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Solution thermodynamics of aqueous nicotinic acid solutions in the presence of tetrabutylammonium hydrogen sulphate

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Abstract: In this study, we investigated the effects of tetrabutylammonium hydrogen sulphate (Bu_4NHSO_4) on the solute–solute and solute–solvent interactions in the aqueous solutions of nicotinic acid in terms of the apparent molar volumes (ϕ_V), standard partial molar volumes (ϕ_V^0) and viscosity B -coefficients at 298.15, 308.15 and 318.15 K under ambient pressure. These interactions are further discussed in terms of ion–dipolar, hydrophobic–hydrophobic, hydrophilic–hydrophobic group interactions. The activation parameters of viscous flow for Bu_4NHSO_4 in the aqueous solutions of nicotinic acid are discussed in terms of the transition state theory. The overall results indicated that ion–hydrophilic and hydrophilic–hydrophilic group interactions are predominant in aqueous solutions of nicotinic acid and that Bu_4NHSO_4 has a dehydration effect on hydrated nicotinic acid.

Keywords: Partial molar volumes; viscosity B -coefficients; tetrabutylammonium hydrogen sulphate; nicotinic acid.

INTRODUCTION

Nicotinic acid has gained huge attention over the years since it was synthesised in 1867 by Huber.¹ This is because of its versatility in terms of chemical, biochemical and therapeutic applications.¹ This derivative of pyridine has the molecular formula $\text{C}_6\text{H}_5\text{NO}_2$ with a carboxyl group ($-\text{COOH}$) at the 3-position and it is sometimes called niacin or vitamin B_3 in combination with nicotinamide.^{2,3} It is a colourless, water-soluble compound and it can be converted to nicotinamide adenine dinucleotide (NAD^+) and nicotinamide adenine dinucleotide 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.^{4,5}

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Many effective components of drugs are weak organic electrolytes and their degree of dissociation is determined mainly by the media, especially aqueous medium since biochemical actions generally occur in the aqueous phase. In pharmaceutical techniques, materials of pharmaceutical aids are usually introduced to enhance the bioavailability of the drugs. The effects of the composition of the solvent on the dissociation and diffusion of drugs are therefore crucial. It has also been found that salt concentration has large effects on vitamins, such as on their solubilities, stabilities and biological activities in different manners. The behaviour of vitamins in solution phase is governed by a combination of many specific interactions, namely ion–dipolar, hydrophobic–hydrophobic and hydrophilic–hydrophobic group interactions. Tetra-alkylammonium salts are bulky in nature and are known to orient water molecules around themselves depending on their alkyl chain lengths.^{6,7} Therefore, aqueous solutions of symmetrical tetra-alkylammonium cations (R_4N^+) are considered to provide model systems for the study of hydrophobic hydration⁸ and salts such as tetrabutylammonium hydrogen sulphate (Bu_4NHSO_4) can provide better information about the effects of electrostatic, hydrophilic and hydrophobic interactions on the stabilities of vitamins, because such salts can influence the macromolecular conformations by affecting inter and intra charge–charge interactions and hydrophobic interactions.

Although extensive studies^{9–19} are available on various properties of nicotinic acid in solution phase, a study on solution thermodynamics of aqueous solution of nicotinic acid in presence of Bu_4NHSO_4 is not available in the literature. Hence, in this work, the effects of Bu_4NHSO_4 on the solute–solute, solute–co-solute and solute–solvent or co-solute–solvent interactions in the aqueous solution of nicotinic acid were studied in terms of apparent molar volumes (ϕ_V), standard partial molar volumes (ϕ_V^0) and viscosity B -coefficients as a function of concentrations of Bu_4NHSO_4 and nicotinic acid in aqueous solution at 298.15, 308.15 and 318.15 K under ambient pressure.

EXPERIMENTAL

Materials

Nicotinic acid (Sigma Aldrich, USA, mass fraction purity > 99.5 %) and Bu_4NHSO_4 (S. D. Fine Chemicals, India, mass fraction purity > 98.5 %) were used in the present study. Deionized, doubly distilled, degassed water with a specific conductance of 1×10^{-6} S cm^{-1} was used for the preparation of all aqueous solutions. Nicotinic acid was used as received from the vendor and its melting point was found to be 236.5 °C. The physical properties of different aqueous solutions of nicotinic acid are reported in Table S-I of the Supplementary material to this paper. No comparable literature data were found on the densities (ρ_0) and viscosities (η_0) for aqueous solutions of nicotinic acid (used as solvents) in this work. Bu_4NHSO_4 was purified by dissolving it in 1:1 (v/v) mixture of methanol and ethanol and recrystallized from diethyl ether. After filtration, the salt was dried *in vacuo* for few hours and its melting point was measured to be 171.5 °C. Stock solutions of Bu_4NHSO_4 in different aqueous solutions of nicotinic acid were prepared by mass and then further diluted to obtain different working

solutions. The pH of the working solutions decreased from 3.33–2.32 as the concentration of Bu_4NHSO_4 increased from 0.005–0.020 mol dm⁻³. Molalities (m) were converted into molarities (c) using experimental densities. All solutions are prepared fresh before use and adequate precautions were taken to avoid evaporation losses during the measurements. The uncertainty in the molarity of the Bu_4NHSO_4 solutions was evaluated to be within ± 0.0001 mol dm⁻³.

