ThermodynamicProperties of Nicotinicacid in Dilute HCl and inaqueous NaCl solutions at (293.15, 298.15, 303.15 and 308.15)K

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Abstract:

Apparent molar volume, V_{φ}, and viscosity B-coefficient of nicotinc acid in water and in aqueous NaCl solutions have been determined from density and viscosity measurements at (293.15, 298.15, 303.15 and 308.15) K. The experimental density data were evaluated by Masson equation, and the derived, apparent molar volume at infinite dilution, V^{o}_{φ}, and the slope S_v, were interpreted in term of solute-solvent and solute- solute interactions. Transfer apparent molar volumes at infinite dilution of nicotinic acid from water to NaCl solutions at various temperatures have been calculated.The viscosity data have been analyzed using Jones-Dole equation, and the derived parameters, Jones-Dolecoefficient, B,and Falkenhagen coefficient,A, have been also interpreted in terms of solute-solvent and solute-solute interactions respectively. The variation of *B* coefficient with temperature, (d*B*/d*T*), was also determined, the negative values indicate that nicotinic acid in aqueous NaCl solution is structure making. The results were interpreted in terms of complex vitamin-water-co-solute (NaCl) interactions. The free energy, enthalpy, andentropy of activation were calculated using the Nightingale, Benck, and Eyring equations. Free energies of activation of viscous flow ($\Delta\mu^*_1$) per mole, and, ($\Delta\mu^*_2$) per mole,of solvent and solute, respectively, were also calculated. The effects of soluteson the structure of water were interpreted in terms of viscositiesand the thermodynamic parameters.

Key words: Apparent molar volume. Density.Solute- solute and solute- solvent interactions.nicotinic acid . Viscosity.sodium chloride.

Introduction:

Nicotinic acid, commonly known as vitamin B3, is a water soluble vitamin, anessential micronutrient, and a reactive moiety of the coenzyme nicotinamide adeninedinucleotide (NAD). It is an essential part of the coenzyme nicotinamide adeninedinucleotide phosphate (NADP) [1]. It plays a very important role to maintain the normalfunction of the digestive systems and cholesterol levels in the human body. The combination of nicotinic acid and nicotinamide is clinically referred to as niacin, since nicotinic acid is converted in the body into the amide very fast, and fornutritional purposes, both of them have equal biological activities [1]. Nicotinamide is aninteresting molecule because of its two nitrogen atoms- one in the heterocyclic ringand the other as the amide group. It is necessary to study aqueous solution properties in order to understand the mechanisms of their actions in detail.The influence of electrolyte on the behavior of protein is one of the important topics in physical chemistry of the substances. It has long been known that there is a strong interaction

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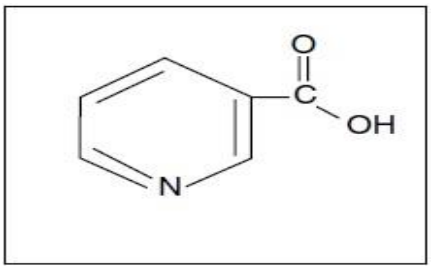
between electrolytes and proteins, which causes a departure from ideal behavior. To understand the fine details, the interactions of the building blocks of the protein with electrolytes must be studied owing to the complex structural organization of the biological macromolecules [2].Volumetric,viscometric, and other thermodynamic data provide valuable information regarding solute-solvent and solute-solute interactions.These interactions help in better understanding of the nature of solute and solvent, whether the added of solute modifies or distort the structure of solvent[3].In this paper, the experimental values ofdensities and viscosities of nicotinicacid have been reported in different aqueousNaCl solutions at 293.15, 298.15, 303.15 and 308.15 K. The density data has been utilized toobtain apparent molar volumes, V_φ from apparent molarvolumes, partial molar volumes, V^0_φ and transfer molarvolumes, V^0_φ of nicotinicacids have been evaluated. Theviscosity data have been used to obtain viscosity coefficients,A and B of Jones-Dole equation [4], the free energies ofactivation of viscous flow per mole of solvent, $\Delta\mu_1^{\#}$ and $\Delta\mu_2^{\#}$ respectively; enthalpy, $\Delta H^{\#}$, and entropy ofactivation, $\Delta S^{\#}$, of viscous flow.The resultshave been discussed in terms of solute-solute and solute-solvent interactions in electrolytic media.

