

## CHAPTER VII

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# INVESTIGATION ON MOLECULAR INTERACTIONS OF NICOTINAMIDE IN AQUEOUS CITRIC ACID SOLUTIONS WITH REFERENCE TO MANIFESTATION OF PARTIAL MOLAR VOLUME AND VISCOSITY *B*- COEFFICIENT MEASUREMENTS

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### 7.1 Introduction:

Enzymes are the functional unit of cell metabolism as they catalyze different reactions to degrade nutrient molecules into simple ones. Many enzymes require a non-protein cofactor for their catalytic activities. Vitamins are essential precursors for various coenzymes. These coenzymes are therefore required in almost all metabolic pathways [1]. NA, commonly known as vitamin B3 [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. It also serves to maintain normal function of the digestive systems and cholesterol levels in human body [1]. The combination of nicotinic acid and nicotinamide is clinically referred as niacin [3-5], since nicotinic acid is converted in the body into the amide very fast and for nutritional purposes both of them have equal biological activities. NA is an interesting molecule because of its two nitrogen atoms – one in the heterocyclic ring and the other as the amide group.

Polybasic acids play an important role in biological and industrial processes and accurate knowledge of their properties is therefore required. Citric acid,  $C_6H_8O_7 \cdot H_2O$  i.e., 2-hydroxypropane-1,2,3-tricarboxylic acid, is a tribasic, environmentally acceptable, and versatile chemical. As it occurs in metabolism of almost all living things, 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. In industry, it is used in the manufacture of the alkyl resins, as a sequestering agent to remove trace metals, in special inks, in electroplating, a chelate to form stable complexes with multivalent metal ions [6, 7]. It is used in personal care products [7, 8].

**Nicotinamide****Citric acid****Water**

Literature survey shows that there are few data on thermodynamic and transport properties for aqueous citric acid solutions. Marcia [9] reported the water activities and pH for aqueous solutions of citric acid at 298.15 K. The measurements were made from 5 to 50 mass % of citric acid. Apelblat [10, 11] and Parmer [12] 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. Sijpkens [13] measured heat capacities and partial molar heat capacities at infinite dilution of citric acid in water at 298.15 K. Levien [14] carried the studies of apparent osmotic coefficients and molar conductivities. Although there have been extensive studies on various properties of NA [1,5,15-19], 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 [19,20] 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.

## 7.2 Experimental Section:

### 7.2.1 Materials

NA was purchased from ACROS Organics Company and used as such. Its mass purity as supplied is 98%. Citric acid, monohydrate (Himedia) was used after drying over P<sub>2</sub>O<sub>5</sub> in a desiccator for more than 48 h. The reagents were always placed in the

desiccator over  $P_2O_5$  to keep them in dry atmosphere. Freshly distilled conductivity water (sp. cond.  $\approx 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ ) 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.

### 7.2.2 Apparatus and Procedure

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  $\pm 0.0001 \text{ mol} \cdot \text{dm}^{-3}$ .

Density measurements of ternary mixtures were performed at atmospheric pressure at  $T = (298.15, 308.15, \text{ and } 318.15) \text{ K}$  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  $\pm 0.00002 \text{ g} \cdot \text{cm}^{-3}$ . The temperature was automatically kept constant within  $\pm 0.01 \text{ K}$ . The mixtures were prepared by mass in  $10 \text{ cm}^3$  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  $T = (298.15, 308.15, \text{ and } 318.15) \text{ K}$  with triply distilled water and purified methanol. It was filled with experimental liquid and placed vertically in a glass sided thermostat maintained constant to  $\pm 0.01 \text{ K}$ . After attainment of thermal equilibrium, the efflux times of flow of liquids were recorded with a stopwatch correct to  $\pm 0.1 \text{ s}$ . Viscosity of the solution,  $\eta$ , is given by the following equation:

$$\eta = (Kt - L/t) \cdot \rho \quad (1)$$

where  $K$  and  $L$  are the viscometer constants and  $t$  and  $\rho$  are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within  $\pm 0.002 \text{ mPa} \cdot \text{s}$ . Details of the methods and techniques of density and viscosity measurements have been described elsewhere [21,22].

The nicotinamide solutions studied here were prepared by mass and the conversion of molality in molarity was accomplished [21,22] using experimental density values. The experimental values of concentrations  $c$ , densities  $\rho$ , viscosities  $\eta$ , and derived parameters at various temperatures are reported in Table 2.

