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Physico-chemical analysis on binary liquid mixture of Nicotinic acid at different temperatures

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The ultrasonic velocity (u), density (ρ) and viscosity (η) of Nicotinic acid in methanol solutions have been investigated at 288, 298 and 308 K. From these experimental measurement, thermo acoustical parameters such as acoustical impedance (Z), adiabatic compressibility (β_a), intermolecular free length (L_f), relaxation time (τ), internal pressure (π_{in}) and free volume (V_f) have been computed. The variation of these acoustical parameters with molar concentration and temperature indicates the existence of strong molecular interaction in the systems studied. The acoustical analysis revealed the possibility of intermolecular hydrogen bonding in the binary liquid solution of Nicotinic acid and Methanol.

Keywords: Ultrasonic velocity, binary liquid solution, molecular interaction, hydrogen bonding

1 Introduction

In recent years, ultrasonic method has become a powerful tool in providing information regarding physicochemical properties of the liquid mixtures[1]. These physicochemical properties of pure and liquid mixtures are having great importance in the field of science and industrial engineering[2] for processing and product formulations[3-9] and also developing reliable predictive models for understanding the nature of intermolecular interactions in the mixtures[10].

The aim of present investigation is to study the variation of thermo acoustical parameters of binary liquid mixture of nicotinic acid and methanol with molar concentrations and temperatures. The variation of these parameters with molar concentration may be helpful in pharmaceutical and food industries to prepare various drug dosages, solution, tablets, capsule, gel and injection in solution form[11]. Also, the variation of these parameters with temperatures may be helpful to preserve various drugs and solution in pharmaceutical and food industry[12]. Nicotinic acid is one of the water soluble vitamin mostly occur in cereals and red meat[13]. The methanol used as a solvent is a natural constituent in blood, urine, saliva and expired air[14] and widely available in our diet principally from fresh citrus fruits and juices, vegetables and certain artificial sweeteners aspartame[15]. Therefore, nicotinic acid and methanol and its liquid mixtures are normally found in our human body so the choice of this liquid mixture was done keeping in mind to study physico-chemical properties by ultrasonic measurement technique at a desired temperature range of human body.

In review of literature, it has been found that most of the studies on physicochemical properties of liquid mixtures have been reported by various ultrasonic researchers[16-21]. However, best of our knowledge no significant effort has been made to investigate the physico-chemical properties of binary liquid mixture of nicotinic acid and methanol at different concentrations and temperatures. Therefore, present investigation has been undertaken to measure the values of ultrasonic velocity (u), density (ρ) and viscosity (η) in the binary mixtures of nicotinic acid and methanol in the concentration range (0 to 0.1 M) and at temperatures of 288, 298 and 308 K using ultrasonic interferometer having fixed frequency of 2 MHz. The various parameters like adiabatic compressibility (βa), acoustic impedance (Z), free length (L_f), relaxation time (τ), free volume (V_f) and internal pressure (π_{in}) were calculated from density, viscosity and ultrasonic velocity data. All these parameters were discussed in terms of solute solvent interaction and complex formation through intermolecular hydrogen bonding in the binary mixture of nicotinic acid & methanol at different concentrations and temperatures.

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2 Materials and Methods

The chemicals nicotinic acid and methanol used in the present work were the products of AR grade with minimum assay of 99.9%. Therefore, all these chemicals were used without further purification. The different molar concentrations of the liquid mixture of nicotinic acid and methanol were made immediately before use. The viscosity of the liquids was measured by an Ostwald Viscometer. The viscometer was suspended in a thermostatic water bath. An electronic digital stopwatch with uncertainty of ± 0.01 s was used for flow time measurement. The density of the solution was measured using pycno meter. The measurements were made at different concentrations (0 to 0.1 molar) and temperatures 288, 298 and 308K.The ultrasonic velocities of liquid mixture of nicotinic acid and methanol were measured by ultrasonic interferometer at a fixed frequency of 2 MHz with an overall accuracy of ± 0.03%. The temperature of liquid mixture was maintained constant by digitally operated constant temperature water bath with an accuracy of ± 0.1 K.

2.1 Physical Parameters

Thermodynamic parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f), acoustic impedance (Z), relaxation time (τ), free Volume (V_f) and internal pressure (π_{in}) were calculated from empirical Jacobson's relations[22-23].