2. Experimental

2.1. Materials

Nicotinic acid (99%) of molar mass 123.11 g mol^{-1} was supplied by Himedia. The structural formula of nicotinic acid was shown inScheme 1. NaClused was from Merk, with a quoted purity > 99.5 %. HCl was reagent grade. Deionized water was used in all experiments.The solvent used was0.01 M HCl. The experimentswere carried out at 293.15, 298.15, 303.15 and 308.15 K.



Scheme 1: The structure of nicotinic acid

2.2 Density and ViscosityMeasurements

The sample densities were measured by an Anton Paar DMA 60/602 vibrating-tube digital densimeter. The density data determined are reproducible to $3X10^{-6}g.cm^{-3}$. The temperature around the density meter cell was controlled by circulating water from the Schott thermostat. Viscosity measurements were carried out with a suspended level Ubbelhode viscometer, which has an efflux time of nearly 110 s for water at 298.15 K. Flow time measurements are performed by a Schott AVS 310 photoelectric time unit with a resolution of 0.01 s. At least three time recordings were obtained, and the average value was used as the experimental flow time. The reproducibility of flow time was 0.02 s. The viscometer was thermostated in aSchott thermostat, the temperature of which was controlled to be 293.15, 298.15, 303.15 and 308.15,with an accuracy in temperature ±0.005 K. The experimental details are given elsewhere [5].

Result and Discussion:

The experimental results of densities (ρ)and viscosities (η) measurements of nicotinicacid in 0.01M HCl and in NaCl solutions at different molarities prepared in 0.01 HCl at (293.15,

298.15, 303.15 and 308.15) K are presented in **table 1.**Apparent molar volumes,V_ϕ,were determined from the measured densities of solvent, ρ_o, and of solution, ρ, using the following equation:

$$V_\phi = [1000(\rho_o - \rho)/C\,\rho_o] + M_2/\rho_o \quad (1)$$

Whereis, C, the molarity of the solution and M_2 is the molecular weight of nicotinicacid. Solvent was taken as 0.01 M HCl solution. For the determination of $V_\phi$of thevitaminin the presence of NaCl, the solvent was taken as the solution containing HCl,(0.01 M), andNaCl at various molarities.The V_ϕ values are included in **table 2**.The apparent molar volumes were least - squares fitted to Masson's empirical relation [6]:

$$V_\phi = V^0{}_\phi + Sv\,C^{1/2} \quad (2)$$

Where $V^0{}_\phi$, is the apparent molar volume at infinite dilutionof nicotinicacid and, by definition, provides information regarding solute - solvent interactions;S_v is the experimental slope and is a measure of solute – soluteinteractions.The, $V^0{}_\phi$and Sv values were obtained from the intercepts and slopes of V_ϕ versus $C^{1/2}$ plots and are given in **table 3** at different temperatures.A typical plotof V_ϕ vs. $C^{1/2}$ for nicotinic acid in the solventsunder studies at 298.15 K is given in **figure 1.**

Table 3shows that, $V^o{}_\varphi$, values are generally positive and increased with an increase in the temperature and molality of NaCl in the solutions but the increasing in molality of NaCl causes decreasing in the, $V^o{}_\varphi$, this indicates that the presence of strong solute–solvent interactions and these interactions are further strengthened at higher temperatures and lower concentrations of NaCl in the solutions. On the other hand, S_v values are negative, this indicates that the investigated solutions are characterized by weak solute–solute interactions.The standard volumes of transfer for the nicotinic acids from 0.01 M HCl to aqueous sodium chloride solutionswere Calculatedusing the following equation [7]:

$$\Delta_t V^0{}_\phi = V^0{}_\phi(\text{in aqueous NaCl}) - V^0{}_\phi(\text{in 0.01 HCl}) \quad (3)$$

Where V^0(in aqueous NaCl) and V^0(in 0.01MHCl) values were presented in **table 3**.The standard volumes of transfer values are reported in **table 5.**

Table1: Densities and viscosities of nicotinicacid in 0.01M HCl and in NaCl solutions at various molarities and temperatures

