotinic acid solutions in presence of the ionic liquids (IL), 1-butyl-2, 3 – dimethylimidazolium tetrafluoroborate ($BdmimBF_4$) and 1-ethyl-3-methylimidazolium tosylate (EmimOTs) at 298 K, 303 K and 308 K are shown in Table 4 and 5 respectively.

Masson (1929) found that the apparent molar volumes, ϕ_V, vary with the square root of the molal concentration, $\sqrt{m}$ by the linear equation:

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \qquad \text{......................(2)}$$

Where ϕ_V^0 is the limiting apparent molar volume and S_V* is the experimental slope. The plots of ϕ_V against $\sqrt{m}$ of aqueous nicotinic acid solutions at 298 K, 303 K and 308 K in presence of the ILs, ($BdmimBF_4$) and (EmimOTs) was linear with positive slopes and the ϕ_V^0 values increase with increasing concentration of nicotinic acid. The values of ϕ_V^0 and S_V* of nicotinic acid solutions at 298 K, 303 K and 308 K in presence of 1-butyl-2, 3 – dimethylimidazolium tetrafluoroborate ($BdmimBF_4$) and 1-ethyl-3-methylimidazolium tosylate (EmimOTs) are reported in Table-6 and **7** respectively.

Table 6. Limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V*), viscosity A, *B*-coefficients *of* aqueous nicotinic acid solution in ($BdmimBF_4$) at different temperatures

Temperature(K)	ϕ_V^0 x 10^6 (m^3. mol^{-1})	$\Delta\ \phi_V^0$ (m^3. mol^{-1})	S_V^* x 10^6 (m^3. $mol^{-3/2}$.$kg^{1/2}$)	*B* ($kg^{1/2}$. $mol^{-1/2}$)	*A* (kg. mol^{-1})
0.01 m NA					
298K	79.7	0..2	6.228	0.525	0.030
303K	80.9	.22	6.073	0.683	0.020
308K	81.79	.24	5.915	0.805	0.015
0.03 m NA					
298K	80.03	.53	6.039	0.663	0.022
303K	81.30	.62	5.882	0.762	0.014
308K	82.03	.64	5.55	0.868	0.009
0.05 m NA					
298K	80.34	.84	5.845	0.721	0.014
303K	81.76	1.08	5.169	0.812	0.008
308K	82.66	1.11	4.817	0.928	0.005

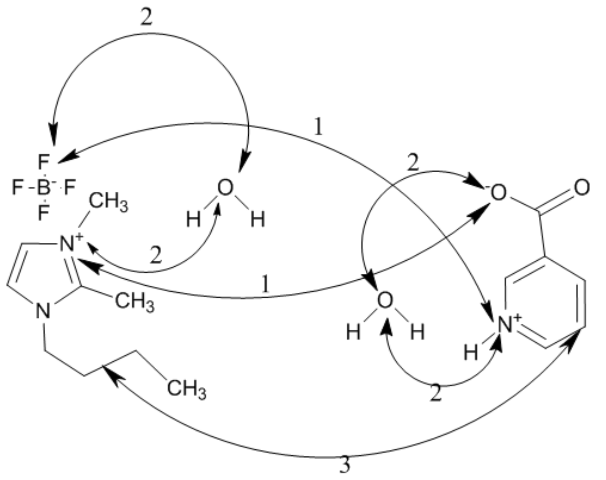
Table 7. Limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V*), viscosity A, *B*-coefficients *of* aqueous nicotinic acid solution in (EmimOTs) at different temperatures

Temperature(K)	ϕ_V^0 x 10^6 (m^3. mol^{-1})	$\Delta\phi_V^0$ x 10^6 (m^3. mol^{-1})	S_V^* x 10^6 (m^3. $mol^{-3/2}$.$kg^{1/2}$)	*B* ($kg^{1/2}$. $mol^{-1/2}$)	*A* (kg. mol^{-1})
0.01 m NA					
298K	80.04	0.54	6.044	0.555	0.020
303K	81.24	0.56	5.889	0.722	0.007
308K	82.13	0.58	5.730	0.839	0.004
0.03 m NA					
298K	80.37	0.87	5.856	0.7	0.011
303K	81.64	0.96	5.695	0.796	0.003
308K	82.53	0.98	5.363	0.905	-0.002
0.05 m NA					
298K	80.69	1.19	5.663	0.755	0.003
303K	82.1	1.42	4.986	0.845	-0.002
308K	83.01	1.46	4.633	0.97	-0.007

