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Study on Diverse Interactions of Vitamin Molecules Insight into H₂O + [Epy] Bf₄ Systems by Physicochemical Contrivance

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ABSTRACT

Physicochemical, such as volumetric, viscometric, refractometric, and acoustic study of solute-solvent interactions of nicotinic acid and ascorbic acid prevailing in aqueous solution of 1-ethyl pyridinium tetrafluoroborate ([Epy] BF₄), have been reported at different temperatures. Using the density data, Masson equation has been employed to obtain the limiting values at infinite dilution by the extrapolated to zero concentration of the apparent molar volumes (ϕ_V^0) and experimental slopes (S_V^*), which interpreted the solute-solvent and solute-solute interactions, respectively. Using the Jones-Dole equation, the viscosity data were analyzed to determine the viscosity A and B- coefficient, which have also been interpreted the solute-solute and solute-solvent interaction respectively in the solutions. The Lorentz-Lorenz equation has been employed to determine the molar refractions (R_M). The temperature dependence behavior of partial molar quantities has been determined for the vitamins. At infinite dilution, limiting apparent molar adiabatic compressibilities (ϕ_K^0) of these vitamins were evaluated and discussed. The role of the solvent (aqueous ionic liquid mixture), and the extent of solute-solute and solute-solvent interactions to the solution complexes have also been analyzed and discussed through the derived properties.

Key words: Apparent molar volume, Solute-solvent interaction, Solute-solute interaction, Vitamins, Ionic Liquid.

1. INTRODUCTION

A vitamin is an organic compound requisite by an organism as a vital nutrient in restricted amounts. An organic chemical compound is called a vitamin when it cannot be produced in sufficient quantities. Vitamins are necessary precursors for various coenzymes. These coenzymes are therefore required in almost all metabolic pathways [1]. Nicotinic acid has gained huge attention over the years since it was synthesized in 1867 by Huber [2]. This is because of its versatility in terms of chemical, biochemical, and therapeutic applications [2]. This derivative of pyridine has the molecular formula C₆H₅NO₂ with a carboxyl group (-COOH) at the 3-position. The molecular structure of nicotinic acid is presented in Scheme 1. It is sometimes called niacin or vitamin B₃ in combination with nicotinamide [3,4]. 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 [5,6]. Ascorbic acid, known as vitamin C is water soluble vitamin, essential for the synthesis of collagen, the intercellular "cement" which gives the structure of muscles, vascular tissues, bones, and tendon. Vitamin C plays an important role for the synthesis of several important peptide hormones neurotransmitters and creatinine. It also enhances the eye's ability and delay the progression of advanced age-related muscular degeneration [7]. Importantly, ascorbic acid (vitamin C) is also able to regenerate other antioxidants as vitamin E. Vitamin C with Zn is also important for the healing of wounds. It is also needed for the metabolism of bile acids, which may have implications for blood cholesterol levels and gallstones. The molecular structure of ascorbic acid is depicted in Scheme 2.

Ionic liquids (ILs) 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"

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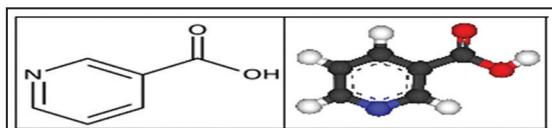
and “green” replacements, i.e. alternative solvents to volatile organic solvents [8-10] used in reactions involving inorganic compounds as well as biocatalysts. They are also used as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells) [11-13]. The molecular structure of the studied IL is represented in Scheme 3. The volumetric, viscometric, refractometric, and acoustic 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 [14-18].

In extension of our earlier study [8,19-23], we have attempted to ascertain the nature of solute-solvent/cosolute interactions of vitamins (nicotinic acid and ascorbic acid) in $w_f=0.001, 0.003, 0.005$ mass fraction of aqueous IL ([1-ethyl pyridinium tetrafluoroborate [EPy]] BF_4^-) binary mixtures at 298.15, 308.15, and 318.15 K, respectively, as literature survey reveals that no work has been carried out in the present ternary systems. We have attempted to report the limiting apparent molar volume (ϕ_v^0), experimental slopes (S_v^*), viscosity B -coefficients, molar refraction (R_M), and limiting apparent molar adiabatic compressibility (ϕ_K^0) in terms of solute-solvent/cosolute interactions for the cited vitamins in aqueous IL solution.

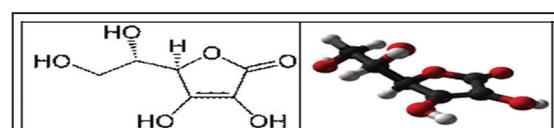
2. EXPERIMENTAL SECTION

2.1. Source and Purity of Samples

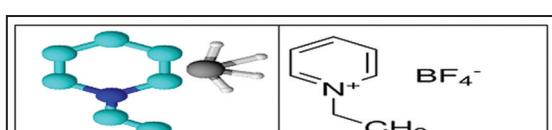
The studied salts (nicotinic acid and ascorbic acid) and co-solute IL, puriss grade was purchased from Sigma-Aldrich, Germany and was used as purchased. The mass purity of salts was ≥ 0.99 . The salts were dried



Scheme 1: Molecular structure of nicotinic acid.



Scheme 2: Molecular structure of ascorbic acid.



Scheme 3: Molecular structure of 1-ethylpyridinium tetrafluoroborate (IL).

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

2.2. Apparatus and Procedure

Aqueous binary solution of IL was prepared by mass (Mettler Toledo AG-285 with uncertainty ± 0.0003 g), which are used as a solvent. Stock solutions of the salts (vitamins) were also prepared by mass and the working solutions were obtained by mass dilution. The conversion of molarity into molality was accomplished using experimental density values. All solutions were prepared afresh before use. The uncertainty in molality of the solutions is evaluated to $\pm 0.0001 \text{ mol kg}^{-3}$.

The densities of the solutions (ρ) were measured by means of vibrating-u-tube Anton Paar digital density meter (DMA 4500 M) with a precision of $0.00005 \text{ g cm}^{-3}$ maintained at $\pm 0.01 \text{ K}$ of the desired temperature. It was calibrated by triply distilled water and passing dry air.