C / (mol.L^{-1})	ρ(g.cm^{-3})				η(mPas.s)			
	293.15K	298.15K	303.15K	308. 15K	293.15K	298.15K	303.15K	308. 15K
0.01 M HCl								
0.000	0.998393	0.997231	0.995834	0.994302	1.002192	0.922724	0.832449	0.758844
0.014	0.999245	0.998078	0.996673	0.99514	1.010543	0.929339	0.836024	0.761777
0.028	1.000105	0.998933	0.997519	0.996003	1.020322	0.932336	0.837888	0.763777
0.042	1.000988	0.999811	0.998388	0.996872	1.026854	0.935358	0.839772	0.765305
0.056	1.001862	1.00068	0.999249	0.997733	1.032919	0.938376	0.841651	0.766828
0.070	1.002772	1.001585	1.000144	0.998628	1.039122	0.94143	0.843562	0.76838
0.084	1.003704	1.002511	1.001061	0.999545	1.049876	0.94451	0.845494	0.76995
0.098	1.004613	1.003415	1.001956	1.00044	1.051392	0.947572	0.847408	0.771503
0.112	1.005533	1.004329	1.002861	1.001345	1.056975	0.950648	0.849334	0.773067
0.126	1.006452	1.005243	1.003765	1.002249	1.063509	0.953727	0.851261	0.774631
0.1 M NaCl in 0.01 M HCl								
0.000	1.002561	1.00135	0.999912	0.998263	1.03507	0.930499	0.836382	0.765468
0.014	1.003281	1.00207	1.000614	0.998972	1.04032	0.93414	0.839653	0.769462
0.028	1.004082	1.002871	1.001396	0.999761	1.045758	0.94156	0.842421	0.774003
0.042	1.004905	1.003694	1.002199	1.000571	1.050937	0.946291	0.845977	0.778566
0.056	1.005824	1.004613	1.003097	1.001477	1.055745	0.950444	0.849618	0.78321
0.070	1.006737	1.005526	1.003987	1.002376	1.060648	0.954596	0.853258	0.787857
0.084	1.007652	1.006441	1.004880	1.003278	1.065079	0.958756	0.856905	0.792512
0.098	1.00868	1.007469	1.005883	1.00429	1.069733	0.96303	0.860652	0.797262
0.112	1.009784	1.008573	1.00696	1.005377	1.074861	0.967384	0.864468	0.80208
0.126	1.011027	1.009816	1.008174	1.006602	1.08092	0.97188	0.868408	0.807017
0.2 M NaCl in 0.01M HCl								
0.000	1.006595	1.005337	1.003856	1.002174	1.047478	0.94517	0.864555	0.775352
0.014	1.007314	1.006056	1.004574	1.002891	1.052289	0.949707	0.868462	0.778349
0.028	1.008107	1.006847	1.005363	1.003679	1.058098	0.954484	0.872021	0.781171
0.042	1.008925	1.007664	1.006178	1.004492	1.063772	0.959288	0.876831	0.784066
0.056	1.009839	1.008577	1.007091	1.005402	1.069492	0.964128	0.880756	0.787004
0.070	1.010747	1.009483	1.007994	1.006305	1.075232	0.968992	0.884774	0.789939
0.084	1.011656	1.010391	1.008900	1.00721	1.081048	0.973897	0.888838	0.793023
0.098	1.012678	1.011411	1.009918	1.008226	1.086874	0.97886	0.892863	0.796016
0.112	1.013775	1.012507	1.011012	1.009318	1.092784	0.983869	0.89694	0.799032
0.126	1.015012	1.013742	1.012245	1.010549	1.098687	0.988877	0.90128	0.802202
0.3 M NaCl in 0.01 M HCl								
0.000	1.010688	1.009381	1.007863	1.006146	1.052652	0.973615	0.898701	0.792735
0.014	1.01142	1.010106	1.008584	1.006866	1.059688	0.979242	0.902823	0.794849
0.028	1.0121	1.010772	1.009248	1.007528	1.065722	0.983493	0.906731	0.79866
0.042	1.01273	1.011411	1.009901	1.008163	1.071697	0.988244	0.910582	0.801486
0.056	1.01335	1.012029	1.010498	1.008776	1.077676	0.99301	0.91441	0.804298
0.070	1.01391	1.012585	1.011051	1.009329	1.083594	0.99772	0.918204	0.807064
0.084	1.01444	1.013122	1.011585	1.009862	1.089498	1.002415	0.921983	0.809817
0.098	1.01495	1.013628	1.012089	1.010365	1.095375	1.007085	0.925739	0.812549
0.112	1.01545	1.014125	1.012583	1.010858	1.101246	1.011749	0.929489	0.815274
0.126	1.01591	1.014582	1.013038	1.011313	1.107081	1.016378	0.933207	0.817971

