

Exploring the Molecular Interactions of Nicotinic Acid Prevailing in Salicylic Acid + H₂O, Anthranilic Acid + H₂O and o-Nitrobenzoic Acid + H₂O Mixed System at Different Temperatures

Kalipada Sarkar¹, Mahendra Nath Roy^{2*}

¹Department of ???, Islampur College, Islampur, Uttar Dinajpur, West Bengal, India, ²Department of Chemistry, University of North Bengal, Darjeeling, West Bengal, India.

ABSTRACT

Molecular interactions of some o-substituted benzoic acids, namely, salicylic acid, anthranilic acid, and o-nitrobenzoic acid with nicotinic acid are examined by physicochemical properties as density (ρ) and viscosity (η) at 298 K, 203 K, and 208 K. The limiting apparent molar volume (ϕ_V^0) and experimental slopes (S_V^*) determined from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The limiting apparent molar volume of transfer ($\Delta\phi_V^0$) has been determined to examine the ionic-ionic, hydrophilic-hydrophilic, and hydrophobic-hydrophobic interaction taking place in the solution. The viscosity data were examined using the Jones–Dole equation and the parameters viscosity A and B coefficients have also been interpreted in terms of solute-solute and solute-solvent interactions, respectively. Molar free energy of activation of viscous flow of the solvent, $\Delta\mu_1^0$ and solute, $\Delta\mu_2^0$ has been deduced to understand the stability of ground state over transition state.

Key words: Nicotinic acid, Limiting apparent molar volume, Solute-solvent interaction, Viscosity A and B coefficients, Hydrophobic-hydrophobic interaction

1. INTRODUCTION

Vitamins are very vital organic nutrients essential for any organism in the limited amount [1,2]. Vitamins exert important functions for the synthesis of varieties of coenzymes and are required in about all metabolic process [3-5]. Nicotinic acid (NA) has gotten enormous importance since it was manufactured in 1867 by Huber [6]. This is because of its usefulness in terms of chemical, biochemical, and therapeutic applications. It also plays an important role in restoring DNA and also in the manufacture of steroid hormones [7,8]. NA lessens the level of “bad” cholesterol and triglycerides in the blood thereby reducing the possibility of heart attack. It has extensive application as an additive in foods and cosmetics [9-11]. It is a pyridine derivative with a carboxyl group (–COOH) at the 3-position. It is also known as niacin, and it is Vitamin B₃. In this paper, we tried to find out the nature of solute-solvent interactions of NA in 0.01, 0.03, and 0.05 mass with o-substituted benzoic acids, namely, salicylic acid, anthranilic acid, and o-nitrobenzoic acid in aqueous medium at 298 K, 203 K, and 208 K. The acidity of substituted benzoic acids not only depends on the others groups present in the aromatic ring but also the position of the substituted groups. In our present study, the substituted groups are present in o-position. Hence, the main focus is to find the effect of inductive effect of these groups of substituted benzoic acids to examine the interaction of these compounds with NA. The densities and viscosities of aqueous NA and NA in an aqueous solution of salicylic acid, anthranilic acid, and o-nitrobenzoic acid are shown in Tables 1-4, respectively [Scheme 1].

2. EXPERIMENTAL SECTION

2.1. Source and Purity of Samples

Salicylic acid, anthranilic acid, and o-nitrobenzoic acids were purchased from Sd. Fine Chemicals, India and purified using standard methods as their mass fraction purity were 0.98. NA was procured

from Acros Organics, New Jersey, U.S.A. Its mass purity was.995 and was used as purchased. Deionized, doubly distilled water was used for the preparation of different aqueous solutions.

2.2. Apparatus and Procedure

Measurement of mass was carried out by Mettler Toledo AG-285 with uncertainty ± 0.0003 g. The density, ρ , was determined with an Anton Paar density meter (DMA 4500M) with a precision of 0.00005 g cm⁻³ kept at ± 0.01 K of the desired temperature. Double-distilled water and dry air were used for its calibration [12]. The viscosity, η , was determined by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol [13]. A thoroughly cleaned and perfectly dried viscometer with the experimental solution was placed vertically in a glass-walled thermostat (Bose Panda Instruments Pvt. Ltd.) maintained to ± 0.01 K. Efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. Three repetitions of each data point were recorded to get the average flow time. Viscosity of the solution may be calculated using the equation:

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

Stock solutions of NA in water were prepared by mass (Mettler Toledo AG285 with uncertainty ± 0.0003 g), and the solutions were prepared

*Corresponding author:

E-mail: mahendraroy2002@yahoo.co.in

ISSN NO: 2320-0898 (p); 2320-0928 (e)

DOI: 10.22607/IJACS.2018.603001

Received: 22nd February 2018;

Revised: 27th February 2018;

Accepted: 27th February 2018

Table 1: Experimental values of density (ρ), viscosity (η) of different molality of aqueous NA solution at 298 K, 303 K, and 308 K.

Aqueous solvent molality	$\rho \times 10^{-3} / \text{kg.m}^{-3}$			$\eta / \text{mP.s}$		
	298 K	303 K	308 K	298 K	303 K	308 K
0.01 m	0.99735	0.996145	0.995009	0.9007	0.8067	0.72911
0.03 m	0.99817	0.99680	0.995162	0.9049	0.811	0.7337
0.05 m	0.99898	0.99764	0.995993	0.9111	0.8172	0.7397

NA: Nicotinic acid

Table 2: Density (ρ) and viscosity (η) of NA in an aqueous solution of o-nitrobenzoic acid at 298 K, 303 K, and 308 K.

Molality Mol.kg ⁻¹	$\rho \times 10^{-3} \text{ kg.m}^{-3}$			$\eta / \text{mP.s}$		
	298 K	303 K	308 K	298 K	303 K	308 K
0.01m NA solution						
0.013	0.99778	0.99657	0.99542	0.9069	0.8129	0.7353
0.025	0.99821	0.99699	0.99583	0.9122	0.8184	0.7410
0.050	0.99906	0.99782	0.99665	0.9221	0.8295	0.7531
0.03 m NA solution						
0.013	0.99860	0.99722	0.99557	0.9111	0.8172	0.7399
0.025	0.99903	0.99764	0.99598	0.9164	0.8233	0.7463
0.050	0.99988	0.99848	0.99680	0.9273	0.8348	0.7592
0.05 m NA solution						
0.013	0.99941	0.99806	0.99640	0.9172	0.8234	0.7459
0.025	0.99984	0.99848	0.99681	0.9233	0.8301	0.7533
0.050	1.00069	0.99931	0.99763	0.9361	0.8440	0.7688

NA: Nicotinic acid

Table 3: Density (ρ) and viscosity (η) of NA in an aqueous solution of salicylic acid at 298 K, 303 K, and 308 K.