ϕ_V^0 value specifies the extent of solute-solvent interaction (Millero, 1973). It is observed that ϕ_V^0 values for nicotinic acid in presence of ILs, ($BdmimBF_4$) and (EmimOTs) are positive and increase with the increasing molarities nicotinic acid and also with temperature which is shown in Table 6, 7 and Fig 1. This trend signifies the existence of strong solute-solvent interactions which is found to be maxima in 0.05 m nicotinic acid solution at 308 K in both the ionic liquids. So the interactions between the ILs and nicotinic acid intensify with increase in temperature and molality of nicotinic acid solution. The ϕ_V^0 values of (EmimOTs) are greater than that of ($BdmimTF_4$) in all the temperatures and molalities. This indicates that (EmimOTs) interacts strongly with nicotinic acid than ($BdmimBF_4$) in aqueous medium. This may be described by the structural features of the ILs. There are three alkyl groups in ($BdmimTF_4$) and two alkyl groups in (EmimOTs) .The presence of one extra methyl group having +I effect in C_2 of ($BdmimBF_4$) makes nitrogen less positive than (EmimOTs). The positively charged N-atom of imidazolium moiety of ionic liquids interacts with negatively charged corboxilate ion of nicotinic acid in aqueous medium. Due to the presence of higher +ve character on N-atom of (EmimOTs) than ($BdmimBF_4$), the former interacts strongly with nicotinic acid than the later. The interaction of the ILs with nicotinic acid in aq. solution is manifested in Scheme-2 and 4. The parameter S_V* is the volumetric virial coefficient describing the pair-wise interaction of solvated species in solution. The sign of S_V* is determined by the interaction between the solute species (Roy, 2011). In our present study S_V* values weaken with increase in temperature and molality of nicotinic acid. This is just opposite findings than the ϕ_V^0 values discussed earlier where ϕ_V^0 values increase with increasing concentrations of nicotinic acid as well as temperatures.

In fact the solute-solute/ solute-co solute interaction will increase with decreasing solute-solute interaction in a solution. This inclination of S_V* values signify poor solute-solute interactions in their aqueous solution. In our present study the S_V* value is minimum in 0.05 m nicotinic acid at 308 K and maximum in 0.01 m nicotinic acid at 298 K for both the ionic liquids. So the interactions between the ILs molecules decrease with increase in temperature as well as molality nicotinic acid in water. It is also observed that S_v* values of

($BdmimBF_4$) is larger than that of (EmimOTs) in all temperatures and molalities which specify that solute-solute interaction is higher in case of former IL than the later.



1 = ion-ion , 2 = ion-hydrophilic and 3 = hydrophobic-hydrophobic interactions

Scheme 2. Molecular interactions between the ionic liquids and nicotinic acid

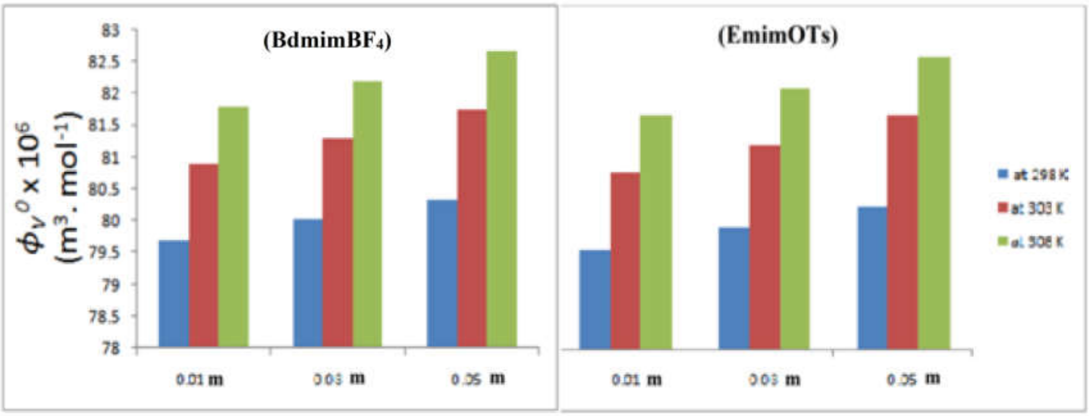


Fig. 1. Variation of limiting apparent molar volumes (ϕ_V^0) *of* the ILs with molalities of aqueous nicotinic acid solution at with temperature in K