The viscosities were measured using a Brookfield DV-III Ultra Programmable Rheometer with fitted spindle size-42. The viscosities were obtained using the following equation

$$\eta = (100/\text{RPM}) \times \text{TK} \times \text{torque} \times \text{SMC} \quad (1)$$

Where RPM, TK (0.09373), and SMC (0.327) are the speed, viscometer torque constant, and spindle multiplier constant, respectively. The instrument was calibrated against the standard viscosity samples supplied with the instrument, water, and aqueous CaCl_2 solutions [24]. Temperature of the solution was maintained within $\pm 0.01^\circ\text{C}$ using Brookfield Digital TC-500 temperature thermostat bath. The viscosities were measured with an accuracy of $\pm 1\%$. Each measurement reported herein is an average of triplicate reading with a precision of 0.3%.

Refractive index was measured with the help of a Digital Refractometer Mettler Toledo. The light source was liquid emitting device, $\lambda=589.3 \text{ nm}$. The refractometer was calibrated twice using distilled water and calibration was checked after every few measurements. The uncertainty of refractive index measurement was ± 0.0002 units.

The ultrasonic speed (u) was measured by multi-frequency ultrasonic interferometer (Model M-81) from Mittal Enterprises, India. The interferometer working at 5 MHz is based on the same principle as was used by Freyer et al. [25] and Kiyohara et al. [26]. The obtained speeds were corrected for diffraction errors as given by Subrahmanyam and Murthy [27]. The uncertainty in the speed is 0.5 m s^{-1} . The temperature was controlled within $\pm 0.01 \text{ K}$ using a Lauda thermostat during the measurement.

3. RESULTS AND DISCUSSIONS

3.1. Apparent Molar Volume

The salts are freely soluble in all proportions of the solvent mixtures. The physical properties of binary mixtures in different mass fractions ($w_I=0.001, 0.003, 0.005$) of aqueous IL solutions at 298.15, 308.15, and 318.15 K are reported in Table 1. The measured experimental values of densities, viscosities, refractive index, and ultrasonic speeds of simple two vitamins in different mass fractions ($w_I=0.001, 0.003, 0.005$) of aqueous IL mixtures at 298.15-318.15 K as a function of concentration (molality) are listed in Table 2.

Volumetric properties, such as, ϕ_V , ϕ_V^0 , are regarded as sensitive tools for the understanding of interactions in solutions. The apparent molar volume can be considered to be the sum of the geometric volume of the solute molecule and changes in the solvent volume due to its interaction with the solute. For this purpose, the apparent molar volumes ϕ_V were determined from the solutions densities using the following equation and the values are given in Table 3.

$$\phi_V = M / \rho - (\rho - \rho_0) / m \rho_0 \rho \quad (2)$$

Where M is the molar mass of the solute, m is the molality of the solution, ρ and ρ_0 are the densities of the solution and aqueous IL mixture, respectively. Table 3 shows that the values of ϕ_V are large and positive for the two systems, suggesting strong solute - solvent interactions. The apparent molar volumes ϕ_V were found to decrease with increasing molality (m) of vitamins in aqueous IL ([EPy] BF₄) and increase with increasing temperature for the vitamins under study. It is also found that the ϕ_V values are greater for ascorbic acid than nicotinic acid.

As the ϕ_V values are independent of the concentrations of the vitamins for extremely dilute solutions, it may

be assumed that the ϕ_V values are equal to the apparent molar volume (ϕ_V^0) at infinite dilution. The plots of the ϕ_V values against the square root of the molar concentrations ($m^{1/2}$) of vitamins were found to be linear. Hence, the apparent molar volumes (ϕ_V^0) at infinite dilution and the experimental slopes (S_V^*) were determined by using least squares fitting of the ϕ_V values to the Masson equation [28].

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{m} \quad (3)$$

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 the square root of the molar concentration $m^{1/2}$ were found to be linear with negative slopes. The values of ϕ_V^0 and S_V^* are reported in Table 4.

The variation of ϕ_V^0 for these two vitamins with the mass fraction of the IL at different temperatures is shown in Figure 1.

Table 4 shows that ϕ_V^0 values for vitamins are positive and increase with increasing concentrations and with increasing temperature in aqueous IL mixture, indicating the presence of strong solute-solvent interactions and these interactions are further reinforced as increases the mass fraction of IL in the mixture. Interaction of vitamins with IL solution increases with increasing interacting center of vitamins.

From this study, we can say that the trend in the solute-solvent interaction is

Nicotinic acid < ascorbic acid

The S_V^* values are found to be negative under investigations, which suggest that the pairwise

Table 1: Values of density (ρ), viscosity (η), refractive index (n_D), and ultrasonic speed (u) of aqueous IL in different mass fraction (w_I), at 298.15 K-318.15 K^a.

Mass fraction of aqueous IL (w_I)	Temperature/K	$\rho \cdot 10^{-3}/\text{kg m}^{-3}$		$\eta/\text{mPa s}$		n_D		$u/\text{m s}^{-1}$	
		Expt	Lit	Expt	Lit	Expt	Lit	Expt	Lit
$w_I=0.001$	298.15	0.99760	-	0.89	-	1.3320	-	1500.8	-
	308.15	0.99748	-	0.85	-	-	-	-	-
	318.15	0.99737	-	0.82	-	-	-	-	-
$w_I=0.003$	298.15	0.99771	-	0.93	-	1.3325	-	1504.5	-
	308.15	0.99758	-	0.87	-	-	-	-	-
	318.15	0.99743	-	0.85	-	-	-	-	-
$w_I=0.005$	298.15	0.99792	-	0.96	-	1.3328	-	1509.4	-
	308.15	0.99773	-	0.89	-	-	-	-	-
	318.15	0.99765	-	0.88	-	-	-	-	-

^auncertainty of the density $u(\rho)=0.00005 \times 10^{-3} \text{ kg m}^{-3}$, viscosity $u(\eta)=0.01 \text{ mPa s}$, refractive index $u(n_D)=0.0002$, speed of sound $u(u)=0.5 \text{ ms}^{-1}$, temperature $u(T)=0.01 \text{ K}$, 95% level of confidence, IL: Ionic liquid

Table 2: Experimental values of density (ρ), viscosity (η), refractive index, and ultrasonic speed (u) of vitamins in different mass fraction of aqueous IL (w_I) at 298.15 K to 318.15 K^a, respectively.

