Int J Thermophys (2009) 30:515–528
DOI 10.1007/s10765-009-0567-5

Partial Molar Volumes and Viscosity B-Coefficients of Nicotinamide in Aqueous Resorcinol Solutions at $T = (298.15, 308.15, \text{and } 318.15)\,\text{K}$

Mahendra Nath Roy · Ashis Banerjee · Pran Kumar Roy

Received: 4 April 2008 / Accepted: 31 January 2009 / Published online: 24 February 2009

Abstract Partial molar volumes ($\phi_{\mathrm{v}}^{\mathrm{o}}$) and viscosity *B*-coefficients for nicotinamide in (0.00, 0.05, 0.10, 0.15, and 0.20) $\text{mol} \cdot \text{dm}^{-3}$ aqueous resorcinol solutions have been determined from solution density and viscosity measurements at (298.15, 308.15, and 318.15) K as a function of the concentration of nicotinamide (NA). Here the relation $\phi_v^{\mathrm{o}} = a_0 + a_1 T + a_2 T^2$, has been used to describe the temperature dependence of the partial molar volume ϕ_v^{o}. These results and the results obtained in pure water were used to calculate the standard volumes of transfer $\Delta\phi_v^{\mathrm{o}}$ and viscosity *B*-coefficients of transfer of nicotinamide from water to aqueous resorcinol solutions to study various interactions in the ternary solutions. The partial molar volume (ϕ_v^{o}) and experimental slopes obtained from the Masson equation have been interpreted in terms of solute–solvent and solute–solute interactions, respectively. The viscosity data have been analyzed using the Jones–Dole equation, and the derived parameters *B* and *A* have also been interpreted in terms of solute–solvent and solute–solute interactions, respectively, in the ternary solutions.The structure making or breaking ability of nicotinamide has been discussed in terms of the sign of $(\delta^2\phi_v^o/\delta T^2)_P$. The activation parameters of viscous flow for the ternary solutions studied were also calculated and explained by the application of transition state theory.

Keywords Density · Nicotinamide · Partial molar volume · Resorcinol · Solute–solvent and solute–solute interactions · Viscosity · Viscosity *B*-coefficient

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M. N. Roy (✉) · A. Banerjee · P. K. Roy
Department of Chemistry, North Bengal University,
Darjeeling 734013, India
e-mail: mahendraroy2002@yahoo.co.in

1 Introduction

Nicotinamide, commonly known as vitamin B_3 [1,2], is a water soluble vitamin, an essential micronutrient, and a reactive moiety of the coenzyme nicotinamide adenine dinucleotide (NAD). It is an essential part of the coenzyme nicotinamide adenine dinucleotide phosphate (NADP). It plays a very important role to maintain the normal function of the digestive systems and cholesterol levels in the human body [3]. The combination of nicotinic acid and nicotinamide is clinically referred to as niacin [4,5], since nicotinic acid is converted in the body into the amide very fast, and for nutritional purposes, both of them have equal biological activities. Nicotinamide is an interesting molecule because of its two nitrogen atoms—one in the heterocyclic ring and the other as the amide group.

Resorcinol is an important organic compound, used externally as an antiseptic and disinfectant. It is also used as a chemical intermediate for the synthesis of pharmaceuticals and some organic compounds. An emerging use of resorcinol is as a template molecule in supramolecular chemistry. The –OH groups on resorcinol form hydrogen bonds to target molecules holding them in the proper orientation for a reaction resorcinol and is readily soluble in water through hydrogen bonding.

Although there have been extensive studies on various properties of nicotinamide [1,2,6–10], to the best of our knowledge, the properties of this ternary solution have not been reported. As partial molar volumes and viscosity *B*-coefficients of a solute provide valuable information about solute–solute, solute–solvent, and solvent–solvent interactions [11–13] in solutions, in this paper we attempted to study these properties for nicotinamide in aqueous solutions of resorcinol at (298.15, 308.15, and 318.15) K to explain the various interactions prevailing in the ternary systems under investigation.

2 Experimental

Nicotinamide was purchased from ACROS Organics Company and used as delivered. Its mass purity, as supplied was 98 %. Resorcinol was purchased from Sd. Fine Chemical Limited. Resorcinol was purified by a reported procedure [13,14], and the compound was dried and stored in a vacuum desiccator. Freshly distilled conductivity water was used for the preparation of different aqueous resorcinol solutions. The physical properties of different aqueous resorcinol solutions are listed in Table 1.