Methods

The mass measurements were realised on a digital electronic analytical balance (Mettler, AG 285, Switzerland) with a precision of ± 0.01 mg. The densities were measured with a vibrating-tube density meter (Anton Paar DMA 4500M), which was maintained at ± 0.01 K of the desired temperature and calibrated with doubly distilled water and dry air. The uncertainty in the density was estimated to be ± 0.0001 g cm⁻³. The viscosities were measured by means of a suspended Ubbelohde type viscometer, which was calibrated at the experimental temperature with doubly distilled water and purified methanol. A thoroughly cleaned and perfectly dried viscometer (filled with the experimental solution) was placed vertically in a glass-walled thermostat maintained at ± 0.01 K of the desired temperature. After attainment of thermal equilibrium, efflux times of flow were recorded with a digital stopwatch that measured time correct to ± 0.01 s. At least three repetitions of each data (reproducible to ± 0.02 s) were taken to average the flow times. Based on previous work on several pure liquids, the precision of the viscosity measurements was evaluated to be within ± 0.003 mPa s and the total uncertainty in the viscosity measurements was 0.05 %. Details of the methods and techniques of the density and viscosity measurements were described elsewhere.^{20–22} The absorption spectra were recorded on JascoV-530 double beam UV-Vis spectrophotometer (coupled with a thermostatic arrangement) at ambient temperature using a quartz cell of 1 cm path length. Doubly distilled water was used as the reference solvent for the spectroscopic measurements. The melting points of the solid solutes were determined by the open capillary method. The pH values of the working solutions were measured with a Systronics MK-VI 5631 digital pH meter, which had been calibrated with a commercially available buffer capsule (Merck, India) of pH 4.00 at 298.15 K before the readings were taken.

RESULTS AND DISCUSSION

The apparent molar volumes (ϕ_V) of Bu_4NHSO_4 in different aqueous solutions of nicotinic acid were determined from the solution densities using the following equation:²³

$$\phi_V = (M / \rho_0) - 1000(\rho - \rho_0) / (c\rho_0) \quad (1)$$

where M and c are the molar mass and molarity of Bu_4NHSO_4 in the aqueous solutions of nicotinic acid; ρ_0 and ρ are the densities of the solvent and the solution, respectively. The experimental densities (ρ), viscosities (η) and derived parameters at 298.15, 308.15 and 318.15 K are reported in Table S-II of the Supplementary material. As the ϕ_V values are independent of the concentrations of Bu_4NHSO_4 for extremely dilute solutions, it may be assumed that the ϕ_V values are equal to the partial molar volume (ϕ_V^0) at infinite dilution. The plots of the ϕ_V values against the square root of the molar concentrations (\sqrt{c}) of Bu_4NHSO_4 were found to be linear. Hence, the partial molar volumes (ϕ_V^0) at

infinite dilution and the experimental slopes (S_V^*) were determined by using least squares fitting (as shown in Fig. 1) of the φ_V values to the Masson Equation:²⁴

$$\varphi_V = \varphi_V^0 + S_V^* \sqrt{c} \quad (2)$$

The φ_V^0 and S_V^* values are reported in Table I, from which it could be seen that the φ_V^0 values are positive and increase with increasing molarity of the nicotinic acid in the mixtures and decrease with increasing temperature of the respective mixtures. This trend in φ_V^0 values indicates the presence of strong solute–solvent interactions and such interactions further strengthen at higher concentrations of nicotinic acid in the ternary solutions and decrease when the temperature increases, probably due to greater thermal agitation leading to disruption of the developing specific interactions between the solute and solvent molecules at higher temperatures. These trends in φ_V^0 values are clear manifestations of the trends in the φ_V values (as listed in Table S-II of the Supplementary material).

The parameter S_V^* is a volumetric virial coefficient and characterizes the pair-wise interactions between solvated species^{25–27} in the solution. Its sign is determined by the interactions between solute species. Table I shows that the S_V^* values are positive for all the ternary solutions and such values increase when the experimental temperatures increase but decrease when the nicotinic acid concentration in the ternary solutions increases. For ionic species such as Bu_4NHSO_4 or zwitterionic nicotinic acid, the positive S_V^* values suggest that the pair-wise interactions (between solute–solute or solute–co-solute) were dominated by the charged end groups or ions and the S_V^* values just reciprocate the trends in φ_V^0 values for the studied experimental aqueous solutions.

Apparent molar volumes (φ_V) and densities (ρ) were used to derive the apparent molar expansibilities (φ_E) of nicotinic acid solutions by using the relation:²⁸

$$\varphi_E = \alpha\varphi_V + 1000(\alpha - \alpha_0) / (m\rho_0) \quad (3)$$

where α and α_0 are the coefficients of isobaric thermal expansion of the solvent and solution, respectively and the other symbols have their usual significances. The coefficients α and α_0 are defined as: $\alpha = -\rho_0^{-1}(\text{d}\rho/\text{d}T)_P$ and $\alpha_0 = -\rho^{-1}(\text{d}\rho/\text{d}T)_P$, respectively.

The uncertainty of α and α_0 values was $\pm 5 \times 10^{-6} \text{ K}^{-1}$. The uncertainty of apparent molar expansibilities (φ_E) was within $\pm 0.001 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1}$. The partial molar expansibilities (φ_E^0) were derived from the relation:²⁸

$$\varphi_E = \varphi_E^0 + S_E \sqrt{m} \quad (4)$$

The φ_E^0 values for the experimental solutions at different temperatures are reported in Table II, from which it could be seen that the φ_E^0 values are negative and further decrease with increasing temperature and nicotinic acid concentration.