M/mol kg ⁻¹	$\rho \cdot 10^{-3}/\text{kgm}^{-3}$	η/mPas	n_D	u/ms^{-1}	M/mol kg ⁻¹	$\rho \cdot 10^{-3}/\text{kgm}^{-3}$	η/mPas	n_D	u/ms^{-1}
$w_I=0.001$									
Nicotinic acid+aqueous IL									
T=298.15 K									
0.0100	0.99775	0.91	1.3320	1505.0	0.0100	0.99758	0.86	-	-
0.0251	0.99836	0.92	1.3323	1517.5	0.0251	0.99809	0.87	-	-
0.0402	0.99926	0.93	1.3327	1534.7	0.0402	0.99879	0.88	-	-
0.0554	1.00027	0.94	1.3331	1556.9	0.0554	0.99984	0.91	-	-
0.0705	1.00143	0.96	1.3336	1582.5	0.0705	1.00102	0.93	-	-
0.0858	1.00269	0.98	1.3341	1613.8	0.0858	1.00212	0.96	-	-
T=318.15 K									
0.0100	0.99742	0.83	-	-					
0.0251	0.99794	0.84	-	-					
0.0402	0.99865	0.85	-	-					
0.0554	0.99978	0.87	-	-					
0.0705	1.00089	0.89	-	-					
0.0858	1.00197	0.91	-	-					
Ascorbic acid+aqueous IL									
T=298.15 K									
0.0100	0.99798	0.90	1.3321	1509.0	0.0100	0.99776	0.87	-	-
0.0251	0.99866	0.92	1.3325	1521.5	0.0251	0.99853	0.91	-	-
0.0402	0.99947	0.95	1.3329	1537.7	0.0402	0.99908	0.92	-	-
0.0554	1.00035	0.97	1.3334	1559.9	0.0554	0.99972	0.95	-	-
0.0705	1.00131	0.99	1.3339	1585.5	0.0705	1.00102	0.97	-	-
0.0858	1.00231	1.03	1.3344	1617.8	0.0858	1.00205	0.99	-	-
T=318.15 K									
0.0100	0.99762	0.83	-	-					
0.0251	0.99824	0.84	-	-					
0.0402	0.99887	0.87	-	-					
0.0554	0.99966	0.89	-	-					
0.0705	1.00057	0.92	-	-					
0.0858	1.00159	0.95	-	-					
$w_I=0.003$									
Nicotinic acid+aqueous IL									
T=298.15 K									
0.0100	0.99786	0.93	1.3324	1507.0	0.0100	0.99765	0.84	-	-
0.0251	0.99849	0.94	1.3327	1519.5	0.0251	0.99834	0.86	-	-
0.0402	0.99944	0.96	1.3330	1537.7	0.0402	0.99917	0.88	-	-
0.0554	1.00058	0.98	1.3335	1559.9	0.0554	1.00019	0.91	-	-
0.0705	1.00182	1.00	1.3340	1586.5	0.0705	1.00126	0.93	-	-
0.0858	1.00331	1.02	1.3345	1615.8	0.0858	1.00277	0.95	-	-
T=318.15 K									
0.0100	0.99749	0.82	-	-					
0.0251	0.99803	0.85	-	-					

(Contd...)

Table 2: (Continued...)

M/mol kg ⁻¹	$\rho \cdot 10^{-3}/\text{kgm}^{-3}$	η/mPas	n_D	u/ms^{-1}	M/mol kg ⁻¹	$\rho \cdot 10^{-3}/\text{kgm}^{-3}$	η/mPas	n_D	u/ms^{-1}
0.0402	0.99879	0.88	-	-					
0.0554	0.99993	0.91	-	-					
0.0705	1.00143	0.93	-	-					
0.0858	1.00252	0.95	-	-					
Ascorbic acid+aqueous IL									
T=298.15 K									
0.0100	0.99802	0.94	1.3328	1508.0	0.0100	0.99784	0.88	-	-
0.0251	0.99891	0.95	1.3332	1521.5	0.0251	0.99842	0.92	-	-
0.0402	0.99969	0.98	1.3337	1539.7	0.0402	0.99939	0.95	-	-
0.0554	1.00053	1.01	1.3342	1561.9	0.0554	1.00022	0.98	-	-
0.0705	1.00173	1.03	1.3347	1588.5	0.0705	1.00139	1.01	-	-
0.0858	1.00302	1.05	1.3352	1618.8	0.0858	1.00264	1.04	-	-
T=318.15 K									
0.0100	0.99768	0.86	-	-					
0.0251	0.99822	0.87	-	-					
0.0402	0.99893	0.90	-	-					
0.0554	1.00032	0.93	-	-					
0.0705	1.00142	0.95	-	-					
0.0858	1.00219	0.98	-	-					
$w_I=0.005$									
Nicotinic acid+aqueous IL									
T=298.15 K									
0.0100	0.99801	0.990	1.333	1511.0	0.0100	0.99779	0.890	-	-
0.0251	0.99868	1.020	1.3333	1524.5	0.0251	0.99831	0.920	-	-
0.0402	0.99957	1.060	1.3337	1543.7	0.0402	0.99915	0.940	-	-
0.0554	1.00079	1.090	1.3342	1563.9	0.0554	1.00007	0.960	-	-
0.0705	1.00215	1.120	1.3347	1590.5	0.0705	1.00172	0.980	-	-
0.0858	1.00379	1.140	1.3353	1621.8	0.0858	1.00303	0.990	-	-
T=318.15 K									
0.0100	0.99773	0.870	-	-					
0.0251	0.99809	0.890	-	-					
0.0402	0.99889	0.920	-	-					
0.0554	0.99997	0.940	-	-					
0.0705	1.00154	0.970	-	-					
0.0858	1.00296	0.990	-	-					
Ascorbic acid+aqueous IL									
T=298.15 K									
0.0100	0.99829	0.990	1.3333	1515.0	0.0100	0.99798	0.920	-	-
0.0251	0.99889	1.020	1.3337	1527.5	0.0251	0.99862	0.950	-	-
0.0402	0.99979	1.060	1.3342	1547.7	0.0402	0.99934	0.980	-	-
0.0554	1.00092	1.090	1.3347	1567.9	0.0554	1.00013	1.000	-	-
0.0705	1.00216	1.120	1.3353	1595.5	0.0705	1.00154	1.040	-	-
0.0858	1.00369	1.140	1.3359	1627.8	0.0858	1.00311	1.070	-	-

(Contd...)