Molality Mol.kg ⁻¹	$\rho \times 10^{-3} \text{ kg.m}^{-3}$			$\eta \text{ mP.s}$		
	298 K	303 K	308 K	298 K	303 K	308 K
0.01 m NA solution						
0.013	0.99778	0.99657	0.99542	0.9067	0.8127	0.7351
0.025	0.99821	0.99699	0.99584	0.9116	0.8177	0.7405
0.050	0.99906	0.99783	0.99666	0.9209	0.8283	0.7519
0.03 m NA solution						
0.013	0.99860	0.99722	0.99558	0.9109	0.8171	0.7396
0.025	0.99903	0.99764	0.99599	0.9156	0.8219	0.7456
0.050	0.99989	0.99848	0.99681	0.9260	0.8334	0.7580
0.05 m NA solution						
0.013	0.99941	0.99806	0.99641	0.9170	0.8232	0.7457
0.025	0.99984	0.99848	0.99682	0.9227	0.8295	0.7527
0.050	1.00069	0.99932	0.99763	0.9349	0.8428	0.7676

NA: Nicotinic acid

by mass dilution. The change of molarity into molality was done using density values.

3. RESULTS AND DISCUSSION

3.1. Density Calculation

Apparent molar volumes (ϕ_v) were evaluated from the densities of the solution using the following equation [14,15].

$$\phi_v = M/\rho - 1000 (\rho - \rho_0)/m\rho\rho_0 \quad (1)$$

Where M is the molar mass of the solute, m is the molality of the solution ρ_0 and ρ are the densities of the mixture and the solution, respectively. The values of apparent molar volume and $(\eta_r - 1)/\sqrt{m}$ of NA in an aqueous solution of o-substituted benzoic acids at various temperatures are reported in Tables 5-7.

Table 4: Density (ρ) and viscosity (η) of NA in an aqueous solution of anthranilic acid at 298 K, 303 K, and 308 K.

Molality Mol.kg ⁻¹	$\rho \times 10^{-3} \text{ kg.m}^{-3}$			$\eta \text{ mP.s}$		
	298 K	303 K	308 K	298 K	303 K	308 K
0.01 m NA solution						
0.013	0.99778	0.99657	0.99542	0.9065	0.8125	0.7349
0.025	0.99821	0.99699	0.99584	0.9110	0.8171	0.7399
0.050	0.99907	0.99783	0.99666	0.9195	0.8271	0.7507
0.03 m NA solution						
0.013	0.99860	0.99722	0.99558	0.9107	0.8169	0.7394
0.025	0.99903	0.99764	0.99599	0.9150	0.8213	0.7450
0.050	0.99989	0.99848	0.99681	0.9248	0.8322	0.7568
0.05 m NA solution						
0.013	0.99941	0.99806	0.99641	0.9168	0.8230	0.7455
0.025	0.99984	0.99848	0.99682	0.9221	0.8289	0.7521
0.050	1.00070	0.99932	0.99764	0.9337	0.8416	0.7664

NA: Nicotinic acid

Table 5: Apparent molar volume, (ϕV) and $(\eta/\eta_0-1)/\sqrt{m}$ of NA in an aqueous solution of o-nitrobenzoic acid at different temperature.

Molality of IL	$\phi V \times 10^6$ (m ³ . Mol ⁻¹)	$(\eta/\eta_0-1)/\sqrt{m}$ (mol. kg ⁻¹) ^{-1/2}	$\phi V \times 10^6$ (m ³ . mol ⁻¹)	$(\eta/\eta_0-1)/\sqrt{m}$ (mol. kg ⁻¹) ^{-1/2}	$\phi V \times 10^6$ (m ³ . mol ⁻¹)	$(\eta/\eta_0-1)/\sqrt{m}$ (mol. kg ⁻¹) ^{-1/2}
	298K		303K		308 K	
0.01 m NA						
0.0125	80.0744	0.069	81.0259	0.077	81.9791	0.0849
0.025	80.1404	0.090	81.0773	0.103	82.0210	0.1153
0.05	80.2224	0.119	81.1501	0.141	82.0796	0.1645
0.03 m NA						
0.0125	80.0942	0.069	81.1012	0.076	82.0740	0.085
0.025	80.1500	0.090	81.1526	0.107	82.1158	0.121
0.05	80.2294	0.124	81.2128	0.147	82.1618	0.174
0.05 m NA						
0.0125	80.1645	0.067	81.1691	0.076	82.1410	0.084
0.025	80.2203	0.095	81.2204	0.112	82.1727	0.130
0.05	80.2871	0.137	81.2680	0.164	82.2162	0.197

NA: Nicotinic acid

The limiting apparent molar volume, ϕ_V^0 was computed using a least-square treatment to the plots of ϕ_V versus \sqrt{m} from the Masson equation.

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \quad (2)$$

Where ϕ_V^0 is the limiting apparent molar volume at infinite dilution and S_V^* is the experimental slope [16].

The plots of ϕ_V against square root of molal concentration (\sqrt{m}) were found to be linear. Values of ϕ_V^0 and S_V^* of NA in an aqueous solution of o-nitrobenzoic acid are reported in Tables 8-10. It is noticed that ϕ_V^0 is large positive and increases with increase in molality of NA in an aqueous solution of salicylic acid, anthranilic acid, and o-nitrobenzoic acid (Figure 1). It proves that solute-solvent interaction strengthens with an increase in molality of NA in the mixture. It is also seen that ϕ_V^0

of NA in o-substituted benzoic acids follow the order o-nitrobenzoic acid > salicylic acid > anthranilic acid. The order of -I effect of the o-substitute groups are $-\text{NO}_2 > -\text{OH} > -\text{NH}_2$, hence the order of acidity will also be o-nitrobenzoic acid > salicylic acid > anthranilic acid. Hence, in our present study, the solute-solvent interactions of NA in an aqueous solution of o-substituted benzoic acids increases with increasing acidity of o-substituted benzoic acids. This indicates that ion-ion interaction is acting between the solute and solvent. With increasing acidity of o-substituted benzoic acids, more ions are formed which interact with NA.

It is also noticed that ϕ_V^0 values increase with increasing temperature. With the increase in temperature, the H-bonding between water and solute molecule decreases hence more cosolute molecules can interact with NA.

Table 6: Apparent molar volume, (ϕV) and $(\eta/\eta_0-1)/\sqrt{m}$ of NA in an aqueous solution of salicylic acid at a different temperature.