### 7.3 Result and Discussion:

The densities, for the solutions of NA in aqueous CA measured at 298.15, 308.15, and 318.15K, have been used to calculate the apparent molar volumes ( $V_\phi$ ) of the solute using the following expression [21] and listed in Table 2

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

where  $c$  is the molar concentration of the solution;  $M_2$  is the molecular weight of the solute;  $\rho$  and  $\rho_0$  is the densities of the solution and solvent, respectively. The plots of  $V_\phi$  against square root of molar concentration  $c^{1/2}$ , were non-linear and  $V_\phi$  values were fitted to the following equation [14]:

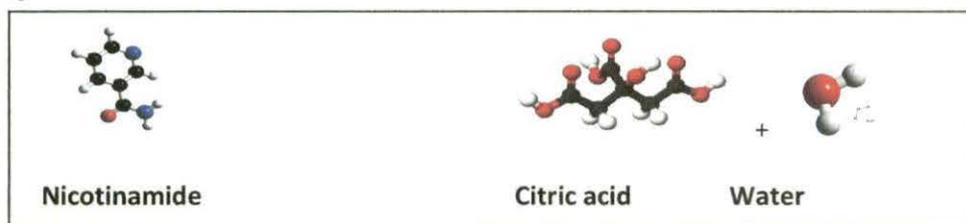
$$V_\phi = V_\phi^0 + A_v c^{1/2} + B_v c \quad (3)$$

where  $V_\phi^0$  is the partial molar volume at infinite dilution,  $A_v$  and  $B_v$  are two adjustable parameters. The  $V_\phi^0$  values were calculated applying a least squares technique to the plots of  $V_\phi$  vs.  $c^{1/2}$  using equation (3). The values of  $V_\phi^0$ ,  $A_v$  and  $B_v$  at each temperature are listed in Table 3. The estimated uncertainties in  $V_\phi^0$  values are represented by standard deviation  $\sigma$ , which is equal to the root mean square of the deviations between the experimental and calculated  $V_\phi$  for each data point.  $V_\phi^0$  values for the aqueous NA solutions at 298.15, 308.15 and 318.15 K were in good agreement with the  $V_\phi^0$  values reported earlier [23]. Table 3 shows that  $V_\phi^0$  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 [24]. 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

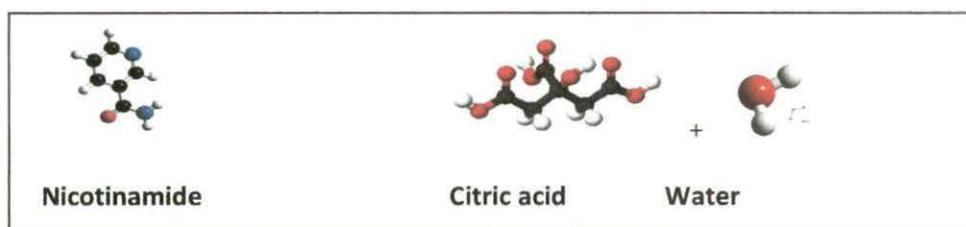
molecule and to the ring N-atom of another molecules in such a fashion that a two-dimensional network parallel to (010) plane is formed with a inter-planer distance of 0.3579 nm at  $T = 295.15$  K. Charman et al.[25] reported the structure of NA in aqueous solution. They studied the concentration-dependent self-association of NA in solution by  $^1\text{H}$  and  $^{13}\text{C}$  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 interactions 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, partial molar volume of NA, the values of which along with the values of  $(\text{CA}+\text{water})$  are provided in Table 4, increases gradually with increasing temperature and higher molarity of  $(\text{CA}+\text{water})$  mixtures. Hence, NA fits into  $(\text{CA}+\text{water})$  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  $(\text{CA}+\text{water})$  mixtures. This is in excellent agreement with the conclusion drawn from the values of  $V_\phi^0$  as well as viscosity  $B$ -coefficient. Schematic representations of the relevant molecules, in connection with solute-solvent interactions, are shown below:

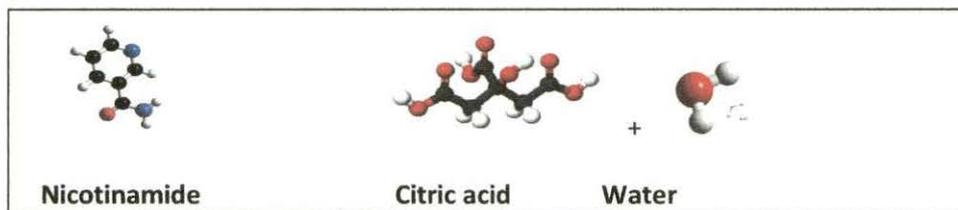
0.03(M):



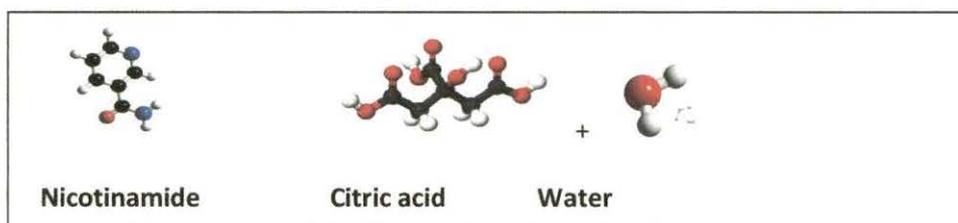
0.05(M):



0.07(M):



0.1(M):



The partial molar volumes  $V_{\phi}^0$  were fitted to a polynomial of the following type in terms of absolute temperature T:

$$V_{\phi}^0 = a_0 + a_1 + a_2 T^2 \quad (4)$$

Values of the coefficients  $a_0$ ,  $a_1$ ,  $a_2$  of the above equation for different NA solutions are reported in Table 5.