Table 2: (Continued...)

M/mol kg ⁻¹	$\rho \cdot 10^{-3}/\text{kgm}^{-3}$	η/mPas	n_D	u/ms^{-1}	M/mol kg ⁻¹	$\rho \cdot 10^{-3}/\text{kgm}^{-3}$	η/mPas	n_D	u/ms^{-1}
T=318.15 K									
0.0100	0.99789	0.890	-	-					
0.0251	0.99841	0.910	-	-					
0.0402	0.99931	0.930	-	-					
0.0554	1.00036	0.960	-	-					
0.0705	1.00168	0.990	-	-					
0.0858	1.00296	1.030	-	-					

^auncertainty of the molality $u(m)=0.0002 \text{ molkg}^{-1}$, density $u(\rho)=0.00005 \times 10^{-3} \text{ kg m}^{-3}$, viscosity $u(\eta)=0.01 \text{ mPa s}$, refractive index $u(n_D)=0.0002$, speed of sound $u(u)=0.5 \text{ ms}^{-1}$, temperature $u(T)=0.01 \text{ K}$, 95% level of confidence, IL: Ionic liquid

Table 3: Molality (m), apparent molar volume (\square_v), $(\eta_r - 1) / \sqrt{m}$, molar refraction, and apparent molar adiabatic compressibility (\square_k) of vitamins in different mass fraction of aqueous Ionic Liquid (w_I) at different temperatures, respectively.

$m/\text{mol.kg}^{-1}$	$\square_v \cdot 10^6/\text{m}^3$ mol^{-1} $/\text{kg}^{1/2} \cdot \text{mol}^{-1/2}$	$(\eta_r - 1) / \sqrt{m}$	R_M	$\square_k \cdot 10^{11}/\text{m}^3$ $\text{mol}^{-1} \cdot \text{Pa}^{-1}$	$m/\text{mol/kg}$	$\square_v \cdot 10^6/\text{m}^3$ mol^{-1} $/\text{kg}^{1/2} \cdot \text{mol}^{-1/2}$	$(\eta_r - 1) / \sqrt{m}$	R_M	$\square_k \cdot 10^{11}/$ $\text{m}^3 \cdot \text{mol}^{-1}$ Pa^{-1}
$w_I=0.001$									
Nicotinic acid+aqueous IL									
T=298.15 K									
0.0100	108.37	0.116	25.287	-2.066	0.0100	113.39	0.122	-	-
0.0251	92.93	0.220	25.311	-3.621	0.0251	98.95	0.308	-	-
0.0402	81.803	0.348	25.316	-4.682	0.0402	90.58	0.365	-	-
0.0554	74.743	0.395	25.321	-5.605	0.0554	80.40	0.467	-	-
0.0705	68.560	0.438	25.323	-6.320	0.0705	72.72	0.505	-	-
0.0858	63.379	0.476	25.328	-7.036	0.0858	68.69	0.583	-	-
T=318.15 K									
0.0100	118.42	0.253	-	-					
0.0251	100.57	0.320	-	-					
0.0402	91.35	0.379	-	-					
0.0554	79.50	0.431	-	-					
0.0705	73.01	0.478	-	-					
0.0858	69.17	0.520	-	-					
Ascorbic acid+aqueous IL									
T=298.15 K									
0.0100	138.45	0.112	36.215	-13.14	0.0100	148.49	0.235	-	-
0.0251	134.04	0.213	36.216	-31.81	0.0251	134.45	0.446	-	-
0.0402	129.68	0.336	36.229	-46.80	0.0402	136.46	0.411	-	-
0.0554	126.42	0.382	36.236	-59.66	0.0554	135.73	0.500	-	-
0.0705	123.41	0.424	36.250	-70.90	0.0705	125.86	0.532	-	-
0.0858	120.99	0.538	36.253	-81.60	0.0858	122.66	0.563	-	-

(Contd...)

Table 3: (Continued...)

$m/\text{mol} \cdot \text{kg}^{-1}$	$\square_v \cdot 10^6 / \text{m}^3$ mol^{-1} $/\text{kg}^{1/2} \cdot \text{mol}^{-1/2}$	$(\eta_r - 1) / \sqrt{m}$	R_M	$\square_k \cdot 10^{11} / \text{m}^3$ $\text{mol}^{-1} \cdot \text{Pa}^{-1}$	$m/\text{mol/kg}$	$\square_v \cdot 10^6 / \text{m}^3$ mol^{-1} $/\text{kg}^{1/2} \cdot \text{mol}^{-1/2}$	$(\eta_r - 1) / \sqrt{m}$	R_M	$\square_k \cdot 10^{11} /$ $\text{m}^3 \cdot \text{mol}^{-1}$ Pa^{-1}
T=318.15 K									
0.0100	151.51	0.121	-	-					
0.0251	141.69	0.153	-	-					
0.0402	138.98	0.303	-	-					
0.0554	134.83	0.362	-	-					
0.0705	130.74	0.458	-	-					
0.0858	126.80	0.541	-	-					
$w_I=0.003$									
Nicotinic acid+aqueous IL									
T=298.15 K									
0.0100	108.35	0.220	25.319	-3.34	0.0100	116.391	0.120	-	-
0.0251	92.121	0.208	25.332	-17.02	0.0251	92.9349	0.228	-	-
0.0402	80.043	0.274	25.337	-26.45	0.0402	83.5622	0.301	-	-
0.0554	71.091	0.327	25.337	-35.09	0.0554	75.8390	0.410	-	-
0.0705	64.543	0.373	25.343	-42.18	0.0705	70.7097	0.454	-	-
0.0858	57.359	0.413	25.346	-49.57	0.0858	62.2017	0.494	-	-
T=318.15 K									
0.0100	117.41	0.123	-	-					
0.0251	99.365	0.312	-	-					
0.0402	89.339	0.431	-	-					
0.0554	77.855	0.525	-	-					
0.0705	66.137	0.558	-	-					
0.0858	63.390	0.590	-	-					
Ascorbic acid+aqueous IL									
T=298.15 K									
0.0100	145.45	0.107	36.260	-18.56	0.0100	150.484	0.1148	-	-
0.0251	128.41	0.135	36.281	-39.45	0.0251	142.865	0.3626	-	-
0.0402	126.91	0.268	36.293	-55.76	0.0402	131.187	0.4584	-	-
0.0554	125.13	0.365	36.311	-70.00	0.0554	128.430	0.5371	-	-
0.0705	118.96	0.404	36.319	-82.51	0.0705	121.986	0.6055	-	-
0.0858	113.91	0.440	36.324	-95.78	0.0858	116.873	0.7060	-	-
T=318.15 K									
0.0100	151.50	0.117	-	-					
0.0251	144.89	0.148	-	-					
0.0402	138.97	0.293	-	-					
0.0554	123.89	0.399	-	-					
0.0705	119.42	0.442	-	-					
0.0858	120.42	0.521	-	-					

(Contd...)