(i) Adiabatic Compressibility (β_a)

Adiabatic compressibility determines the orientation of the solvent molecules around the liquid molecules[24-25]. It can be calculated by using ultrasonic velocity and density as:

$$\beta_a = 1/\rho U^2 \; N^{-1}.m^2 \qquad \ldots (1)$$

Where, *U* is the ultrasonic velocity of solution at fixed experimental temperature.

ρ is the density of the solution at fixed experimental temperature.

(ii) Intermolecular Free Length (L_f)

The intermolecular free length (L_f) is an important physical property of the liquid mixtures[26-27]. It gives the distance between the surfaces of the neighbouring molecules which mainly affects the sound velocity[28-29]. Intermolecular free length can be given by[30]

$$L_f = k.(\beta_a)^{1/2} \; Å \qquad \ldots (2)$$

Where, k is Jacobson's constant.

$= (93.875+0.345\times T) \times 10^{-8}$
(T is temperature in Kelvin)

(iii) Acoustical Impedance (Z)

Acoustic impedance is an important physical property to determine the absorption of sound in the material medium[31]. It experiences the resistance of ultrasonic beam, as it passes through a medium[32]. The acoustic impedance can be given by following relation

$$Z = U.\,\rho \; Kg/m^2.\,Sec \qquad \ldots (3)$$

(iv) Relaxation time (τ)

Relaxation time is the time at which molecules return to their original positions after being displaced by the force. The relaxation time is estimated from the following relation[33]

$$\tau = \frac{4}{3}\eta\,\beta_a \; Sec \qquad \ldots (4)$$

(v) Free Volume (V_f)

Free volume can be calculated on the basis of dimensional analysis in terms of experimentally measurable parameters like ultrasonic velocity and viscosity and is given by[34].

$$V_f = \left(\frac{M.U}{K.\eta}\right) m^3/mole \qquad \ldots (5)$$

Where, K–Temperature independent constant

$= 4.28 \times 10^9$.

M – Effective molecular weight of mixture

$= m_1x_1 + m_2x_2$

(Where -m_1 & m_2 are molecular weight of solute and solvent respectively.

x_1 & x_2 are mole fraction of solute and solvent resp.

η - viscosity of solution at fixed experimental temperature

vi) Internal Pressure (π_{in}):

Internal pressure is a fundamental property of a liquid, which provides an excellent basis for examining the solution phenomenon and studying various properties of the liquid state[35]. The internal pressure of the liquid mixture is obtained from the experimental values of ultrasonic velocity, density and viscosity using the following relation[34].

$$\pi_{in} = bRT\,[K\eta/U]^{1/2}\,[\rho^{2/3}/M^{7/6}] \; N.m^{-2} \qquad (6)$$

Where: b- Cubic Packing factor
(Assume to be 2 for all liquids and solutions)
R- Universal gas constant
T- Absolute temperature (in Kelvin)

K-Temperature independent constant
= 4.28 x 10^9

3 Results and Discussions

The measured experimental value of ultrasonic velocity (U), density (ρ) and viscosity (η) of pure solvent methanol is used in the present work and compared with the available literature data[36-47] at 288, 298 and 308 K. These values are reported in Table. 1 and a satisfactory agreement was found.

With a view to understand the effect of concentration, temperature and nature of solvent on structure forming or structure-breaking tendency various acoustical parameters like acoustical impendence (Z), adiabatic compressibility (βa), intermolecular free path length (L_f),relaxation time (τ), internal pressure (π_{in}) and free volume (V_f) were determined by using the experimental data of ultrasonic velocity (U), density (ρ) and viscosity (η) at three different temperatures 288, 298 and 308K using standard Eqs. 1-6. These parameters were tabulated in Table. 2.

Ultrasonic Velocity

In the present investigation, it has been observed that, ultrasonic velocity decreasing up to 0.04 molar concentration and then increases and attains a maximum value at 0.08 M. On further increasing the concentration, the ultrasonic velocity decreases. The non-linear variation of ultrasonic velocity with increase in molar concentrations indicates occurrence of complex formation between nicotinic acid and

Table 1 — Ultrasonic velocity, density (ρ) and viscosity (η) of Pure solvent methanol and comparison with literature data at 288K, 298 K and 303K

Solvent	Temperature [K]	U ($m.s^{-1}$) × 10^3		ρ ($Kg.m^{-3}$)		η (Pa.Sec)	
Methanol		Experimental	Literature	Experimental	Literature	Experimental	Literature
	288 K	1.148	1.175[41]	796.4	790[41]	0.000637	0.000635[47]
	298 K	1.108	1.102[36,38] 1.108[41,42]	785.2	786.6[36-37] 786.9[39,40,46] 786.30[42] 786.37[43]	0.000548	0.000547[39,40,46] 0.000551[42-43]
	308 K	1.096	1.074[36] 1.069[38] 1.076[42] 1.073[44]	778.1	777.23[37] 776.60[42] 777.05[43] 776.9[45]	0.000470	0.000480[43]