So the interaction between the solute molecules is stronger at lower temperature whereas the interaction between the solute and solvent molecules is greater at higher temperature and solute-solvent interaction of nicotinic acid is stronger with (EmimOTs) than ($BdmimBF_4$) in aqueous medium. The variation of ϕ_V^0 with temperature of nicotinic acid in presence of IL in aqueous medium follows the polynomial (Sheng Fang, 2017).

$$\phi_V^0 = a_0 + a_1T + a_2T^2 \quad \text{………………(3)}$$

Where a_0, a_1 and a_2 are the coefficients and T is the temperature in K. Values of the coefficients of the above equation for aqueous nicotinic acid solutions in presence of the ILs, ($BdmimBF_4$) and (EmimOTs) are reported in Table-8 and 9 respectively.

The limiting apparent molar expansibilities (Φ_E^0) can be calculated by the following equation (Shekaari, 2010):

$$\Phi_E^0 = (\delta\phi_V^0/\delta T)_P = a_1 + 2a_2T \quad \text{…………………(4)}$$

The values of Φ_E^0 of the studied compounds at 298 K, 303 K and 308 K are evaluated and reported in Table 8 and 9. The S_V* is not the sole condition for determining the structure-making or breaking nature of any solute (Parmar, 2005). Hepler provided a technique of studying the sign of $(\delta^2\phi_V^0/\delta T^2)_P$ for the solute in terms of structure-making and breaking ability of the solute in aqueous solution using the following thermodynamic expression (Hepler, 1969).

$$(\delta\Phi_E^0/\delta T)_P = (\delta^2\phi_V^0/\delta T^2)_P = 2a_2 \quad \text{…………….(5)}$$

It has been considered that the structure making solutes should have positive $(\delta\Phi_E^0/\delta T)_P$ values, whereas structure-breaking solutes should have negative values (Banipal, 2008 and Hossain, 2014). The $(\delta\Phi_E^0/\delta T)_P$ values of nicotinic acid in aqueous solution of ($BdmimBF_4$) and (EmimOTs) have been given in Table-8 and 9. It is evident that $(\delta^2\phi_V^0/\delta T^2)_P$ values are negative for aq. nicotinic acid solution in presence of both the ILs, suggesting thereby that the ILs act as structure breaker in aq. nicotinic acid solution. The limiting apparent molar volume of transfer, $\Delta\phi_V^0$ for NA from pure water to IL solution is defined by

$$\Delta\phi_V^0 \text{ (amino acid)} = \phi_V^0 \text{ (amino acid in aq. IL solution)} - \phi_V^0 \text{ (in water)} \quad \text{…………………(6)}$$

The value of $\Delta\phi_V^0$ gives an idea about the solute–solvent interactions.

Table 8. Values of empirical coefficients (a_0, a_1, and a_2) of 0.01 m, 0.03 m and 0.05 m aqueous nicotinic acid solution in ($BdmimBF_4$)

Molality of NA	$a_0 \times 10^6$ ($m^3 . mol^{-1}$)	$a_1 \times 10^6$ ($m^3 . mol^{-1} . K^{-1}$)	$a_2 \times 10^6$ ($m^3 . mol^{-1} . K^{-2}$)	$(\delta\Phi_E^0/\delta T)_P$
0.01m	-1964	13.82	-0.022	-0.044
0.03m	-1418	10.21	-0.0.016	-0.088
0.05m	-475.4	4.086	-0.006	-0.012

