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Investigation on molecular interactions of nicotinamide in aqueous citric acid monohydrate solutions with reference to manifestation of partial molar volume and viscosity *B*-coefficient measurements

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ABSTRACT

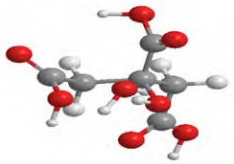
Apparent molar volumes (V_ϕ), viscosity *B*-coefficients for nicotinamide in 0.03, 0.05, 0.07 and 0.10 mol dm^{-3} aqueous citric acid monohydrate solutions have been determined from solution density and viscosity measurements at 298.15, 308.15 and 318.15 K as function of concentration of nicotinamide. The apparent molar volumes have been extrapolated to zero concentration to obtain the limiting values at infinite dilution using Masson equation. The infinite dilution partial molar expansibilities have also been calculated from the temperature dependence of the limiting apparent molar volumes. This results have, in conjunction with the results obtained in pure water, been used to calculate the standard volumes of transfer ΔV_ϕ^0 and viscosity *B*-coefficients of transfer for nicotinamide from water to aqueous citric acid monohydrate solutions for rationalizing various interactions in the ternary solutions. The structure making or breaking ability of nicotinamide has been discussed in terms of the sign of $\left[\partial^2 V_\phi^0/\partial T^2\right]_p$ and dB/dT. An increase in the transfer volume of nicotinamide with increasing citric acid monohydrate concentration has been explained by Friedman–Krishnan co-sphere model. The activation parameters of viscous flow for the ternary solutions studied have also been calculated and explained by the application of transition state theory.

1. Introduction

Vitamins are essential precursors for various coenzymes. These coenzymes are therefore required in almost all metabolic pathways [1]. Nicotinamide (NA), commonly known as vitamin B_3 [2], is a water-soluble vitamin, an essential micronutrient and a reactive moiety of the coenzyme nicotinamide adenine dinucleotide (NAD). It is sometimes referred to as nothing more than vitamin PP (Pellagra Preventive) [3,4], since its deficiency in human diet causes pellagra. It is an essential part of the coenzyme—nicotinamide adenine dinucleotide phosphate (NADP), its reduced form NADPH, NAD and its reduced form NADH. The combination of nicotinic acid and NA is clinically referred as niacin [3–5]. NA is an interesting molecule because of its two nitrogen atoms—one in the heterocyclic ring and the other as the amide group.

Citric acid monohydrate $C_6H_8O_7{\cdot}H_2O$ (CA) i.e., 2-hydroxypropane-1,2,3-tricarboxylic acid monohydrate, is a tribasic, environmentally acceptable, and versatile chemical. As it occurs in metabolism of almost all living beings, its interactions in an aqueous solution is of great value to the biological scientists. In pharmaceutical industry, citric acid is used as a stabilizer in various formulations, as a drug component and as an anticoagulant in blood for transfusions and also used as an acidifier in many pharmaceuticals. It is used in personal care products [6,7].

Nicotinamide



Citric acid monohydrate

Water

Literature survey shows that there are few data on thermodynamic and transport properties for aqueous citric acid solutions. Maffia and Meirelles [8] reported the water activities and pH

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Table 1
Density ρ, and viscosity η, of different aqueous CA solution at different temperatures.

Aqueous CA solution ($\mathrm{mol\,dm^{-3}}$)	T (K)	ρ ($\times10^{-3}\,\mathrm{kg\,m^{-3}}$)	η (mPa s)
0.03	298.15	0.9995	0.8766
	308.15	0.9963	0.7136
	318.15	0.9925	0.6253
0.05	298.15	1.0009	0.8921
	308.15	0.9977	0.7353
	318.15	0.9938	0.6371
0.07	298.15	1.0026	0.9048
	308.15	0.9993	0.7595
	318.15	0.9954	0.6527
0.10	298.15	1.0048	0.9254
	308.15	1.0018	0.7855
	318.15	0.9979	0.6766

for aqueous solutions of citric acid at 298.15 K. The measurements were made from 5 to 50 mass% of citric acid. Apelblat and Manzurola [9,10] and Parmar et al. [11] studied partial molar volumes of citric acid in water at 298.15 and 298.15, 303.15, 308.15, 308.15, and 313.15 K respectively. Sijpkes et al. [12] measured heat capacities and partial molar heat capacities at infinite dilution of citric acid in water at 298.15 K. Levien [13] carried the studies of apparent osmotic coefficients and molar conductivities. Although there have been various studies on various properties of NA [2,14,15,20–22], to the best of our knowledge, the properties of this ternary solution have not been reported earlier. As apparent molar volumes and viscosity *B*-coefficients of a solute gives cumulative effects [16,17] of solute–solute, solute–solvent and solvent–solvent interactions in solutions, in this paper we attempted to study these properties for NA in aqueous solutions of CA at 298.15, 308.15 and 318.15 K to explain the various interactions prevailing in the ternary systems under investigation.

