Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.yu • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 73 (12) 1235–1246 (2008) UDC 547.581.2+547.831–32:532.13:541.25
JSCS–3802 *Original scientific paper*

Study of solute–solvent interactions of nicotinic acid and benzoic acid in methanol and its binary solvent systems

MAHENDRA NATH ROY*, LOVELY SARKAR and BIPUL KUMAR SARKAR

Department of Chemistry, University of North Bengal, Darjeeling-734013, India

(Received 22 November 2007, revised 23 April 2008)

Abstract: The apparent molar volumes, ϕ_V, and viscosity B-coefficients, B, for nicotinic acid (NA) and benzoic acid (BA) in mixed solvents containing 10, 20, 30 mass % of *n*-amyl alcohol (*n*-AmOH) or isoamyl alcohol (i-AmOH) in methanol and in pure methanol (MeOH) were determined from the solution density and viscosity measurements at 298.15 K as function of concentrations of NA and BA. These results were, in conjunction with the results obtained in pure methanol, used to deduce the partial molar volumes of transfer, $\Delta\phi_V^0$, and viscosity B-coefficients of transfer, ΔB, for NA and BA from methanol to different mixed methanol solvents, in order to rationalize various interactions in the ternary solutions. An increase in the transfer properties of NA and BA with increasing mass % of *n*-AmOH and i-AmOH in methanol was observed and explained by the effect of structural changes and preferential solvation. Also, the free energies of viscous flow, $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$, per mole of solvent and solute, respectively, were calculated and analyzed on the basis of the transition state theory of relative viscosity.

Keywords: apparent molar volumes; viscosity B-coefficients; nicotinic acid; benzoic acid; solute–solvent interactions.

INTRODUCTION

Many enzymes require a non-protein co-factor for their catalytic activities. Vitamins are essential precursors for various co-enzymes. These co-enzymes are therefore required in almost all metabolic pathways.[1] Nicotinic acid (pyridine-3-carboxylic acid) is an essential micro-nutrient, a reactive moiety of the co-enzyme nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP).[2] NAD is involved in the catabolism of carbohydrates, fats, and proteins with simultaneous energy production. The NADP functions consist especially of anabolic processes of fatty acids and cholesterol synthesis.[3–5] Sometimes nicotinic acid is referred to as nothing more than vitamin PP (Pellagra Preventive),[2,6,7] since its deficiency in human diet causes pellagra.

---

* Corresponding author. E-mail: mahendraroy2002@yahoo.co.in
doi: 10.2298/JSC0812235R

Benzoic acid is a good adsorbing reagent for insulin[8,9] and is used in medicine as a urinary antiseptic and in the vapor form for disinfecting bronchial tubes.[10] This acid also finds many important applications in the manufacture of alkyl resins, plasticizers and pharmaceuticals.[11]

Volumetric properties of the binary or ternary mixtures have recently been studied extensively. In particular, much effort has gone into the determination of partial molar volumes at infinite dilution, as they are the key to solvation phenomena. Although there are studies on various properties of nicotinic acid (NA) [7,12–17,20] and benzoic acid (BA) [9,18–22] in the literature, studies on partial molar volumes and viscosities of these compounds in mixed solvent systems are still scarce. Hence in this study an attempt was made to study these properties for NA and BA in binary mixtures of methanol with *n*-amyl (*n*-AmOH) and isoamyl alcohol (i-AmOH) at 298.15 K to unravel the various interactions prevailing in the ternary systems under investigation.

EXPERIMENTAL

Nicotinic acid and benzoic acid were purchased from the Sigma Chemical Company, USA and used as received. Their purity as supplied by the vendor was 99 %. A. R. Grade methanol, *n*-amyl alcohol and isoamyl alcohol were purchased from Merck, India. The purity of the alcohols as given by the vendor was also 99 %. The purification of methanol was cited in an earlier paper.[23] Both *n*-AmOH and i-AmOH were dried with anhydrous K_2CO_3 and fractionally distilled. The middle fraction was collected and kept free from humidity with 3 Å molecular sieves.[24] The physical properties of the different pure liquids and mixed methanol solvents are listed in Table I.