Table 9. Values of empirical coefficients (a_0, a_1, and a_2) of 0.01 m, 0.03 m and 0.05 m aqueous nicotinic acid solution in (EmimOTs)

Molality of NA	$a_0 \times 10^6$ ($m^3 . mol^{-1}$)	$a_1 \times 10^6$ ($m^3 . mol^{-1} . K^{-1}$)	$a_2 \times 10^6$ ($m^3 . mol^{-1} . K^{-2}$)	$(\delta\Phi_E^0/\delta T)_P$
0.01m	-1780	12.62	-0.02	-0.04
0.03m	-1228	8.994	-0.014	-0.028
0.05m	-472	4.086	-0.006	-0.012

Table 10. Pair, V_{AB}, and Triplet, V_{ABB}, Interaction Coefficients of nicotinic acid in aqueous solution of ionic liquids at 298 K, 303 K and 308 K temperatures

IL in aq. NA solution	V_{AB} $m^3 \cdot mol^{-2} \cdot kg$	V_{ABB} $m^3 \cdot mol^{-2} \cdot kg^2$	V_{AB} $m^3 \cdot mol^{-2} \cdot kg$	V_{ABB} $m^3 \cdot mol^{-2} \cdot kg^2$	V_{AB} $m^3 \cdot mol^{-2} \cdot kg$	V_{ABB} $m^3 \cdot mol^{-2} \cdot kg^2$
	298 K		303 K		308 K	
($BdmimTF_4$)	10.583	-38.888	11.3330	-22.22	12.67	-44.44
(EmimOTs)	33.25	-416.66	34.0000	-400.00	35.50	-433.33

The limiting apparent molar volumes of transfer are also shown in Table 6 and 7. The change in transfer volume may be interpreted on the basis of co-sphere overlap model proposed by Friedman and Krishnan (Friedman, 1974). According to the model the effect of overlap of hydration co-sphere is destructive. The positive $\Delta\phi_V^0$ value indicates the existence of hydrophilic–hydrophilic, ion- hydrophilic and ion–ion interactions, whereas the negative $\Delta\phi_V^0$ value is an indication of the hydrophobic–hydrophobic interactions (Dhondge, 2011 and Sarkar, 2012). The interactions between nicotinic acid and ionic liquids in aqueous medium may be of few types.

i) Ionic-ionic interaction of the H^+ ion of water and zwitterionic NH^+ groups of nicotinic acid with anionic part of ILs [BF_4^- of ($BdmimBF_4$) and OTs^- of (EmimOTs)]
ii) Ionic-ionic interaction of and OH^- of water and $-COO^-$ ion of nicotinic acid with N^+ ion of imidazolium part of each IL.
iii) Ionic-hydrophilic interaction of polar end of water with the all +ve and -ve ion of nicotinic acid and IL
iv) Ionic–hydrophobic interactions between ions of IL and non-polar part of nicotinic acid molecules.
(v) Hydrophobic-hydrophobic interaction of non-polar part of IL and non-polar part of NA.

The interactions of types (i), (ii) and (iii) impart positive contributions to ϕ_V^0 values while interaction of types (iv) and (v) impart negative contribution to ϕ_V^0 values (Pal, 2012; Zafarani-Moattar, 2011 and Riyazuddeen, 2012). The $\Delta\phi_V^0$ for NA in aqueous ILs are positive; hence the hydrophilic–hydrophilic and ion–ion interactions are in domination over hydrophobic-hydrophobic and ionic–hydrophobic interactions. As a result, the apparent molar volumes of NA in solution will be increased. It is observed that $\Delta\phi_V^0$ values increase with increasing molalities of nicotinic acid as well as the temperature. The intermolecular distance between the solute and co-solute decreases with increasing concentration of NA as a result the hydrophobic-hydrophobic and ionic–hydrophobic interactions increase with molality. Similarly, with increasing temperature, the H-bonding between water and solute molecules will decrease as a result the hydrophobic-hydrophobic and ionic–hydrophobic interactions among the solute molecules will increase with temperature.