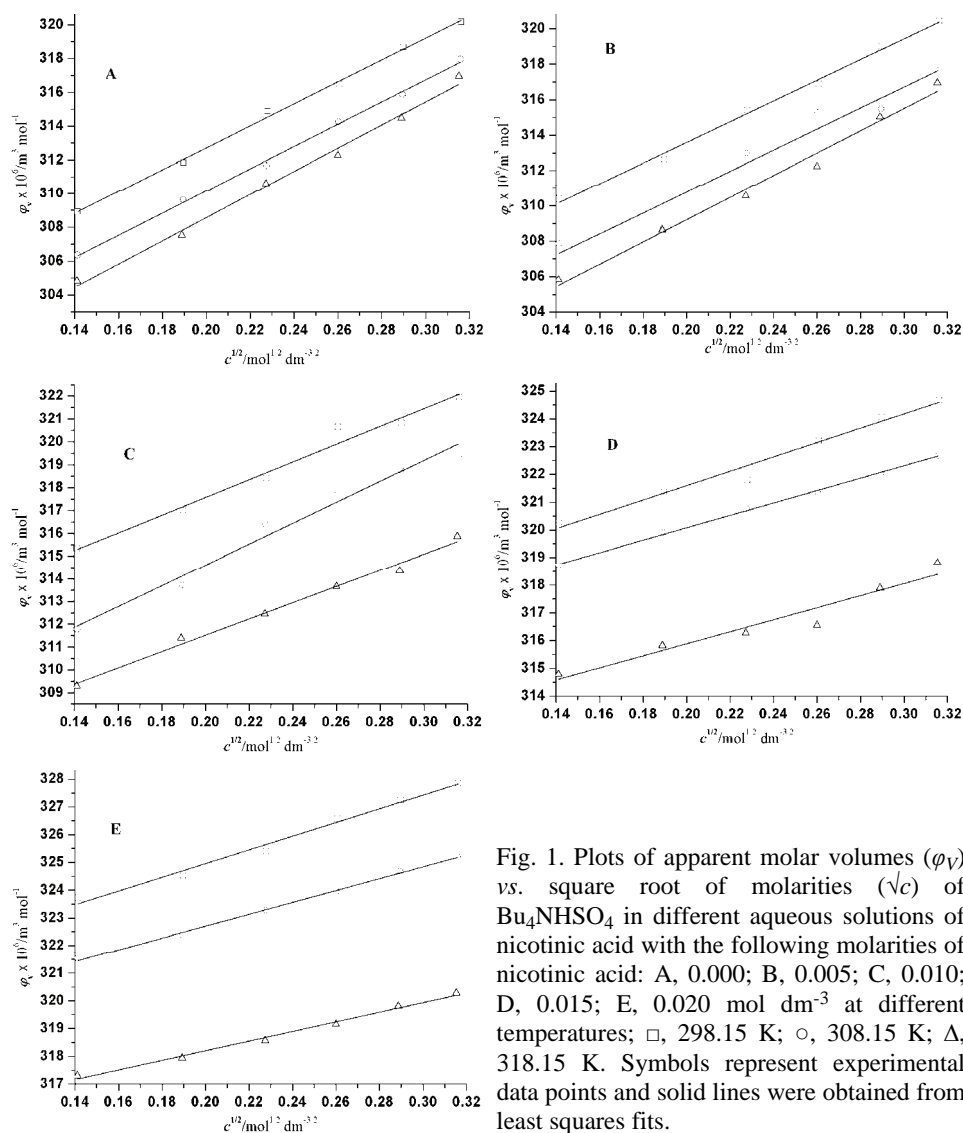


Fig. 1. Plots of apparent molar volumes (ϕ_V) vs. square root of molarities (\sqrt{c}) of Bu_4NHSO_4 in different aqueous solutions of nicotinic acid with the following molarities of nicotinic acid: A, 0.000; B, 0.005; C, 0.010; D, 0.015; E, 0.020 mol dm^{-3} at different temperatures; \square , 298.15 K; \circ , 308.15 K; Δ , 318.15 K. Symbols represent experimental data points and solid lines were obtained from least squares fits.

Such a trend in the ϕ_E^0 values may be attributed to structural perturbations caused by the addition of nicotinic acid or to the appearance of caging or packing effects.^{29,30} However, such effects gradually decrease and lead to the release of solvated H_2O molecules in favour of the bulk water structure. Thus, the volume of the solution decreases and the density increases, as given in Table S-II of the Supplementary material. According to Heplar,³² the long-range structure making or breaking ability of solutes in solutions can be better characterized by the sign of the $(d\phi_E^0/dT)_P$ terms. If the sign of $(d\phi_E^0/dT)_P$ is slightly negative or posi-

tive, the solute is a structure maker, otherwise it is a structure breaker. The $(d\phi_E^0/dT)_P$ values were obtained from the slopes of linear fits of ϕ_E^0 values against the experimental temperatures (T), which have coefficient of regression (R^2) values lying within the range of 0.99998–0.99999. From the values of $(d\phi_E^0/dT)_P$ reported in Table II, it is evident that Bu_4NHSO_4 acts as a mild structure maker and its structure making ability decreases to some extent with increasing nicotinic acid concentrations in the studied solutions.

TABLE I. Partial molar volumes (ϕ_V^0) and the experimental slopes (S_V^*) of Eq. (2) for Bu_4NHSO_4 in aqueous solutions of nicotinic acid with corresponding standard deviations (σ) at different temperatures

T / K	$\phi_V^0 \times 10^6 / \text{m}^3 \text{mol}^{-1}$	$S_V^* \times 10^6 / \text{m}^{9/2} \text{mol}^{-3/2}$	$\sigma^b \times 10^6 / \text{m}^3 \text{mol}^{-1}$
$c_{\text{NA}}^a = 0.000$			
298.15	299.73 (± 0.81)	64.94 (± 3.33)	0.09 (0.99755)
308.15	297.02 (± 0.80)	65.74 (± 3.28)	0.09 (0.99774)
318.15	294.84 (± 1.07)	68.64 (± 4.40)	0.29 (0.99338)
$c_{\text{NA}} = 0.005$			
298.15	301.92 (± 0.88)	58.39 (± 3.63)	0.13 (0.99571)
308.15	298.94 (± 1.66)	59.24 (± 6.80)	1.68 (0.95124)
318.15	296.62 (± 1.21)	62.96 (± 4.99)	0.48 (0.98703)
$c_{\text{NA}} = 0.010$			
298.15	309.80 (± 1.07)	38.85 (± 4.40)	0.29 (0.98703)
308.15	305.45 (± 1.20)	45.77 (± 4.90)	0.45 (0.97948)
318.15	304.38 (± 0.84)	35.69 (± 3.44)	0.11 (0.99085)
$c_{\text{NA}} = 0.015$			
298.15	316.42 (± 0.91)	25.88 (± 3.70)	0.15 (0.97684)
308.15	315.61 (± 0.44)	22.33 (± 1.80)	0.01 (0.99822)
318.15	311.55 (± 1.08)	21.67 (± 4.45)	0.01 (0.93418)
$c_{\text{NA}} = 0.020$			
298.15	320.03 (± 0.75)	24.66 (± 3.06)	0.07 (0.98794)
308.15	318.43 (± 0.45)	21.39 (± 1.84)	0.01 (0.99788)
318.15	314.73 (± 0.56)	17.53 (± 2.31)	0.02 (0.99205)