TABLE I. Physical properties of different pure and mixed methanol solvents at 298.15 K

Solvent	ρ / g cm^{-3}		η / mPa s	
	Experimental	Literature	Experimental	Literature
Methanol	0.7869	0.7869[26]	0.547	0.547[26]
n-Amyl alcohol	0.8115	0.8110[24]	3.350	3.350[24]
Isoamyl alcohol	0.8071	0.8071[24]	3.475	3.480[24]
10 mass % of *n*-amyl alcohol	0.7883	–	0.569	–
20 mass % of *n*-amyl alcohol	0.7898	–	0.645	–
30 mass % of *n*-amyl alcohol	0.7923	–	0.732	–
10 mass % of isoamyl alcohol	0.7882	–	0.574	–
20 mass % of isoamyl alcohol	0.7900	–	0.648	–
30 mass % of isoamyl alcohol	0.7911	–	0.720	–

Stock solutions of NA and BA in different mixed methanol solvents and in pure methanol were prepared by mass and the working solutions were prepared by mass dilution. The conversion of molality into molarity was accomplished using the experimental density values. Great care was taken in minimizing evaporation losses and preventing moisture pick-up. The uncertainty in the molarity of the nicotinamide solutions was evaluated to ±0.0001 mol dm^{-3}.

The densities were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water and purified benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at ±0.01 K of the desired temperature. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed. The mass measurements accurate to ±0.01 mg were made on a digital electronic analytical balance (Mettler Toledo, AG 285, Switzerland). The total uncertainty in density was estimated to be ±0.0001 g cm^{-3} and that of the temperature ±0.01 K.

The viscosity was measured by means of a suspended Ubbelohde type viscometer, which had been thoroughly cleaned, dried and calibrated at 298.15 K with triply distilled water and purified methanol. It was filled with experimental liquid and placed vertically in a glass sided thermostat bath maintained constant to ±0.01 K. The efflux times of flow of the liquids were recorded with a stopwatch correct to ±0.1 s. The viscosity of a solution, η, is given by the following equation:

$$\eta = (kt - \frac{L}{t})\rho \tag{1}$$

where k and L are viscometer constants and t and ρ are the efflux time of flow and the density of the experimental liquid, respectively. The uncertainty in the viscosity measurements was within ±0.003 mPa s. Details of the methods and techniques of density and viscosity measurements were described elsewhere.[25,26] The experimental values of concentrations c, densities viscosities, and derived parameters of the studied ternary solutions at 298.15 K are reported in Table II.

TABLE II. Concetration, density, viscosity, apparent molar volume, ϕ_V, and $(\eta_r - 1)/\sqrt{c}$ for nicotinic acid and benzoic acid in methanol and mixed methanol solvents at 298.15 K

c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s	ϕ_V / cm^3 mol^{-1}	$(\eta_r - 1)/\sqrt{c}$
		Nicotinic acid		
		In methanol		
0.0197	0.7880	0.551	88.32	0.0521
0.0320	0.7886	0.553	87.09	0.0613
0.0517	0.7898	0.559	85.57	0.0965
0.0690	0.7908	0.563	84.28	0.1113
0.0779	0.7913	0.565	83.91	0.1179
0.0821	0.7916	0.566	83.70	0.1212
		In 10 mass % of *n*-AmOH + MeOH		
0.0200	0.7893	0.575	93.55	0.0746
0.0325	0.7900	0.579	92.20	0.0975
0.0524	0.7910	0.584	90.45	0.1152
0.0699	0.7920	0.590	89.08	0.1396
0.0874	0.7930	0.596	87.95	0.1605
0.0901	0.7932	0.597	87.80	0.1639
		In 20 mass % of *n*-AmOH + MeOH		
0.0200	0.7908	0.647	92.90	0.0219
0.0325	0.7915	0.651	90.04	0.0516
0.0524	0.7927	0.656	86.29	0.0745
0.0699	0.7938	0.662	83.76	0.0996
0.0874	0.7949	0.668	81.67	0.1206
0.0900	0.7951	0.669	81.31	0.1240