This trend can also be interpreted by the following expression given below by Franks et al (1985):

$$\phi_V^0 = \phi W + \phi V - \phi S \quad \ldots\ldots\ldots\ldots\ldots\ldots..(7)$$

Where ϕW is the van der Waals volume, ϕV is the volume associated with voids or empty space and ϕS is the shrinkage volume due to electrostriction. For the same class of solutes, the value ϕW and ϕV will remain same in aqueous ionic liquid solutions and only the value due to electrostriction will be changed. The hydrophilic–hydrophilic and ion–ion interactions will increase with increase in molalities of NA and as a result ϕS value will decrease (Frrtier, 1974). This is the reason why ϕ_V^0 values increase with increase in molalities of nicotinic acid.

The volumetric pair and triple ion interaction were evaluated from the expression proposed by McMillan–Mayer (McMillan, 1945).

$$\Delta\phi_V^0 = 2Y_{AB}m + 3Y_{ABB}m^2 \quad \ldots\ldots\ldots\ldots\ldots.(8)$$

Where $\Delta\phi_V^0$, Y_{AB} and Y_{ABB} are the limiting apparent molar volume of transfer, pair and triple ion interaction coefficients respectively and A and B represent nicotinic acids and ionic liquid respectively. The interaction coefficients Y_{AB} and Y_{ABB} are calculated by putting the $\Delta\phi_V^0$ values of different molalities of nicotinic acid in presence of ILs in the above expression and summarized in Table 10. It is observed that Y_{AB} values are positive whereas Y_{ABB} values are negative for nicotinic acid in presence of both the ionic liquids in aqueous medium at different temperatures. The positive values of □□□ suggest that existing interactions in our studied solutions are mostly pair wise (Banipal, 2010).

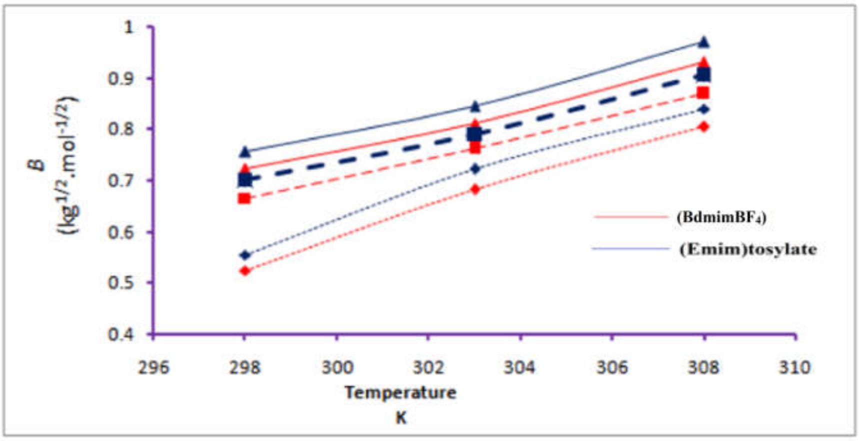
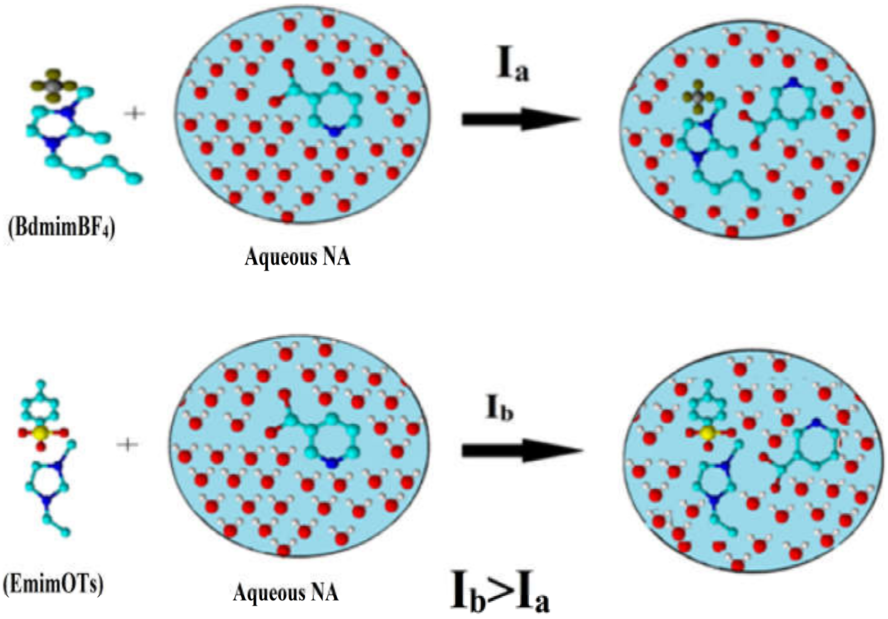