Molality of IL	$\phi V \times 10^6$ ($m^3 \cdot mol^{-1}$)	$(\eta/\eta_0-1)/\sqrt{m}$ ($mol \cdot kg^{-1}$) ^{-1/2}	$\phi V \times 10^6$ ($m^3 \cdot mol^{-1}$)	$(\eta/\eta_0-1)/\sqrt{m}$ ($mol \cdot kg^{-1}$) ^{-1/2}	$\phi V \times 10^6$ ($m^3 \cdot mol^{-1}$)	$(\eta/\eta_0-1)/\sqrt{m}$ ($mol \cdot kg^{-1}$) ^{-1/2}
	298K		303K		308 K	
0.01 m NA						
0.0125	79.9738	0.067	80.9250	0.074	81.8781	0.0822
0.025	80.0398	0.086	80.9764	0.096	81.9199	0.1105
0.05	80.1343	0.112	81.0618	0.134	81.9910	0.1563
0.03 m NA						
0.0125	79.9938	0.066	81.0005	0.075	81.9729	0.080
0.025	80.0496	0.084	81.0519	0.095	82.0148	0.115
0.05	80.1415	0.117	81.1246	0.138	82.0733	0.166
0.05 m NA						
0.0125	80.0642	0.065	81.0686	0.073	82.0402	0.081
0.025	80.1200	0.090	81.1199	0.106	82.0719	0.124
0.05	80.1992	0.131	81.1800	0.157	82.1279	0.189

NA: Nicotinic acid

Table 7: Apparent molar volume, (ϕV) and $(\eta/\eta_0-1)/\sqrt{m}$ of NA in an aqueous solution of anthranilic acid at a different temperature.

Molality of IL	$\phi V \times 10^6$ ($m^3 \cdot mol^{-1}$)	$(\eta/\eta_0-1)/\sqrt{m}$ ($mol \cdot kg^{-1}$) ^{-1/2}	$\phi V \times 10^6$ ($m^3 \cdot mol^{-1}$)	$(\eta/\eta_0-1)/\sqrt{m}$ ($mol \cdot kg^{-1}$) ^{-1/2}	$\phi V \times 10^6$ ($m^3 \cdot mol^{-1}$)	$(\eta/\eta_0-1)/\sqrt{m}$ ($mol \cdot kg^{-1}$) ^{-1/2}
	298K		303K		308 K	
0.01 m NA						
0.0125	79.8732	0.064	80.8545	0.072	81.7770	0.0794
0.025	79.9392	0.081	80.9310	0.091	81.8188	0.1046
0.05	80.0462	0.104	81.0028	0.126	81.9025	0.1481
0.03 m NA						
0.0125	79.8934	0.064	80.8999	0.073	81.8719	0.078
0.025	79.9492	0.079	80.9512	0.090	81.9137	0.109
0.05	80.0535	0.110	81.0364	0.131	81.9848	0.157
0.05 m NA						
0.0125	79.9640	0.063	80.9681	0.071	81.9393	0.078
0.025	80.0197	0.085	81.0193	0.101	81.9710	0.119
0.05	80.1114	0.124	81.0919	0.149	82.0395	0.180

NA: Nicotinic acid

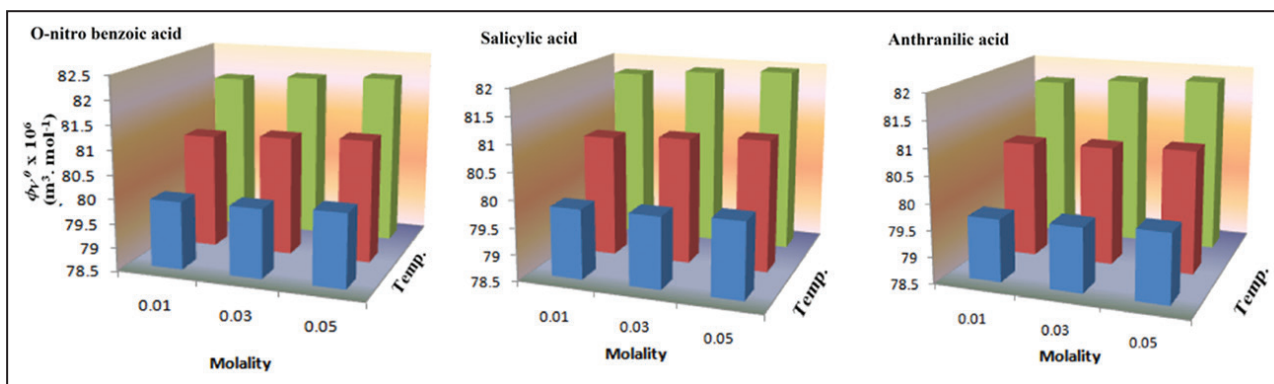


Figure 1: Variation of limiting apparent molar volumes (ϕV^0) of nicotinic acid with molality in an aqueous solution of o-substituted benzoic acids at different temperatures.

The volumetric virial coefficient S_V^* describes solute-solute interaction in solution [17]. In our present studies, the S_V^* values of NA in an aqueous solution of o-substituted benzoic acids are positive and decrease as the temperature and mass fraction of NA increase. The magnitude of ϕ_V^0 value is higher than that of S_V^* for all the solutions and at all experimental temperatures which indicate that solute-solvent interaction dominates over solute-solute interaction. The S_V^* values of NA in an aqueous o-substituted benzoic acids solution follows the order, o-nitrobenzoic acid < salicylic acid < anthranilic. It signifies that solute-solute interaction of NA decreases with increasing acidity of o-substituted benzoic acids.

The ϕ_V^0 is related with temperature as per follows the polynomial equation [18],

$$\phi_V^0 = a_0 + a_1T + a_2T^2 \quad (3)$$

Where a_0 , a_1 , and a_2 are coefficients and T is the temperature in K. The a_0 , a_1 , and a_2 values of the above equation for NA in an aqueous solution of o-substituted benzoic acids at 298 K, 303 K, and 308 K, respectively, are summarized in Table 10.

The limiting apparent molar expansibilities (Φ_E^0) can be evaluated from the above equation as follows [19]:

$$\Phi_E^0 = (\delta\phi_V^0/\delta T)_P = a_1 + 2a_2T \quad (4)$$

Many scientists stated that S_V^* is not the only condition for determining the structure-making or breaking capacity of any solute [20]. Hepler presented a procedure of examining the sign of $(\delta^2\phi_V^0/\delta T^2)_P$ for the solute to clarify the structure-making and breaking the ability of the solute in an aqueous medium by the following expression [21];

$$(\delta\Phi_E^0/\delta T)_P = (\delta^2\phi_V^0/\delta T^2)_P = 2a_2 \quad (5)$$

Table 8: Limiting apparent molal volumes (ϕV^0), experimental slopes (SV^*), limiting apparent molal volumes of transfer ($\Delta\phi V^0$), viscosity A and B-coefficients of NA in an aqueous solution of o-nitrobenzoic acid at different temperature.