TABLE II. Continued

c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s	ϕ_V / cm^3 mol^{-1}	$(\eta_r - 1)/\sqrt{c}$
Nicotinic acid				
In 30 mass % of *n*-AmOH + MeOH				
0.0199	0.7931	0.737	104.64	0.0484
0.0325	0.7937	0.742	101.01	0.0758
0.0524	0.7948	0.752	95.17	0.1194
0.0698	0.7957	0.760	93.90	0.1448
0.0812	0.7964	0.765	91.65	0.1582
0.0815	0.7964	0.765	91.89	0.1579
In 10 mass % of i-AmOH + MeOH				
0.0198	0.7893	0.579	83.32	0.0619
0.0321	0.7900	0.582	83.12	0.0778
0.0519	0.7912	0.589	82.85	0.1147
0.0692	0.7922	0.595	82.68	0.1391
0.0865	0.7932	0.601	82.50	0.1599
0.0878	0.7933	0.601	82.49	0.1587
In 20 mass % of i-AmOH + MeOH				
0.0197	0.7909	0.651	98.01	0.0330
0.0321	0.7916	0.655	92.74	0.0603
0.0518	0.7927	0.662	89.86	0.0949
0.0690	0.7938	0.668	86.12	0.1175
0.0780	0.7943	0.671	86.05	0.1271
0.0822	0.7946	0.673	85.00	0.1346
In 30 mass % of i-AmOH + MeOH				
0.0197	0.7920	0.729	97.87	0.0891
0.0321	0.7927	0.738	92.61	0.1395
0.0518	0.7941	0.754	82.41	0.2075
0.0691	0.7954	0.765	76.96	0.2378
0.0839	0.7967	0.777	72.00	0.2733
0.0849	0.7967	0.778	71.70	0.2765
Benzoic acid				
In methanol				
0.0200	0.7885	0.553	88.60	0.0776
0.0320	0.7890	0.556	88.45	0.0920
0.0519	0.7898	0.560	88.25	0.1043
0.0719	0.7907	0.564	88.11	0.1159
0.0878	0.7915	0.567	88.01	0.1234
0.0999	0.7919	0.569	87.96	0.1272
In 10 mass % of *n*-AmOH + MeOH				
0.0204	0.7894	0.573	86.51	0.0492
0.0325	0.7901	0.576	84.66	0.0682
0.0528	0.7913	0.580	82.84	0.0841
0.0732	0.7926	0.585	80.40	0.1039
0.0894	0.7936	0.588	79.71	0.1117
0.0996	0.7943	0.591	78.50	0.1225

TABLE II. Continued

c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s	ϕ_V / cm^3 mol^{-1}	$(\eta_r - 1)/\sqrt{c}$
Benzoic acid				
In 20 mass % of *n*-AmOH + MeOH				
0.0200	0.7906	0.648	101.50	0.0329
0.0320	0.7912	0.650	99.46	0.0433
0.0521	0.7922	0.656	97.10	0.0747
0.0722	0.7932	0.661	95.06	0.0923
0.0883	0.7941	0.665	93.60	0.1043
0.0983	0.7946	0.668	92.79	0.1137
In 30 mass % of *n*-AmOH + MeOH				
0.0200	0.7931	0.734	103.65	0.0193
0.0320	0.7938	0.738	100.59	0.0458
0.0520	0.7947	0.743	97.13	0.0659
0.0719	0.7957	0.749	94.19	0.0866
0.0879	0.7968	0.755	91.73	0.1060
0.0999	0.7971	0.759	90.57	0.1167
In 10 mass % of i-AmOH + MeOH				
0.0199	0.7891	0.577	95.84	0.0370
0.0318	0.7897	0.579	94.86	0.0488
0.0518	0.7907	0.583	93.57	0.0689
0.0716	0.7917	0.587	92.55	0.0846
0.0876	0.7926	0.590	91.67	0.0942
0.0995	0.7932	0.593	91.14	0.1049
In 20 mass % of i-AmOH + MeOH				
0.0199	0.7910	0.650	104.64	0.0219
0.0318	0.7914	0.652	102.54	0.0346
0.0516	0.7924	0.657	99.67	0.0611
0.0716	0.7933	0.662	97.32	0.0807
0.0874	0.7941	0.666	95.69	0.0940
0.0994	0.7945	0.670	94.75	0.1077
In 30 mass % of i-AmOH + MeOH				
0.0199	0.7918	0.725	109.90	0.0492
0.0319	0.7923	0.729	106.82	0.0700
0.0517	0.7932	0.736	103.02	0.0977
0.0716	0.7944	0.743	96.11	0.1194
0.0875	0.7950	0.749	98.03	0.1362
0.0994	0.7956	0.755	97.14	0.1542

RESULT AND DISCUSSION

For the analysis of the solvation state of NA and BA in mixed methanol solvents and the interactions existing between different components in the studied solutions, the apparent molar volumes (ϕ_V) were determined from the solution densities using the following equation:[25,27]

$$\phi_V = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{\rho_0 c} \tag{2}$$

where M is the molar mass of the solute, c is the concetration of the solution and ρ_0 and ρ are the densities of the solvent and solution, respectively. The experimental ϕ_V values were fitted to Masson Equation:[28]

$$\phi_V = \phi_V^0 + S_V^* \sqrt{c} \tag{3}$$

where ϕ_V^0 is the partial molar volume at infinite dilution and S_V^* is the experimental slope. The ϕ_V^0 values were determined by fitting the dilute data ($c < 0.1$) to Eq. (3) using the least-square fit. The values of ϕ_V^0 and S_V^* at the experimental temperature are reported in Table III. The estimated uncertainties in ϕ_V^0 are equal to standard deviation, σ, the root mean square of the deviations between the experimental and calculated ϕ_V for each data point. Table III shows that the ϕ_V^0 values are generally positive and increase with increasing amount of *n*-AMOH/i-AmOH in the ternary solutions. This indicates the presence of strong solute–solvent interactions which are further strengthened at higher amounts of *n*-AMOH/i-AmOH in the ternary solutions. Also, the ϕ_V^0 values are comparatively more positive for the solutions containing BA than for those containing NA. This is a clear manifestation that solute–solvent interactions are more prominent in BA solutions. The negative S_V^* values indicated that the investigated solutions are characterized by weak solute–solute interactions.