2. Experimental

NA was purchased from ACROS Organics Company and used as such. Its mass purity as supplied is 98%. Citric acid monohydrate was purchased from Himedia. Its mass purity as supplied is 99%. The reagents were always placed in the desiccator over P_2O_5 to keep them in dry atmosphere. Freshly distilled conductivity water (specific conductance $\approx 10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$) was used as standard solvent and for making binary aqueous mixtures of CA. The physical properties of different aqueous CA solutions are listed in Table 1.

Stock solutions of NA in different aqueous CA 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 molarity of the NA solutions is evaluated to $\pm0.0001\,\mathrm{mol\,dm^{-3}}$.

Density measurements of ternary mixtures were performed at atmospheric pressure at T = 298.15, 308.15, and 318.15 K by means of vibrating-tube densimeter (Anton Paar, DMA 4500) which was calibrated with distilled water and air. The uncertainty in the density measurement was $\pm0.0002\,\mathrm{g\,cm^{-3}}$. The temperature was automatically kept constant within ±0.01 K. The mixtures were prepared by mass in 10 $\mathrm{cm^3}$ bottles and precautions were taken to minimize evaporation losses. The apparatus was calibrated once a day with dry air and double-distilled freshly degassed water.

The viscosity was measured by means of a suspended Ubbelohde type viscometer thoroughly cleaned, dried and calibrated at T = 298.15, 308.15, and 318.15 K with triply 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

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

c ($\mathrm{mol\,dm^{-3}}$)	ρ ($\times10^{-3}\,\mathrm{kg\,m^{-3}}$)	η (mPa s)	V_ϕ ($\times10^{6}\,\mathrm{m^3\,mol^{-1}}$)	$(\eta_r-1)/c^{1/2}$
0.03[a]				
T = 298.15 K				
0.0120	0.9998	0.8836	97.65	0.0723
0.0240	1.0001	0.8878	97.20	0.0822
0.0400	1.0005	0.8940	96.86	0.0988
0.0560	1.0009	0.8992	96.63	0.1085
0.0720	1.0013	0.9048	96.51	0.1198
0.0840	1.0016	0.9085	96.43	0.1255
T = 308.15 K				
0.0119	0.9966	0.7189	101.02	0.0678
0.0239	0.9968	0.7233	100.37	0.0879
0.0398	0.9972	0.7285	99.93	0.1041
0.0558	0.9976	0.7340	99.59	0.1211
0.0717	0.9980	0.7397	99.31	0.1363
0.0837	0.9983	0.7440	99.14	0.1469
T = 318.15 K				
0.0119	0.9927	0.6292	103.85	0.0571
0.0238	0.9929	0.6335	102.58	0.0858
0.0397	0.9933	0.6394	101.52	0.1132
0.0556	0.9937	0.6451	100.66	0.1343
0.0715	0.9941	0.6501	100.10	0.1487
0.0834	0.9944	0.6546	99.88	0.1624
0.05[a]				
298.15 K				
0.0120	1.0012	0.8974	98.69	0.0542
0.0240	1.0015	0.9016	98.05	0.0689
0.0400	1.0019	0.9075	97.56	0.0863
0.0561	1.0023	0.9144	97.31	0.1056
0.0721	1.0027	0.9198	97.16	0.1158
0.0841	1.0030	0.9234	97.07	0.1211
308.15 K				
0.0119	0.9979	0.7387	102.94	0.0422
0.0239	0.9982	0.7421	102.00	0.0594
0.0399	0.9985	0.7475	101.05	0.0828
0.0559	0.9989	0.7525	100.33	0.0989
0.0719	0.9993	0.7585	99.78	0.1178
0.0839	0.9996	0.7622	99.50	0.1261
318.15 K				
0.0119	0.9940	0.6384	106.83	0.0191
0.0238	0.9942	0.6419	105.28	0.0494
0.0398	0.9945	0.6470	104.23	0.0778
0.0557	0.9949	0.6522	103.55	0.1009
0.0716	0.9952	0.6576	103.13	0.1204
0.0835	0.9955	0.6607	102.87	0.1283
0.07[a]				
T = 298.15 K				
0.0120	1.0028	0.9055	101.54	0.0072
0.0240	1.0031	0.9082	100.77	0.0244
0.0400	1.0034	0.9132	100.21	0.0467
0.0560	1.0038	0.9187	99.75	0.0649
0.0721	1.0042	0.9255	99.45	0.0853
0.0841	1.0045	0.9298	99.31	0.0954
T = 308.15 K				
0.0119	0.9995	0.7605	105.52	0.0116
0.0239	0.9998	0.7639	104.23	0.0372
0.0399	1.0001	0.7695	103.38	0.0657
0.0558	1.0004	0.7763	102.87	0.0933
0.0718	1.0007	0.7828	102.45	0.1144
0.0838	1.0010	0.7883	102.19	0.1309
T = 318.15 K				
0.0119	0.9956	0.6532	109.91	0.0076
0.0238	0.9958	0.6570	108.52	0.0429
0.0397	0.9960	0.6634	107.31	0.0823
0.0556	0.9963	0.6698	106.77	0.1115
0.0715	0.9966	0.6778	106.30	0.1440
0.0834	0.9968	0.6845	106.09	0.1688