Stock solutions of nicotinamide in different aqueous resorcinol solutions were prepared by mass, and the working solutions were prepared by mass dilution. The conversion of molality into molarity was accomplished using experimental density values. All solutions were prepared afresh before use. The uncertainty in the molarity of the nicotinamide solutions is evaluated to be $0.0001\ \mathrm{mol \cdot dm^{-3}}$

The densities were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of $25\ \mathrm{cm^3}$ and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at $T = (298.15, 308.15,\ \text{and}\ 318.15)$ K with double distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at ±0.01 K of the desired temperatures. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed. Adequate

Table 1 Density ρ and viscosity η of different aqueous resorcinol solutions at different temperatures

Aqueous resorcinol solutions ($\mathrm{mol \cdot dm^{-3}}$)	T (K)	$\rho \times 10^{-3}$ ($\mathrm{kg \cdot m^{-3}}$)	η ($\mathrm{mPa \cdot s}$)
0.05	298.15	0.9992	0.900
	308.15	0.9985	0.740
	318.15	0.9975	0.621
0.10	298.15	1.0005	0.950
	308.15	1.0003	0.801
	318.15	0.9986	0.697
0.15	298.15	1.0017	1.001
	308.15	1.0015	0.862
	318.15	1.0004	0.750
0.20	298.15	1.0032	1.051
	308.15	1.0027	0.901
	318.15	1.001	0.801

precautions were taken to avoid evaporation losses during the course of actual measurements. The mass measurements, accurate to ±0.01 mg, were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The total uncertainty in density was estimated to be $0.0002\ \mathrm{g \cdot cm^{-3}}$, and that of the temperature is 0.01 K.

The viscosity was measured by means of a suspended Ubbelohde type viscometer thoroughly cleaned, dried, and calibrated at $T = (298.15, 308.15, \text{and } 318.15)$ K with triple distilled water and purified methanol. It was filled with experimental liquid and placed vertically in a glass-sided thermostat maintained constant to 0.01 K. After attainment of thermal equilibrium, the efflux times of flow of liquids were recorded with a stopwatch correct to ±0.1 s. The viscosity of the solution, η is given by the following equation:

$$\eta = (Kt - L/t)\,\rho \tag{1}$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow (in s) and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within $0.002\ \mathrm{mPa \cdot s}$. Details of the methods and techniques of density and viscosity measurements have been described elsewhere [15,16].

The nicotinamide solutions studied here were prepared by mass, and the conversion of molality to molarity was accomplished [15,16] using experimental density values. The experimental values of concentrations c, densities ρ, viscosities η, and derived parameters at various temperatures are reported in Table 2.

3 Discussion

To study the solvation state of nicotinamide in aqueous resorcinol solutions and the interaction between nicotinamide and resorcinol, data for partial molar volumes are important. For this purpose, the apparent molar volumes (ϕ_v) were determined from the solution densities using the following equation [15,17]:

Table 2 Molarity c, density ρ, viscosity η, apparent molar volumes ϕ_v, and $(\eta_r - 1)/c^{1/2}$ for nicotinamide in different aqueous resorcinol solutions at different temperatures

c $(\text{mol} \cdot \text{dm}^{-3})$	$\rho \times 10^{-3}$ $(\text{kg} \cdot \text{m}^{-3})$	η $(\text{mPa} \cdot \text{s})$	$\phi_v \times 10^6$ $(\text{m}^3 \cdot \text{mol}^{-1})$	$(\eta_r - 1)/c^{1/2}$
0.05[a]				
$T = 298.15\,\text{K}$				
0.0252	1.0019	0.9081	13.30	0.0555
0.0453	1.0041	0.9122	14.55	0.0628
0.0654	1.0057	0.9165	22.30	0.0710
0.0755	1.0061	0.9185	30.51	0.0738
0.0855	1.0062	0.9200	40.72	0.0753
0.0956	1.0063	0.9219	48.23	0.0780
$T = 308.15\,\text{K}$				
0.0250	1.0009	0.7453	27.21	0.0419
0.0450	1.0027	0.7496	28.27	0.0586
0.0649	1.0042	0.7541	34.18	0.0726
0.0749	1.0045	0.7569	42.41	0.0814
0.0850	1.0046	0.7595	50.33	0.0885
0.0949	1.0047	0.7619	57.32	0.0942
$T = 318.15\,\text{K}$				
0.0250	0.9998	0.6225	31.49	0.0061
0.0450	1.0016	0.6259	31.81	0.0305
0.0649	1.0032	0.6298	34.21	0.0500
0.0749	1.0035	0.6319	41.60	0.0587
0.0850	1.0037	0.6336	49.46	0.0644
0.0950	1.0038	0.6360	56.45	0.0737
0.10[a]				
$T = 298.15\,\text{K}$				
0.0250	1.0030	0.9563	21.20	0.0393
0.0450	1.0050	0.9604	21.95	0.0498
0.0650	1.0065	0.9644	29.41	0.0578
0.0750	1.0068	0.9661	37.63	0.0604
0.0850	1.0069	0.9681	46.71	0.0637
0.0950	1.0070	0.9699	53.33	0.0664
$T = 308.15\,\text{K}$				
0.0249	1.0023	0.8042	41.40	0.0205
0.0449	1.0039	0.8083	41.71	0.0394
0.0650	1.0054	0.8127	44.15	0.0543
0.0749	1.0058	0.8151	49.12	0.0613
0.0849	1.0059	0.8175	56.63	0.0680
0.0950	1.0061	0.8199	61.51	0.0742
$T = 318.15\,\text{K}$				
0.0250	1.0003	0.6991	52.97	0.0154
0.0449	1.0017	0.7035	53.11	0.0412
0.0650	1.0031	0.7090	52.35	0.0655
0.0749	1.0033	0.7115	59.50	0.0736
0.0850	1.0034	0.7144	66.01	0.0838
0.0949	1.0035	0.7172	70.15	0.0920
0.15[a]				
$T = 298.15\,\text{K}$				
0.0251	1.0041	1.0078	26.72	0.0423
0.0452	1.0060	1.0126	27.30	0.0540
0.0652	1.0075	1.0174	33.63	0.0636
0.0753	1.0077	1.0199	41.80	0.0686
0.0853	1.0079	1.0226	48.81	0.0735
0.0953	1.0080	1.0251	56.42	0.0777