Temperature (K)	$\phi V^0 \times 10^6$ ($m^3 \cdot mol^{-1}$)	$\Delta \phi V^0$ ($m^3 \cdot mol^{-1}$)	$SV^* \times 10^6$ ($m^3 \cdot mol^{-3/2} \cdot kg^{1/2}$)	B ($kg^{1/2} \cdot mol^{-1/2}$)	A ($kg \cdot mol^{-1}$)
0.01 m NA					
298 K	79.92	0.42	1.475	0.498	0.019
303 K	80.9	0.22	1.243	0.645	0.011
308 K	81.87	0.29	1.004	0.799	0.004
0.03 m NA					
298 K	79.95	0.45	1.352	0.544	0.012
303 K	80.99	0.31	1.11	0.7	0.007
308 K	81.98	0.4	0.872	0.892	0.004
0.05 m NA					
298 K	80.04	0.54	1.22	0.704	-0.004
303 K	81.07	0.39	0.977	0.881	-0.012
308 K	82.06	0.48	0.751	1.129	-0.029

NA: Nicotinic acid

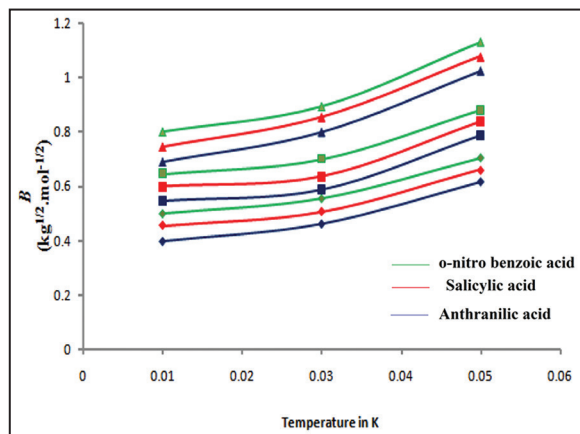
Table 9: Limiting apparent molal volumes (ϕV^0), experimental slopes (SV^*), limiting apparent molal volumes of transfer ($\Delta\phi V^0$), viscosity A and B-coefficients of NA in an aqueous solution of salicylic acid at a different temperature.

Temperature (K)	$\phi V^0 \times 10^6$ ($m^3 \cdot mol^{-1}$)	$\Delta \phi V^0 \times 10^6$ ($m^3 \cdot mol^{-1}$)	$SV^* \times 10^6$ ($m^3 \cdot mol^{-3/2} \cdot kg^{1/2}$)	B ($kg^{1/2} \cdot mol^{-1/2}$)	A ($kg \cdot mol^{-1}$)
0.01 m NA					
298 K	79.81	0.31	1.606	0.455	0.021
303 K	80.78	0.1	1.373	0.598	0.013
308 K	81.76	0.18	1.135	0.744	0.006
0.03 m NA					
298 K	79.84	0.34	1.483	0.506	0.014
303 K	80.87	0.19	1.241	0.635	0.009
308 K	81.87	0.29	1.003	0.853	0.005
0.05 m NA					
298 K	79.92	0.42	1.35	0.66	0.002
303 K	80.96	0.28	1.107	0.833	-0.01
308 K	81.95	0.37	0.882	1.076	-0.027

NA: Nicotinic acid

Table 10: Limiting apparent molal volumes (ϕV^0), experimental slopes (SV^*), limiting apparent molal volumes of transfer ($\Delta\phi V^0$), viscosity A and B-coefficients of NA in an aqueous solution of anthranilic acid at a different temperature.

Temperature (K)	$\phi V^0 \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$\Delta\phi V^0 \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$SV^* \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-3/2} \cdot \text{kg}^{1/2}$)	B ($\text{kg}^{1/2} \cdot \text{mol}^{-1/2}$)	A ($\text{kg} \cdot \text{mol}^{-1}$)
0.01 m NA					
298K	79.69	0.19	1.736	0.399	0.024
303K	80.71	0.03	1.466	0.549	0.015
308K	81.64	0.06	1.266	0.69	0.009
0.03 m NA					
298K	79.72	0.22	1.613	0.463	0.016
303K	80.76	0.08	1.371	0.587	0.011
308K	81.75	0.17	1.134	0.799	0.002
0.05 m NA					
298K	79.81	0.31	1.48	0.617	0.00
303K	80.84	0.16	1.238	0.785	-0.008
308K	81.83	0.25	1.012	1.023	-0.024

**Figure 2:** Variation of viscosity B coefficient of nicotinic acid (NA) with temperature in an aqueous solution of o-substituted benzoic acids (-♦- for 0.01 m, -■- for 0.03 m, and -▲- for 0.05 m nicotinic acid solution)

It is considered that the structure-making solutes should have positive $(\delta\Phi_E^0/\delta T)_P$ values, whereas structure-breaking solutes should have negative values [22,23]. The $(\delta\Phi_E^0/\delta T)_P$ values of NA in aqueous solution of salicylic acid, anthranilic acid, and o-nitrobenzoic acid have been shown in Table 11 it is apparent that $(\delta^2\phi V^0/\delta T^2)_P$ values are negative for NA solution in the presence of salicylic acid, anthranilic acid, and o-nitrobenzoic acid in aqueous medium. It signifies that o-substituted benzoic acid performs as structure breaker in aqueous NA solution.

The limiting apparent molar volumes of transfer, $\Delta\phi V^0$ for NA from water to o-substituted benzoic acids solution have been calculated by the following relation [24].

$$\Delta\phi V^0(\text{NA}) = \phi V^0(\text{NA in aqueous o-substituted benzoic acid solution}) - \phi V^0(\text{NA in water}) \quad (6)$$

$\Delta\phi V^0$ gives the information about the solute-solvent interactions. The values of limiting apparent molar volumes of transfer of NA in an aqueous solution of salicylic acid, anthranilic acid, and o-nitrobenzoic acid are given in Tables 8-10, respectively. The change in transfer

volume was explained by Friedman and Krishnan on the basis of cosphere overlap model [25,26]. According to the model, the effect of overlap of hydration cosphere is destructive. The positive $\Delta\phi V^0$ values show the presence of hydrophilic-hydrophilic, ion-ion, and ion-hydrophilic interactions, but the negative $\Delta\phi V^0$ values signify the presence of hydrophobic-hydrophobic interactions [27,28]. There are few kinds of interaction acting between NA and o-substituted benzoic acids in an aqueous medium (Scheme 2).