Table 2 (*Continued*)

c (mol dm^{-3})	ρ ($\times 10^{-3}$ kg m^{-3})	η (mPa s)	V_ϕ ($\times 10^6$ m^3 mol^{-1})	$(\eta_r - 1)/c^{1/2}$
0.10[a]				
T = 298.15 K				
0.0121	1.0051	0.9258	102.67	0.0043
0.0243	1.0053	0.9292	101.92	0.0262
0.0404	1.0057	0.9357	101.30	0.0556
0.0567	1.0060	0.9423	100.81	0.0766
0.0729	1.0064	0.9502	100.55	0.0992
0.0850	1.0066	0.9563	100.39	0.1146
T = 308.15 K				
0.0121	1.0020	0.7863	108.47	0.0087
0.0242	1.0022	0.7903	107.38	0.0392
0.0403	1.0025	0.7972	106.28	0.0744
0.0565	1.0027	0.8049	105.54	0.1036
0.0726	1.0031	0.8133	105.08	0.1312
0.0847	1.0033	0.8198	104.84	0.1498
T = 318.15 K				
0.0121	0.9980	0.6771	113.84	0.0061
0.0241	0.9981	0.6824	112.56	0.0547
0.0402	0.9983	0.6898	111.57	0.0972
0.0563	0.9985	0.6981	110.98	0.1337
0.0724	0.9987	0.7059	110.44	0.1609
0.0844	0.9989	0.7119	110.18	0.1793

[a] Molarity of CA in water in mol dm^{-3}.

of flow of liquids were recorded with a stopwatch correct to ± 0.1 s. Viscosity of the solution, η is given by the following equation:

$$\eta = \left(Kt - \frac{L}{t}\right)\rho \tag{1}$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within ±0.002 mPa s. Details of the methods and techniques of density and viscosity measurements have been described elsewhere [18,19].

The nicotinamide solutions studied here were prepared by mass and the conversion of molality in molarity was accomplished [18,19] 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

The densities, for the solutions of NA in aqueous CA measured at 298.15, 308.15, and 318.15 K, have been used to calculate the apparent molar volumes (V_ϕ) of the solute using the following expression [18] and listed in Table 2:

$$V_\phi = \frac{M_2}{\rho_0} - \frac{1000}{c}\left(\frac{\rho - \rho_0}{\rho_0}\right) \tag{2}$$

where c is the molar concentration of the solution, M_2 is the molecular weight of the solute, ρ and ρ_0 are the densities of the solution and solvent, respectively. The plots of V_ϕ against square root of molar concentration $c^{1/2}$, were non-linear and V_ϕ values were fitted to the following equation [20]:

$$V_\phi = V_\phi^0 + A_V c^{1/2} + B_V c \tag{3}$$

where V_ϕ^0 is the partial molar volume at infinite dilution. A_v and B_v are two adjustable parameters. The V_ϕ^0 values were calculated applying a least squares technique to the plots of V_ϕ vs. $c^{1/2}$ using Eq. (3). The values of V_ϕ^0, A_V and B_V at each temperature are listed in Table 3. The estimated uncertainties in V_ϕ^0 values are represented by standard deviation σ, which is equal to the root mean square of the deviations between the experimental and calculated V_ϕ for each data point. V_ϕ^0 values for the aqueous NA solutions at 298.15, 308.15 and 318.15 K were in good agreement with the V_ϕ^0 values reported earlier [20]. Table 3 shows that V_ϕ^0 values are generally positive and increase with a rise in both the temperature and molarity of CA in the solutions. This indicates the presence of strong solute–solvent interactions and these interactions are further strengthened at higher temperatures and higher concentration of CA in the solutions. The crystal structure of NA was reported by Wright and King [21]. In the crystal, NA is linked by two weak hydrogen bonds from the hydrogen atoms of amide N-atom to the O-atom of one neighbouring molecule and to the ring N-atom of another molecules in such a fashion that a two-dimensional network parallel to (0 1 0) plane is formed with a inter-planer distance of 0.3579 nm at T = 295.15 K. Charman et. al. [22] reported the structure of NA in aqueous solution. They studied the concentration-dependent self-association of NA in solution by ^{1}H and ^{13}C NMR spectroscopy and osmometric measurements. Their results revealed that NA associates in aqueous solution with the amide groups of each NA molecule creating large associated species at higher concentrations. This fact justifies the observed changes in the values of parameters A_v and B_v.