Fig. 2. Variation of viscosity B coefficient with temperature in K *of* aqueous nicotinic acid solution in presence ILs [….. for 0.01 m, - - - for 0.03 m and —— for 0.05 m aq. NA solution]



Scheme 3. Solute-solvent interaction of ILs in aqueous NA solution

The pair wise volumetric interaction arises due to the Ionic-ionic interaction between nicotinic acid and the ILs in aqueous medium.

Viscosity calculation

The viscosity data has been analyzed using the Jones–Dole equation (Jones, 1992).

$$(\eta /\eta_0 - 1) / \sqrt{m} = A + B \sqrt{m} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(9)$$

Where, η_0 and η are the viscosities of the solvent and solution respectively. A plot of $(\eta /\eta_0 - 1) / \sqrt{m}$ against $\sqrt{m}$ give a straight line with an intercept “A” and a slope of “B”. The $(\eta /\eta_0 - 1) / \sqrt{m}$ values of 0.01 m, 0.03 m and 0.05 m nicotinic acid solutions in presence of ILs, $(BdmimBF_4)$ and (EmimOTs) at 298 K, 303 K and 308 K respectively are reported in Table-4 and 5 respectively. The viscosity coefficients A and B values of aqueous solution of nicotinic acid in presence of $(BdmimBF_4)$ and (EmimOTs) estimated by a least square method are reported in Table-6 and 7 respectively and the variation of B with temperature of both the ILs are shown in Fig. 2. The values of the *A* coefficient are positive and decrease with the increase in molarity of nicotinic acid solutions and also with the increase in temperature for both the ionic liquids. The viscosity *B*-coefficient is also a valuable tool to provide information concerning the solvation of the solute in solution (Millero, 1971 and Millero, 1978). It is evident in our present study that the values of the *B*-coefficient are positive, thereby suggesting the presence of strong solute–solvent interactions which strengthened with increasing molality as well as temperature of nicotinic acid solutions. So, IL in 0.05 m nicotinic acid solutions at 308 K shows maximum solute-solvent interactions and in 0.01 m nicotinic acid solutions at 298 K gives minimum solute-solute interactions. This is in conformity with the results obtained from density measurements. It is also reported that (EmimOTs) in aqueous solution of nicotinic acid has greater B values than that of $(BdmimBF_4)$ which signifies that the solute-solvent interactions in case of former IL is greater than the later. This result is also in good agreement with the density study. It has been stated that *dB/dT* is a better factor for determining the structure-making/breaking nature of any solute rather than simply the value of the *B*-coefficient (Kant, 2009 and Yan, 2004)). It is found from Table-6 and 7 that the values of the *B*-coefficient increase with rise in temperature (positive *dB/dT*) for both the ionic liquids suggesting the structure-breaking tendency of the ionic liquids in aq. nicotinic acid solutions. Molar free energy of activation of viscous flow of the solvent μ_1^0 is related to the viscosity of the solvent at any temperature as per the following equation proposed by Feaking et al (1974) (Feakins, 1974; Nain, 2011 and Kumar, 2012).

$$\eta□ = \frac{hN}{V_1^0} \exp\left(\frac{\Delta\mu 1_1^0}{RT}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

Table 11. $(V_2^0 - V_1^0)$, Δ□$_1^0$, Δ□$_2^0$ and ΔG^0 $(1\rightarrow 1^*)$ of nicotinic acid in aqueous solution of ionic liquids at 298 K, 303 K and 308 K temperatures