TABLE III. Limiting partial molar volume (ϕ_V^0) and experimental slope (S_V^*) for nicotinic acid and benzoic acid in methanol and different mixed methanol solvents with standard deviations (σ) at 298.15 K

Solute	Solvent	ϕ_V^0 / cm^3 mol^{-1}	S_V^* / cm^2 dm$^{1/2}$ mol$^{-3/2}$	σ
NA	MeOH	92.81	–31.99	0.01
	10 mass % of *n*-AmOH+MeOH	98.74	–36.46	0.01
	20 mass % of *n*-AmOH+MeOH	103.17	–73.07	0.01
	30 mass % of *n*-AmOH+MeOH	116.75	–88.25	0.22
	10 mass % of i-AmOH+MeOH	84.07	–5.35	0.02
	20 mass % of i-AmOH+MeOH	108.99	–84.42	1.74
	30 mass % of i-AmOH+MeOH	123.23	–175.74	0.45
BA	MeOH	89.11	-3.70	0.01
	10 mass % of *n*-AmOH+MeOH	92.97	–45.35	1.21
	20 mass % of *n*-AmOH+MeOH	108.55	–50.28	0.02
	30 mass % of *n*-AmOH+MeOH	114.16	–74.96	0.02
	10 mass % of i-AmOH+MeOH	99.66	–26.87	0.01
	20 mass % of i-AmOH+MeOH	112.73	–57.38	0.01
	30 mass % of i-AmOH+MeOH	120.69	–79.33	0.02

Partial molar volumes of transfer from methanol to different mixed methanol solvents, $\Delta\phi_V^0$, were determined using the relation:[29,30]

$$\Delta\phi_V^0 = \phi_V^0\,(\text{mixed methanol solvent}) - \phi_V^0\,(\text{methanol}) \tag{4}$$

The $\Delta\phi_V^0$ value is, by definition, free from solute–solute interactions and therefore provides information regarding solute–co-solute interactions.[29] Alcohols are characterized by the presence of extensive intermolecular hydrogen bonding in the pure state,[31] as well as in their mixtures. However, the strength of hydrogen bonding depends on the position of the –OH group and molecular shape. Due to the branched structure of i-AmOH, intermolecular hydrogen bonding is less[32,33] in i-AmOH + MeOH mixtures than in the *n*-AmOH + MeOH system. This fact may also be due to the order of the +I-effect: MeOH < *n*-AmOH < < i-AmOH and thereby decreasing the polarity of the alcoholic O–H bonds. This decreased polarity of the alcoholic O–H bonds decreases the degree of intermolecular hydrogen bonding in the mixtures but increases the solvation of the studied solutes, predominantly by hydrophobic–hydrophobic group interactions.[34] As can be seen from Table IV, the value of $\Delta\phi_V^0$ is positive and increases monotonically with the amount of *n*-AmOH/i-AmOH in the ternary mixtures, indicating increased solute–solvents interactions in the mixed methanol solvents. Also, it is evident that this increasing trend is, on average, greater for the i-AmOH + methanol system than for the *n*-AmOH + methanol system. This suggests that NA and BA are preferentially more solvated by *n*-AmOH/i-AmOH than by methanol and the branched structure of i-AmOH renders it a more efficient solvent for the studied solutes. Also, the $\Delta\phi_V^0$ values are generally more positive for mixtures containing BA, *i.e.*, the solute–solvent interactions are comparatively more prominent for the BA mixtures than for the NA mixtures. This may be attributed to their structural difference and, inasmuch as the local structure in solutions depends on the forces between molecules and on the form and volume of the molecules, it will change with the composition. The $\Delta\phi_V^0$ values are depicted graphically in Figs. 1 and 2 as a function of mass % of *n*-AmOH/i-AmOH in the solutions for the studied solutes at 298.15 K.

A perusal of Table V shows that the values of the *A* coefficient are generally negative for all the investigated solutions at the experimental temperature. These results indicate the presence of weak solute–solute interactions and that these interactions further decrease with increasing mass % of *n*-AmOH/i-AmOH in the solutions. The viscosity B-coefficient[36] reflects the effects of solute–solvent interactions on the solution viscosity. Table V illustrates that the values of the viscosity B-coefficient for selected solutes in the studied solvent systems are positive, thereby suggesting the presence of strong solute–solvent interactions and these interactions are further strengthened with increasing mass % of *n*-AmOH/i-AmOH in the ternary solutions.