The partial molar expansibilities  $\phi_E^0$  can be obtained by the following equation [26]:

$$\phi_E^0 = \left( \frac{\delta V_{\phi}^0}{\delta T} \right)_P = a_1 + a_2 T \quad (5)$$

The values of  $\phi_E^0$  for different ternary solutions at  $T = (298.15, 308.15, \text{ and } 318.15)$  K are given in Table 5 and it shows that  $\phi_E^0$  value increases as the temperature increases.

According to Hepler [27], the sign of  $\left( \frac{\delta \phi_E^0}{\delta T} \right)_P$  or  $\left( \frac{\delta^2 V_{\phi}^0}{\delta T^2} \right)_P$  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:

$$\left( \frac{\delta \phi_E^0}{\delta T} \right)_P = \left( \frac{\delta^2 \phi_V^0}{\delta T^2} \right)_P = 2a_2 \quad (6)$$

If the sign of  $\left(\frac{\delta\phi_E^0}{\delta T}\right)_P$  is positive, the solute is a structure maker, otherwise it is

a structure breaker. It is seen from Table 6, 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 resorcinol in the mixtures. This fact may be attributed to gradual disappearance of caging or packing effect [28,29] in the ternary solutions. This observation is in line with the observation made by Kundu and Kishore [23]. They suggested that NA acts as a water-structure promoter due to hydrophobic hydration. The small negative values of  $\left(\frac{\delta\phi_E^0}{\delta T}\right)_P$  at (0.10 and 0.15) mol·dm<sup>-3</sup> aqueous CA solutions are probably due to higher structure promoting ability of CA than nicotinamide with comparatively higher  $V_\phi^0$  value in aqueous solution [7] originating from hydrophobic hydration with greater degree of hydrogen bonding than the bulk water [30].

Partial molar volumes  $\Delta V_\phi^0$  of transfer from water to different aqueous CA solutions have been determined using the relations [31,32]:

$$\Delta V_\phi^0 = V_\phi^0 \text{ (aqueous CA solution)} - V_\phi^0 \text{ (water)} \quad (7)$$

The  $\Delta V_\phi^0$  value is free from solute-solute interactions and therefore provides information regarding solute-cosolute interactions [31]. It can be seen from Table 8, the value of  $\Delta V_\phi^0$  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 [33], 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  $\Delta V_\phi^0$  indicate 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 as shown in Fig.1(a), Fig.1(b) and Fig.1(c)

( $\Delta V_\phi^0$  versus molarity of CA in solution). In addition, standard partial molar volumes of the solute have also been explained by a simple model [34,35]:

$$V_\phi^0 = V_{vw} + V_{void} - V_s \quad (8)$$

where  $V_{vw}$  is the van der Waals volume,  $V_{void}$  is the volume associated with voids or empty space, and  $V_s$  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 [36], the increase in  $V_\phi^0$  values and the positive  $\Delta V_\phi^0$  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 [23], pyridine has been stated as a structure-breaker in aqueous solution and the structure-promoting tendency of NA has been assigned to the  $-\text{CONH}_2$  group. Thus the interactions between NA and CA in water can roughly be summarized as follows: (i) interaction of H-atom of  $-\text{OH}$  group of CA with the N-atom in the heterocyclic ring of NA, (ii) interaction of H-atom of  $-\text{OH}$  group of CA with the N-atom in the amide group of NA, (iii) interaction of H-atom of  $-\text{OH}$  group of CA with the O-atom in the amide group of NA. Therefore, the overall positive  $V_\phi^0$  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  $\Delta V_\phi^0$ .

The viscosity data of the aqueous and aqueous CA solutions of NA have been analyzed using the Jones-Dole [37] equation:

$$\frac{(\eta/\eta_0 - 1)}{\sqrt{c}} = \frac{(\eta_r - 1)}{\sqrt{c}} = A + B\sqrt{c} \quad (9)$$

where  $\eta_r = \eta/\eta_0$ , and  $\eta$  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 7.

Table 7 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 [38] 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 7 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.