Table 2 continued

c ($\mathrm{mol \cdot dm^{-3}}$)	$\rho \times 10^{-3}$ ($\mathrm{kg \cdot m^{-3}}$)	η ($\mathrm{mPa \cdot s}$)	$\phi_v \times 10^6$ ($\mathrm{m^3 \cdot mol^{-1}}$)	$(\eta_r - 1)/c^{1/2}$
$T = 308.15\,\mathrm{K}$				
0.0249	1.0034	0.8653	46.91	0.0235
0.0449	1.0049	0.8701	47.00	0.0440
0.0650	1.0062	0.8755	50.51	0.0609
0.0750	1.0063	0.8783	57.40	0.0685
0.0849	1.0065	0.8811	63.42	0.0754
0.0949	1.0066	0.8840	68.73	0.0823
$T = 318.15\,\mathrm{K}$				
0.0250	1.0017	0.7517	69.71	0.0135
0.0449	1.0031	0.7568	63.11	0.0420
0.0649	1.0036	0.7628	72.75	0.0663
0.0750	1.0037	0.7657	78.30	0.0757
0.0849	1.0038	0.7685	82.32	0.0843
0.0949	1.0039	0.7720	85.46	0.0949
0.20[a]				
$T = 298.15\,\mathrm{K}$				
0.0250	1.0052	1.0577	40.31	0.0385
0.0451	1.0068	1.0629	40.98	0.0520
0.0650	1.0083	1.0682	43.15	0.0631
0.0751	1.0087	1.0711	48.30	0.0687
0.0850	1.0089	1.0740	54.82	0.0740
0.0951	1.0091	1.0769	60.33	0.0789
$T = 308.15\,\mathrm{K}$				
0.0249	1.0041	0.9048	64.70	0.0232
0.0449	1.0053	0.9099	65.16	0.0440
0.0650	1.0064	0.9159	65.11	0.0626
0.0749	1.0067	0.9192	68.02	0.0716
0.0850	1.0068	0.9218	73.70	0.0773
0.0950	1.0069	0.9251	78.20	0.0851
$T = 318.15\,\mathrm{K}$				
0.0249	1.0021	0.8031	79.71	0.0142
0.0450	1.0030	0.8084	76.73	0.0420
0.0649	1.0039	0.8150	76.80	0.0669
0.0750	1.0040	0.8186	82.19	0.0788
0.0849	1.0041	0.8217	85.29	0.0873
0.0949	1.0042	0.8252	88.71	0.0967

[a] Molarity of resorcinol in water in $\mathrm{mol \cdot dm^{-3}}$

$$\phi_v = M/\rho_0 - 1000\,(\rho - \rho_0)/c\rho_0 \tag{2}$$

Here M is the molar mass of the solute, c is the molarity of the solution, and ρ_0 and ρ are the densities of the solvent and solution, respectively. The plots of ϕ_v against the square root of molar concentration $c^{1/2}$, were nonlinear and ϕ_v values were fitted to the following equation [8]:

$$\phi_v = \phi_v^{\mathrm{o}} + A_v c^{1/2} + B_v c, \tag{3}$$

where ϕ_v^{o} is the partial molar volume at infinite dilution, and A_v and B_v are two adjustable parameters. The ϕ_v^{o} values were calculated applying a least-squares technique to

Table 3 Partial molar volume ϕ_v^{o}, and adjustable parameters A_v and B_v for nicotinamide in different aqueous resorcinol solutions with standard deviations σ at different temperatures