The viscosity B-coefficients of transfer (ΔB) from methanol to different mixed methanol solvents were determined using the relation:[29,30]

$$\Delta B = B(\text{mixed methanol solvent}) - B(\text{methanol}) \tag{6}$$

The ΔB values, shown in Table IV, and depicted graphically in Figs. 1 and 2 as a function of mass % of *n*-AmOH/i-AmOH in solutions at 298.15 K, support the results obtained from the $\Delta\phi_V^0$ values discussed above.

TABLE IV. Values of $\Delta\phi_V^0$ and ΔB of transfer from methanol to different mixed methanol solvents for NA and BA at 298.15 K. The viscosity data of the studied non-aqueous solutions of NA and BA were analyzed using the Jones–Dole Equation:[35]

$$(\frac{\eta}{\eta_0} - 1)c^{-1/2} = (\eta_r - 1)c^{-1/2} = A + Bc^{1/2} \tag{5}$$

where $\eta_r = \eta/\eta_0$; η_0 and η are the viscosities of the solvent and solution, respectively. *A* and *B* are constants estimated by the least-squares method and reported in Table V

Solute	Solvent	$\Delta\phi_V^0$ / cm^3 mol^{-1}	ΔB / cm^3 mol^{-1}
NA	10 mass % of *n*-AmOH	5.93	0.052
	20 mass % of *n*-AmOH	10.36	0.127
	30 mass % of *n*-AmOH	23.94	0.270
	10 mass % of i-AmOH	–8.74	0.152
	20 mass % of i-AmOH	16.18	0.183
	30 mass % of i-AmOH	30.42	0.721
BA	10 mass % of *n*-AmOH	3.86	0.127
	20 mass % of *n*-AmOH	19.44	0.202
	30 mass % of *n*-AmOH	25.05	0.259
	10 mass % of i-AmOH	10.55	0.106
	20 mass % of i-AmOH	23.62	0.213
	30 mass % of i-AmOH	31.58	0.304

TABLE V. Values of viscosity *A* and *B* coefficients with standard errors in parenthesis for NA and BA in methanol and different mixed methanol solvents at 298.15 K

Solute	Solvent	*A* / cm$^{3/2}$ mol$^{-1/2}$	*B* / cm^3 mol^{-1}
NA	MeOH	–0.022 (±0.007)	0.502 (±0.031)
	10 mass % of *n*-AmOH	–0.005 (±0.011)	0.554 (±0.030)
	20 mass % of *n*-AmOH	–0.066 (±0.006)	0.629 (±0.022)
	30 mass % of *n*-AmOH	–0.061 (±0.002)	0.772 (±0.007)
	10 mass % of i-AmOH	–0.034 (±0.006)	0.654 (±0.010)
	20 mass % of i-AmOH	–0.063 (±0.004)	0.685 (±0.015)
	30 mass % of i-AmOH	–0.080 (±0.007)	1.223 (±0.018)
BA	MeOH	0.040(±0.000)	0.281 (±0.001)
	10 mass % of *n*-AmOH	–0.008(±0.007)	0.408 (±0.015)
	20 mass % of *n*-AmOH	–0.038(±0.001)	0.483 (±0.013)
	30 mass % of *n*-AmOH	–0.055(±0.002)	0.540 (±0.007)
	10 mass % of i-AmOH	–0.019(±0.001)	0.387 (±0.002)
	20 mass % of i-AmOH	–0.051(±0.006)	0.494 (±0.017)
	30 mass % of i-AmOH	–0.035(±0.012)	0.585 (±0.040)