The  $\Delta B$  values shown in Table 8 and depicted graphically in Fig.1(a), Fig.1(b) and Fig.1(c) ( $\Delta B$  versus molarity of CA in solution) as a function of molarity of CA in solutions at the experimental temperatures support the results obtained from  $\Delta V_\phi^0$  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.[39] using equation (11):

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

where the  $\bar{V}_1^0$  and the  $\bar{V}_2^0$  are the partial molar volumes of the solvent and solute respectively.  $\Delta\mu_2^{0\ddagger}$  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  $\Delta\mu_1^{0\ddagger}$  is the free energy of activation per mole of solvent mixture is calculated by the following relation [39]:

$$\Delta\mu_1^{0\ddagger} = \Delta G_1^{0\ddagger} = RT \ln\left(\frac{\eta_0 \bar{V}_1^0}{h N_A}\right) \quad (11)$$

where  $h$  is Planck's constant,  $N_A$  is Avogadro's number and  $\Delta G_1^{0\ddagger}$  is the free-energy of activation per-mole of solvent mixture. From Table 9, it is seen that  $\Delta\mu_1^{0\ddagger}$  is almost constant at all temperatures and solvent compositions. It implies that  $\Delta\mu_2^{0\ddagger}$  is dependent mainly on the values of viscosity  $B$ -coefficients and  $(\bar{V}_2^0 - \bar{V}_1^0)$  terms.  $\Delta\mu_2^{0\ddagger}$  values were 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. [39],  $\Delta\mu_2^{0\ddagger} > \Delta\mu_1^{0\ddagger}$  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 [40]. The entropy of activation for electrolytic solutions has been calculated using the following relation [39]:

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

$\Delta S_2^{0\ddagger}$  has been calculated from the slope of the plots of  $\Delta\mu_2^{0\ddagger}$  versus  $T$  by using a least-square treatment. The enthalpy of activation has been determined by using the following relation [39]:

$$\Delta H_2^{0\ddagger} = \Delta\mu_2^{0\ddagger} + T\Delta S_2^{0\ddagger} \quad (13)$$

The values of  $\Delta S_2^{0\ddagger}$  and  $\Delta H_2^{0\ddagger}$  are reported in Table 9. 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.

#### 7.4 Conclusion:

In summary,  $V_\phi^0$  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.

**Tables:****Table 1: Density  $\rho$  and viscosity  $\eta$ , of different aqueous CA solution at different temperatures**

Aqueous CA solution / (mol·dm <sup>-3</sup> )	T/K	$\rho \times 10^{-3}$ / (kg·m <sup>-3</sup> )	$\eta$ / (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	0.7253
	318.15	0.9938	0.6261
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

**Table 2: Molarity  $c$ , density  $\rho$ , viscosity  $\eta$ , apparent molar volumes  $V_{\phi}^0$ , and  $(\eta_r - 1)/c^{1/2}$  for NA in different aqueous CA solutions at different temperatures**

$c$ / (mol·dm <sup>-3</sup> )	$\rho \times 10^{-3}$ / (kg·m <sup>-3</sup> )	$\eta$ / (mPa·s)	$V_{\phi}^0 \times 10^6$ / (m <sup>3</sup> ·mol <sup>-1</sup> )	$(\eta_r - 1) / c^{1/2}$
0.03 <sup>a</sup>				
T=298.15 K				
0.01200	0.9998	0.8836	97.65	0.0723
0.02401	1.0001	0.8878	97.20	0.0822
0.04001	1.0005	0.8940	96.86	0.0988
0.05601	1.0009	0.8992	96.63	0.1085
0.07201	1.0013	0.9048	96.51	0.1198
0.08402	1.0016	0.9085	96.43	0.1255

## T=308.15 K

0.01197	0.9966	0.7189	101.02	0.0678
0.02392	0.9968	0.7233	100.37	0.0879
0.03989	0.9972	0.7285	99.93	0.1041
0.05584	0.9976	0.7340	99.59	0.1211
0.07179	0.9980	0.7397	99.31	0.1363
0.08376	0.9983	0.7440	99.14	0.1469

## T=318.15 K

0.01192	0.9927	0.6292	103.85	0.0571
0.02384	0.9929	0.6335	102.58	0.0858
0.03973	0.9933	0.6394	101.52	0.1132
0.05562	0.9937	0.6451	100.66	0.1343
0.07151	0.9941	0.6501	100.10	0.1487
0.08343	0.9944	0.6546	99.88	0.1624

0.05<sup>a</sup>

## 298.15 K

0.01202	1.0012	0.8974	98.69	0.0542
0.02405	1.0015	0.9016	98.05	0.0689
0.04008	1.0019	0.9075	97.56	0.0863
0.05611	1.0023	0.9144	97.31	0.1056
0.07214	1.0027	0.9198	97.16	0.1158
0.08417	1.0030	0.9234	97.07	0.1211

## 308.15 K

0.01199	0.9979	0.7287	102.94	0.0422
0.02397	0.9982	0.7320	102.00	0.0594
0.03996	0.9985	0.7373	101.05	0.0828
0.05594	0.9989	0.7423	100.33	0.0989
0.07192	0.9993	0.7482	99.78	0.1178
0.08390	0.9996	0.7518	99.50	0.1261