- Interaction of zwitterionic $=\text{NH}^+$ groups of NA and the H^+ ion of water with $-\text{COO}^-$ group of o-substituted benzoic acids which are of ionic-ionic in nature.
- Interaction of an OH^- of water with $=\text{NH}^+$ groups of NA which is of ionic-ionic in nature.
- Interaction of polar end of water with all +ve and -ve ion of NA and o-substituted benzoic acids which is of ionic-hydrophilic in nature.
- Interactions between ions of o-substituted benzoic acids and non-polar part of NA molecules which are of ionic-hydrophilic in nature.
- Interaction of non-polar part of o-substituted benzoic acids and non-polar part of NA which is of Hydrophobic-hydrophobic in nature.

The interactions of types (i), (ii), and (iii) have positive contributions to ϕV^0 while the interaction of types (iv) and (v) have negative contribution to ϕV^0 [29-31]. Since the $\Delta\phi V^0$ values of NA in all the aqueous solutions of o-substituted benzoic acids are positive; hence, the hydrophilic-hydrophilic and ion-ion interactions dominate over hydrophobic-hydrophobic and ionic-hydrophobic interactions. The ϕV^0 of NA in an aqueous solution of o-substituted benzoic acids is higher than that of NA in aqueous solution. This is due to the electrostriction effect of NA that makes a certain amount of contraction in volume of water. This effect of electrostriction of NA becomes lesser on the addition of o-substituted benzoic acids. As a result, NA exerts low electrostriction in the presence of o-substituted benzoic acids.

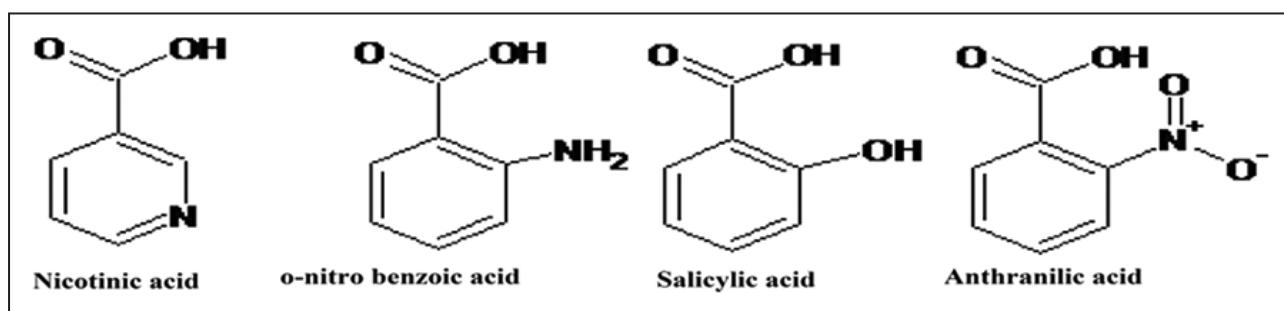
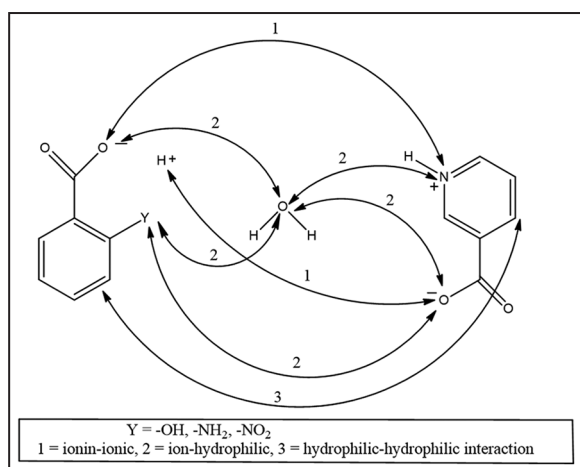
This trend can also be interpreted by the following expression given below by Franks *et al.* [32]:

$$\phi V^0 = \phi W + \phi V - \phi S \quad (7)$$

Table 11: Values of empirical coefficients (a_0 , a_1 , and a_2) of NA in an aqueous solution of o-nitrobenzoic acid, salicylic acid, and anthranilic acid.

Molality of NA	$a_0 \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$a_1 \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	$a_2 \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$)	$(\delta\Phi_E^0/\delta T)_P$
o-nitrobenzoic acid				
0.01 m	3.4532	0.3162	-0.0002	-0.0004
0.03 m	-72.328	0.809	-0.001	-0.002
0.05 m	-53.5832	0.6868	-0.0008	-0.0016
Salicylic acid				
0.01 m	40.0568	0.0738	-0.0002	-0.0004
0.03 m	-35.7244	0.5666	-0.0006	-0.0012
0.05 m	-72.358	0.809	-0.001	-0.002
Anthranilic acid				
0.01 m	-143.6312	1.2858	-0.0018	-0.0036
0.03 m	-72.558	0.809	-0.001	-0.002
0.05 m	-53.8132	0.6868	-0.0008	-0.0016

NA: Nicotinic acid

**Scheme 1:** Structure of nicotinic acid, salicylic acid, anthranilic acid, and o-nitrobenzoic acid.**Scheme 2:** Molecular interactions of nicotinic acid with o-substitution benzoic acids in an aqueous medium.

So, ϕ_V^0 is related with Van der Waals volume (ϕ_W), voids or empty space in solution (ϕ_V) and shrinkage volume due to electrostriction (ϕ_S). The value ϕ_W and ϕ_V will remain equal for the same class of solutes in aqueous solutions whereas, the volume due to electrostriction will vary. With increasing concentration of NA in o-substituted benzoic acids, the ionic-ionic interactions between NA and o-substituted benzoic acids will increase as a result ϕ_S value

will decrease [33]. Hence, ϕ_V^0 values enhance with an increase in molalities of NA.

3.2. Viscosity Calculation

The relative viscosity of any solution is related with molality as per following Jones–Dole equation [34]:

$$\eta_r = \eta/\eta_0 = 1 + A\sqrt{m} + Bm \quad (8)$$

Where, η_0 and η are the viscosity of the solvent and solution, respectively, and m is the concentration of the solution in molality. The above equation may be rearranged as

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

If we plot a graph of $(\eta/\eta_0 - 1)/\sqrt{m}$ against \sqrt{m} , we will get a straight line with the intercept "A" and a slope of "B." A and B are known as viscosity coefficients. The $(\eta/\eta_0 - 1)/\sqrt{m}$ values of NA in the presence of three o-substituted benzoic acids in an aqueous medium at different temperatures are shown in Tables 5-7, respectively. The A and B values of NA are evaluated by a least square method and are reported in Tables 8-10, and the change of B with temperature is shown in Figure 2.