. Table 2: Apparent molar volumes of nicotinicacid in 0.01M HCl and in NaCl solutions at Various molarities and temperatures

C / (mol. L^{-1})	V_ϕ($cm^3.mol^{-1}$)			
	293.15K	298.15K	303.15 K	308.15K
0.01M HCl				
0.014	62.33421	62.76309	63.46269	63.60004
0.028	62.05494	62.48512	63.39597	63.27483
0.042	61.42592	61.85904	62.88269	62.50920
0.056	61.25371	61.68764	62.81898	62.20325
0.070	60.64725	61.08402	62.33087	61.65752
0.084	59.97515	60.41506	61.78052	61.03266
0.098	59.73548	60.17652	61.65381	60.82391
0.112	59.45879	59.90112	61.49166	60.54460
0.126	59.24818	59.69149	61.39445	60.37956
0.1M NaCl in 0.01 M HCl				
0.014	71.57072	71.74284	72.18879	73.23806
0.028	68.64902	68.82249	69.28378	70.61277
0.042	67.18394	67.35809	67.82708	68.45164
0.056	64.71704	64.89233	65.37428	66.21429
0.070	63.33864	63.51457	64.00376	64.68606
0.084	62.39471	62.57107	63.06522	63.72605
0.098	60.57259	60.74979	61.25351	61.92814
0.112	58.5272	58.70534	59.21982	61.34099
0.126	55.82952	56.0089	56.53755	58.44065
0.2M NaCl in 0.01 M HCl				
0.014	71.29078	71.34882	71.54927	71.75486
0.028	68.6437	68.80705	69.01145	69.21765
0.042	67.1918	67.35543	67.56046	67.76668
0.056	64.74708	64.91118	65.11729	65.32352
0.070	63.38107	63.54544	63.75215	63.95839
0.084	62.44563	62.61017	62.8173	63.02354
0.098	60.63989	60.80478	61.01271	61.21896
0.112	58.61289	58.77817	58.98699	59.19326
0.126	55.93946	56.10525	56.31526	56.52155
0.3M NaCl in 0.01 M HCl				
0.014	70.3508	70.65673	71.02133	71.22874
0.028	71.77921	72.75505	73.08234	73.29158
0.042	73.78311	74.07915	74.00646	74.63916
0.056	74.82251	75.11556	75.46444	75.67194
0.070	76.32937	76.61807	76.96166	77.16919
0.084	77.56128	77.84644	78.18569	78.39324
0.098	78.7466	79.02834	79.36343	79.57101
0.112	79.7256	80.00452	80.33617	80.54376
0.126	80.79209	81.06794	81.39584	81.60346

Table 3: limiting apparent molar volumes of nicotinicacid in 0.01M HCland in NaCl solutions at various molarities and various temperatures.

C (mol. L^{-1})	Sv ($cm^3.kg.mol^{-2}$)			
	293.15 K	298.15 K	303.15 K	308.15 K
0.0	-14.23	-14.16	-10.17	-14.84
0.1	-62.39	-62.36	-62.03	-59.38
0.2	-61.15	-60.86	-60.83	-60.82
0.3	45.22	43.86	44.17	43.79

Table 4: Experiment slope, Sv, of nicotinic acid in 0.01M HCland in NaCl solutions at various molarities and various temperatures.