## 318.15 K

0.01194	0.9940	0.6274	106.83	0.0191
0.02388	0.9942	0.6308	105.28	0.0494

0.03980	0.9945	0.6358	104.23	0.0778
0.05572	0.9949	0.6410	103.55	0.1009
0.07164	0.9952	0.6462	103.13	0.1204
0.08357	0.9955	0.6493	102.87	0.1283
0.07 <sup>a</sup>				
T=298.15 K				
0.01201	1.0028	0.9055	101.54	0.0072
0.02402	1.0031	0.9082	100.77	0.0244
0.04003	1.0034	0.9132	100.21	0.0467
0.05604	1.0038	0.9187	99.75	0.0649
0.07206	1.0042	0.9255	99.45	0.0853
0.08407	1.0045	0.9298	99.31	0.0954
T=308.15 K				
0.01197	0.9995	0.7605	105.52	0.0116
0.02394	0.9998	0.7639	104.23	0.0372
0.03991	1.0001	0.7695	103.38	0.0657
0.05587	1.0004	0.7763	102.87	0.0933
0.07183	1.0007	0.7828	102.45	0.1144
0.08380	1.0010	0.7883	102.19	0.1309
T=318.15 K				
0.01193	0.9956	0.6532	109.91	0.0076
0.02385	0.9958	0.6570	108.52	0.0429
0.03975	0.9960	0.6634	107.31	0.0823
0.05565	0.9963	0.6698	106.77	0.1115
0.07154	0.9966	0.6778	106.30	0.1440
0.08347	0.9968	0.6845	106.09	0.1688
0.10 <sup>a</sup>				
T=298.15 K				
0.01215	1.0051	0.9258	102.67	0.0043
0.02430	1.0053	0.9292	101.92	0.0262
0.04049	1.0057	0.9357	101.30	0.0556
0.05669	1.0060	0.9423	100.81	0.0766

0.07289	1.0064	0.9502	100.55	0.0992
0.08504	1.0066	0.9563	100.39	0.1146
T=308.15 K				
0.01211	1.0020	0.7863	108.47	0.0087
0.02422	1.0022	0.7903	107.38	0.0392
0.04037	1.0025	0.7972	106.28	0.0744
0.05651	1.0027	0.8049	105.54	0.1036
0.07265	1.0031	0.8133	105.08	0.1312
0.08477	1.0033	0.8198	104.84	0.1498
T=318.15 K				
0.01206	0.9980	0.6771	113.84	0.0061
0.02413	0.9981	0.6824	112.56	0.0547
0.04021	0.9983	0.6898	111.57	0.0972
0.05629	0.9985	0.6981	110.98	0.1337
0.07237	0.9987	0.7059	110.44	0.1609
0.08443	0.9989	0.7119	110.18	0.1793

<sup>a</sup> Molarity of CA in water in mol·dm<sup>-3</sup>

**Table 3. Limiting Partial molar volume  $V_{\phi}^0$ , and adjustable parameters  $A_v$  and  $B_v$  for NA in different aqueous CA acid solutions with standard deviations  $\sigma$  at different temperatures**

T/K	$V_{\phi}^0 \times 10^6$ (m <sup>3</sup> ·mol <sup>-1</sup> )	$A_v$ /(m <sup>3</sup> ·mol <sup>-1.5</sup> )	$B_v$ /(m <sup>3</sup> ·mol <sup>-2</sup> )	$\sigma$ (%)
0.03 <sup>a</sup>				
298.15	99.11	-15.92	-23.05	0.004
308.15	102.74	-18.04	-19.54	0.007
318.15	107.78	-40.87	-46.23	0.016
0.05 <sup>a</sup>				
298.15	100.85	-23.88	-37.50	0.006
308.15	105.74	-27.62	-20.52	0.013
318.15	111.64	-52.84	-78.23	0.015
0.07 <sup>a</sup>				
298.15	103.80	-23.81	-28.52	0.008
308.15	109.28	-40.99	-57.59	0.012
318.15	114.65	-51.72	-76.65	0.014
0.10 <sup>a</sup>				
298.15	105.04	-24.79	-30.19	0.009
308.15	112.17	-38.18	-44.21	0.014
318.15	117.64	-40.23	-50.50	0.013

<sup>a</sup> Molarity of CA in water in mol·dm<sup>-3</sup>

**Table 4. Partial molar volume of NA and (CA + Water) mixtures at different temperatures**

T/K	Partial molar volume of NA $\times 10^6/(\text{m}^3\cdot\text{mol}^{-1})$	Partial molar volume of (CA + Water) $\times 10^6/(\text{m}^3\cdot\text{mol}^{-1})$
0.03 <sup>a</sup>		
298.15	99.11	18.13
308.15	102.74	18.19
318.15	107.78	18.26
0.05 <sup>a</sup>		
298.15	100.85	18.17
308.15	105.74	18.23
318.15	111.64	18.30
0.07 <sup>a</sup>		
298.15	103.80	18.21
308.15	109.28	18.27
318.15	114.65	18.34
0.10 <sup>a</sup>		
298.15	105.04	18.27
308.15	112.17	18.33
318.15	117.64	18.40