This can also be explained in view of molar volume of the solute and that of the solvent mixtures. Solute–solvent interac-

Table 3

Limiting partial molar volume V_ϕ^0 (NA), and adjustable parameters A_v and B_v for NA in different aqueous CA acid solutions with standard deviations σ, Limiting Partial molar volume V_ϕ^0 (CA + water) at different temperatures.

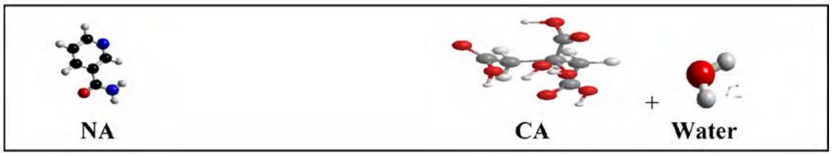
T (K)	V_ϕ^0 (NA) ($\times 10^6$ m^3 mol^{-1})	A_v (m^3 mol$^{-1.5}$)	B_v (m^3 mol^{-2})	σ (%)	V_ϕ^0 (CA + water) ($\times 10^6$ m^3 mol^{-1})
0.03[a]					
298.15	99.11	−15.92	−23.05	0.004	18.13
308.15	102.74	−18.04	−19.54	0.007	18.19
318.15	107.78	−40.87	−46.23	0.016	18.26
0.05[a]					
298.15	100.85	−23.88	−37.50	0.006	18.17
308.15	105.74	−27.62	−20.52	0.013	18.23
318.15	111.64	−52.84	−78.23	0.015	18.30
0.07[a]					
298.15	103.80	−23.81	−28.52	0.008	18.21
308.15	109.28	−40.99	−57.59	0.012	18.27
318.15	114.65	−51.72	−76.65	0.014	18.34
0.10[a]					
298.15	105.04	−24.79	−30.19	0.009	18.27
308.15	112.17	−38.18	−44.21	0.014	18.33
318.15	117.64	−40.23	−50.50	0.013	18.40

[a] Molarity of CA in water in mol dm^{-3}.

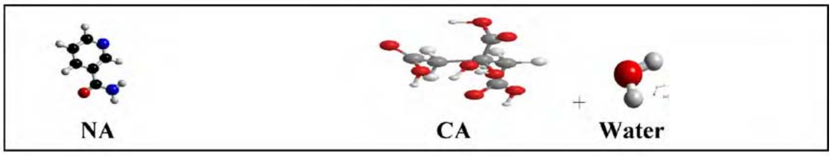
tions depend on the fitness of solute molecules into the solvent molecules. Greater the difference of molar volumes between solute and solvent molecules, higher is the fitness of solute molecules into solvent molecules. In this paper, the values of limiting partial molar volume of NA and (CA + water) is provided in Table 3, with the former increasing gradually with increasing temperature and higher molarity of (CA + water) mixtures. Hence, NA fits into (CA + water) mixture in the same order, resulting in more solute–solvent interactions i.e., they are more closely packed, with increasing temperature as well as concentration of (CA + water) mixtures. This is in excellent agreement with the conclusion drawn from the values of V_ϕ^0 as well as viscosity *B*-coefficient. Schematic representations of the relevant molecules, in connection with solute–solvent interactions, are shown below:

0.03(M):

0.05(M):



0.07(M):



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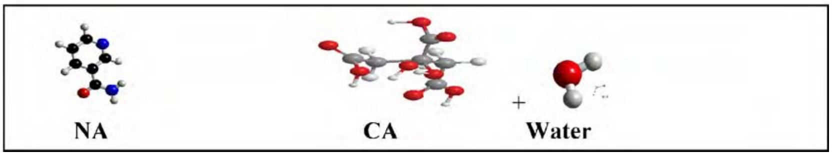

The partial molar expansibilities ϕ_E^0 can be obtained by the following equation [23]:

$$\phi_E^0 = \left(\frac{\delta V_\phi^0}{\delta T}\right)_P = a_1 + 2a_2 T \tag{4}$$

The values of ϕ_E^0 for different ternary solutions at $T = 298.15$, 308.15, and 318.15 K are given in Table 4 and it shows that ϕ_E^0 value increases as the temperature increases.