^aMolarity of nicotinic acid in water; ^bvalues of coefficient of regression (R^2) in parentheses

The partial molar volumes of transfer ($\Delta\phi_V^0$) from water to an aqueous solution of nicotinic acid were determined from the relation:^{27,33}

$$\Delta\phi_V^0 = \phi_V^0[\text{Aqueous solution of nicotinic acid}] - \phi_V^0[\text{Water}] \quad (5)$$

The $\Delta\phi_V^0$ values are depicted in Fig. 2 as a function of the molarity of the aqueous nicotinic acid solutions. The $\Delta\phi_V^0$ values are free from solute–solute interactions and, therefore, provide valuable information about solute–co-solute interactions.³³ Figure 2 shows that the $\Delta\phi_V^0$ values were positive at all the experimental temperatures and increase monotonically with increasing nicotinic acid concentration in the ternary solutions. According to the co-sphere model,³⁴

while the overlap of hydration co-spheres of two ionic species results in a volume increase, those of hydration co-spheres of hydrophobic–hydrophobic and ion–hydrophobic groups result in a net volume decrease. The positive $\Delta\phi_V^0$ values indicate that ion–hydrophilic and hydrophilic–hydrophilic group interactions are predominant over ion–hydrophobic, hydrophobic–hydrophobic and hydrophilic–hydrophobic interactions and the overall effect of the overlap of the hydration co-spheres of Bu_4NHSO_4 and zwitterionic nicotinic acid reduces the electrostriction of water by Bu_4NHSO_4 . Such reduced electrostriction results in a concomitant increase in volume and this effect increases further with increasing molarities of nicotinic acid in the ternary solutions.

TABLE II. Limiting partial molar expansibilities (ϕ_E^0) for Bu_4NHSO_4 in aqueous solutions of nicotinic acid at different temperatures; standard errors are given in parentheses

c_{NA}^a mol dm ⁻³	$\phi_E^0 \times 10^4 / \text{m}^3 \text{mol}^{-1} \text{K}^{-1}$			$S_E \times 10^4 / \text{m}^3 \text{mol}^{-1} \text{K}^{-1}$			$(d\phi_E^0 / dT)_P \times 10^6$ m ³ mol ⁻¹ K ⁻²
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	
0	-3.458 (±0.001)	-3.480 (±0.001)	-3.351 (±0.001)	1.572 (±0.001)	1.543 (±0.001)	1.612 (±0.001)	-0.363 (±0.001)
0.005	-6.676 (±0.001)	-6.740 (±0.001)	-6.817 (±0.001)	11.773 (±0.001)	11.877 (±0.001)	12.025 (±0.001)	-0.700 (±0.001)
0.010	-8.058 (±0.001)	-8.153 (±0.001)	-8.231 (±0.001)	11.873 (±0.001)	12.062 (±0.001)	12.141 (±0.001)	-0.863 (±0.001)
0.015	-5.362 (±0.001)	-5.378 (±0.001)	-5.439 (±0.002)	4.139 (±0.001)	4.203 (±0.002)	4.242 (±0.001)	-0.567 (±0.001)
0.020	-5.326 (±0.001)	-5.384 (±0.002)	-5.444 (±0.001)	1.027 (±0.002)	1.089 (±0.001)	1.073 (±0.001)	-0.589 (±0.002)

^aMolarity of nicotinic acid in aqueous solutions

The partial molar volumes (ϕ_V^0) of a solute can also be explained by the simple model^{25,35} given by the relation:

$$\phi_V^0 = \phi_{\text{vw}} + \phi_{\text{void}} - \phi_S \quad (6)$$

where ϕ_{vw} , ϕ_{void} and ϕ_S are the van der Waals volumes, the volumes associated with voids or empty spaces and the shrinkage volumes due to electrostriction, respectively. Assuming the values of ϕ_{vw} and ϕ_{void} are of same magnitude in water and in aqueous nicotinic acid solutions of for the same solute, the increase in the ϕ_V^0 values and the concomitant positive $\Delta\phi_V^0$ values can be attributed to decreases in the shrinkage volumes (ϕ_S) of water by Bu_4NHSO_4 in presence of nicotinic acid. This fact suggests that Bu_4NHSO_4 has a dehydration effect on hydrated nicotinic acid. It was already reported in the literature^{36–38} that HSO_4^- readily achieves the equilibrium: $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$ in aqueous solution at low temperatures (<100 °C) under ambient pressure. According to Sharnin *et al.*³⁹ nicotinic acid exists in the zwitterionic form in aqueous solution and within the pH range of the experimental aqueous solutions, nicotinic acid remains in equi-