<sup>a</sup> Molarity of CA in water in  $\text{mol}\cdot\text{dm}^{-3}$ **Table 5. Values of various coefficients of Eq. 4 for NA in different aqueous CA solutions.**

Aqueous CA solution/ $(\text{mol}\cdot\text{dm}^{-3})$	$a_0/(\text{m}^3\cdot\text{mol}^{-1})$	$a_1/(\text{m}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	$a_2/(\text{m}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-2})$
0.03	638.60	-3.911	0.007
0.05	419.02	-2.573	0.005
0.07	-110.12	0.882	-0.001
0.10	-870.10	5.747	-0.008

**Table 6. Partial molar expansibility  $\phi_E^0$  for NA in different aqueous CA solutions at different temperatures**

Aqueous CA solution/(mol·dm <sup>-3</sup> )	$\phi_E^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$			$\left( \frac{\delta \phi_E^0}{\delta T} \right)_P \times 10^6$ /(m <sup>3</sup> ·mol <sup>-1</sup> ·K <sup>-2</sup> )
	298.15K	308.15K	318.15K	
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

**Table 7. Values of A and B coefficients with standard errors for NA in different aqueous CA solutions at different temperatures.**

Aqueous CA solution /(mol·dm <sup>-3</sup> )	$A \times 10^{-3} / (\text{m}^{3/2} \cdot \text{mol}^{-1/2})$			$B \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
0.03	0.0375 (±0.002)	0.0196 (±0.002)	-0.0046 (±0.002)	0.3036 (±0.009)	0.4347 (±0.010)	0.5814 (±0.012)
0.05	0.0105 (±0.003)	-0.0121 (±0.003)	-0.0466 (±0.004)	0.3877 (±0.015)	0.4768 (±0.013)	0.6172 (±0.016)
0.07	-0.0507 (±0.004)	-0.0643 (±0.003)	-0.0927 (±0.006)	0.4986 (±0.019)	0.6669 (±0.017)	0.8870 (±0.027)
0.10	-0.0664 (±0.004)	-0.0807 (±0.004)	-0.0960 (±0.004)	0.6116 (±0.019)	0.7833 (±0.018)	0.9567 (±0.018)

**Table 8. Partial molar volumes  $V_{\phi}^0$ , Partial molar volumes of transfer,  $\Delta V_{\phi}^0$ , viscosity  $B$ -coefficients, and Viscosity  $B$ -coefficients of transfer,  $\Delta B$ , from water to different aqueous CA solutions for NA at three different temperatures.**

Aqueous CA solutions /(mol·dm <sup>-3</sup> )	$V_{\phi}^0 \times 10^6$ /(m <sup>3</sup> ·mol <sup>-1</sup> )	$\Delta V_{\phi}^0 \times 10^6$ /(m <sup>3</sup> ·mol <sup>-1</sup> )	$B \times 10^6$ /(m <sup>3</sup> ·mol <sup>-1</sup> )	$\Delta B \times 10^6$ /(m <sup>3</sup> ·mol <sup>-1</sup> )
T= 298.15 K				
0.03	96.87[41]	0	0.221[41]	0
0.05	99.11	2.24	0.334	0.113
0.07	100.85	3.98	0.388	0.187
0.10	103.80	6.93	0.499	0.298
T= 308.15 K				
0.03	97.71[41]	0	0.424[41]	0
0.05	102.74	5.03	0.435	0.011
0.07	105.74	8.03	0.477	0.053
0.10	109.28	11.57	0.667	0.243
T= 318.15 K				
0.03	100.86[41]	0	0.538[41]	0
0.05	107.78	6.92	0.581	0.043
0.07	111.64	10.78	0.617	0.079
0.10	114.65	13.79	0.887	0.349

**Table 9. Values of  $\bar{V}_1^0$ ,  $\Delta\mu_1^{0*}$ ,  $\bar{V}_2^0 - \bar{V}_1^0$ ,  $\Delta\mu_2^{0*}$ ,  $T\Delta S_2^{0*}$ , and  $\Delta H_2^{0*}$  for NA in different aqueous CA solutions at different temperatures**

Parameters	298.15 K	308.15 K	318.15 K
0.03 mol·dm <sup>-3</sup>			
$\bar{V}_1^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	18.08	18.14	18.21
$\Delta\mu_1^{0*} / (\text{kJ} \cdot \text{mol}^{-1})$	9.13	8.62	8.31
$(\bar{V}_2^0 - \bar{V}_1^0) \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	81.03	84.60	89.57
$\Delta\mu_2^{0*} / (\text{kJ} \cdot \text{mol}^{-1})$	45.90	61.49	84.55