Table 3: (Continued...)

$m/\text{mol} \cdot \text{kg}^{-1}$	$\square_v \cdot 10^6 / \text{m}^3$	$(\eta_r - 1) / \sqrt{m}$	R_M	$\square_k \cdot 10^{11} / \text{m}^3 \cdot \text{Pa}^{-1}$	$m/\text{mol/kg}$	$\square_v \cdot 10^6 / \text{m}^3$	$(\eta_r - 1) / \sqrt{m}$	R_M	$\square_k \cdot 10^{11} / \text{m}^3 \cdot \text{mol}^{-1/2} \cdot \text{Pa}^{-1}$
$w_I=0.005$									
Nicotinic acid+aqueous IL									
T=298.15 K									
0.0100	114.34	0.108	25.341	-3.94	0.0100	117.376	0.230	-	-
0.0251	92.903	0.340	25.377	-17.30	0.0251	100.137	0.363	-	-
0.0402	82.030	0.429	25.379	-27.01	0.0402	87.8093	0.402	-	-
0.0554	71.076	0.503	25.383	-36.35	0.0554	80.7478	0.440	-	-
0.0705	62.812	0.567	25.385	-44.06	0.0705	66.2604	0.476	-	-
0.0858	54.163	0.624	25.388	-51.27	0.0858	60.8953	0.471	-	-
T=318.15 K									
0.0100	117.38	0.357	-	-	0.0100	117.376	0.230	-	-
0.0251	106.55	0.376	-	-	0.0251	100.137	0.363	-	-
0.0402	92.826	0.475	-	-	0.0402	87.8093	0.402	-	-
0.0554	81.481	0.506	-	-	0.0554	80.7478	0.440	-	-
0.0705	67.982	0.583	-	-	0.0705	66.2604	0.476	-	-
0.0858	61.016	0.610	-	-	0.0858	60.8953	0.471	-	-
Ascorbic acid+aqueous IL									
T=298.15 K									
0.0100	139.41	0.312	36.282	-23.06	0.0100	151.463	0.337	-	-
0.0251	137.60	0.395	36.329	-48.49	0.0251	140.839	0.426	-	-
0.0402	129.63	0.520	36.345	-67.37	0.0402	136.179	0.505	-	-
0.0554	121.82	0.576	36.358	-82.40	0.0554	132.785	0.526	-	-
0.0705	115.78	0.629	36.361	-96.85	0.0705	121.968	0.635	-	-
0.0858	108.46	0.642	36.371	109.17	0.0858	113.082	0.691	-	-
T=318.15 K									
0.0100	152.47	0.114	-	-	0.0100	151.463	0.337	-	-
0.0251	146.06	0.215	-	-	0.0251	140.839	0.426	-	-
0.0402	134.93	0.283	-	-	0.0402	136.179	0.505	-	-
0.0554	127.14	0.386	-	-	0.0554	132.785	0.526	-	-
0.0705	118.82	0.471	-	-	0.0705	121.968	0.635	-	-
0.0858	113.91	0.582	-	-	0.0858	113.082	0.691	-	-

IL: Ionic liquid

interaction is restricted by the interaction of the interacting group of one molecule to side chain of the other vitamins molecules. The S_V^* values of the vitamin solution given in Table 4 decreases with increase in the interactive centers of the studied vitamins and with the increase in the mass fraction of IL in the solvent mixture interpreting the minimum solute-solute interaction.

From Table 4, a quantitative comparison between ϕ_V^0 and S_V^* values show that, the magnitude of ϕ_V^0 values is higher than S_V^* suggesting that the

solute-solvent interactions dominate over the solute-solute interactions in all solutions at the investigated temperatures. Furthermore, S_V^* values are negative at all temperatures, and the values slight increase with the increase of experimental temperatures which may be attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of solute-solute interactions.

According to Sharnin et al. [29,30] nicotinic acid exists in the zwitterionic form in aqueous solution.

Table 4: Limiting apparent molal volumes (ϕ_V^0), experimental slopes (S_V^*), viscosity A, B-coefficients, limiting partial molal adiabatic compressibilities (ϕ_K^0), and experimental slopes (S_K^*) of vitamins in different mass fraction of aqueous IL (w_I) at 298.15K to 318.15K, respectively.

Temp/K	$\phi_V^0 \cdot 10^6 / \text{m}^3$	$S_V^* \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-3/2} \cdot \text{kg}^{1/2}$	$B / \text{kg}^{1/2} \cdot \text{mol}^{-1/2}$	$A / \text{kg} \cdot \text{mol}^{-1}$	$\phi_K^0 \cdot 10^{11} / \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$	$S_K^* \cdot 10^{11} / \text{kg}^{1/2}$
mol^{-1}						
$w_I=0.001$						
Nicotinic acid+aqueous IL						
298.15	130.46	-92.048	1.9188	0.0683	28.66	-328.18
308.15	137.01	-117.24	2.2917	0.0869	-	-
318.15	143.17	-121.62	2.5504	0.1059	-	-
Ascorbic acid+aqueous IL						
298.15	148.08	-233.86	2.1178	0.1076	34.98	-502.96
308.15	158.47	-237.29	2.3987	0.1238	-	-
318.15	162.87	-260.94	2.6664	0.1498	-	-
$w_I=0.003$						
Nicotinic acid+aqueous IL						
298.15	134.13	-144.59	2.1108	0.073	29.05	-333.25
308.15	139.3	-176.07	2.3095	0.0848	-	-
318.15	146.12	-185.64	2.6605	0.0901	-	-
Ascorbic acid+aqueous IL						
298.15	156.69	-264.46	2.3246	0.1152	35.18	-527.74
308.15	168.79	-266.74	2.5654	0.1391	-	-
318.15	172.09	-289.92	2.8394	0.1471	-	-
$w_I=0.005$						
Nicotinic acid+aqueous IL						
298.15	143.61	-166.46	2.3013	0.1107	29.57	-363.63
308.15	147.3	-185.92	2.4321	0.1366	-	-
318.15	151.6	-210.32	2.8765	0.1881	-	-
Ascorbic acid+aqueous IL						
298.15	160.25	-306.89	2.4321	0.1277	35.62	-591.88
308.15	171.59	-311.23	2.5994	0.1427	-	-
318.15	176.2	-315.39	2.9321	0.1538	-	-