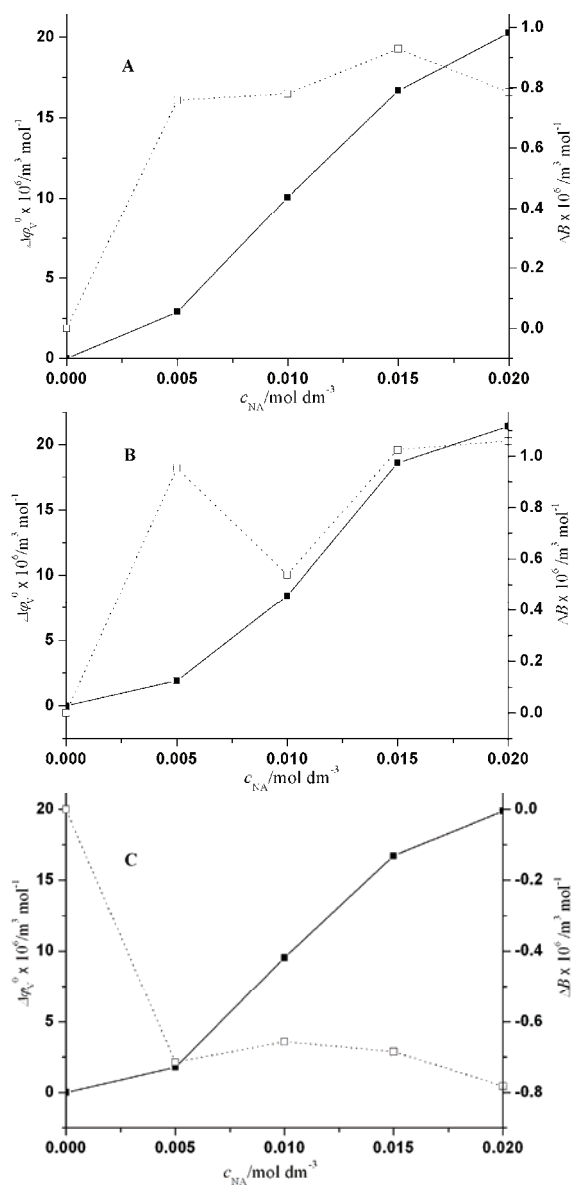


Fig. 2. Plots of partial molar volumes of transfer ($\Delta\phi_v^0$) and viscosity B -coefficients of transfer (ΔB) from water to aqueous solutions of nicotinic acid for Bu_4NHSO_4 at different temperatures: A, 298.15 K; B, 308.15 K; C, 318.15 K; $-\blacksquare-$, $\Delta\phi_v^0$; $\dots\square\dots$, ΔB .

librium with its four possible forms:⁴⁰ a positively charged form (AH_2^+), two isoelectric forms (AH^\pm and AH^0) and a negatively charged form (A^-). Changes in UV–Vis absorption spectra of nicotinic acid ($4.0 \times 10^{-5} \text{ mol dm}^{-3}$) in different aqueous solutions of Bu_4NHSO_4 and of nicotinic acid as a function of its concentration in aqueous solution of Bu_4NHSO_4 ($4.0 \times 10^{-5} \text{ mol dm}^{-3}$) at 298.15 K are shown in Figs. 3 and 4, respectively. The UV–Vis absorption spectra show

only one peak at 260 nm corresponding to an $n \rightarrow \pi^*$ transition that involves the molecular orbitals of $\equiv N$: and the pyridine ring. The UV-Vis absorption spectra also show that the intensity of this peak increases with increasing nicotinic acid concentration and decreases with increasing Bu_4NHSO_4 concentration. 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 HSO_4^- , SO_4^{2-} and HO^- , *ii*) polar $-\text{COO}^-$ group (through both the O-atoms) of zwitterionic nicotinic acid and Bu_4N^+ and H^+ ions and *iii*) ionic-hydrophobic interaction between ions of Bu_4NHSO_4 and the non polar part of zwitterionic nicotinic acid molecules. While type *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 (depicted in Fig. 5) predominate over ionic-hydrophobic interactions. This predominance of ionic group interactions reduces the electrostriction of water by Bu_4NHSO_4 and imparts positive contributions to the $\Delta\phi_V^0$ values.

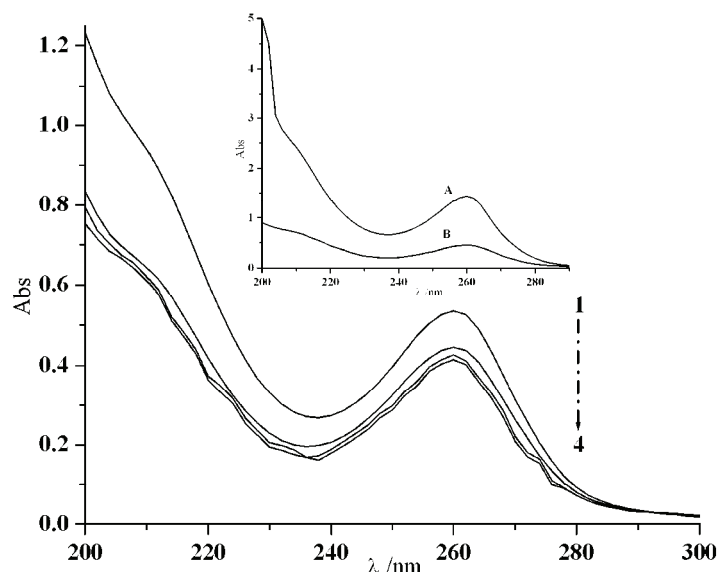


Fig. 3. Changes in the UV-Vis absorption spectra of $4.0 \times 10^{-5} \text{ mol dm}^{-3}$ nicotinic acid in ternary solutions (Bu_4NHSO_4 + nicotinic acid + H_2O) with the following molarities of Bu_4NHSO_4 : 1, $2.0 \times 10^{-5} \text{ mol dm}^{-3}$; 2, $4.0 \times 10^{-5} \text{ mol dm}^{-3}$; 3, $6.0 \times 10^{-5} \text{ mol dm}^{-3}$ and 4, $8.0 \times 10^{-5} \text{ mol dm}^{-3}$. Inset: A, $4.0 \times 10^{-5} \text{ mol dm}^{-3}$ nicotinic acid in aqueous solution; B, average spectrum of 1-4.