The values of the A-coefficient are positive in case of o-nitrobenzoic acid and salicylic acid but negative in case of anthranilic acid. In all the cases, A values decrease with the increase in molality of NA and also

Table 12: ($V_2^0 - V_1^0$), $\Delta \mu_1^0$, $\Delta \mu_2^0$, and $\Delta G^0 (1 \rightarrow 1^*)$ of NA in aqueous solution of o-nitrobenzoic acid, salicylic acid, and anthranilic acid at different temperature.

Temperature in K	$(V_2^0 - V_1^0) \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$\Delta \mu_1^0$ kJ mol^{-1}	$\Delta \mu_2^0$ kJ mol^{-1}	$\Delta G^0 (1 \rightarrow 1^*)$ kJ mol^{-1}
0.01 m NA+o-nitrobenzoic acid)				
298 K	61.901	9.180451	76.99468	67.8136
303 K	62.88	9.056825	98.97466	89.9178
308 K	63.77	8.947319	122.6308	113.6835
0.03 m NA+o-nitrobenzoic acid				
298 K	61.89	9.197171	84.51619	75.319
303 K	63.93	9.075498	106.4479	97.3725
308 K	63.92	8.968757	135.5731	126.6046
0.05 m NA+o-nitrobenzoic acid				
298 K	61.945	9.219267	104.8855	95.666
303 K	62.975	9.099949	131.4306	122.33
308 K	63.965	8.994966	168.8359	159.840
0.01m NA+salicylic acid				
298 K	61.791	9.180451	71.06712	61.886
303 K	62.761	9.056825	92.38703	83.33
308 K	63.741	8.947319	114.799	105.851
0.03 m NA+salicylic acid				
298 K	61.783	9.197171	77.915	68.717
303 K	62.813	9.075498	97.36285	88.287
308 K	63.813	8.968757	130.0267	121.057
0.05 m NA+salicylic acid				
298 K	61.825	9.219267	98.8444	89.625
303 K	62.865	9.099949	125.568	116.468
308 K	63.855	8.994966	161.3199	152.324
0.01 m NA+anthranilic acid				
298 K	61.67108	9.180451	63.35071	54.17026
303 K	62.69108	9.056825	85.10736	76.05054
308 K	63.62108	8.947319	107.1079	98.16058
0.03 m NA+anthranilic acid				
298 K	61.66	9.197171	71.99848	62.80131
303 K	62.70	9.075498	90.6509	81.5754
308 K	63.69	8.968757	122.3517	113.3829
0.05 m NA+anthranilic acid				
298 K	61.7155	9.219267	92.94161	83.72234
303 K	62.7455	9.099949	118.0333	108.9334
308 K	63.7355	8.994966	153.8024	144.8074

NA: Nicotinic acid

with temperature. The viscosity B-coefficient provides information about the solvation of the solute in solution [35,36]. In our present study, it is observed that B-coefficient values are positive suggesting the existence of strong solute-solvent interactions. It is also evident that the B values increase with increasing molality of NA which signifies that solute-solvent interactions strengthen with increasing molality. Hence, NA of 0.05 m solution at 308 K has highest solute-solvent interactions, and NA of 0.01 m solution at 298 K has least

solute-solvent interactions. The B values of NA in the presence of aqueous o-substituted benzoic acids follow the order

o-nitrobenzoic acid > salicylic acid > anthranilic

The acidity of these three acids will also follow the same order. With increasing acidity of o-substituted benzoic acids, more ions will be formed which will interact with NA. This is the reason why result solute-solvent interaction of NA strengthens with increasing the acidity

of o-substituted benzoic acids. The similar result was also obtained from density measurements.

The structure-making/breaking nature of any solute may be explained better with the thermodynamic property, dB/dT [37,38]. The dB/dT value for structure-making solute is negative whereas for structure-breaking solute it is positive. It is revealed from Figure 2 that the B-coefficient values increase with increasing temperature for NA in the presence of three o-substituted benzoic acids in aqueous medium signifying positive dB/dT. It indicates that NA in the presence of three o-substituted benzoic acids has structure-breaking capacity.

According to Feaking *et al.* (1974), molar free energy of activation of viscous flow of any solute in pure solvent, $\Delta\mu_1^\circ$ may be evaluated as follows [39-41].

$$\eta_0 = \frac{hN}{V_1^0} \exp\left(\frac{\Delta\mu_1^0}{RT}\right) \quad (10)$$

Where V_1^0 is the average molar volume of NA in water, and the others symbols have usual meaning. From the above equation, we can compute $\Delta\mu_1^\circ$ as follows [42]

$$\Delta\mu_1^0 = RT \ln \left[\frac{V_1^0 \eta_0}{hN} \right] \quad (11)$$

The $\Delta\mu_1^\circ$ values are given in Table 12.

Molar activation energy of viscous flow of the NA in an aqueous solution of o-substituted benzoic acids is related to the viscosity B-coefficient as given below proposed by Feanins *et al.*

$$B = \frac{V_1^0 - V_2^0}{1000} + V_1^0 \left(\frac{\Delta\mu_1^0 - \Delta\mu_2^0}{1000RT} \right) \quad (12)$$

Where V_2^0 is limiting the apparent molar volume of the NA in an aqueous solution of o-substituted benzoic acids calculated from density measurements and $\Delta\mu_2^\circ$ is the change in free energy of activation of viscous flow per mole of NA in an aqueous solution of o-substituted benzoic acids. $\Delta\mu_2^\circ$ can be calculated from the above equation as

$$\Delta\mu_2^\circ = \Delta\mu_1^\circ + \frac{RT}{V_1^0} [1000B - (V_1^0 - V_2^0)] \quad (13)$$

The $\Delta\mu_2^\circ$ and $(V_1^0 - V_2^0)$ values are given in Table 12. According to the transition state theory, the solvent molecule moves through its viscous transition state. $\Delta\mu_2^\circ$ is the summation of free energy of activation of solvent from its ground state to transition state $\Delta G^0(1 \rightarrow 1^*)$ and free energy of transfer of NA from the ground state to transition state $\Delta G^0(2 \rightarrow 2^*)$ [43]. It is revealed from Table 12 that $\Delta\mu_2^\circ$ values of the NA in an aqueous solution of o-substituted benzoic acids are large positive than $\Delta\mu_1^\circ$ [44]. It points out that the ground state NA is favored over the transition state in the presence of o-substituted benzoic acids. The solute and the solvent molecules are organized in ground state and breaking, and distortion of intermolecular bonds occur in the transition state of viscous flow. The increase of $\Delta\mu_1^\circ$ values with molality of NA indicates that the ground state becomes more organized with increasing molality of NA in the presence of o-substituted benzoic acids.