According to Hepler [24], the sign of $\left(\delta\phi_E^0/\delta T\right)_P$ or $\left(\delta^2 V_\phi^0/\delta T^2\right)_P$ is a better criterion in characterizing the long-range structure making and breaking ability of the solutes in solution. The general thermodynamic expression is as follows:

$$\left(\frac{\delta\phi_E^0}{\delta T}\right)_P = \left(\frac{\delta^2 V_\phi^0}{\delta T^2}\right)_P = 2a_2 \tag{5}$$

If the sign of $\left(\delta\phi_E^0/\delta T\right)_P$ is positive, the solute is a structure maker, otherwise it is a structure breaker. It is seen from Table 4, NA predominantly acts as a structure maker and its structure making ability increases with a rise in both the temperature and molarity of CA in the solutions. But its structure making ability decreases to some extent at higher concentration of CA in the mixtures. This fact may be attributed to gradual disappearance of caging or packing effect [25,26] in the ternary solutions. This observation is in good agreement to the observations made by Kundu and Kishore [20]. They suggested that NA acts as a water-structure promoter due to hydrophobic hydration. The small negative values of $\left(\delta\phi_E^0/\delta T\right)_P$ at 0.10 and 0.15 mol dm^{-3} aqueous CA solutions are probably due to higher structure-promoting ability of CA than NA with comparatively higher V_ϕ^0 value in aqueous solution originating from hydrophobic hydration with greater degree of hydrogen bonding than the bulk water [27].

Partial molar volumes ΔV_ϕ^0 of transfer from water to different aqueous CA solutions have been determined using the relations [28,29]:

$$\Delta V_\phi^0 = V_\phi^0(\text{aqueous CA solution}) - V_\phi^0(\text{water}) \tag{6}$$

The ΔV_ϕ^0 value is free from solute–solute interactions and therefore provides information regarding solute–cosolute interactions [28]. It can be seen from Table 5, the value of ΔV_ϕ^0 is positive at all the experimental temperatures and increases with the molarity of CA in the ternary solutions. The concentration dependence of the thermodynamic properties of the solutes in aqueous solutions can be explained in terms of overlap of hydration co-spheres. According to the co-sphere model, as developed by Friedman and Krishnan [30], the effect of overlap 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 ΔV_ϕ^0 indicate

Table 4
Partial molar expansibility, ϕ_E^0, for NA in different aqueous CA solutions at different temperatures.

Aqueous CA solution (mol dm^{-3})	ϕ_E^0 (m^3 mol^{-1} K^{-1})			$\left(\frac{\delta\phi_E^0}{\delta T}\right)_P$ (m^3 mol^{-1} K^{-2})
	298.15 K	308.15 K	318.15 K	
0.03	0.322	0.464	0.606	0.014
0.05	0.409	0.509	0.609	0.010
0.07	0.583	0.573	0.563	−0.001
0.10	0.798	0.632	0.466	−0.016

that solute–solvent interactions are predominant and the overall effect of the overlap of the hydration co-spheres of NA and CA reduce the effect of electrostriction of water by NA molecules and this effect increases with the molarity of CA in the ternary mixtures. In addition, standard partial molar volumes of the solute have also been explained by a simple model [31,32]:

$$V_\phi^0 = V_{\mathrm{VW}} + V_{\mathrm{Void}} - V_{\mathrm{S}} \tag{7}$$

where V_{VW} is the van der Waals volume, V_{Void} is the volume associated with voids or empty space, and V_{S} is the shrinkage volume due to electrostriction. Assuming the V_{VW} and V_{Void} have the same magnitudes in water and in aqueous CA solutions for the same solute [33], the increase in V_ϕ^0 values and the positive ΔV_ϕ^0 values can be attributed to the decrease in the shrinkage volume of water by NA in presence of CA. This fact suggests that CA has a dehydration effect on the hydrated NA.

In the literature [20], pyridine has been stated as a structure-breaker in aqueous solution and the structure-promoting tendency of NA has been assigned to the –CONH$_2$ group. Thus the interactions between NA and CA in water can roughly be summarized as follows: (i) interaction of H-atom of –OH group of CA with the N-atom in the heterocyclic ring of NA, (ii) interaction of H-atom of –OH group of CA with the N-atom in the amide group of NA, (iii) interaction of H-atom of –OH group of CA with the O-atom in the amide group of NA. Nicotinamide is prone to some acid–base equilibria. Leaving apart the protonation of the amide group, which occurs at high acidity levels, the protonation of the ring Nitrogen atom is endowed with a pK = 5.00 value [34]. Likewise, the ionization constants for citric acid have been reported as: pK_1 = 3.13, pK_2 = 4.76 and pK_3 = 6.40 [35]. This means that all these ionizations occur within quite close acidity ranges to each other and, under the experimental conditions used in this work, strong (and maybe prevailing) acid–base interactions can be surmised. Therefore, the overall positive V_ϕ^0 values indicate that solute–solvent interactions predominate over solvent–solvent interactions and thus reduce the electrostriction of water molecules by NA imparting positive values of ΔV_ϕ^0.