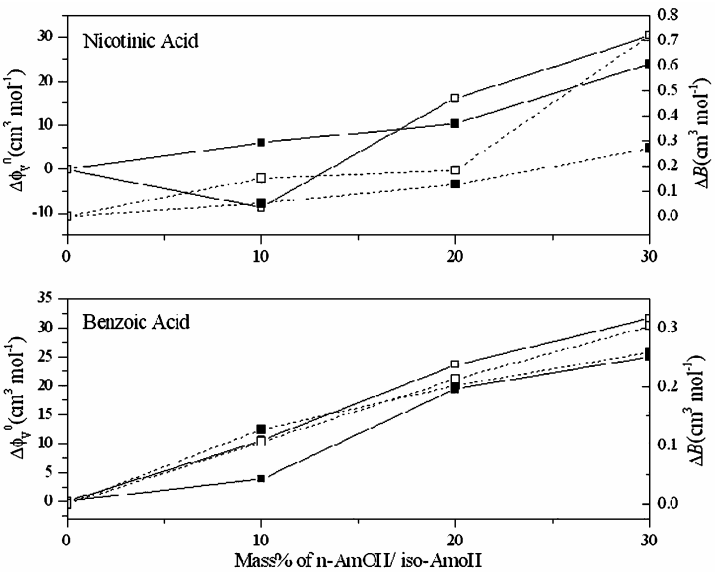

Fig. 1. Plots of partial molar volume of transfer, $\Delta\phi_V^0$, and viscosity B-coefficient of transfer, ΔB, from methanol to methanol + *n*-AmOH (■)/i-AmOH (□) solvents for nicotinic acid and benzoic acid at 298.15 K; Solid and dotted lines are for $\Delta\phi_V^0$ and ΔB, respectively.

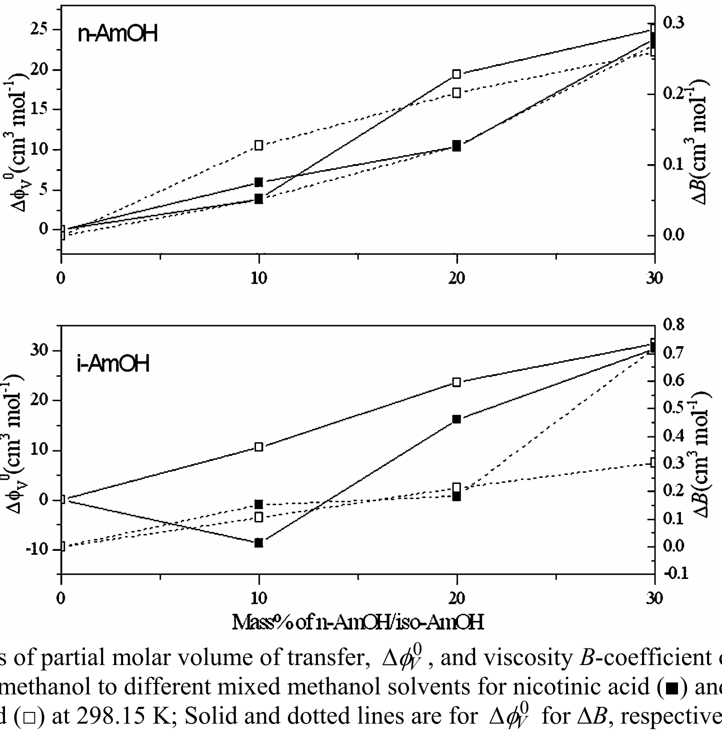

Fig. 2. Plots of partial molar volume of transfer, $\Delta\phi_V^0$, and viscosity *B*-coefficient of transfer, ΔB, from methanol to different mixed methanol solvents for nicotinic acid (■) and benzoic acid (□) at 298.15 K; Solid and dotted lines are for $\Delta\phi_V^0$ for ΔB, respectively.

The viscosity data were also analyzed on the basis of the transition state theory of relative viscosity as suggested by Feakings *et al.*[37] using the following equation:

$$\Delta\mu_2^{0\neq} = \Delta\mu_2^{0\neq} + \frac{RT(1000B + \overline{V}_2^0 - \overline{V}_1^0)}{\overline{V}_1^0} \tag{7}$$

where $\Delta\mu_2^{0\neq}$ is the contribution per mole of the solute to the free energy of activation of viscous flow of the solutions. $\overline{V}_1^0$ and $\overline{V}_2^0$ are the partial molar volumes of the solvent and solute, respectively. $\Delta\mu_2^{0\neq}$ of the solutions was determined from the above relation. The free energy of activation of viscous flow for the pure solvent/solvent mixture, $\Delta\mu_1^{0\neq}$, is given by the relation:[37,38]

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln\left(\frac{\eta_0\overline{V}_1^0}{hN_A}\right) \tag{8}$$

where N_A is the Avogadro constant, h the Planck constant, η_0 the viscosity of the solvent, R the gas constant and T the absolute temperature. The values of the parameters $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ are given in Table VI. They show that $\Delta\mu_1^{0\neq}$ is almost constant at all the solvent compositions, implying that $\Delta\mu_2^{0\neq}$ is dependent mainly on the viscosity B-coefficients and the $\overline{V}_2^0 - \overline{V}_1^0$ terms. However, the $\Delta\mu_2^{0\neq}$ values were found to be positive at the experimental temperature and this suggests that the process of viscous flow becomes more difficult as the amount of *n*-AmOH/i-AmOH increases in the ternary solutions. Thus, the viscous behavior of the studied solutes reinforces the earlier contention that strong solute–solvent interaction exists in the present systems. According to Feakings *et al.*,[37] $\Delta\mu_2^{0\neq} >$