T (K)	$\phi_v^o \times 10^6$ ($\mathrm{m^3 \cdot mol^{-1}}$)	$\mathrm{A}_v \times 10^6$ ($\mathrm{m^3 \cdot mol^{-1.5}}$)	$B_v \times 10^6$ ($\mathrm{m^3 \cdot mol^{-2}}$)	σ (%)
0.00[a]				
298.15	94.975	−23.75	81.3	0.002
308.15	95.847	−28.60	83.8	0.001
318.15	97.085	−30.09	105.2	0.002
0.05[a]				
298.15	95.670	−902.74	2428.1	0.030
308.15	100.310	−799.89	2145.6	0.028
318.15	112.070	−847.19	2160.1	0.067
0.10[a]				
298.15	97.343	−839.25	2266.9	0.026
308.15	105.260	−673.25	1723.3	0.044
318.15	120.580	−697.66	1734.2	0.105
0.15[a]				
298.15	99.948	−798.65	2131.4	0.016
308.15	109.540	−671.38	1751.4	0.028
318.15	135.420	−702.67	1775.3	0.124
0.20[a]				
298.15	101.050	−641.70	1649.7	0.040
308.15	116.371	−529.24	1307.5	0.058
318.15	138.480	−592.39	1401.3	0.027

[a] Molarity of resorcinol in water in $\mathrm{mol \cdot dm^{-3}}$

the plots of ϕ_v versus $c^{1/2}$ using Eq. 3. The values of ϕ_v^{o}, A_v, and B_v at each temperature are listed in Table 3. The estimated uncertainties in ϕ_v^{o} values are represented by the standard deviation σ, which is equal to the root mean square of the deviation between the experimental and calculated ϕ_v for each data point. The ϕ_v^{o} values for the aqueous nicotinamide solutions at (298.15, 308.15, and 318.15) K were in good agreement with ϕ_v^{o} values reported earlier [7]. Table 3 shows that ϕ_v^{o} values are generally positive and increase with an increase in both the temperature and molarity of resorcinol in the solutions. This indicates the presence of strong solute–solvent interactions, and these interactions are further strengthened at higher temperatures and higher concentrations of resorcinol in the solutions. The crystal structure of nicotinamide was reported by Wright and King [9]. In the crystal, nicotinamide is linked by two weak hydrogen bonds from the hydrogen atoms of the amide N-atom to the O-atom of one neighbouring molecule and to the ring N-atom of other molecules in such a fashion that a two-dimensional network parallel to the (010) plane is formed with a inter-planar distance of 0.3579 nm at $T = 295.15$ K. Charman et al. [10] reported the structure of nicotinamide in aqueous solution. They studied the concentration-dependent self-association of nicotinamide in solution by ^{1}H- and ^{13}C-NMR spectroscopy and osmometric measurements. Their results revealed that nicotinamide associates in aqueous solutions with the amide groups of each nicotinamide molecule creating large associated species at higher concentrations. This behavior is consistent with the observed changes in the values of parameters A_v and B_v.

Table 4 Values of various coefficients of Eq. 4 for nicotinamide in different aqueous resorcinol solutions

Aqueous resorcinol solution ($\mathrm{mol \cdot dm^{-3}}$)	$a_o \times 10^6$ ($\mathrm{m^3 \cdot mol^{-1}}$)	$a_1 \times 10^6$ ($\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}}$)	$a_2 \times 10^6$ ($\mathrm{m^3 \cdot mol^{-1} \cdot K^{-2}}$)
0.00	237.10	−1.02	0.001
0.05	3228.07	−21.12	0.035
0.10	3262.04	−21.65	0.037
0.15	7296.25	−48.41	0.081
0.20	2846.12	−19.59	0.034s

Table 5 Partial molar expansibility ϕ_E^o for nicotinamide in different aqueous resorcinol solutions at different temperatures

Aqueous resorcinol solution ($\mathrm{mol \cdot dm^{-3}}$)	$\phi_E^o \times 10^6$ ($\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}}$)			$(\delta\phi_E^o/\delta T)_P \times 10^6$ ($\mathrm{m^3 \cdot mol^{-1} \cdot K^{-2}}$)
	298.15 K	308.15 K	318.15 K	
0.00	0.0510	0.0870	0.1230	0.0036
0.05	0.1080	0.8200	1.5320	0.0712
0.10	0.4126	1.1526	1.8926	0.0740
0.15	0.1209	1.7489	3.3769	0.1628
0.20	1.2133	1.9113	2.6093	0.0698

The partial molar volumes ϕ_v^o were fitted to a polynomial of the following type

$$\phi_v^o = a_0 + a_1 T + a_2 T^2 \tag{4}$$

Values of the coefficients a_0, a_1, and a_2 of the above equation for different nicotinamide solutions are reported in Table 4.