C (mol. L^{-1})	$V^0\varphi$ ($cm^3.mol^{-1}$)			
	T/K			
	293.15	298.15	303.15	308.15
0.0	64.29	64.71	64.93	65.54
0.1	79.44	79.53	79.81	80.43
0.2	79.17	79.25	79.45	79.65
0.3	64.50	65.21	65.43	65.79

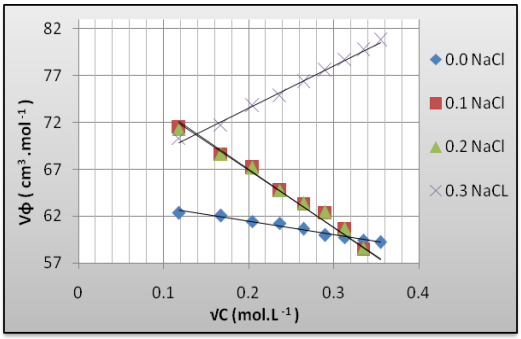


Figure 1: Apparent molar volumes (V_ϕ) as a function of square root of molar concentration (√C) ofnicotinic acid at 298.15 K

Table 5: The standard volumes of transfer for the nicotinic acids from 0.01 HCl to aqueous sodium chloride solutions at different temperatures.

C ($mol.L^{-1}$)	$\Delta_t V^0_\phi$ (cm^3mol^{-1})			
	293.15 K	298.15 K	303.15 K	308.15 K
0.1	15.15	14.82	14.88	14.89
0.2	14.88	14.54	14.52	14.11
0.3	0.21	0.5	0.5	0.25

It was observed from the table that $\Delta_t V^0_\phi$ values are positive but negative at 0.2 NaCl. However, no clear regular trend is observed in variation of $\Delta_t V^0_\phi$ transfer values withmolarity of NaCl or with temperature. This shows the complexity of interactions in a solution containing a background HCl and a co-solute beside the vitamin (the solute under study.The following points can still be noted on the transfer volume data presented in **table 5**. Positive values for $\Delta_t V^0_\phi$ transfer of nicotinic acid probably result from the overlapof hydration cospheres of NaCl and the vitamin. Some of the water previously electrostricted in the hydration spheres of individual solutes, NaCl and vitamin, returns to normal structure upon overlap of co-spheres causing an increase in volume in coexistence of the two solutes.The viscosity data of solutions for nicotinic acid in 0.01M HCl and in different molarities of NaCl aqueous solutions have been analyzed using the Jones–Dole [8, 9] equation:

$$\eta/\eta^0=\eta_r=1+AC^{1/2}+BC= (\eta/\eta^0-1)/C^{1/2}= A+BC^{1/2} \quad (4)$$

Where $\eta_r$is the relative viscosity, C,is the molar concentration, η and η^o are the respective viscosities of solution and solvent. A is the Falkenhagen coefficient, which accounts for solute − solute interactions and B, the Jones-Dole coefficient is empirical and is a measure of the structural modification induced by solute-solvent interactions [10]. The viscosity coefficients, A and B, were obtained from the intercepts and slopes of the plots $(\eta_r - 1)/C^{1/2}$vs. $C^{1/2}$. The values of A and B are listed in **table 6.**

Table 6: Values of Falkenhagen coefficient A, Jones-Dole coefficient Bof nicotinic acids in 0.01MHCl and in NaCl solutions at variousmolalities and different temperatures**.**

T/ (K)	A/ ($L^{-1.5}.mol^{-0.5}$)	B/ ($L.mol^{-1}$)	A/ ($L^{-1.5}.mol^{-0.5}$)	B/ ($L.mol^{-1}$)	A/ ($L^{-1.5}.mol^{-0.5}$)	B/ ($L.mol^{-1}$)	A/ ($L^{-1.5}.mol^{-0.5}$)	B/ ($L.mol^{-1}$)
0.0 M NaCl			0.1M NaCl		0.2MNaCl		0.3MNaCl	
293.15	0.037	0.219	0.02	0.372	-0.019	0.446	0.011	0.378
298.15	0.029	0.18	0.012	0.355	-0.012	0.405	0.008	0.324
303.15	0.01	0.151	0.017	0.317	-0.003	0.346	0.004	0.293
308.15	0.015	0.117	0.034	0.300	-0.006	0.259	0.008	0.226

Viscosity B-coefficient is an important factor for two reasons; first its provide information about the solvation of solutes and its effects on the structure of the solvent in the near environment of the solute molecules. Second, some activation parameters of viscous flow can be obtained using the viscosity B-coefficient. The viscosity B-coefficient, originally introduced as an empirical term, was found to depend on solute–solvent interactions and on the relative size of the solute and solvent molecules. Larger and positive viscosity B-coefficient values indicate a structure making action (hydrogen bonded actions) of the solute on solvents. It can be seen from **table6** that the viscosity B-coefficient values are positive, indicating the structure-making ability of nicotinic acid and the presence of strong ion–solvent interactions.The viscosity B-coefficient values decrease with increasing temperature; hence, their temperature derivatives, i.e., dB/dT, are negative.