Table 2 — The measured parameters ultrasonic velocity(U), density (ρ), viscosity (η) and the derived parameters adiabatic compressibility (β_a), intermolecular free length (L_f), free Volume (V_f) internal pressure (π_{in}),acoustic impedance (Z) and relaxation time (τ) for Nicotinic acid and methanol solution at 288K, 298K and 308K

Temp (K)	Conc. (mole/dm^3)	U× 10^3 ($m.s^{-1}$)	ρ ($Kg.m^{-3}$)	η (PaSec)	β_a × 10^{-10} ($N^{-1}.m^2$)	L_f(A^0)	V_f × 10^{-8} (m^3/mole)	π_{in} X 10^9 N/m^2	Z X 10^5 ($Kg.m^{-2}sec^{-1}$)	τ X 10^{-13} (Sec)
288K	0	1.148	796.4	0.000637	9.53	0.5965	4.9553	1.11	9.14	8.092
	0.02	1.144	786.9	0.00072	9.71	0.6022	4.1372	1.16	9	9.322
	0.04	1.144	786.4	0.000725	9.72	0.6024	4.1292	1.16	9	9.392
	0.06	1.152	792.4	0.000736	9.51	0.5959	4.1138	1.16	9.13	9.332
	0.08	1.160	796.7	0.000745	9.33	0.5902	4.1159	1.16	9.24	9.266
	0.1	1.152	787	0.000736	9.58	0.5979	5.837	0.883	9.07	9.396
298K	0	1.108	785.2	0.000548	10.37	0.6335	5.888	1.07	8.7	7.58
	0.02	1.108	784.4	0.000592	10.38	0.6338	5.2892	1.11	8.69	8.197
	0.04	1.108	783	0.000591	10.4	0.6344	5.3477	1.1	8.68	8.198
	0.06	1.112	787	0.000594	10.28	0.6305	5.38105	1.1	8.75	8.138
	0.08	1.124	792.4	0.000603	9.989	0.6216	5.3913	1.1	8.91	8.031
	0.1	1.116	784.1	0.000601	10.24	0.6294	7.5426	0.836	8.75	8.206
308K	0	1.096	778.1	0.000470	10.7	0.6546	7.2936	1.03	8.53	6.705
	0.02	1.080	781.4	0.000492	10.97	0.6629	6.7182	1.05	8.44	7.198
	0.04	1.080	780.7	0.000487	10.98	0.6632	6.8798	1.04	8.43	7.131
	0.06	1.076	785.4	0.000494	11	0.6637	6.7533	1.05	8.45	7.244
	0.08	1.104	789.5	0.000501	10.39	0.6452	6.92975	1.04	8.72	6.942
	0.1	1.088	781.7	0.000505	10.81	0.6579	9.4264	0.801	8.5	7.277

methanol molecules[48].The occurrence of maximum velocity at 0.08 M concentration and subsequent decrease of ultrasonic velocity with further increase in molar concentrations of nicotinic acid. This may occur, as maximum associated nicotinic acid molecules are broken into their monomers and the hydrogen bonds (O-H..O) are formed between the hydrogen atom of methanol molecules and the oxygen atom of nicotinic acid monomers, thus association may be possible between nicotinic acid and methanol molecules through hydrogen bonding as shown in Fig. 1. It is likely that the molecules of nicotinic acid may stay in associated form. These associated molecules are fairly larger in size as compared to methanol molecules and have to be accommodated in the system and this may cause some structural changes resulting in the weakening of the intermolecular forces. This probably would be the reason for the decrease in ultrasonic velocity above 0.08 molar concentrations.

Acoustic Impedance

In the present investigation, it has been observed that acoustic impedance (Z) exhibited similar trends as that of ultrasonic velocity with increase in molar concentration of nicotinic acid which support the possibility of molecular interactions and complex formation between the nicotinic acid and methanol molecules[49-50].

The ultrasonic velocity and acoustic impedance decreases with increase in temperature this is due to breaking of hetero association and homo association of interacting molecules.