The partial molar expansibilities of ϕ_E^o can be obtained by the following equation [13]:

$$\phi_E^o = (\delta\phi_v^o/\delta T)_p = a_1 + 2a_2 T \tag{5}$$

The values of ϕ_E^o for different ternary solutions at $T =$ (298.15, 308.15, and 318.15) K are given in Table 5. Table 5 shows that ϕ_E^o values increase as the temperature increases.

According to Hepler [18], the sign of $(\delta\phi_E^o/\delta T)_P$ is a better criterion in characterizing the long-range structure-making and -breaking ability of the solutes in the solution. The general thermodynamic expression is as follows:

$$(\delta\phi_E^o/\delta T)_P = -(\delta^2\phi_v^o/\delta T^2)_P = 2a_2 \tag{6}$$

If the sign of $(\delta\phi_E^o/\delta T)_P$ is positive, the solute is either a structure maker or a structure breaker. It is seen from Table 5, that nicotinamide predominantly acts as a structure maker, and its structure-making ability increases with an increase in both the temperature and molarity of resorcinol in the solutions. But its structure-making ability decreases some what at higher concentrations of resorcinol in the mixtures. This fact may be attributed to the gradual disappearance of the caging or packing effect [19,20] in ternary solutions. This observation is in line with the observation made by Kundu and Kishore [8]. They suggested that nicotinamide acts as a water-structure promoter due to hydrophobic hydration.

Partial molar volumes $\Delta\phi_v^{\text{o}}$ of transfer from water to different aqueous resorcinol solutions have been determined using the relation [21,22]:

$$\Delta\phi_v^{\text{o}} = \phi_v^{\text{o}}(\text{aqueous resorcinol solution}) - \phi_v^{\text{o}}(\text{water}) \tag{7}$$

The $\Delta\phi_v^{\text{o}}$ value is independent of the solute–solute interactions and therefore provides information regarding solute–co-solute interactions [21]. It can be seen from Table 7, that the value of $\Delta\phi_v^{\text{o}}$ is positive at all experimental temperatures and increases with the molarity of resorcinol in the ternary solutions. The concentration dependence of the thermodynamic properties of the solutes in aqueous solutions can be explained in terms of the overlapping of hydration co-spheres. According to the co-sphere model, as developed by Friedman and Krishnan [23], the effect of overlappping of the hydration co-spheres is destructive, i.e., the overlap of hydration co-spheres of hydrophobic–hydrophobic groups results in a net volume decrease. However, in the present study, the positive values of $\Delta\phi_v^{\text{o}}$ indicate that solute–solvent interactions are predominant and the overall effect of the overlap of the hydration co-spheres of nicotinamide and resorcinol reduce the effect of electrostriction of water by nicotinamide molecules, and this effect increases with the molarity of resorcinol in the ternary mixtures as shown in Fig. 1 ($\Delta\phi_v^{\text{o}}$ versus molarity of resorcinol in solution). In addition, standard partial molar volumes of the solute have also been explained by a simple model [24,25]:

$$\phi_v^{\text{o}} = \phi_{\text{vw}} + \phi_{\text{void}} - \phi_{\text{s}} \tag{8}$$

where, ϕ_{vw} is the van der Waals volume, ϕ_{void} is the volume associated with voids or empty space, and ϕ_{s} is the shrinkage volume due to electrostriction. Assuming that ϕ_{vw} and ϕ_{void} have the same magnitudes in water and in aqueous resorcinol solutions for the same solute [26], the increase in ϕ_v^{o} values and the positive $\Delta\phi_v^{\text{o}}$ values can be attributed to the decrease in the shrinkage volume of water by nicotinamide in the presence of resorcinol. This fact suggests that resorcinol has a dehydration effect on the hydrated nicotinamide.

In the literature [8], pyridine has been noted as a structure breaker in aqueous solutions, and the structure-promoting tendency of nicotinamide has been assigned to the –CONH$_2$ group. Thus, the interactions between nicotinamide and resorcinol in water can roughly be summarized as follows: (i) interaction of H-atom of –O–H group of resorcinol with the N-atom in the heterocyclic ring of nicotinamide, (ii) interaction of H-atom of –O–H group of resorcinol with the N-atom in the amide group of nicotinamide, and (iii) interaction of H-atom of –O–H group of resorcinol with the O-atom in the amide group of nicotinamide, Therefore, the overall positive ϕ_v^{o} values indicate that solute–solvent interactions predominate over solvent–solvent interactions and thus reduce the electrostriction of water molecules by nicotinamide imparting positive values of $\Delta\phi_v^{\text{o}}$.