IL: Ionic liquid

Hence, it could be assumed that nicotinic acid exists in a zwitterionic form and limits the possible interactions involving: (i) Polar $-\text{NH}^+$ group of zwitterionic nicotinic acid and BF_4^- and HO^- , (ii) polar $-\text{COO}^-$ group (through both the O-atoms) of zwitterionic nicotinic acid and positive (+) nitrogen center of the IL and H^+ ions, and (iii) ionic-hydrophobic interaction

between ions of the IL ($[\text{EPy}] \text{BF}_4^-$) and the nonpolar part of zwitterionic nicotinic acid molecules. While types (i) and (ii) interactions impart positive contributions, type (iii) interactions impart negative contributions to ϕ_V^0 values. Therefore, the overall positive ϕ_V^0 values indicate that ionic group interactions predominate over ionic-hydrophobic interactions.

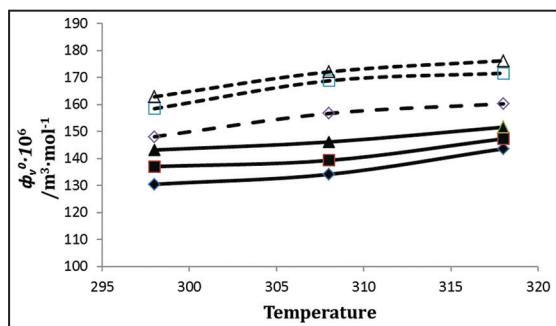


Figure 1: Plot of limiting apparent molar volume (ϕ_V^0) for nicotinic acid at 298.15 K (♦), 308.15 K (■), 318.15 K (▲), and ascorbic acid at 298.15K (◊), 308.15 (□), 318.15K (Δ), against studied temp (T) in $w_1=0.001, 0.003$, and 0.005 mass fraction of aq. IL, respectively.

Ascorbic acid, vitamin C, is a weak electrolyte. Its molecular formula is $C_6H_8O_6$. In aqueous solution, ascorbic acid ionizes to form H^+ and $C_6H_8O_6^-$. Plausible interaction occurring in ascorbic acid and IL ($[Epy]BF_4^-$) is (i) OH grs of ascorbic acid and positive nitrogen center of the IL, (ii) H^+ ions of water molecule and –OH gr of ascorbic acid (iii) BF_4^- of the IL and H^+ of water molecule. (iii) Ionic-hydrophobic interaction between ions of the IL and nonpolar part of the ascorbic acid.

The observed ϕ_V^0 positive values (Table 4) are due to the effect of ion-hydrophilic interactions (between positive nitrogen center of the IL and –OH grs of ascorbic acid and between polar $-NH^+$ group of zwitterionic nicotinic acid and BF_4^-) is greater for ascorbic acid than nicotinic acid.

Nicotinic acid < ascorbic acid

Greater interaction in ascorbic acid than nicotinic acid may be due to the greater number of –OH grs present in the ascorbic acid. The schematic representation of solute-solvent interaction, for the studied vitamins in aqueous IL binary mixtures, in view of various derived parameters is depicted in Scheme 4.

3.2. Temperature Dependent Limiting Apparent Molar Volume

The variation of ϕ_V^0 with the temperature of the vitamins in aqueous IL mixture can be expressed by the general polynomial equation as follows,

$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \quad (4)$$

Where a_0 , a_1 , a_2 are the empirical coefficients depending on the solute, mass fraction (w_1) of the cosolute IL, and T is the temperature range under study in Kelvin. The values of these coefficients of the above

equation for the vitamins in aqueous IL mixtures are reported in Table 5.

The limiting apparent molar expansibilities, ϕ_E^0 , can be obtained by the following equation:

$$\phi_E^0 = (\delta\phi_V^0 / \delta T)_P = a_1 + 2a_2 T \quad (5)$$

The limiting apparent molar expansibilities, ϕ_E^0 , change in magnitude with the change of temperature. The values of ϕ_E^0 for different solutions of the studied vitamins at (298.15, 308.15, and 318.15) K are reported in Table 6. The table reveals that ϕ_E^0 is positive for all the vitamins in aqueous IL and studied temperatures. This fact can be ascribed to the absence of caging or packing effect for the vitamins in solutions.

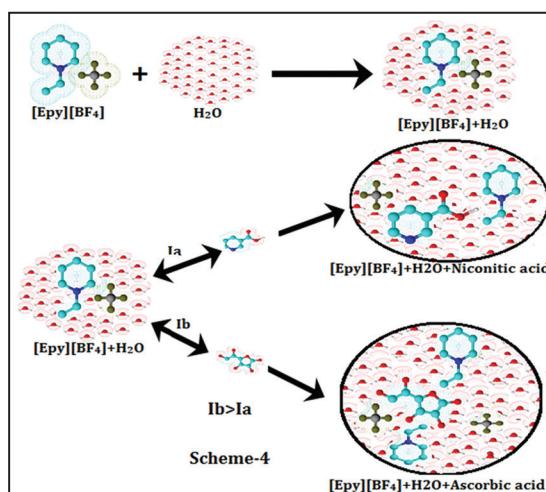
During the past few years, it has been emphasized by different workers that S_V^* is not the sole criterion for determining the structure making or -breaking nature of any solute. Hepler [31] developed a technique of examining the sign of $(\delta\phi_E^0 / \delta T)_P$ for the solute in terms of long-range structure-making and -breaking capacity of the solute in the mixed solvent systems using the general thermodynamic expression,

$$(\delta\phi_E^0 / \delta T)_P = (\delta^2\phi_V^0 / \delta T^2)_P = 2a_2 \quad (6)$$

If the sign of $(\delta\phi_E^0 / \delta T)_P$ is positive or a small negative, the molecule is a structure maker; otherwise, it is a structure breaker [32]. As is evident from Table 6 and Figure 2, the $(\delta\phi_E^0 / \delta T)_P$ values for all vitamins are positive under investigation are predominantly structure makers in all of the experimental solutions.