The sign of dB/dTgives the information of structure making/breaking property of the solute in the solvent media, rather than simply the viscosity B-coefficient [11]. It can be seen from**figure2** that dB/dTare negative for nicotinic acid in all aqueous solutions, thereby showing the structure- making ability of nicotinic acid. Thus, nicotinic acid can be classified as a structure maker in aqueous 0.01 HCl and in NaCl solutions.

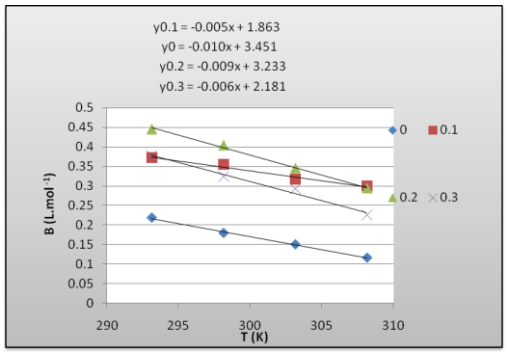


Figure 2: dependence of B-coefficient on Temperature

Eyring and co-workers [12] proposed that the average Gibbs energy of activation of a solute for viscous flow in a solvent, $\Delta\mu1$, can be calculated from the following equation.

$$\eta o = [h N_A / V^0\phi 1] \exp [\_\Delta\mu_1^{\#} RT] \quad (5)$$

Where h and $N_A$are the Planck's constant and Avogadro's number, respectively, and $V^0\phi 1$is the average molar volume of the aqueous NaCl solutions at (293.15, 298.15, 303.15 and 308.15) K (calculated from density data).According to Feakinset al. [13, 14], the activation Gibbs energy,$\Delta\mu2^{\#}$, for viscous flow of the nicotinic acid in aqueous NaCl solutions is related to the viscosity B-coefficient by following equation,

$$B = [(V^o_{\varphi,1} - V^o_{\varphi,2})/1000] + V^o_{\varphi,2}[(\Delta\mu_2^{\#} \_ \Delta\mu_1^{\#}) / 1000RT] \quad (6)$$

Eq. (6) can be rearranged to give

$$\Delta\mu2^{\#} = \Delta\mu1^{\#} + (RT/V^o_{\varphi,1})[1000B - (V^o_{\varphi,1} - V^o_{\varphi,2})] \quad (7)$$

WhereR is gas constantand T is the absolute temperaturerespectively. The calculated values of $\Delta\mu1^{\#}$and $\Delta\mu2^{\#}$ are displayed in **table 7.**

Table 7: Values of $\Delta\mu_1^{\#}$ and $\Delta\mu_2^{\#}$ of nicotinic acids in 0.01M HCl and in NaCl solutions at various molarities and different temperatures**.**

T/ (K)	$\Delta\mu1^{\#}$/ (J mol^{-1})	$\Delta\mu2^{\#}$/ (J mol^{-1})	$\Delta\mu1^{\#}$/ (J mol^{-1})	$\Delta\mu2^{\#}$/ (J mol^{-1})	$\Delta\mu1^{\#}$/ (J mol^{-1})	$\Delta\mu2^{\#}$/ (J mol^{-1})	$\Delta\mu1^{\#}$/ (J mol^{-1})	$\Delta\mu2^{\#}$/ (J mol^{-1})
0.0 MNaCl			0.1 M NaCl		0.2M NaCl		0.3 MNaCl	
293.15	61521.06	77990.52	62739.43	79179.03	62758.69	82368.18	62760.81	62878.58
298.15	62368.46	76480.77	63548.52	79530.49	63577.45	81748.43	62878.58	63743.77
303.15	63158.43	75534.23	64349.09	78951.09	64422.67	80321.76	64510.26	64603.47
308.15	63966.86	74158.68	65183.73	79297.92	65210.52	79108.61	65257.19	65257.19