The viscosity data of the aqueous and aqueous CA solutions of NA have been analyzed using the Jones–Dole [36] equation:

$$(\eta/\eta_0 - 1)/\sqrt{c} = (\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \tag{8}$$

where $\eta_r = \eta/\eta_0$, and η are the viscosities of solvent and solution respectively, c is the molar concentration of a solution. A and B are the Jones–Dole constants estimated by a least squares method and reported in Table 5.

Table 5 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 CA in the mixtures.

The viscosity B-coefficient [37] 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 5 shows that the values of the viscosity B-coefficient for NA in the studied solvent systems are positive, thereby suggesting the presence of strong solute–solvent interaction and these types of interactions are strengthened with an increase in both the temperature and molarity of CA in the mixtures.

Viscosity B-coefficients of transfer ΔB from water to different aqueous CA solutions have been determined using the relations [28,29]:

$$\Delta B = B(\text{aqueous CA solution}) - B(\text{water}) \tag{9}$$

Table 5
Partial molar volumes, V_ϕ^0, Partial molar volumes of transfer, ΔV_ϕ^0, viscosity A-coefficients, viscosity B-coefficients, and Viscosity B-coefficients of transfer, ΔB, from water to different aqueous CA solutions for NA at three different temperatures.

Aqueous CA solutions (mol dm^{-3})	V_ϕ^0 ($\times 10^6$ m^3 mol^{-1})	ΔV_ϕ^0 ($\times 10^6$ m^3 mol^{-1})	A (dm$^{3/2}$ mol$^{-1/2}$)	B (dm^3 mol^{-1})	ΔB (dm^3 mol^{-1})
T = 298.15 K					
0.00	96.87 [40]	0	0.042 [40]	0.221 [40]	0
0.03	99.11	2.24	0.038 (±0.002)	0.304 (±0.009)	0.113
0.05	100.85	3.98	0.011 (±0.003)	0.388 (±0.015)	0.187
0.07	103.80	6.93	−0.051 (±0.004)	0.499 (±0.019)	0.298
0.10	105.04	8.17	−0.066 (±0.004)	0.612 (±0.019)	0.411
T = 308.15 K					
0.00	97.71 [40]	0	0.030 [40]	0.424 [40]	0
0.03	102.74	5.03	0.019 (±0.002)	0.435 (±0.010)	0.011
0.05	105.74	8.03	−0.012 (±0.003)	0.477 (±0.013)	0.053
0.07	109.28	11.57	−0.064 (±0.003)	0.667 (±0.017)	0.243
0.10	112.17	14.46	−0.081 (±0.004)	0.783 (±0.018)	0.359
T = 318.15 K					
0.00	100.86 [40]	0	−0.014 [40]	0.538 [40]	0
0.03	107.78	6.92	−0.005 (±0.002)	0.581 (±0.012)	0.043
0.05	111.64	10.78	−0.047 (±0.004)	0.617 (±0.016)	0.079
0.07	114.65	13.79	−0.093 (±0.006)	0.887 (±0.027)	0.349
0.10	117.64	16.78	−0.096 (±0.004)	0.957 (±0.018)	0.419

The values within () parenthesis indicate standard errors.

Table 6
Values of $\bar{V}_1^0$, $\Delta\mu_1^{0\neq}$, $\bar{V}_2^0 - \bar{V}_1^0$, $\Delta\mu_2^{0\neq}$, $T\Delta S_2^{0\neq}$, and $\Delta H_2^{0\neq}$ for NA in different aqueous CA solutions at different temperatures.