3.3. Viscosity Calculation

The experimental viscosity data for the studied systems are listed in Table 2. The relative



Scheme 4: The schematic representation of solute-solvent interaction, for the studied vitamins in aqueous IL binary mixtures.

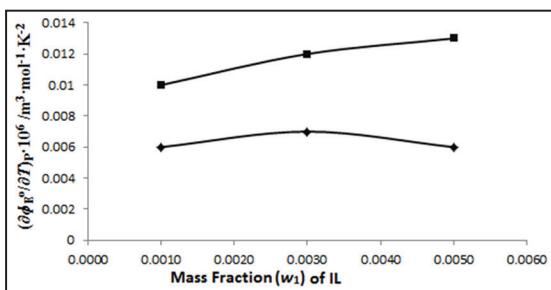


Figure 2: Plot of $(d\phi_E^0 / dT)_P$.nicotinic acid (♦) and ascorbic acid (■) against studied temp (T) in $w_1=0.001, 0.003$, and 0.005 mass fraction of aq. ionic liquid.

Table 5: Values of empirical coefficients (a_0 , a_1 , and a_2) of Equation 4 for vitamins in different mass fraction of aqueous IL (w_I) at 298.15 K to 318.15 K, respectively.

Solvent mixture	$a_0 \cdot 10^6 \cdot \text{m}^3 \cdot \text{mol}^{-1}$	$a_1 \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$a_2 \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$
Nicotinic acid+aqueous IL			
$w_I=0.001$	294.84	-1.494	0.0030
$w_I=0.003$	339.21	-1.654	0.0033
$w_I=0.005$	313.81	-1.480	0.0031
Ascorbic acid+aqueous IL			
$w_I=0.001$	478.16	-2.623	0.0050
$w_I=0.003$	611.51	-3.328	0.0060
$w_I=0.005$	609.26	-3.416	0.0064

IL: Ionic liquid

viscosity (η_r) has been analyzed using the Jones-Dole equation [33].

$$(\eta / \eta_o - 1) / \sqrt{m} = (\eta_r - 1) / \sqrt{m} = A + B \sqrt{m} \quad (7)$$

Where $\eta_r = \eta / \eta_o$, η and η_o are the relative viscosities, the viscosities of the ternary solutions (vitamins + aq. IL) and binary aqueous mixture (aq. IL) and m is the molality of the vitamins in ternary solutions. A and B are experimental constants known as viscosity A- and B-coefficients, which are specific to solute-solute and solute-solvent interactions, respectively. The values of A and B coefficients are projected by least-squares method by plotting $(\eta_r - 1) / \sqrt{m}$ against \sqrt{m} , and reported in Table 4. The values of the A coefficient are found to increase slightly with temperature and with the increase in mass of IL in the solvent mixture. These results designate the presence of very weak solute-solute interactions. These results are in an excellent arrangement with those obtained from S_V^* values.

Table 6: Limiting apparent molal expansibilities (ϕ_E^0) for vitamins in different mass fraction of aqueous IL (w_I) at 298.15 K to 318.15 K, respectively.

Solvent mixture	$\phi_E^0 \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	$(\partial \phi_E^0 / \partial T)_P \cdot 10^6 / \text{m}^3 \cdot \text{K}^{-1}$		
		K^{-1}	$\text{mol}^{-1} \text{K}^{-2}$	
Nicotinic acid+aqueous IL				
T/K	298.15	308.15	318.15	
$w_I=0.001$	0.295	0.355	0.415	0.006
$w_I=0.003$	0.314	0.380	0.446	0.007
$w_I=0.005$	0.339	0.400	0.461	0.006
Ascorbic acid+aqueous IL				
T/K	298.15	308.15	318.15	
$w_I=0.001$	0.359	0.459	0.559	0.010
$w_I=0.003$	0.250	0.370	0.490	0.012
$w_I=0.005$	0.370	0.497	0.624	0.013

IL: Ionic liquid

The extent of solute-solvent interaction in the solution calculated from the viscosity B-coefficient [34] gives valuable information regarding the solvation of the solvated solutes and their effects on the structure of the solvent in the local vicinity of the solute molecules in the solutions. From Table 4 and Figure 3, it is evident that the values of the B-coefficient are positive and much higher than A-coefficient, thereby suggesting the solute-solvent interactions are dominant over the solute-solute interactions. The higher B-coefficient values for higher viscosity values is due to the solvated solutes molecule associated by the solvent molecules all round to the formation of associated molecule by solute-solvent interaction, would present greater resistance, and this type of interactions are strengthened with a rise in temperature and also increase with an increase of mass fraction (w_I) of IL in the solvent mixtures. These results are in good agreement with those obtained from ϕ_V^0 values discussed earlier in Section 3.1.

Table 7 shows that the values of the B coefficients of all vitamins slightly increase with increasing temperature, i.e., the dB/dT values are positive. From Table 7, small positive dB/dT values for the present vitamins behave almost as structure-makers.

3.4. Refractive Index Calculation

The molar refraction R_M can be evaluated from the Lorentz-Lorenz relation [35].

$$R_M = \{(n^2_D - 1) / (n^2_D + 2)\}(M / \rho) \quad (8)$$

where R_M , n^D , M and ρ are the molar refraction, the refractive index, the molar mass, and the density of solution, respectively. The refractive index of a substance is defined as the ratio c_0/c , where c is the speed of light in the medium and c_0 the speed of light in vacuum. Stated more simply, the refractive index of a compound describes its ability to refract light as it moves from one medium to another and thus, the higher the refractive index of a compound, the more the light is refracted [36] as stated by Deetlefs et al. [37].

