Ultrasonic Studies of Molecular Interactions in the Mixture of Pyridine with 1-Propanol at Different Temperatures

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Abstract: *Ultrasonic velocity (U), density (ρ) and viscosity (η) values of the mixture of pyridine with 1-propanol have been measured at 303K, 313K and 323K temperatures. From these data, acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) have been estimated using the standard relations. The excess parameters such as β^E, $L_f^{\ E}$, $V_f^{\ E}$ and $\pi_i^{\ E}$ are also determined from the experimental data. The results are interpreted in terms of molecular interaction between the components of the mixture. The ultrasonic velocity decreases with the mole fraction of 1-propanol in the binary mixture at all temperatures. The adiabatic compressibility (β) shows an inverse behaviour as compared to ultrasonic velocity at all temperatures.*

Keywords: Ultrasonic velocity, acoustical parameters, adiabatic compressibility, free length, free volume, internal pressure

1. Introduction

The ultrasonic velocities (U), viscosity (η) and Density (ρ) measurements find wide applications in characterizing the physico - chemical behaviour of the binary liquid mixtures [1-3]. These properties are extensively used to estimate the thermodynamics properties and predict the intermolecular interactions. Further, the measurements of excess thermodynamic properties are found to be greatly significant in studying the structural changes associated with the liquids. One of the constituent of the binary liquid mixture under study is Pyridine (C_5H_5N), recognized as the non aqueous aprotic solvent having dielectric constant 12.40 at 25^0C, dipole moment 2.22 D at 25^0C, and boiling point 115^0C^{12}. Pyridine is used as a precursor to agrochemicals and pharmaceuticals and is also an important solvent and reagent. Pyridine has also been used as the major constituents of binary mixtures of required characteristics. 1-Propanol (1-PrOH), on the other hand is associative liquid and is useful in variety of industrial fields like oil industry, refrigeration, air conditioning and others. 1-PrOH has an OH group that might be expected to lead to the formation of a hydrogen-bonded complex with pyridine at the nitrogen site and perhaps electrostatic bonding at other sites. These liquid mixtures are of interest to organic chemists who want to know about the type of bond and the number of each kind of molecule in the pyridine complex.

In present paper, an attempt to investigate the molecular interaction in the binary mixture of pyridine with 1-PrOH through ultrasonic studies is made. We have measured density (ρ), ultrasonic velocity (u), viscosity (η) of mixtures of Pyridine + 1-PrOH at 303 K, 313 K and 323 K temperatures. From this data, acoustical parameters like adiabatic compressibility (β), inter molecular free length (L_f), free volume (V_f), internal pressure (π_i) and their excess values are computed. Results are used to explain the nature of molecular interactions between mixing compounds.

2. Material and Sample Preparation

1-Propanol (AR grade) and pyridine (AR grade) were commercially obtained from S D Fine-chem Limited (India) and were used without further purification. Binary mixtures of 1-propanol and pyridine were prepared at nine concentrations by volume. Assuming ideal mixing behaviour the concentration was converted in to the mol fraction using relation [4]

$$x_1 = \frac{\rho_1 \times v_1 / M_1}{\rho_1 \times v_1 / M_1 + \rho_2 \times v_2 / M_2} \quad (1)$$

Where, M is molecular weight, v is volume and ρ is density. 1 represents 1-PrOH and 2 represent pyridine. The mole fraction is accurate to ± 0.1%.

3. Experimental Details

The speeds of sound waves were measured by using digital ultrasonic pulse echo velocity meter [Model no. VCT-70A, VI Microsystems Pvt. Ltd., Chennai (India)] at a fixed frequency of 2 MHz with an accuracy of ± $2ms^{-1}$. Electronically operated digital constant temperature bath for ultrasonic [Supplied by Vi Microsystems Pvt. Ltd., Chennai (India)] was used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature.

The density of pure liquids and liquid mixtures was determined using a pyknometer by relative measurement method. The pyknometer was calibrated at 303 K, 313 K and 323 K with double distilled water and gave an estimated reproducibility ± $0.0001 gcm^{-3}$. An Ostwald's Viscometer of 10 ml capacity was used for the viscosity measurement of pure liquids and liquid mixtures. The viscometer was calibrated with double distilled water immersed in the water bath which was kept at the experimental temperature. The time of flow (t_w) of water and the time flow (t_s) of solution was measured with digital stop clock having an accuracy ± 0.1 s. The temperature of the samples was maintained within ± 0.1 K in an electronically controlled thermostatic water

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bath. All the measurements have been done at three different temperatures 303 K, 313 K and 323 K.