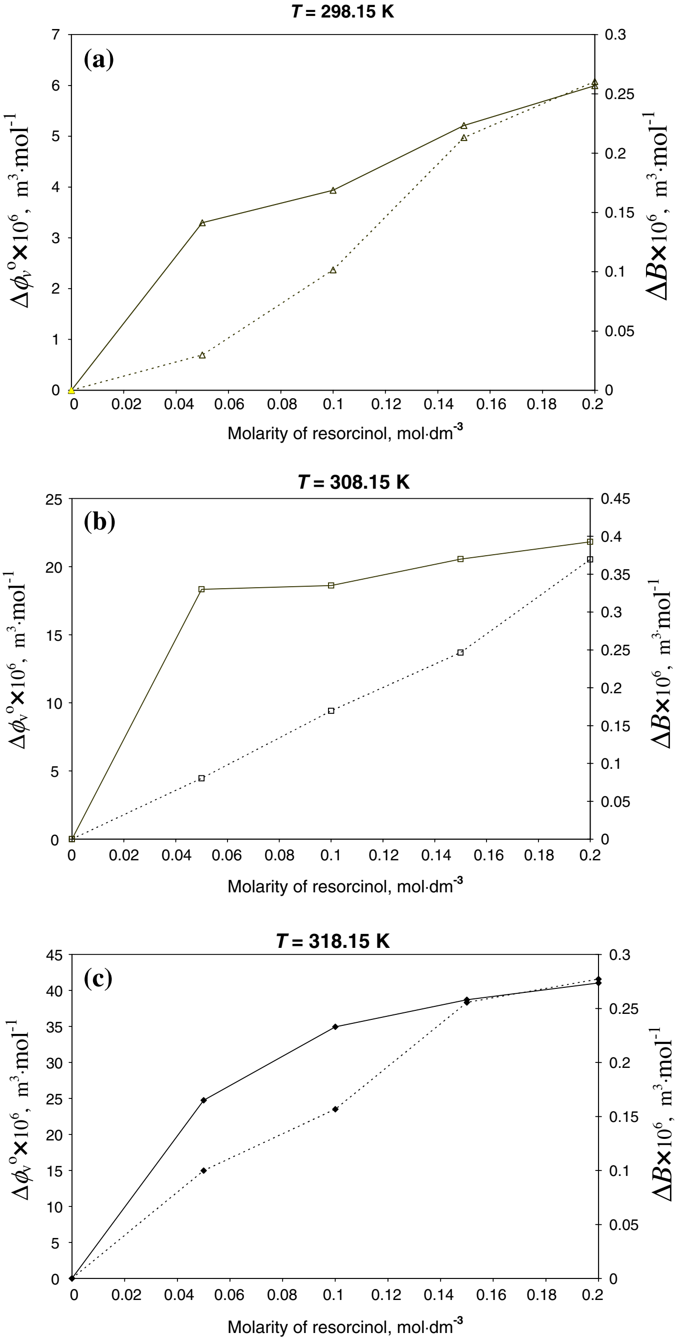

Fig. 1 Plots of partial molar volume ($\Delta\phi_v^{\text{o}}$) and viscosity B-coefficients (ΔB) against molarity for the transfer from water to different aqueous resorcinol solutions for nicotinamide; dotted lines for $\Delta\phi_v^{\text{o}}$ and solid lines for ΔB: (a) $T = 298.15$ K, (b) $T = 308.15$ K, and (c) $T = 318.15$ K

The viscosity data of the aqueous and aqueous resorcinol solutions of nicotinamide have been analyzed using the Jones–Dole [27] equation,

$$(\eta/\eta_0 - 1)/c^{1/2} = (\eta_\mathrm{r} - 1)/c^{1/2} = A + Bc^{1/2}, \tag{9}$$

where, $\eta_\mathrm{r} = \eta/\eta_\mathrm{o}$ and η are the viscosities of the solvent and solution, respectively, and c is the molar concentration of a solution. The A and B are the Jones–Dole constants estimated by a least-squares method and are reported in Table 6.

Table 6 shows that the values of the A-coefficient are generally negative. These results indicate the presence of weak solute–solute interactions, and these interactions further decrease with an increase in both the temperature and molarity of resorcinol in the mixtures.

The viscosity B-coefficient [28] reflects the effects of solute–solvent interactions on the solution viscosity.The viscosity B-coefficient is a valuable tool to provide information concerning the solvation of solutes and their effects on the structure of the solvent in the local vicinity of the solute molecules. Table 6 shows that the values of the viscosity B-coefficient for nicotinamide in the studied solvent systems are positive, thereby suggesting the presence of strong solute–solvent interactions and these types of interactions are strengthened with an increase in both the temperature and the molarity of resorcinol in the mixtures.

Viscosity B-coefficients of transfer ΔB from water to different aqueous resorcinol solutions have been determined using the relations [21,22],

$$\Delta B = B(\text{aqueous resorcinol solution}) - B(\text{water}) \tag{10}$$

The ΔB values shown in Table 7 and depicted graphically in Fig. 1 (ΔB versus molarity of resorcinol in solution) as a function of molarity of resorcinol in solutions at the experimental temperatures support the results obtained from $\Delta\phi_\mathrm{v}^\mathrm{o}$ values as discussed above.