Table 7: Values of dB/dT for the vitamins in different mass fraction of aqueous IL (w_I) at 298.15 to 318.15 K, respectively.

Solvent mixture	dB/dT
Nicotinic acid+aqueous IL	
$w_I=0.001$	0.0316
$w_I=0.003$	0.0275
$w_I=0.005$	0.0288
Ascorbic acid+aqueous IL	
$w_I=0.001$	0.0274
$w_I=0.003$	0.0257
$w_I=0.005$	0.0250

IL: Ionic liquid

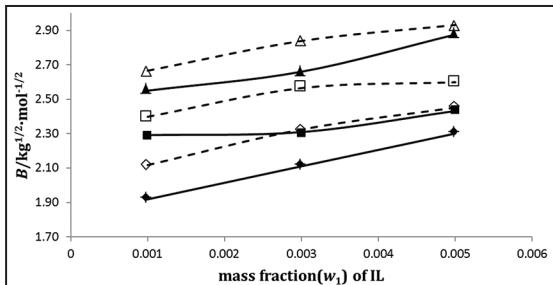


Figure 3: The plots of viscosity B-coefficient fornicotinic acid at 298.15 K (♦), 308.15 K (■), 318.15 K (▲), and ascorbic acid at 298.15 K (◊), 308.15 (□), 318.15 K (Δ), against mass fraction ($w_I = 0.001, 0.003$, and 0.005) of aq. ionic liquid, respectively.

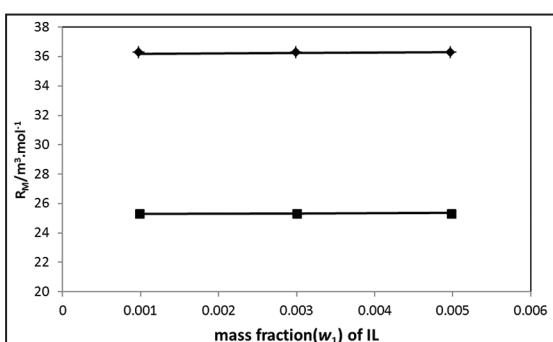


Figure 4: The plots of R_M fornicotinic acid (—■—) and ascorbic acid (—◆—) in different mass fractions (w_I) of ionic liquid in aqueous mixture at 298.15 K.

The refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser and with the increase of mass fraction of IL in solvent mixture refractive index value also increases. Hence, a perusal of Tables 2 and 3 we found that the refractive index and the molar refraction values, respectively, are higher for ascorbic acid than nicotinic acid, indicating the fact that the molecules are more tightly packed in the mixture. Figure 4 also supports the same fact that the ascorbic acid has higher molar refraction values than the nicotinic acid. The interaction in the solution is basically solute-solvent interaction and a small amount of solute-solute interaction. This is also good agreement with the results obtained from density and viscosity parameters discussed above. The trend in the package of the studied vitamins in aqueous mixture of IL is:

Nicotinic acid < ascorbic acid

3.5. Ultrasonic Speed Calculation

The adiabatic compressibility, defined by the thermodynamic relation:

$$\beta_s = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S \quad (9)$$

Where V is volume, P is pressure and S is entropy, is related to the solution density ρ , and the ultrasonic speed (u), by the Newton-Laplace's equation:

$$\beta_s = 1/u^2 \rho \quad (10)$$

providing the relation between thermodynamics and acoustics. The apparent molar adiabatic compressibility ϕ_E of the solution was determined from the relation

$$\phi_K = M\beta / \rho + (\beta\rho_0 - \beta_0\rho) / m\rho\rho_0 \quad (11)$$

where β_0 and β are the adiabatic compressibility of the solvent and solution, respectively and m is the molality of the solution. Limiting molar adiabatic compressibilities (ϕ_E^0) and experimental slopes (S_V^*) were obtained by fitting ϕ_K against the square root of molality (\sqrt{m}) using the least squares method.

$$\phi_K = \phi_E^0 + S_V^* \sqrt{m} \quad (12)$$

The values of ϕ_K^0 and S_V^* are presented in Table 4. The values of ϕ_K^0 and S_V^* are important parameter provided information about the extent of solute-solvent and solute-solute interaction respectively. The behavior is useful in the characteristic of solvation and electrostriction (the contraction of the solvent around the solute) of salt in solutions.

From Table 4 and Figure 5, it is observed that the value of limiting apparent molar isentropic compressibility ϕ_K^0 are positive and increases with the increase in

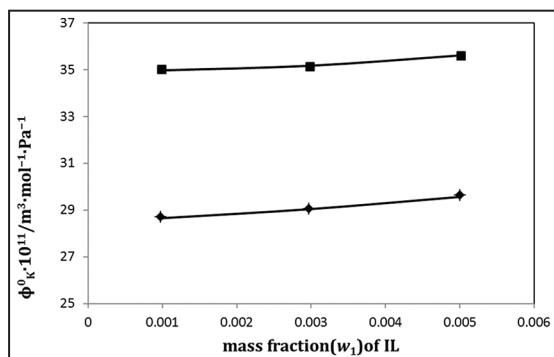


Figure 5: The plots limiting molar adiabatic compressibilities (ϕ_K^0) for nicotinic acid (—◆—) and ascorbic acid (—■—) in different mass fractions (w_1) of ionic liquid in aqueous mixture at 298.15 K.

concentration (w_1) of IL for all the studied solution, and shows the stronger solute-solvent interaction. The result is good agreement with the ϕ_V^0 value discussed earlier.

4. CONCLUSION

Extensive study of thermophysical and thermodynamic properties of simple vitamins in aqueous IL binary mixture were done. It is specified from the values of the limiting apparent molar volume (ϕ_V^0), viscosity B -coefficients, molar Refraction (R_M) and limiting partial isentropic compressibility (ϕ_K^0), the presence of strong solute-solvent interactions which increases with the increase of interacting centers (groups) of vitamins and mass fraction of IL in the aqueous mixture. The refractive index and the molar refraction values imply that ascorbic acid molecules are more tightly packed in the solution leading to higher solute-solvent interaction than the other vitamin. Above all this study demands a novelty of some vitamins prevailing in the aqueous solutions of IL mixture.

5. ACKNOWLEDGMENT

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