Parameters	298.15 K	308.15 K	318.15 K
0.03 mol dm^{-3}			
$\bar{V}_1^0$ ($\times 10^6$ m^3 mol^{-1})	18.08	18.14	18.21
$\Delta\mu_1^{0\neq}$ (kJ mol^{-1})	9.13	8.62	8.31
$(\bar{V}_2^0 - \bar{V}_1^0)$ ($\times 10^6$ m^3 mol^{-1})	81.03	84.60	89.57
$\Delta\mu_2^{0\neq}$ (kJ mol^{-1})	45.90	61.49	84.55
$T\Delta S_2^{0\neq}$ (kJ mol^{-1})	–576.09	–595.41	–614.73
$\Delta H_2^{0\neq}$ (kJ mol^{-1})	–530.18	–533.92	–530.18
0.05 (mol dm^{-3})			
$\bar{V}_1^0$ ($\times 10^6$ m^3 mol^{-1})	18.09	18.15	18.22
$\Delta\mu_1^{0\neq}$ (kJ mol^{-1})	9.17	8.67	8.31
$(\bar{V}_2^0 - \bar{V}_1^0)$ ($\times 10^6$ m^3 mol^{-1})	82.76	87.59	93.42
$\Delta\mu_2^{0\neq}$ (kJ mol^{-1})	53.21	67.39	89.69
$T\Delta S_2^{0\neq}$ (kJ mol^{-1})	–543.80	–562.03	–580.27
$\Delta H_2^{0\neq}$ (kJ mol^{-1})	–490.59	–494.65	–490.59
0.07 mol dm^{-3}			
$\bar{V}_1^0$ ($\times 10^6$ m^3 mol^{-1})	18.10	18.16	18.23
$\Delta\mu_1^{0\neq}$ (kJ mol^{-1})	9.21	8.78	8.42
$(\bar{V}_2^0 - \bar{V}_1^0)$ ($\times 10^6$ m^3 mol^{-1})	85.70	91.12	96.42
$\Delta\mu_2^{0\neq}$ (kJ mol^{-1})	68.37	94.18	128.79
$T\Delta S_2^{0\neq}$ (kJ mol^{-1})	–900.65	–930.86	–961.07
$\Delta H_2^{0\neq}$ (kJ mol^{-1})	–832.28	–836.68	–832.28
0.10 mol dm^{-3}			
$\bar{V}_1^0$ ($\times 10^6$ m^3 mol^{-1})	18.12	18.17	18.24
$\Delta\mu_1^{0\neq}$ (kJ mol^{-1})	9.27	8.87	8.51
$(\bar{V}_2^0 - \bar{V}_1^0)$ ($\times 10^6$ m^3 mol^{-1})	86.92	94.00	99.40
$\Delta\mu_2^{0\neq}$ (kJ mol^{-1})	83.78	110.54	138.82
$T\Delta S_2^{0\neq}$ (kJ mol^{-1})	–820.42	–847.94	–875.45
$\Delta H_2^{0\neq}$ (kJ mol^{-1})	–736.64	–737.40	–736.64

The ΔB values shown in Table 5 as a function of molarity of CA in solutions at the experimental temperatures support the results obtained from ΔV_ϕ^0 values discussed above.

The viscosity data have also been analyzed on the basis of transition state theory for relative viscosity of the solutions as suggested by Feakings et al. [38] using Eq. (10):

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + \frac{RT}{\bar{V}_1^0}(1000B + \bar{V}_2^0 - \bar{V}_1^0) \tag{10}$$

where $\bar{V}_1^0$ and $\bar{V}_2^0$ are the partial molar volumes of the solvent and solute respectively. $\Delta\mu_2^{0\neq}$ is the contribution per mole of the solute to the free energy of activation for the viscous flow of solutions have been determined from the above relation and $\Delta\mu_1^{0\neq}$ is the free energy of activation per mole of solvent mixture is calculated by the following relation [38]:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ \ln\left(\frac{\eta_0\bar{V}_1^0}{hN_A}\right) \tag{11}$$

where h is Planck's constant, N_A is Avogadro's number and $\Delta G_1^{0\neq}$ is the Gibbs energy of activation per mole of solvent mixture. From Table 6, it is seen that $\Delta\mu_1^{0\neq}$ is almost constant at all temperatures and solvent compositions. It implies that $\Delta\mu_2^{0\neq}$ is dependent mainly on the values of viscosity B-coefficients and $(\bar{V}_2^0 - \bar{V}_1^0)$ terms. $\Delta\mu_2^{0\neq}$ values are positive at all experimental temperatures and this and this suggests that the process of viscous flow becomes difficult as the temperature and molarity of CA in solution increases. So the formation of the transition state becomes less favorable. According to Feakins et al. [38] $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$ for solutes having positive viscosity B-coefficients indicates stronger ion-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 [39]. The entropy of activation for electrolytic solutions has been calculated using the following relation [38]:

$$\Delta S_2^{0\neq} = -\frac{d(\Delta\mu_2^{0\neq})}{dT} \tag{12}$$

$\Delta S_2^{0\neq}$ has been calculated from the slope of the plots of $\Delta\mu_2^{0\neq}$ versus T by using a least-square treatment. The enthalpy of activation has been determined by using the following relation [38]:

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \tag{13}$$

The values of $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ are reported in Table 6. 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, V_ϕ^0 and viscosity B-coefficient values for NA indicate the presence of strong solute–solvent interactions and these interactions are further strengthened at higher temperatures and higher concentration of CA in the ternary solutions. This study also reveals that NA acts as a water-structure promoter due to hydrophobic hydration in the presence of CA and CA has a dehydration effect on the hydrated NA.