The viscosities (η) of the different experimental aqueous solutions were analyzed by the Jones-Dole Equation:⁴¹

$$(\eta/\eta_0 - 1)/\sqrt{c} = (\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \quad (7)$$

where $\eta_r = \eta/\eta_0$ is the relative viscosity; η_0 and η are the viscosities of solvent and solution, respectively. A and B are two adjustable parameters that are obtained by a least squares analysis and are reported in Table III. The viscosity B -coefficient⁴² reflects the effects of solute–solvent interactions on the solution viscosity and provides information about the solvation of a solute and the structure of the solvent in the local vicinity of the solute molecules. Table III shows that the viscosity B -coefficients for Bu_4NHSO_4 in the studied solvent systems were positive and thus suggest the presence of strong solute–solvent interactions in the studied solutions. These interactions further increase when both the molarity of Bu_4NHSO_4 in the ternary solutions and the temperature increase. The A -coefficients values are indicative of solute–solute or ion–ion interactions and in the present study their values support the results obtained from viscosity B -coefficients discussed earlier. Viscosity B -coefficients of transfer (ΔB) from water to aqueous solutions of nicotinic acid were determined by using the relation:^{27,33}

$$\Delta B = B [\text{Aqueous solution of nicotinic acid}] - B [\text{Water}] \quad (8)$$

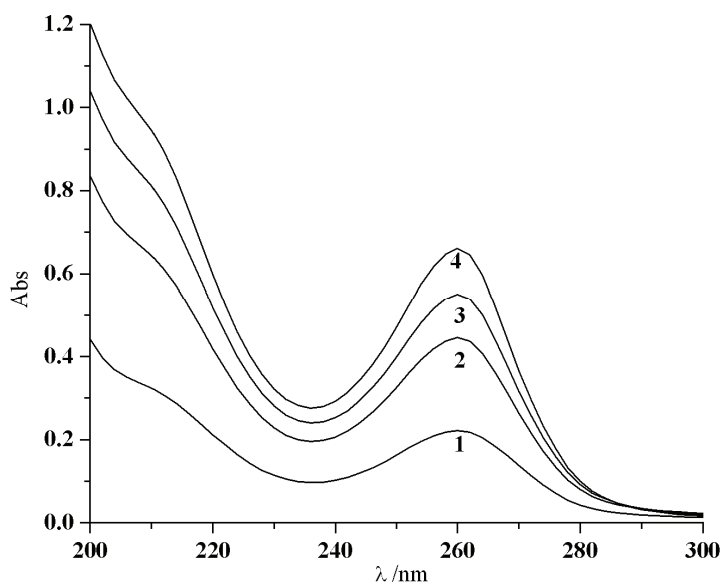


Fig. 4. Changes in the UV–Vis absorption spectra of nicotinic acid ($4.0 \times 10^{-5} \text{ mol dm}^{-3}$) in ternary solutions (Bu_4NHSO_4 + nicotinic acid + H_2O) with the following molarities of nicotinic acid: 1, $2.0 \times 10^{-5} \text{ mol dm}^{-3}$; 2, $4.0 \times 10^{-5} \text{ mol dm}^{-3}$; 3, $6.0 \times 10^{-5} \text{ mol dm}^{-3}$ and 4, $8.0 \times 10^{-5} \text{ mol dm}^{-3}$.

The ΔB values are depicted in Fig. 2 as a function of the molarity of nicotinic acid in the aqueous solutions and they support the results obtained from the $\Delta\phi_V^0$ values discussed earlier.

According to transition state theory of relative viscosity,⁴³ the contribution per mole of a solute to the free energy of activation for viscous flow of the solution ($\Delta\mu_2^{\ominus*}$) is related to the viscosity *B*-coefficients by the following relation:

$$\Delta\mu_2^{\ominus*} = \Delta\mu_1^{\ominus*} + RT(1000B + \varphi_{V,2}^0 - \varphi_{V,1}^0)/\varphi_{V,1}^0 \quad (9)$$

where $\varphi_{V,1}^0$ and $\varphi_{V,2}^0$ are the partial molar volumes of the solvent and solute, respectively. The free energy of activation of viscous flow per mole of the pure solvent or solvent mixture ($\Delta\mu_1^{\ominus*}$) is given by the relation:^{43,44}

$$\Delta\mu_1^{\ominus*} = \Delta G_1^{\ominus*} = RT \ln (\eta_0 \varphi_{V,1}^0)/hN_A \quad (10)$$

where N_A is the Avogadro number and the other symbols have their usual significances.⁴³

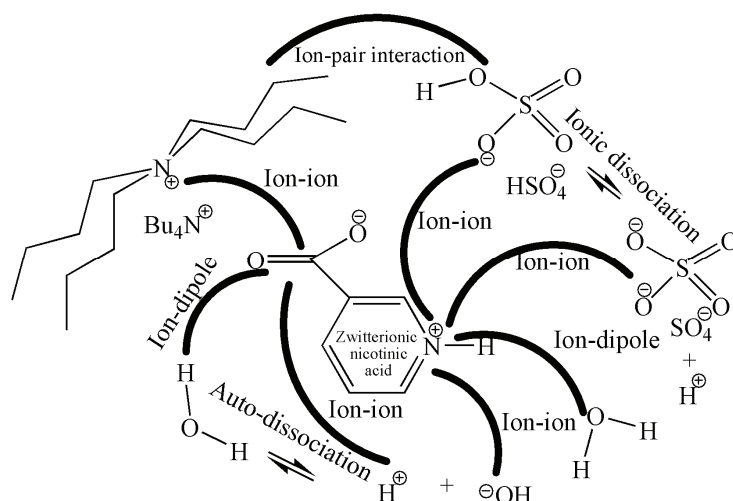


Fig. 5. Different possible ionic group interactions in aqueous solutions of nicotinic acid in presence of Bu_4NHSO_4 .