Table 7shows that $\Delta\mu_1^{\#}$ values are almost constant at all temperatures and solvent compositions. Itmeans that$\Delta\mu2^{\#}$is dependentmainly on the values of viscosity B-coefficients and ($V^o_{\varphi,1}$- $V^o_{\varphi,2}$)terms. The $\Delta\mu_2^{\#}$ valueswere positive at all experimental temperatures. So the formation of the transitionstate becomes less favorable [15]. According to Feakins et al. [13], $\Delta\mu2^{\#} > \Delta\mu1^{\#}$for solutes having positive viscosityB-coefficients indicates stronger solute–solventinteractions, suggesting the formation of a transition state which is accompanied bythe rupture and distortion of the

intermolecular forces in the solvent structure [15].The larger is the value of $\Delta\mu 2^{\#}$,the greater is the structure-making tendency of thesolute, and the positive values of $\Delta\mu 2^{\#}$for nicotinic acid in the different aqueous NaClsolutions suggests nicotinic acid is a net structure promoter in these aqueous solutions.The total free energy of activation of viscous flow of the solution, $\Delta\mu^{\#}$was calculated from the relation:

$$\Delta\mu^{\#} = n_2\Delta\mu_2^{\#} + n1\ \Delta\mu_1^{\#} \qquad (7)$$

Where, n1, and, n2, are the number of moles of mixed solvent and solute, respectively. The values of $\Delta\mu^{\#}$are presented in **table 8**.The enthalpy, $\Delta H^{\#}$and$\Delta S^{\#}$of activation of viscous flow were computed using the equation [8]:

$$\Delta\mu^{\#} = \Delta H^{\#} - T\ \Delta S^{\#} \qquad (8)$$

The values$\Delta H^{\#}$and$\Delta S^{\#}$are obtained from the intercepts and slopes of the plots of $\Delta\mu^{\#}$versus temperatures. . These parameters contribute to the structural information regarding solute species and solute-solvent interactions. The results are summarized in **table 8**. The $\Delta H^{\#}$ values of nicotinic acid are positive in all solutions and increase regularly with increasing in nicotinic solutions, thereby suggesting that viscous flow appears difficult as amount of nicotinic acid due to formation of inactivated species. Negative $\Delta S^{\#}$ values for nicotinic acid in all NaCl solutions suggest that during viscous flow the system is less structured than the initial state [16].

Table 8: Enthalpy, $\Delta H^{\#}$, entropy, $\Delta S^{\#}$ and The total free energy of activation of viscous flow, $\Delta\mu^{\#}$

C/ (mol.L^{-1})	$\Delta S^{\#}$/ (J.K^{-1}. mol^{-1})	$\Delta H^{\#}$/ (kJ.mol^{-1})	$\Delta\mu^{\#}$/ (kJ.mol^{-1})			
			293.15 K	298.15 K	303.15 K	308.15 K
0.0 MNaCl						
0.014	1.507	2.15	1.710615	1.698059	1.695089	1.686477
0.028	5.04	4.279	2.806562	2.768524	2.753804	2.727457
0.042	8.79	6.472	3.904323	3.837103	3.810669	3.766628
0.056	12.75	8.73	5.003981	4.903876	4.865764	4.804055
0.07	16.94	11.052	6.105304	5.968619	5.918868	5.839527
0.084	21.34	13.437	7.208271	7.031314	6.969964	6.87302
0.098	25.96	15.887	8.313194	8.092264	8.01935	7.90483
0.112	30.79	18.402	9.419833	9.151238	9.066798	8.934729
0.126	35.84	20.98	10.52828	10.20832	10.11239	9.962807
0.1 M NaCl						
0.014	-18.46	1.985	7.396855	7.491984	7.5752	7.676781
0.028	-18.41	3.108	8.505761	8.601969	8.67863	8.787041
0.042	-18.26	4.262	9.61784	9.713825	9.783934	9.898902
0.056	-17.98	5.458	10.7335	10.82666	10.89022	11.01207
0.07	-17.53	6.707	11.85369	11.9414	11.99841	12.12696
0.084	-16.93	8.005	12.97834	13.05795	13.10842	13.24378
0.098	-16.18	9.35	14.10589	14.17474	14.21869	14.3609
0.112	-15.41	10.7	15.23654	15.29195	15.32939	15.48098
0.126	-14.34	12.141	16.369	16.4083	16.43923	16.59776
0.2NaCl M						
0.014	-34.05	3.773	13.75363	13.92704	14.09816	14.26409
0.028	-31.22	5.743	14.89245	15.05854	15.21125	15.36193