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References

[1] F.A. Robinson, The Vitamin B-Complexes, Chapman & Hall, London, 1951 (Chapter 4).
[2] S. Cakir, I. Bulut, E. Bicer, O. Cakir, J. Coord. Chem. 56 (2003) 511–521.
[3] A.N. Nesmeyanov, N.A. Nesmeyanov, Fundamentals of Organic Chemistry, third vol., Mir, Moscow, 1981.
[4] 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, fourteenth ed., McGraw-Hill, New York, 1998.
[5] C.R.W. Edwards, I.A.D. Bouchier, C. Haslett, E.R. Chilvers, Davidson's Principles and Practice of Medicine, seventeenth ed., BPC Paulton Books Limited, Great Britain, 1996.
[6] R.E. Kirk, D.F. Othmer, Encyclopedia of Chemical Technology, fourth ed., John Willey and Sons, New York, 1993.
[7] J.A. Kent, Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology, fourteenth ed., Spingerlink, 2008.
[8] M.C. Maffia, J.A. Meirelles, J. Chem. Eng. Data 46 (2001) 582–587.
[9] A. Apelblat, E. Manzurola, Fluid Phase Equilibria 60 (1990) 157–171.
[10] A. Apelblat, E. Manzurola, J. Chem. Thermodyn. 6 (1985) 579–584.
[11] M.L. Parmar, R.K. Awasthi, M.K. Guleria, J. Chem. Sci. 116 (2004) 33–38.
[12] A.H. Sijpkes, P.A. Rossum, J.S. Raad, G. Somsen, Chem. Thermodyn. 9 (1989) 1061–1067.
[13] B.J. Levien, J. Phys. Chem. 59 (1955) 640–644.
[14] H.G. Windmuller, C.J. Ackerman, H. Bakerman, O. Mickelsen, J. Biol. Chem. 234 (1959) 889–894.
[15] M. Iwaki, N.P.J. Cotton, P.G. Quirk, P.R. Rich, J.B. Jackson, J. Am. Chem. Soc. 128 (2006) 2621–2629.
[16] J.M. McDowall, C.A. Vincent, J. Chem. Soc. Faraday Trans. I 70 (1974) 1862–1868.
[17] M.R.J. Deck, K.J. Bird, A.J. Parker, Aust. J. Chem. 28 (1975) 955–963.
[18] M.N. Roy, B. Sinha, V.K. Dakua, J. Chem. Eng. Data 51 (2006) 590–594.
[19] M.N. Roy, B. Sinha, J. Mol. Liq. 133 (2007) 89–99.
[20] A. Kundu, N. Kishore, J. Solution Chem. 32 (2003) 703–717.
[21] W.B. Wright, G.S.D. King, Acta Crystallogr. 7 (1954) 283–288.
[22] W.N. Charman, C.S.C. Lai, D.J. Craik, Aust. J. Chem. 46 (1993) 377–385.
[23] M.N. Roy, B. Sinha, R. Dey, A. Sinha, Int. J. Thermophys. 26 (2005) 1549–1563.
[24] L.G. Hepler, Can. J. Chem. 47 (1969) 4617–4622.
[25] F.J. Millero, in: R.A. Horne (Ed.), Water and Aqueous Solutions, 1972, New York (Chapter 13).
[26] M.L. Parmar, D.S. Banyal, Indian J. Chem. 44 A (2005) 1582–1588.

[27] W.Y. Wen, in: R.A. Horne (Ed.), Water and Aqueous Solutions, Willey–Interscience, New York, 1972 (Chapter 15).
[28] K. Belibagli, E. Agranci, J. Solution Chem. 19 (1990) 867–882.
[29] C. Zhao, P. Ma, J. Li, J. Chem. Thermodyn. 37 (2005) 37–42.
[30] H.L. Friedman, C.V. Krishnan, in: F. Franks (Ed.), Water: A Comprehensive Treatise, third vol., Plenum Press, New York, 1973 (Chapter 1).
[31] R.K. Wadi, P. Ramasami, J. Chem. Soc. Faraday Trans. 93 (1997) 243–247.
[32] R. Bhat, J.C. Ahluwalia, J. Phys. Chem. 89 (1985) 1099–1105.
[33] A.K. Mishra, J.C. Ahluwalia, J. Chem. Soc. Faraday Trans. I 77 (1981) 1469–1483.
[34] B. Garcia, S. Ibeas, J.M. Leal, J. Phys. Org. Chem. 9 (1996) 593–597.
[35] J. Barbosa, J.L. Beltrán, V. Sanz-Nebot, Anal. Chim. Acta 288 (1994) 271–278.
[36] G. Jones, M. Dole, J. Am. Chem. Soc. 51 (1929) 2950–2964.
[37] F.J. Millero, A. Losurdo, C. Shin, J. Phys. Chem. 82 (1978) 784–792.
[38] D. Feakins, D.J. Freemantle, K.G. Lawrence, J. Chem. Soc. Faraday Trans. 70 (1974) 795–806.
[39] B. Samantaray, S. Mishra, U.N. Dash, J. Teach. Res. Chem. 11 (2005) 87–93.
[40] B. Sinha, B.K. Sarkar, M.N. Roy, J. Chem. Thermodyn. 40 (2008) 394–400.