$T\Delta S_2^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	-576.09	-595.41	-614.73
$\Delta H_2^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	-530.18	-533.92	-530.18
0.05 mol·dm <sup>-3</sup>			
$\bar{V}_1^0 \times 10^6 / (\text{m}^3\cdot\text{mol}^{-1})$	18.09	18.15	18.22
$\Delta\mu_1^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	9.17	8.67	8.31
$(\bar{V}_2^0 - \bar{V}_1^0) \times 10^6 / (\text{m}^3\cdot\text{mol}^{-1})$	82.76	87.59	93.42
$\Delta\mu_2^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	53.21	67.39	89.69
$T\Delta S_2^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	-543.80	-562.03	-580.27
$\Delta H_2^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	-490.59	-494.65	-490.59
0.07 mol·dm <sup>-3</sup>			
$\bar{V}_1^0 \times 10^6 / (\text{m}^3\cdot\text{mol}^{-1})$	18.10	18.16	18.23
$\Delta\mu_1^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	9.21	8.78	8.42
$(\bar{V}_2^0 - \bar{V}_1^0) \times 10^6 / (\text{m}^3\cdot\text{mol}^{-1})$	85.70	91.12	96.42
$\Delta\mu_2^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	68.37	94.18	128.79
$T\Delta S_2^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	-900.65	-930.86	-961.07
$\Delta H_2^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	-832.28	-836.68	-832.28
0.10 mol·dm <sup>-3</sup>			
$\bar{V}_1^0 \times 10^6 / (\text{m}^3\cdot\text{mol}^{-1})$	18.12	18.17	18.24
$\Delta\mu_1^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	9.27	8.87	8.51
$(\bar{V}_2^0 - \bar{V}_1^0) \times 10^6 / (\text{m}^3\cdot\text{mol}^{-1})$	86.92	94.00	99.40
$\Delta\mu_2^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	83.78	110.54	138.82
$T\Delta S_2^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	-820.42	-847.94	-875.45
$\Delta H_2^{0*} / (\text{kJ}\cdot\text{mol}^{-1})$	-736.64	-737.40	-736.64

Figures:

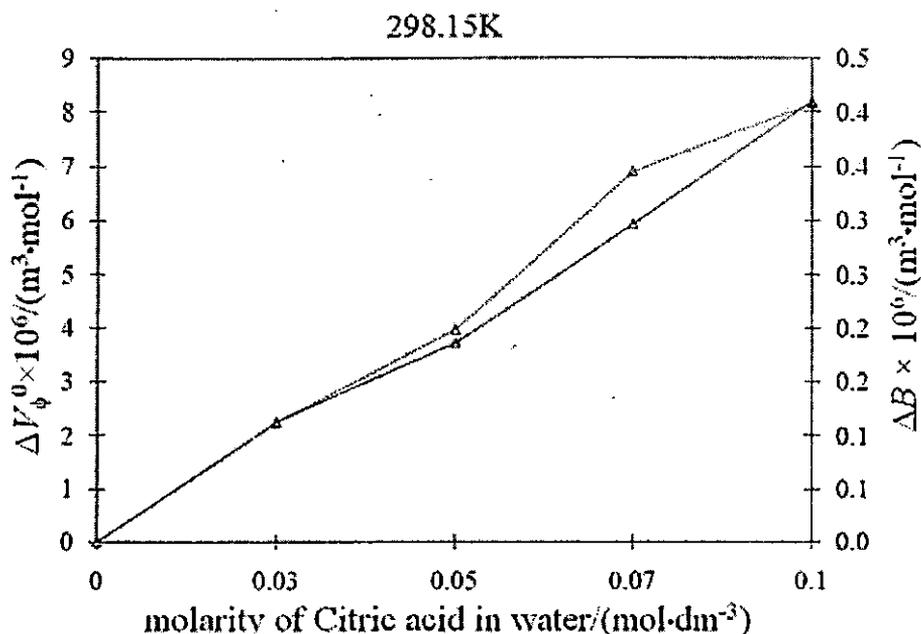


Fig. 1(a) Plots of partial molar volume ( $\Delta V_{\phi}^0$ ) and viscosity  $B$ -coefficients ( $\Delta B$ ) against molarity for the transfer from water to different aqueous CA solutions for NA at  $T = 298.15$  K. Dotted lines for  $\Delta V_{\phi}^0$  and solid lines for  $\Delta B$ .