Temperature in K	$(V_2^0 - V_1^0) \times 10^6$ ($m^3 . mol^{-1}$)	$\Delta\mu_1^0$ kJ mol^{-1}	$\Delta\mu_2^0$ kJ mol^{-1}	ΔG^0 $(1\rightarrow 1^*)$ kJ mol^{-1}
0.01m NA + ($BdmimTF_4$)				
298 K	61.68	9.175	89.842	80.667
303 K	62.88	9.075	113.353	104.278
308 K	63.77	9.008	125.934	116.926
0.03m NA + ($BdmimTF_4$)				
298 K	61.97	9.216	108.964	99.748
303 K	63.24	9.113	124.245	115.131
308 K	63.97	9.029	141.196	132.167
0.05m NA + ($BdmimTF_4$)				
298 K	62.25	9.241	116.486	116.486
303 K	63.67	9.156	131.067	131.067
308 K	64.57	9.068	149.676	149.676
0.01m NA + (EmimOTs				
298 K	62.02	9.175	89.889	80.714
303 K	63.22	9.075	118.853	109.778
308 K	64.11	9.008	137.351	128.343
0.03m NA + (EmimOTs				
298 K	62.31	9.216	113.813	104.597
303 K	63.58	9.113	129.036	119.922
308 K	64.47	9.029	146.514	137.485
0.05m NA + (EmimOTs				
298 K	62.59	9.241	121.189	111.948
303 K	64	9.156	135.709	126.552
308 K	64.94	9.068	155.528	146.459

Where V_1^0 is the average molar volume of aqueous nicotinic acid solution and the others symbols have usual meaning. The above equation can be rearranged as follows (Gaba, 2017).

$$\Delta\mu_1^\circ = RT \ln\left[\frac{V_1^0 \eta_0}{hN}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

The $\Delta\mu 1^\circ$ values are reported in Table-11. Molar activation energy of activation of viscous flow of the nicotinic acids in aqueous IL solution is related to the Jones-Dole B coefficient as given below proposed by Feanins et al.

$$B = \frac{V_1^0 - V_2^0}{1000} + V_1^\circ \left(\frac{\mu_1^0 - \mu_2^0}{1000RT}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

Where V_2° is limiting apparent molar volume of the nicotinic acid in aqueous IL solution and the others symbols have usual meaning. $\Delta\mu_2^\circ$ can be calculated from the above equation as

$$\Delta\mu_2^\circ = \Delta\mu_1^\circ + \frac{RT}{V_1^0}[1000B - (V_1^\circ - V_2^\circ] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

The $\Delta\mu_2^\circ$ and $(V_1^\circ - V_2^\circ)$ values are summarized in Table-11. $\Delta\mu_2^\circ$ is the change in free energy of activation of viscous flow per mole of aqueous NA solution in presence of ionic liquid. According to the transition state theory, the solvent molecule must pass through the viscous transition state. $\Delta\mu_2^\circ$ is the contribution of free energy of transfer of IL molecule from ground state to transition state ΔG^0 $(1\rightarrow 1^*)$ and the movement of IL molecule through its transition state ΔG^0 $(2\rightarrow 2^*)$ (Feakins, 1993). It is observed that $\Delta\mu_2^\circ$ values are large positive than $\Delta\mu_1^\circ$. This indicates that the ground state is more favored than the transition state. The solute and the solvent molecules are held strongly in ground state than in the transition state and breaking and distortion of intermolecular bonds take place in the transition state of viscous flow (Glasstone, 1941). Moreover, the $\Delta\mu_1^\circ$ values increase with molality of NA which signifies that the ground state become more structured with increasing molality of NA in presence of IL.

The values of the limiting apparent molar volume (ϕ_V^0) and viscosity *B*-coefficient point out the existence of strong solute–solvent interactions between of ILs and nicotinic acid in aqueous solutions which enhances with increase in molality of aqueous nicotinic acid and predominates at higher temperature. On the contrary, the solute-solute interactions strengthen at lesser temperature. The study on volumetric pair and triple ion interaction reveals that the interactions in our studied solutions are mostly pair wise. Evaluation of molar free energy of activation of viscous flow of the solvent μ_1^0 and solute $\Delta\mu_2^\circ$ confirms that the ground state is more favored than the transition state.

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