The entropy of activation for viscous flow per mole of the solute in the ternary solutions ($\Delta S_2^{\ominus*}$) can be obtained from the negative slope of the plots of $\Delta\mu_2^{\ominus*}$ against *T*:

$$\Delta S_2^{\ominus*} = -d(\Delta\mu_2^{\ominus*})/dT \quad (11)$$

and the activation enthalpy for viscous flow ($\Delta H_2^{\ominus*}$) can be obtained from the relation:

$$\Delta H_2^{\ominus*} = \Delta\mu_2^{\ominus*} + T\Delta S_2^{\ominus*} \quad (12)$$

TABLE III. Values of viscosity A - and B -coefficients for Bu_4NHSO_4 in aqueous solutions of nicotinic acid at different temperatures

Viscosity coefficients	T / K		
	298.15	308.15	318.15
$c_{\text{NA}}^{\text{a}} = 0.000$			
$A \times 10^{-6} / \text{m}^{3/2} \text{mol}^{-1/2}$	-0.145	-0.087	-0.142
$B \times 10^{-6} / \text{m}^3 \text{mol}^{-1}$	1.004	1.248	1.446
$\sigma \times 10^{-6} / \text{m}^{3/2} \text{mol}^{-1/2}$	0.001	0.001	0.002
$c_{\text{NA}} = 0.005$			
$A \times 10^{-6} / \text{m}^{3/2} \text{mol}^{-1/2}$	-0.096	-0.087	0.212
$B \times 10^{-6} / \text{m}^3 \text{mol}^{-1}$	1.762	2.201	0.731
$\sigma \times 10^{-6} / \text{m}^{3/2} \text{mol}^{-1/2}$	0.002	0.001	0.001
$c_{\text{NA}} = 0.010$			
$A \times 10^{-6} / \text{m}^{3/2} \text{mol}^{-1/2}$	-0.092	-0.017	0.287
$B \times 10^{-6} / \text{m}^3 \text{mol}^{-1}$	1.784	1.787	0.789
$\sigma \times 10^{-6} / \text{m}^{3/2} \text{mol}^{-1/2}$	0.001	0.001	0.002
$c_{\text{NA}} = 0.015$			
$A \times 10^{-6} / \text{m}^{3/2} \text{mol}^{-1/2}$	-0.099	-0.238	0.132
$B \times 10^{-6} / \text{m}^3 \text{mol}^{-1}$	1.933	2.273	0.761
$\sigma \times 10^{-6} / \text{m}^{3/2} \text{mol}^{-1/2}$	0.001	0.004	0.001
$c_{\text{NA}} = 0.020$			
$A \times 10^{-6} / \text{m}^{3/2} \text{mol}^{-1/2}$	-0.078	-0.179	0.189
$B \times 10^{-6} / \text{m}^3 \text{mol}^{-1}$	1.778	2.307	0.664
$\sigma \times 10^{-6} / \text{m}^{3/2} \text{mol}^{-1/2}$	0.001	0.001	0.001

^aMolarity of nicotinic acid in water

The parameters ($\varphi_{V,2}^0 - \varphi_{V,1}^0$), $\Delta\mu_1^{\ominus*}$, $\Delta\mu_2^{\ominus*}$, $\Delta H_2^{\ominus*}$ and $T\Delta S_2^{\ominus*}$ are reported in Table IV, from which it can be seen that the $\Delta\mu_1^{\ominus*}$ values are almost invariant of the solvent composition and temperature, implying also that the $\Delta\mu_2^{\ominus*}$ values are dependent mainly on the viscosity B -coefficient and the ($\varphi_{V,2}^0 - \varphi_{V,1}^0$) deviations. The $\Delta\mu_2^{\ominus*}$ values contain the change in the free energy of activation of the solute in presence of solvent as well as contributions from the movement of the solute molecules. The $\Delta\mu_2^{\ominus*}$ values were found to be positive at all the experimental temperatures and decreased with increasing temperature and increased with increasing nicotinic acid concentration in the ternary solutions. Such trends suggest that the viscous flow process becomes more difficult with increasing nicotinic acid concentration in the solutions but becomes favourable at higher temperatures. Hence the formation of the transition state becomes less favourable in the presence of nicotinic acid but becomes somewhat more favourable at higher temperatures. The ($\Delta\mu_2^{\ominus*} - \Delta\mu_1^{\ominus*}$) deviations reflect the change in the activation energy per mole of solute when one mole of the solvent is replaced by one mole of the solute at infinite dilution. Hence according to Feakins *et al.*,⁴³ for solutes with positive $\Delta S_2^{\ominus*}$, $\Delta H_2^{\ominus*}$ and viscosity B -coefficients, $\Delta\mu_2^{\ominus*} > \Delta\mu_1^{\ominus*}$ indicates stronger solute-solvent interactions and thus

suggests that the formation of the transition state is accompanied by the rupture and distortion of the intermolecular forces in the solvent structure.⁴³ The greater the value of $\Delta\mu_2^{\ominus*}$, the greater is the structure-promoting tendency of a solute and the higher values of $\Delta\mu_2^{\ominus*}$ for Bu₄NHSO₄ in the ternary solutions when compared to those in the aqueous binary solutions suggest that Bu₄NHSO₄ is a better structure promoter for the ternary mixtures than for aqueous binary solutions. Although a detailed mechanism for the formation of such a transition state cannot be easily advanced, it may be suggested that the viscous process is endothermic (positive $\Delta H_2^{\ominus*}$ values) and the slip-plane is in an ordered state (positive $\Delta S_2^{\ominus*}$ values) and involves a centro-symmetric region.^{43,44}

TABLE IV. Values of $(\varphi_{V,2}^0 - \varphi_{V,1}^0) \times 10^6 / \text{m}^3 \text{mol}^{-1}$, $\Delta\mu_1^{\ominus*}$, $\Delta\mu_2^{\ominus*}$, $\Delta H_2^{\ominus*}$ and $T\Delta S_2^{\ominus*}$ for Bu₄NHSO₄ in different aqueous solutions of nicotinic acid at different temperatures