Viscosity

The viscosity is an important tool to determine the structure as well as molecular interaction occurring in the solutions[51]. It has been found that viscosity shows very small variation with increase in molar concentration of nicotinic acid. This may be assumed due to the fact that, when a nicotinic acid is added to a methanol, then the methanol becomes more viscous, so that, the mixture became thick liquid, less fluidity and therefore weak intermolecular forces exist between them. Viscosity also shows decreasing behaviour with increase in temperature indicates decreases in cohesive forces which brings the molecules to a loosely packing. This results the weakening of molecular association between the interacting molecules of nicotinic acid and methanol.

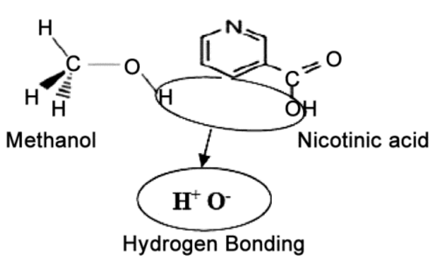

Fig. 1 — Intermolecular interactions in Methanol and Nicotinic acid

Relaxation time

Relaxation time is depending on the viscosity of liquid[52]. The relaxation time show the same variation as that of viscosity. The relaxation time which is order of 10^{-12} sec is due to structural relaxation process[33, 53-54] in such a case it has been suggested that molecules getrearranged due to co-operative process[55].

Adiabatic Compressibility

Compressibility of a material is one the important physical quantities in thermodynamic and fluid mechanics. It is an important parameter to measure relative change in volume with respect to change in pressure. During compression, if the temperature remains constant then the compressibility is known as isothermal compressibility and if it is carried out reversibly without heat exchange with surrounding then we get adiabatic compressibility[56]. In the present investigation, adiabatic compressibility shows an inverse behaviour to that of ultrasonic velocity which confirm complex formation due to hydrogen bond formation between nicotinic acid and methanol molecules. Adiabatic compressibility decreases with increase in molar concentration and shows a minimum at 0.08 molar concentration. This might be due to aggregation of methanol molecules around nicotinic acid molecules supporting strong interaction between interacting components[57].The occurrence of minimum adiabatic compressibility at 0.08 molar concentration, shows maximum complexation. The occurrence of ultrasonic velocity maxima and adiabatic compressibility minima at the same concentration indicates a significant interaction between the molecules of nicotinic acid and methanol.

Intermolecular free length

Intermolecular free length, shows a behavior similar to that of adiabatic compressibility and inversely to that of ultrasonic velocity[58-60]. As there is no linearity observed for the values of intermolecular free length and adiabatic compressibility. This confirms the presence of specific interactions in nicotinic acid and methanol molecules[2].

In the present binary mixture, adiabatic compressibility and intermolecular free length increases with increase in temperature. This might be due to the fact that, as the temperature increases available thermal energy facilitates the breaking of bonds between the associated molecules into their monomers, therefore the molecules in the liquid mixture can move away from each other, reducing the interaction, which may further reduce the cohesive forces. Moreover, increase of thermal energy increases the spacing between the molecules and increases entropy of its structural arrangement which tends to weakens the intermolecular forces.

Free volume and internal pressure

Free volume is one of the significant factors in explaining the variations in physico-chemical properties of the liquid and liquid mixtures. It gives the measure of cohesive or binding forces between the solutes and solvent molecules. The internal pressure gives very much information of thermodynamic properties of liquids and play a crucial role in elucidating the molecular interaction. It also gives the idea of force of attraction and repulsion between the molecules[61]. As observed in Table. 2, free volume and internal pressure shows minute variation up to 0.08 molar concentration, may be due to existence of weak intermolecular forces. However, from 0.08 M concentration free volume increases whereas internal pressure decreases. This may occur because, after 0.08 molar concentration, molecules get disordered due to increasing entropy of the system which leads to decrease interactions between molecules of nicotinic acid and methanol. It also noticed that, with the increase in temperature, free volume increases and internal pressure decreases. As temperature increases molecules get disordered due to increase entropy of the system which leads to decrease interactions between the nicotinic acid and methanol molecules.

4 Conclusions

1. The nonlinear variation of ultrasonic velocity and related acoustical parameters gives the idea of solute-solvent interaction and complex formation in the binary mixture of nicotinic acid and methanol
2. The variation of ultrasonic velocity with temperature indicates breaking of hetero and homo association of molecules in the binary liquid mixture of nicotinic acid and methanol.
3. The strong association of B- complex nicotinic acid and methanol at 0.08 molar concentration may be helpful in pharmaceutical and food industries to prepare various drug dosages, solution, tablets, capsule, gel and injection in solution form.

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