TABLE VI. Values of $\overline{V}_2^0 - \overline{V}_1^0$, $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ for NA and BA in methanol and different mixed methanol solvents at 298.15 K

Solute	Solvent	$(\overline{V}_2^0 - \overline{V}_1^0)\times10^6$ / m³ mol⁻¹	$\Delta\mu_1^{0\neq}$ / kJ mol⁻¹	$\Delta\mu_2^{0\neq}$ / kJ mol⁻¹
NA	MeOH	52.09	9.97	43.72
	10 mass % of *n*-AmOH	55.33	10.23	45.02
	20 mass % of *n*-AmOH	56.69	10.71	47.27
	30 mass % of *n*-AmOH	66.77	11.20	52.80
	10 mass % of i-AmOH	40.65	10.25	49.91
	20 mass % of i-AmOH	62.52	10.72	50.59
	30 mass % of i-AmOH	73.17	11.16	75.35
BA	MeOH	48.39	9.97	30.02
	10 mass % of *n*-AmOH	49.56	10.23	36.35
	20 mass % of *n*-AmOH	62.07	10.71	39.77
	30 mass % of *n*-AmOH	64.18	11.20	41.16
	10 mass % of i-AmOH	56.24	10.25	35.55
	20 mass % of i-AmOH	66.26	10.72	40.60
	30 mass % of i-AmOH	70.63	11.16	43.58

$> \Delta\mu_1^{0\neq}$ for solutes with positive viscosity B-coefficients indicates stronger solute–solvent interactions, thereby suggesting that the formation of the transition state is accompanied by the rupture and distortion of the intermolecular forces in the solvent structure.[37] In the present study, the found relation $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$ suggests an increase in the bulk structure of methanol in the presence of NA and BA due to the preferential solvation of the said solutes by *n*-AmOH/i-AmOH, releasing some methanol molecules to the bulk structure. In fact, Feakings *et al*[37] showed $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$ for solutes that are structure promoters.

CONCLUSION

In summary, the $\Delta\phi_V^0$ and viscosity B-coefficient values for nicotinic acid and benzoic acid indicate the presence of strong solute–solvent interactions and these interactions are further strengthened at higher amount of *n*-AmOH/i-AmOH in the ternary solutions. Also, they were found to act as methanol-structure promoters and their solvation behavior towards the mixed alcoholic solvents were more or less similar to in nature.

Acknowledgements. The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2002, SAP-1) for financial support.

ИЗВОД

ИЗУЧАВАЊЕ ИНТЕРАКЦИЈА РАСТВОРЕНА СУСПСТАНЦА–РАСТВАРАЧ У РАСТВОРИМА НИКОТИНСКЕ И БЕНЗОЕВЕ КИСЕЛИНЕ У МЕТАНОЛУ И БИНАРНОЈ СМЕШИ РАСТВАРАЧА

MAHENDRA NATH ROY, LOVELY SARKAR и BIPUL KUMAR SARKAR

Department of Chemistry, University of North Bengal, Darjeeling-734013, India

На основу зависности густине и вискозности од концентрације никотинске (NA) и бензоеве (BA) киселине у бинарном растварачу, који садржи 10, 20 и 30 mass % *n*-амил алкохола (*n*-AmOH) или изоамил алкохола у метанолу (i-AmOH), и чистом метанолу, на температури 298,15 K, одређене су вредности привидних моларних запремина, ϕ_V, и B коефицијента вискозности. Ови резултати су искоришћени за одређивање парцијалне моларне запремине, $\Delta\phi_V^0$, и B коефицијента вискозности, ΔB, преноса за NA и BA од метанола ка различитим бинарним метанолским растварачима, да би се рационализовале различите интеракције у терцијарним растворима. Уочен је пораст величина преноса NA и BA са порастом садржаја *n*-AmOH или i-AmOH у метанолу, који је објашњен ефектима структурних промена и преференцијалне солватације. Такође, израчунате су и моларне промене хемијског потенцијала за растварач и растворену сустанцу, $\Delta\mu_1^{0\neq}$ и $\Delta\mu_2^{0\neq}$, респективно, и анализиране у складу са теоријом прелазног стања и релативном вискозношћу.