4. CONCLUSION

In this paper, we studied the various types of interactions of NA prevailing in an aqueous solution of three o-substituted benzoic acids at different temperatures from viscosity and density measurements. The limiting apparent molar volume (ϕ_v^0) calculated from densities and viscosity B-coefficient calculated from viscosities proved the presence

of strong solute-solvent interactions which intensify with increasing molality and temperature. The determination of volumetric pair and triple ion interactions proved the presence of pairwise interactions in our studied solutions. The molar free energy of activation of a viscous flow of the solvent μ_1^0 and solute $\Delta\mu_2^\circ$ calculation proved that the ground state is more favored than the transition state.

5. ACKNOWLEDGMENTS

The authors are grateful to the UGC supported Major research project, Ref. No. RP/5032/FCS/2011, New Delhi, for financial support to continue this research work. One of the authors, Prof. M. N. Roy, is thankful to University Grant Commission, New Delhi, Government of India for being awarded one-time grant under Basic Scientific Research through the grant-in-Aid No. F.4-10/2010 (BSR) regarding his active service for augmenting of research facilities to facilitate further research work.

6. REFERENCES

1. A. Kundu, N. Kishore, (2003) Apparent molar heat capacities and apparent molar volumes of aqueous nicotinamide at different temperatures, *Journal of Solution Chemistry*, **32**: 703-717.
2. G. Ayranci, M. Sahin, E. Ayranci, (2007) Volumetric properties of ascorbic acid (vitamin C) and thiamine hydrochloride (vitamin B1) in dilute HCl and in aqueous NaCl Solutions at (283.15, 293.15, 298.15, 303.15, 308.15, and 313.15) K, *Journal of Chemical Thermodynamics*, **39**: 1620-1631.
3. F. A. Robinson. (1951) *The Vitamin B-Complexes*, London: Chapman & Hall Publication.
4. A. W. Hakin, S. A. M. M. Beswick, (1993) The volumetric and thermochemical properties of L-ascorbic acid in water at 288.15, 298.15 and 308.15 K, *Canadian Journal Chemistry*, **71**: 925-929.
5. M. V. Kaulgud, H. G. Dole, K. S. M. Rao, (1978) Apparent molal volume, apparent molal compressibility and transport properties of dilute aqueous solutions of ascorbic acid, *Indian Journal Chemistry*, **16A**: 955-958.
6. C. A. Elvehjem, L. Teply, (1943) The structure and estimation of natural products functionally related to nicotinic acid, *Journal Chemical Reviews*, **33(3)**: 185-208.
7. A. N. Nesmeyanov, (1981) *Fundamentals of Organic Chemistry*, Moscow: Mir Publication.
8. A. S. Fauci, E. Braunwald, K. J. Isselbacher, J. D. Wilson, J. B. Martin, D. L. Kasper, S. L. Hauser, D. L. Long, (1998) *Harrison's Principles of Internal Medicine*, New York: McGraw-Hill.
9. J. Block. (1996) *Kirk-Othmer Encyclopedia of Chemical Technology*, Park Ridge, NJ: Wiley.
10. L. A. Carlson, (2005) Nicotinic acid: The broad-spectrum lipid drug. A 50th Anniversary review, *Journal of Internal Medicine*, **258(2)**: 94-114.
11. Z. Orekhova, M. Ben-Hamo, E. Manzurola, A. Apelblat, (2005) Electrical conductance/volumetric studies in aqueous solutions of nicotinic acid, *Journal of Solution Chemistry*, **34**: 687-700.
12. R. Gopal, M. A. Siddique, (1969) A study of ion-solvent interactions of some tetraalkyl- ammonium and common ions in N-methyl acetamide from apparent molar volume data, *Journal of Physical Chemistry*, **72**: 1814-1817.
13. M. N. Roy, A. Jha, A. Choudhury. (2004) Densities, viscosities and adiabatic compressibilities of some mineral salts in water at different temperatures, *Journal of Chemical and Engineering Data*, **4**: 291-296.