0.042	-28.39	7.717	16.03304	16.19176	16.32604	16.46145
0.056	-25.55	9.693	17.17406	17.3254	17.4412	17.56131
0.07	-22.7	11.672	18.31709	18.46104	18.55834	18.66313
0.084	-19.86	13.654	19.46198	19.59853	19.67732	19.76677
0.098	-17.01	15.637	20.60646	20.7356	20.79584	20.86993
0.112	-14.15	17.621	21.75095	21.87265	21.91432	21.97303
0.126	-11.3	19.604	22.89373	23.00799	23.03108	23.07438
0.3NaCl M						
0.014	-63.6	1.086	19.81658	19.89033	20.42674	20.6978
0.028	-66.1	1.214	20.67687	20.76444	21.31386	21.59542
0.042	-68.52	1.367	21.54088	21.64101	22.20312	22.49561
0.056	-71.01	1.505	22.40661	22.51999	23.09562	23.39828
0.07	-73.5	1.645	23.27574	23.40241	23.99123	24.3045
0.084	-76	1.785	24.1474	24.28739	24.88946	25.21337
0.098	-78.5	1.925	25.0219	25.17526	25.79062	26.12523
0.112	-81.02	2.065	25.89882	26.06559	26.6943	27.03964
0.126	-83.54	2.205	26.77897	26.95919	27.6013	27.95741

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الخواص الثرموديناميكية لحامض النيكوتين في الحامض المخفف للهيدروليك وكذلك في المحاليل المائية لكلوريد الصوديوم عند درجات 293.15 و298.15 و303.15 و308.15 كلفن

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الخلاصة:

تم في هذا البحث تحديد الحجم المولاري الظاهري (V_φ) ومعامل اللزوجة B لحامض النيكوتين في الماء ومحلول كلوريد الصوديوم المائي من خلال قياسات الكثافة واللزوجة في درجات الحرارة (٢٩٣٫١٥، ٢٩٨٫١٥، ٣٠٣٫١٥ و٣٠٨٫١٥) كلفن. تم تقييم البيانات التجريبية للكثافة بواسطة معادلة ماسون وتم حساب حجم المولي الظاهري في التخفيف الى مالانهاية (V^0_φ) وكذلك المنحنى التجريبيالتخفيف الى مالانهاية لحامض النيكوتين من الوسط المائي الى محاليل كلوريد الصوديوم عند درجات حرارية مختلفة. تم تحليل بيانات اللزوجه باستخدام معادله جونز دول، و تم ايجاد قيم معامل جونز دول للزوجة B، و معامل فالكينهاكين، *Sv*, A و فسرت القيم المستحصلة اعتمادا على طبيعة التداخلات الجزيئية الناتجة بين المذاب و المذيب او المذاب و المذاب على التوالي. كما تم دراسة تأثير درجة الحرارة على معامل B للزوجة (dB/dT)و كانت القيم الناتجة سالبة مما يشير الى ان حامض النيكوتين في المحلول المائي لملح كلوريد الصوديوم هو باني للتراكيب و تعزى النتائج كذلك الى التداخلات الجزيئية بين المزيج الثلاثي المكون من الفيتامين – الماء– المذاب المشترك (كلوريد الصوديوم) . تم حساب الطاقة الحرة , الانثالبي($\Delta H^{\#}$), و الانتروبي($\Delta S^{\#}$) للتنشيط الجرياني باستخدام معادلة ايرنك . كما تم حساب الطاقة الحرة للتنشيط الجرياني لكل من المذيب($\Delta\mu_1^{\#}$) و المذاب ($\Delta\mu_2^{\#}$) على التوالي. تم دراسة تأثيرالمذاب على تراكيب الماء باستخدام دوال اللزوجة و الدوال الثرموديناميكية.