The viscosity data have also been analyzed on the basis of transition state theory for the relative viscosity of the solutions as suggested by Feakins et al. [29] using

$$\Delta\mu_2^{\mathrm{o}*} = \Delta\mu_1^{\mathrm{o}*} + RT(1000B + V_2^\mathrm{o} - V_1^\mathrm{o})/V_1^\mathrm{o} \tag{11}$$

where, $\Delta\mu_2^{\mathrm{o}*}$ is the contribution per mole of the solute to the free energy of activation for the viscous flow of solutions and $\Delta\mu_1^{\mathrm{o}*}$ is the free energy of activation per mole of solvent mixture . The values are reported in Table 8. V_1^o is the partial molar volume of the solvent mixture, and V_2^o is the partial molar volume of the solute. $\Delta\mu_1^{\mathrm{o}*}$ is calculated from

$$\Delta\mu_1^{\mathrm{o}*} = \Delta G_1^{\mathrm{o}*} = RT\,\ln(\eta_\mathrm{o} V_1^\mathrm{o}/hN_\mathrm{A}) \tag{12}$$

where h is Planck's constant, N_A is Avogadro's number, and $\Delta G_1^{\mathrm{o}*}$ is the free energy of activation per mole of solvent mixture. From Table 8, it is seen that $\Delta\mu_1^{\mathrm{o}*}$ is almost

Table 6 Values of *A*- and *B*-coefficients with standard errors for nicotinamide in different aqueous resorcinol solutions at different temperatures

Aqueous resorcinol solution $(\mathrm{mol \cdot dm^{-3}})$	$A \times 10^{-3}$ $(\mathrm{m^{3/2} \cdot mol^{-1/2}})$			$B \times 10^{6}$ $(\mathrm{m^{3} \cdot mol^{-1}})$		
	$T = 298.15\,\mathrm{K}$	$T = 308.15\,\mathrm{K}$	$T = 318.15\,\mathrm{K}$	$T = 298.15\,\mathrm{K}$	$T = 308.15\,\mathrm{K}$	$T = 318.15\,\mathrm{K}$
0.00	0.1259	0.1105	0.1014	0.0117	0.0218	0.2812
	(±0.001)	(±0.002)	(±0.001)	(±0.003)	(±0.001)	(±0.001)
0.05	0.0312	−0.015	−0.0642	0.153	0.3518	0.4462
	(±0.000)	(±0.001)	(±0.001)	(±0.001)	(±0.002)	(±0.000)
0.01	0.0112	−0.0362	−0.0665	0.1804	0.3568	0.5142
	(±0.001)	(±0.002)	(±0.002)	(±0.000)	(±0.002)	(±0.002)
0.15	0.0044	−0.0388	−0.0719	0.2351	0.3918	0.5393
	(±0.002)	(±0.000)	(±0.001)	(±0.001)	(±0.001)	(±0.001)
0.20	−0.0046	−0.0429	−0.0743	0.2686	0.4146	0.5548
	(±0.001)	(±0.003)	(±0.001)	(±0.000)	(±0.002)	(±0.001)

Table 7 Partial molar volumes ϕ_v^o, viscosity B-coefficients, and ΔB of transfer from water to different aqueous resorcinol solutions for nicotinamide at three different temperatures

Aqueous resorcinol solution ($\text{mol} \cdot \text{dm}^{-3}$)	$\phi_v^o \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$\Delta\phi_v^o \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$B \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$\Delta B \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)
$T = 298.15\,\text{K}$				
0.00	94.97	0	0.0117	0
0.05	95.67	0.695	0.1530	0.141
0.10	97.34	2.368	0.1804	0.169
0.15	99.94	4.973	0.2351	0.223
0.20	101.05	6.075	0.2686	0.257
$T = 308.15\,\text{K}$				
0.00	95.84	0	0.0218	0
0.05	100.31	4.463	0.3518	0.330
0.10	105.26	9.413	0.3568	0.335
0.15	109.54	13.693	0.3918	0.370
0.20	116.37	20.523	0.4146	0.393
$T = 318.15\,\text{K}$				
0.00	97.08	0	0.2812	0
0.05	112.07	14.985	0.4462	0.165
0.10	120.58	23.495	0.5142	0.233
0.15	135.42	38.335	0.5393	0.258
0.20	138.66	41.575	0.5548	0.274