The various acoustical parameters such as adiabatic compressibility (β), free length (L_f), internal pressure (π_i), acoustic impedance (Z), free volume (V_f) and their excess values have been calculated from the measured data using the following standard expressions[5,6]

$$\beta = \frac{1}{U^2 \rho} \quad (2)$$

$$L_f = K_T \beta^{\frac{1}{2}} \quad (3)$$

$$\pi_i = bRT \left(\frac{K\eta}{U}\right)^{\frac{1}{2}} \left(\frac{\rho^{\frac{2}{3}}}{M_{eff}^{7/6}}\right) \quad (4)$$

$$Z = \rho U \quad (5) \quad V_f = \left(\frac{M_{eff} U}{K\eta}\right)^{3/2} \quad (6)$$

where U is ultrasonic velocity, K_T is the temperature dependent constant, K is a constant equal to 4.28×10^9 independent of temperature for all the liquids, b is the packing fraction of the liquid, which is taken equal to 2 for most of the liquids, M_{eff} (=$x_1 M_1 + x_2 M_2$) is the effective molecular mass and M is the molecular weight of pure liquids.

The excess values (A^E) of all acoustic parameters were computed by the relation,

$$A^E = A_{exp} - A_{id} \quad (7)$$

$$A_{id} = \sum_{i=1}^{n} A_i x_i$$, A_{exp} is experimental value.

A_{id} is the ideal value, A_i is any acoustical parameter and x_i is the mole fraction of the liquid component i. The variations of, excess properties with composition are expressed by Redlich-Kister[7] polynomial equation

$$Q = x_1 x_2 \sum_{r=0}^{n} a_r (x_2 - x_1)^r \quad (8)$$

Where Q refers all excess parameters. The adjustable parameters a_r, were determined by least square fitting methods, fitting the experimental values to eq (8). The standard deviations, σ (Q) were defined as

$$\sigma(Q) = \left|\frac{\Phi_{min}}{P - n}\right|^{0.5} \quad (9)$$

Where, P and n are the experimental points and parameters respectively. Φ_{min} is the minimum value of the objective function Φ defined as

$$\Phi = \sum_{k=1}^{N} (n_k)^2 \quad (10)$$

Where $n_k = Q_{cal} - Q$. Q is the experimental value and Q_{cal} is evaluated using eq (8).

4. Result and Discussion:

Comparison of density (ρ), viscosity (η) and ultrasonic velocity (U) of pure 1-PrOH and Pyridine with literature data at 303 K, 313 K and 323 K are given in Table 1.

Table 1: Comparison of Density, Viscosity and ultrasonic velocity of 1-PrOH and Pyridine with Literature Data at 303 K and 313 K.

Component		Temp. = 303 K			Temp. = 313 K		
		ρ	η	U	ρ	η	U
1- PrOH	Exp.	0.806	1.5523	1202.47	0.798	1.2451	1189.13
	Literature	0.7967[8]	1.7153[8]	1198.5[9]	0.787[10]	1.381[10]	-
Pyridine	Exp.	0.964	1.0668	1396.23	0.948	0.7488	1391.54
	Literature	0.978[8]	1.2054[8]	1390[11]	0.968[8]	1.0098[8]	-

Table 2: Density, Viscosity and Ultrasonic Velocity of Mixtures of Pyridine + 1-PrOH as Function of Mole Fraction (x_1) of 1-PrOH at T = (303, 313 and 323) K.

x1	Density (ρ)			Viscosity (η)			Ultrasonic Velocity (u)		
	g cm^{-3}			mNsm^{-2}			ms^{-1}		
	303 K	313 K	323 K	303 K	313 K	323 K	303 K	313 K	323 K
0	0.964	0.948	0.934	1.0668	0.7488	0.5251	1396.23	1391.54	1374.24
0.083	0.957	0.941	0.924	1.0996	0.7615	0.5329	1381.32	1370.23	1351.96
0.168	0.949	0.928	0.916	1.1209	0.7925	0.5556	1362.27	1358.59	1327.56
0.258	0.933	0.906	0.894	1.1518	0.8206	0.5833	1351.96	1345.46	1295.47
0.351	0.923	0.893	0.873	1.1785	0.8519	0.612	1336.55	1331.33	1280.57
0.447	0.906	0.876	0.86	1.2028	0.8821	0.6368	1318.23	1307.21	1272.19
0.548	0.898	0.864	0.855	1.2327	0.9143	0.6668	1297.71	1281.31	1245.58
0.654	0.877	0.846	0.832	1.2698	0.9523	0.7006	1276.95	1256.43	1221.25
0.764	0.866	0.832	0.816	1.3271	0.9945	0.7379	1255.17	1226.44	1200.16
0.879	0.84	0.814	0.803	1.4026	1.0805	0.8036	1229.66	1202.63	1192.91
1	0.806	0.798	0.782	1.5523	1.2451	0.9851	1202.47	1189.13	1158.29

The experimentally measured values of density, viscosity and ultrasonic velocity of the binary liquid mixtures at 303 K, 313 K and 323 K are presented in Table 2. From the Table 2, it is observed that ultrasonic velocity decreases with mol fraction of 1- PrOH in pyridine at all three temperatures.

Similar trend is observed in the density values. Density decreases due to decreased electrostriction in the solution. This less electrostriction increases the volume and hence decreases the density [12]. Viscosity values are found to increase with increase in concentration of 1-PrOH.

Furthermore, it can be seen from the table that viscosity values at all concentrations decrease with increase in temperature, suggesting more dissociation between solute and solvent molecules with rise in temperature [13].