14. E. Ayranci, (1997) Apparent molar volume and viscosity of compounds with Asymmetric carbon atoms, *Journal of Chemical and Engineering Data*, **42(5)**: 934-937.
15. M. T. Zafarani-Moattar, B. Asadzadeh, (2014) Salting-out behaviour of 1-butyl-3-methylimidazolium bromide, [C4mim][Br], ionic liquid on aqueous L-serine solutions at T = 298.15 K, *Journal of Chemical Thermodynamics*, **83**: 43-51.
16. F. J. Millero, J. H. Knox, (1973) Apparent molal volumes of aqueous sodium fluoride, sodium sulfate, potassium chloride, potassium sulfate, magnesium chloride and magnesium sulfate solutions at 0 deg. and 50 deg, *Journal of Chemical and Engineering Data*, **18**: 407.
17. M. N. Roy, D. Ekka, R. Dewan, (2011) Physico-chemical studies of some bio-active solutes in pure methanoic acid, *Acta Chimica Slovenica*, **58(4)**: 792-796.
18. S. Fang, H. J. Xie, H. Y. Chen, L. Wang, S. Y. Tian, (2017) Solute-solvent interactions of amino acid L-phenylalanine in aqueous 1-butyl-2,3-dimethylimidazolium bromide ionic liquid solutions, *Journal of Chemical Thermodynamics*, **113**: 144-150.
19. H. Shekaari, F. Jebali, (2010) Solute-solvent interactions of amino acids in aqueous lpropyl 3-methylimidazolium bromide ionic liquid solutions at 298.15 K, *Journal of Solution Chemistry*, **39**: 1409-1427.
20. M. L. Parmar, D. S. Banyal, (2005) Effect of temperature on the partial molar volumes of some bivalent transition metal nitrates and magnesium nitrate in DMF + water mixtures, *Indian Journal of Chemistry*, **44A**: 1582-1588.
21. L. G. Hepler, (1969) Thermal expansion and structure in water and aqueous solutions, *Canadian Journal of Chemistry*, **47**: 4617.
22. T. S. Banipal, J. Kaur, P. K. Banipal, K. Singh, (2008) Study of interactions between amino acids and zinc chloride in aqueous solutions through volumetric measurements at T = (288.15 to 318.15) K, *Journal of Chemical and Engineering Data*, **53**: 1803-1816.
23. M. S. Hossain, T. K. Biswas, D. C. Kabiraz, M. N. Islam, M. E. Huque, (2014) Studies on sodium dodecylsulfate in aqueous and in aqueous amino acid solutions: Volumetric and viscometric approaches, *Journal of Chemical Thermodynamics*, **71**: 6-13.
24. H. L. Friedman and C. V. Krishnan, (1973) In: F. Franks, editor, *Water: A comprehensive Treatise*, Vol. 3, Ch. 1. NewYork: Plenum.
25. M. T. Zafarani-Moattar, F. Izadi, (2011) Effect of temperature and concentration of KBr or KNO₃ on the volumetric and transport properties of aqueous solutions of tripotassium citrate, *Journal of Chemical and Engineering Data*, **56**: 2818-2829.
26. S. S. Dhondge, C. P. Pandhurnekar, S. Garade, and K. Dadure, (2011) Volumetric and transport behavior of different carbohydrates in aqueous and aqueous urea mixtures at different temperature, *Journal of Chemical and Engineering Data*, **56**: 3484-3491.
27. A. Pal, B. Kumar, (2012) Volumetric and acoustic properties of binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄] with alkoxyalkanols at different temperatures, *Journal of Chemical and Engineering Data*, **57**: 688-695.
28. B. K. Sarkar, A. Choudhury, B. Sinha, (2012) Excess molar volumes, excess viscosities and ultrasonic speeds of sound of binary mixtures of 1,2-dimethoxyethane with some aromatic liquids at 298.15 K, *Journal of Solution Chemistry*, **41**: 53-74.
29. R. Gaba, A. Pal, H. Kumar, D. Sharma, R. Saini, (2017) Thermodynamic properties of glycine and diglycine in aqueous solutions of 1-pentyl-3-methylimidazolium chloride at different temperatures, *Journal of Molecular Liquids*, **229**: 417-423.
30. V. Dhirand, R. P. S. Grewal, (2014) Investigations of various amino acids in different aqueous solutions of potassium nitrate at various temperatures in terms of partial molar volumes, *International Journal of Engineering and Technical Research*, **2**: 44-51.
31. S. Riyazuddeen, S. Afrin, (2012) Effect of NaCl and NaNO₃ on the partial molar volumes and partial molar isentropic compressibilities of some amino acids at several different temperatures (298.15–328.15) K, *Journal of Solution Chemistry*, **41**: 1144-1155.
32. F. Franks, M. A. J. Quickenden, D. S. Reid, B. Watson, (1970) Calorimetric and volumetric studies of dilute aqueous solutions of cyclic ether derivatives, *Transactions of the Faraday Society*, **66**: 582-589.
33. J. L. Fortier, P. A. Leduc, J. E. Desnoyers, (1974) Thermodynamic properties of alkali halides. II. Enthalpies of dilution and heat capacities in water at 25°C, *Journal of Solution Chemistry*, **3**: 323.
34. W. G. McMillan, J. E. Mayer, (1945) The statistical thermodynamics of multicomponent systems, *Journal of Chemical Physics*, **13**: 276-305.
35. T. S. Banipal, H. S. Parampaul, K. Banipal, (2010) Volumetric and viscometric properties of some sulphadiazine drugs in aqueous solutions of sodium chloride at T=(288.15 to 318.15) K, *Journal of Chemical and Engineering Data*, **55**: 3872-3881.
36. G. Jones, M. Dole, (1929) The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride. *Journal of the American Chemical Society*, **51**: 2950-2964.
37. F. J. Millero, (1971) Molal volumes of electrolytes, *Chemical Reviews*, **71**: 147-176.
38. F. J. Millero, A. Losurdo, C. Shin, (1978) The apparent molal volumes and adiabatic compressibilities of aqueous amino acids at 25°C, *The Journal of Physical Chemistry*, **82**: 784-792.
39. D. Feakins, W. E. Waghorne, K. G. Lawrence, (1974) Transition state treatment of the relative viscosity of electrolytic solutions. Applications to aqueous, non-aqueous and methanol + water systems, *Journal of Chemical Society, Faraday Transactions*, **70**: 795-806.
40. A. K. Nain, M. Lather, R. K. Sharma, (2011) Volumetric, ultrasonic and viscometric behavior of l-methionine in aqueous-glucose solutions at different temperatures, *Journal of Molecular Liquids*, **159**: 180-188.
41. H. Kumar, K. Kaur, (2012) Viscosities of glycine and l-Alanine in (0.2, 0.4, 0.6, and 0.8) mol·kg⁻¹ aqueous dipotassium hydrogen phosphate solutions at different temperatures, *Journal of Chemical & Engineering Data*, **57**: 3416-3421.
42. R. Gaba, A. Pal, D. Sharma, J. Kaur, (2017) Solvation behavior of glycine and glycyl dipeptide in aqueous 1-butyl-3-methylimidazolium bromide ionic liquid solutions at different temperatures, *Journal of Molecular Liquids*, **233**: 38-44.
43. D. Feakins, W. E. Waghorne, K. G. Lawrence, (1993) Relative viscosities and quasi thermodynamics of solutions of tert-butylalcohol in the methanol-water system: A different view of the alkyl water interactions, *Journal of Chemical Society Faraday Transactions*, **89**: 3381-3388.
44. S. Glasstone, K. Laidler, H. Eyring, (1941) *The Theory of Rate Processes*, New York: McGraw-Hill.

***Bibliographical Sketch**

Kalipada Sarkar is an Assistant Professor in the Department of Chemistry, Islampur College, West Bengal, India, and carrying out his research work under the guidance of Dr. Mahendranath Roy, University of North Bengal, Darjeeling, West Bengal, India. His research areas include Solution Chemistry, Inclusion Complexes, and Solution Thermodynamics. He has five research articles published in national and international journals.



Dr. Mahendra Nath Roy is a Professor of Physical Chemistry at the University of North Bengal, Darjeeling. His research interests are in the areas of Ionic Liquids, Solution Thermodynamics, and Polymer Chemistry. His contribution has been recognized by the publication of a large number of high impact research articles (Total-252, International-194, and National-58), Books (Total-5, International-03, and National-03), and Chapters 01. He is the life member of ICS, ISC, CRSI, and JTR. He has been awarded one-time grant amounting Rs.-7.00 lac by UGC, New Delhi, under basic scientific research (BSR), Bronze Medal award from Chemical Research Society of India (CRSI) and Prof. Suresh C Ameta Award from Indian Chemical Society. He has excellently supervised 30 Ph.D. students to confer their Ph.D. degree and still he has been supervising outstandingly 8 (eight) Ph.D. students.