constant at all temperatures and solvent compositions. It means that $\Delta\mu_2^{o*}$ is dependent mainly on the values of viscosity B-coefficients and $(V_2^o - V_1^o)$ terms. The $\Delta\mu_2^{o*}$ values were positive at all experimental temperatures. So the formation of the transition state becomes less favorable [29]. According to Feakins et al. [29], $\Delta\mu_2^{o*} > \Delta\mu_1^{o*}$ for solutes having positive viscosity B-coefficients indicates stronger solute–solvent interactions, suggesting the formation of a transition state which is accompanied by the rupture and distortion of the intermolecular forces in the solvent structure [29]. The larger is the value of $\Delta\mu_2^{o*}$, the greater is the structure-making tendency of the solute, and the positive values of $\Delta\mu_2^{o*}$ for nicotinamide in the different aqueous resorcinol solutions suggests nicotinamide is a net structure promoter in these ternary mixtures. Equation 13 has been used to calculate the entropy of activation (ΔS_2^{o*}) for solutions,

$$\Delta S_2^{o*} = -\text{d}\Delta\mu_2^{o*})/\text{d}T \tag{13}$$

The ΔS_2^{o*} has been calculated from the slope of the plots of $\Delta\mu_2^{o*}$ versus T by using a least square treatment. The enthalpy of activation has been determined by using the following relation [29]:

$$\Delta H_2^{o*} = \Delta\mu_2^{o*} + T\Delta S_2^{o*} \tag{14}$$

Table 8 Values of $V_2^{\mathrm{o}} - V_1^{\mathrm{o}}$, $\Delta\mu_2^{\mathrm{o}}$, $T\Delta S_2^{\mathrm{o}}$, and ΔH_2^{o} for nicotinamide in different aqueous resorcinol solutions at different temperatures

Parameters	298.15 K	308.15 K	318.15 K
$0.00\ \mathrm{mol \cdot dm^{-3}}$			
$(V_2^0 - V_1^0)10^6(\mathrm{m^3 \cdot mol^{-1}})$	80.846	84.511	89.611
$\Delta\mu_1^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	9.175	8.944	8.761
$\Delta\mu_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	21.812	23.902	62.128
$T\Delta S_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	−601.011	−621.169	−641.327
$\Delta H_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	−579.199	−597.267	−579.199
$0.05\ \mathrm{mol \cdot dm^{-3}}$			
$(V_2^0 - V_1^0)10^6(\mathrm{m^3 \cdot mol^{-1}})$	77.555	82.183	93.925
$\Delta\mu_1^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	9.197	9.006	8.840
$\Delta\mu_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	40.746	70.342	87.575
$T\Delta S_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	−698.103	−721.518	−744.932
$\Delta H_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	−657.357	−651.176	−657.357
$0.10\ \mathrm{mol \cdot dm^{-3}}$			
$(V_2^0 - V_1^0)10^6(\mathrm{m^3 \cdot mol^{-1}})$	79.152	87.065	102.354
$\Delta\mu_1^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	9.342	9.219	9.155
$\Delta\mu_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	44.710	71.720	98.636
$T\Delta S_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	−803.902	−830.865	−857.828
$\Delta H_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	−759.192	−759.145	−759.192
$0.15\ \mathrm{mol \cdot dm^{-3}}$			
$(V_2^0 - V_1^0)10^6(\mathrm{m^3 \cdot mol^{-1}})$	81.779	91.367	117.127
$\Delta\mu_1^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	9.468	9.403	9.357
$\Delta\mu_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	52.740	77.519	104.276
$T\Delta S_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	−768.273	−794.041	−819.809
$\Delta H_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	−715.533	−716.522	−715.533
$0.20\ \mathrm{mol \cdot dm^{-3}}$			
$(V_2^0 - V_1^0)10^6(\mathrm{m^3 \cdot mol^{-1}})$	82.808	98.119	120.378
$\Delta\mu_1^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	9.598	9.528	9.53
$\Delta\mu_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	57.350	81.502	107.219
$T\Delta S_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	−743.422	−768.357	−793.291
$\Delta H_2^{\mathrm{o}*}(\mathrm{kJ \cdot mol^{-1}})$	−686.072	−686.855	−686.072

The values of $\Delta S_2^{\mathrm{o}*}$ and $\Delta H_2^{\mathrm{o}*}$ are reported in Table 8. They are negative for all experimental solutions at all temperatures which suggest that the transition state is associated with bond formation and an increase in order.

4 Conclusion

In summary, ϕ_v^{o} and viscosity B-coefficient values for nicotinamide indicate the presence of strong solute–solvent interactions, and these interactions are further strengthened at higher temperatures and higher concentrations of resorcinol in ternary solutions. This study also reveals that nicotinamide acts as a water-structure promoter due to hydrophobic hydration in the presence of resorcinol and resorcinol has a dehydration effect on the hydrated nicotinamide.

Acknowledgments The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2002, SAP-1) and Head, Department of Chemistry, University of North Bengal, Darjeeling, India, for providing various facilities.

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