Parameters	T / K		
	298.15	308.15	318.15
$c_{\text{NA}}^{\text{a}} = 0.000$			
$(\varphi_{V,2}^0 - \varphi_{V,1}^0) \times 10^6 / \text{m}^3 \text{mol}^{-1}$	281.61	278.79	276.47
$\Delta\mu_1^{\ominus*} / \text{kJ mol}^{-1}$	9.17	8.95	8.76
$\Delta\mu_2^{\ominus*} / \text{kJ mol}^{-1}$	185.01	223.53	256.79
$T\Delta S^{\ominus*} / \text{kJ mol}^{-1}$	-1070.04	-1105.93	-1141.82
$\Delta H^{\ominus*} / \text{kJ mol}^{-1}$	-885.03	-882.40	-885.03
$c_{\text{NA}} = 0.005$			
$(\varphi_{V,2}^0 - \varphi_{V,1}^0) \times 10^6 / \text{m}^3 \text{mol}^{-1}$	283.77	280.73	278.24
$\Delta\mu_1^{\ominus*} / \text{kJ mol}^{-1}$	9.14	8.93	8.68
$\Delta\mu_2^{\ominus*} / \text{kJ mol}^{-1}$	288.54	358.15	153.94
$T\Delta S^{\ominus*} / \text{kJ mol}^{-1}$	2006.50	2073.80	2141.10
$\Delta H^{\ominus*} / \text{kJ mol}^{-1}$	2295.04	2431.95	2295.04
$c_{\text{NA}} = 0.010$			
$(\varphi_{V,2}^0 - \varphi_{V,1}^0) \times 10^6 / \text{m}^3 \text{mol}^{-1}$	291.65	287.25	286.01
$\Delta\mu_1^{\ominus*} / \text{kJ mol}^{-1}$	9.24	8.98	8.72
$\Delta\mu_2^{\ominus*} / \text{kJ mol}^{-1}$	292.77	300.94	163.48
$T\Delta S^{\ominus*} / \text{kJ mol}^{-1}$	1927.46	1992.11	2056.76
$\Delta H^{\ominus*} / \text{kJ mol}^{-1}$	2220.24	2293.05	2220.24
$c_{\text{NA}} = 0.015$			
$(\varphi_{V,2}^0 - \varphi_{V,1}^0) \times 10^6 / \text{m}^3 \text{mol}^{-1}$	298.28	297.41	293.18
$\Delta\mu_1^{\ominus*} / \text{kJ mol}^{-1}$	9.28	9.06	8.82
$\Delta\mu_2^{\ominus*} / \text{kJ mol}^{-1}$	314.16	370.98	160.62
$T\Delta S^{\ominus*} / \text{kJ mol}^{-1}$	2288.89	2365.67	2442.44
$\Delta H^{\ominus*} / \text{kJ mol}^{-1}$	2603.06	2736.65	2603.06
$c_{\text{NA}} = 0.020$			
$(\varphi_{V,2}^0 - \varphi_{V,1}^0) \times 10^6 / \text{m}^3 \text{mol}^{-1}$	301.89	300.24	296.37
$\Delta\mu_1^{\ominus*} / \text{kJ mol}^{-1}$	9.31	9.15	8.89
$\Delta\mu_2^{\ominus*} / \text{kJ mol}^{-1}$	293.64	376.45	147.23
$T\Delta S^{\ominus*} / \text{kJ mol}^{-1}$	2182.68	2255.89	2329.09
$\Delta H^{\ominus*} / \text{kJ mol}^{-1}$	2476.33	2632.34	2476.33

^aMolarity of nicotinic acid in water

CONCLUSIONS

In summary, the partial molar volumes (φ_V^0) and viscosity B -coefficients of Bu_4NHSO_4 in aqueous solutions of nicotinic acid indicate the presence of strong solute–solvent interactions and such interactions further strengthen at higher nicotinic acid concentrations but decrease at higher temperatures. These facts may be attributed to the predominance of ion–hydrophilic and hydrophilic–hydrophilic group interactions over ion–hydrophobic, hydrophobic–hydrophobic and hydrophilic–hydrophobic interactions. Moreover, the trends in $(d\varphi_E^0/dT)_P$ and $\Delta\mu_2^{\ominus*}$ for Bu_4NHSO_4 in aqueous solutions of nicotinic acid suggest that Bu_4NHSO_4 is a net structure promoter in the studied aqueous solutions and it has a dehydration effect on hydrated nicotinic acid.

SUPPLEMENTARY MATERIAL

The physical properties of different aqueous solutions of nicotinic acid and experimental densities, viscosities along with derived parameters at the experimental temperatures (listed in Tables S-I and S-II) are available electronically from <http://www.shd.org.rs/JSCS/> or from the author on request.

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ИЗВОД

ТЕРМОДИНАМИКА ВОДЕНОГ РАСТВОРА НИКОТИНСКЕ КИСЕЛИНЕ У ПРИСУСТВУ ТЕТРАБУТИЛАМОНИЈУМ-ХИДРОГЕН-СУЛФАТА

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У овом раду истражен је утицај тетрабутиламонијум-хидроген-сулфата (Bu_4NHSO_4) на интеракције растворена супстанца–растворена супстанца и растворена супстанца–растварач у воденим растворима никотинске киселине, користећи привидне моларне запремине (φ_B), стандардне парцијалне моларне запремине (φ_B^0) и B -кофицијенте на 298,15, 308,15 и 318,15 К и на атмосферском притиску. Ове интеракције су додатно дискутоване преко јон–дипол, хидрофобно–хидрофобних и хидрофилно–хидрофобних група интеракција. Активациони параметри вискозног тока за Bu_4NHSO_4 у воденим растворима никотинске киселине дискутовани су користећи теорију прелазног стања. Укупни резултати су показали да су јон–хидрофилне и хидрофилно–хидрофилне групе интеракција доминантне у воденим растворима никотинске киселине и да Bu_4NHSO_4 има дехидратациони ефекат на хидратисану никотинску киселину.

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