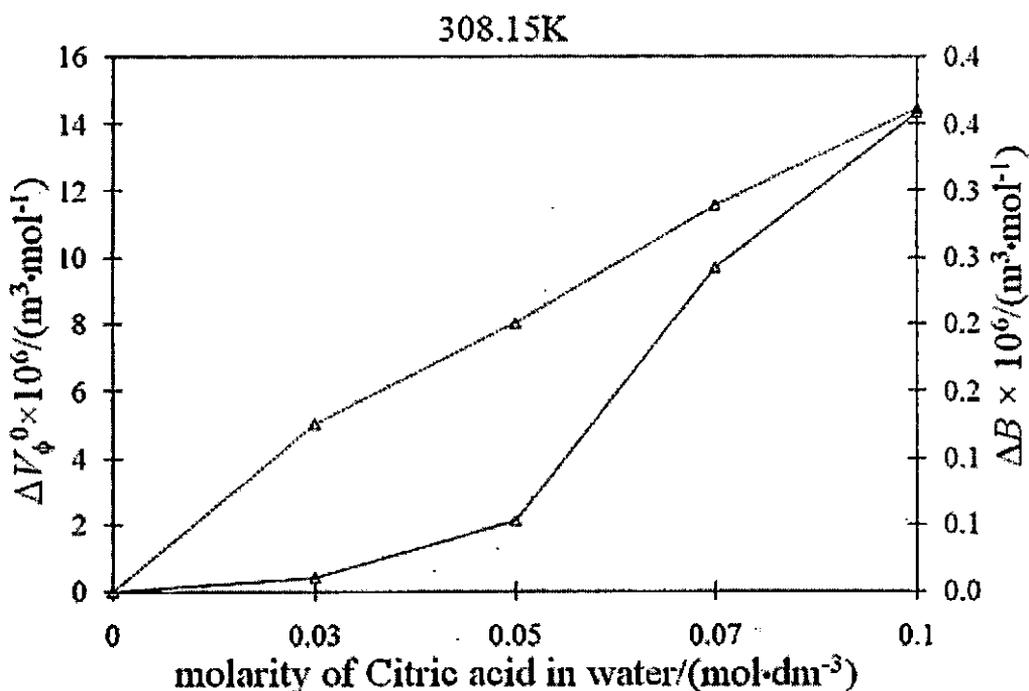
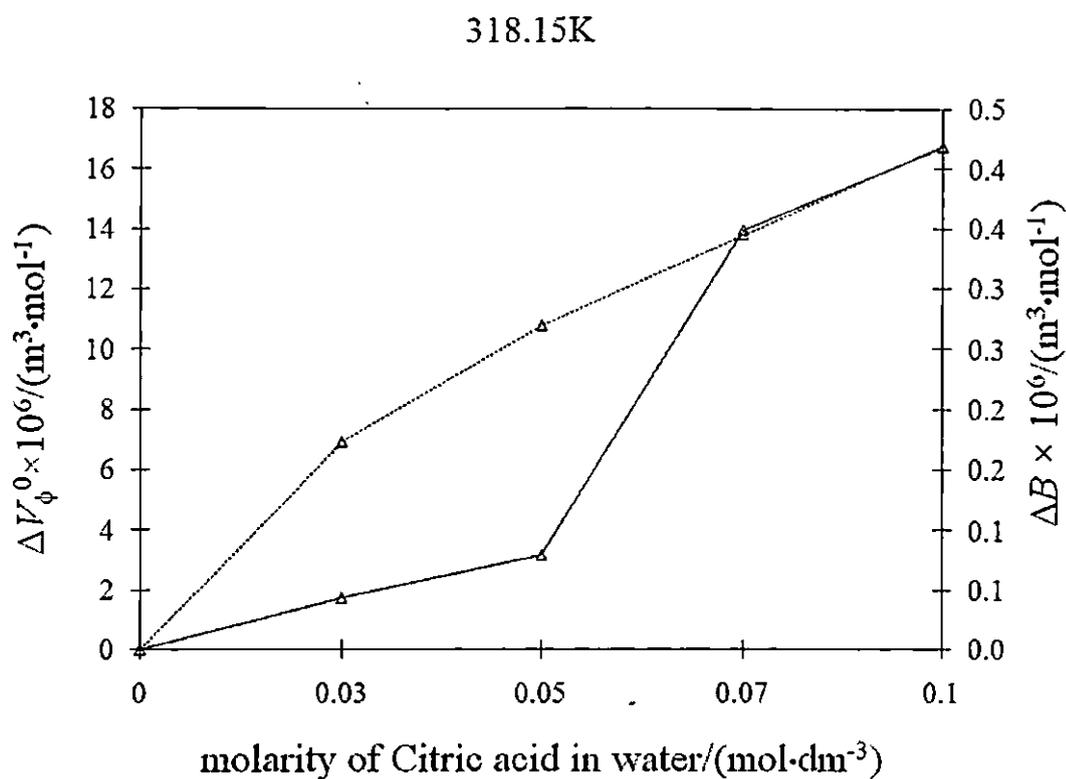


Fig. 1(b) Plots of partial molar volume ( $\Delta V_{\phi}^0$ ) and viscosity  $B$ -coefficients ( $\Delta B$ ) against molarity for the transfer from water to different aqueous CA solutions for NA at  $T = 308.15$  K. Dotted lines for  $\Delta V_{\phi}^0$  and solid lines for  $\Delta B$ .



**Fig. 1(c)** Plots of partial molar volume ( $\Delta V_{\phi}^0$ ) and viscosity  $B$ -coefficients ( $\Delta B$ ) against molarity for the transfer from water to different aqueous CA solutions for NA at  $T = 318.15$  K. Dotted lines for  $\Delta V_{\phi}^0$  and solid lines for  $\Delta B$ .