(Примљено 22. новембра 2007, ревидирано 23. априла 2008)

REFERENCES

1. F. A. Robinson, *The Vitamin B-Complexes*, Chapman & Hall, London, 1951, Ch. 4

2. A. S. Fauci, E. Braunwald, K. J. Isselbacher, J. D. Wilson, J. B. Martin, D. L. Kasper, S. L. Hauser, D. L. Long, *Harrison's Principles of Internal Medicine*, Vol. 1, 14th Ed., McGraw- Hill, New York, 1998
3. T. Brody, *Nutritional Biochemistry*, 2nd Ed., Academic Press, San Diego, CA, 1999
4. M. Shils, J. A. Olson, M. Shike, A. C. Ross, *Nutrition in Health and Diseases*, 9th Ed., Williams & Wilkins, Baltimore, MD, 1999
5. E. E. Snell, D. E. Metzler, *Annu. Rev. Biochem.* **25** (1956) 435
6. A. N. Nesmeyanov, N. A. Nesmeyanov, *Fundamentals of Organic Chemistry*, Vol. 3, Mir Publishers, Moscow, 1981, p. 393
7. D. Cacaval, A. C. Blaga, M. Camarup, A. I. Galaction, *Separation Sci. Technol.* **42** (2007) 389
8. I. L. Finar, *Organic Chemistry*, *Vol 1: The Fundamental Principles*, 6th Ed., Longman Singapore Publishers (Pte) Ltd, Singapore, 1990
9. P. J. Moloney, D. M. Findlay, *J. Biol. Chem.* **67** (1923) 359
10. B. S. Bhal, A. Bhal, *Advanced Organic Chemistry*, S. Chand and Company Ltd., New Delhi, 1981, p. 1097
11. W. A. Sharp, *Dictionary of Chemistry*, 2nd Ed., Penguin Books Ltd., London, 1990, p. 56
12. H. H. Loh, C. P. Berg, *J. Nutrition* **101** (1971) 1601
13. S. Schuette, R. C. Rose, *Am. J. Physiol. Cell. Physiol.* **250** (1986) C694
14. I. Cho, C. L. Chang, X. Quing, *J. Agri. Food. Chem.* **53** (2005) 7307
15. W. I. M. Holman, *Biochemistry* **56** (1954) 513
16. Z. Orekhova, M. Ben-Hamo, E. Manzurola, A. Apelblat, *J. Soln. Chem.* **34** (2005) 687
17. C. Yiyun, X. Tongwen, *Eur. J. Med. Chem.* **40** (2005) 1384
18. K. Sagarik, S. Chaiwongwattana, P. Sisot, *J. Chem. Phys.* **306** (2004) 1
19. P. K. Mandal, D. K. Chatterjee, B. K. Seal, A. K. Basu, *J. Soln. Chem.* **7** (1978) 1572
20. A. G. Kharitonova, O. K. Krasilnikova, R. Sh.Vastapetyan, A. V. Bulanova, *Colloid J.* **67** (2005) 375
21. J. W. Mauger, A. N. Paralta, *J. Pharm. Sci.* **63** (1974) 576
22. E. Ayranci, N. Hoda, E. Bayram, *J. Colloid Interface Sci.* **284** (2005) 83
23. M. N. Roy, B. Sinha, *J. Soln. Chem.* **34** (2005) 1311
24. R. Riggio, H. E. Martinez, H. N. Sollomo, *J. Chem. Eng. Data* **31** (1986) 235
25. M. N. Roy, B. Sinha, V. K. Dakua, *J. Chem. Eng. Data* **51** (2006) 590
26. M. N. Roy, B. Sinha, *J. Mol. Liq.* **133** (2007) 89
27. B. Sinha, V. K. Dakua, M. N. Roy, *J. Chem. Eng. Data* **52** (2007) 1768
28. A. Kundu, N. Kishore, *J. Soln. Chem.* **32** (2003) 703
29. K. Belibagli, E. Agranci, *J. Soln. Chem.* **19** (1990) 867
30. A. Ali, S. Khan, F. Nabi, *J. Serb. Chem. Soc.* **72** (2007) 495
31. Y. Marcus, *Introduction to Liquid State Chemistry*, Wiley, New York, 1977
32. V. K. Dakua, B. Sinha, M. N. Roy, *J. Indian. Chem. Soc*. **84** (2007) 37
33. A. Aucejo, M. C. Burguet, R. Munoz, M. Sanchotello, *J. Chem. Eng. Data* **41**(1996) 508
34. A. Ben-Naim, *Solvation Thermodynamics*, Plenum Press, New York, 1987
35. G. Jones, M. Dole, *J. Am. Chem. Soc.* **51** (1929) 2950
36. F. J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.* **82** (1978) 784
37. D. Feakings, D. J. Freemantle, K. G. Lawrence, *J. Chem. Soc., Faraday Trans. I* **70** (1974) 795
38. S. Glasston, K. Laidler, H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.