From Table 2 it can be seen that viscosity of the mixture is found to increase nonlinearly with increase in mole fraction of 1-PrOH, at all the three temperatures. The excess viscosity gives an estimate of intermolecular interaction. Present system shows negative deviation of excess viscosity (η^E) from ideality over the entire mole fraction range at all the three temperatures (Figure 1). The negative deviation in excess viscosity (η^E) suggests the existence of weak intermolecular interactions between the pyridine and 1-PrOH. According to Fort and Moore [14] negative values of (η^E) occur for system of different molecular sizes due to dispersion forces, responsible for the interactions. Similar temperature dependence has been observed by Gupta et al [15] for tetrahydrofuras with alcohol mixtures.
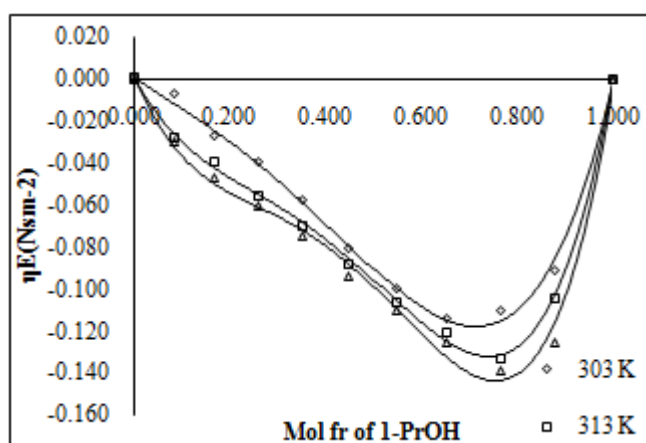

Figure 1 Plot of excess viscosity against mole fraction of 1-PrOH. (–) shows the fitted line of Redlich-Kister equation

Figure 2 shows that the ultrasonic velocity, decrease non-linearly with increasing mole fraction of 1-PrOH. Further, in Pyridine + 1-PrOH binary system the interaction becomes weak with increase in temperature due to thermal agitation of component molecules and this is indicated by the decrease in velocity values.
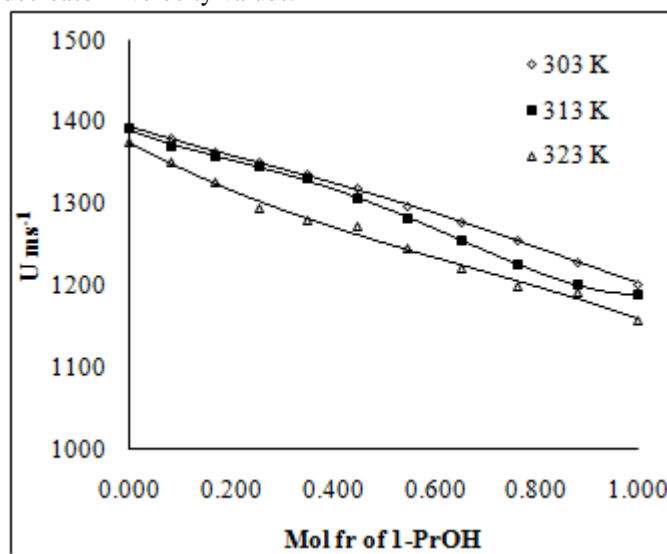

Figure 2: Plot of ultrasonic velocity (U) against mole fraction of 1-PrOH at 303, 313 and 323 K temperatures.

The values of adiabatic compressibility (β), intermolecular free length (L_f), free volume (V_f) and internal pressure (π_i) are presented in the Table 3. The adiabatic compressibility (β) and free length (L_f) show an opposite trend to that of ultrasonic velocity. According to a model proposed by Erying and Kincaid [16], ultrasonic velocity decreases with increase in free length and vice-versa. This is also in accordance with the expected increase in compressibility following a decrease in ultrasonic velocity in these mixtures. Increase of β and L_f with temperature for all compositions suggests breaking of hetero and homo- association of molecules at higher temperature.

Table 3: Values of adiabatic compressibility (β), free length (L_f), internal pressure (π_i) and Free volume (V_f) for Pyridine + 1-PrOH binary system at T = (303, 313 and 323) K

Mol Fraction	β/(x10^{-10} m^{2}N^{-1})			L_f/(x10^{-11}m)			π_i/(x10^6Nm^{-2})			V_f/(x10^{-7} m^{3}mol^{-1})		
X_1	Temperature (K)			Temperature (K)			Temperature (K)			Temperature (K)		
	303	313	323	303	313	323	303	313	323	303	313	323
0.000	5.323	5.449	5.649	4.603	4.658	4.742	7.474	6.407	5.518	1.002	1.914	3.012
0.083	5.479	5.661	5.901	4.670	4.747	4.860	7.366	6.288	5.397	0.806	1.760	2.799
0.168	5.679	5.840	6.194	4.755	4.822	4.966	7.225	6.192	5.336	0.740	1.616	2.581
0.258	5.865	6.097	6.463	4.832	4.927	5.050	7.048	6.042	5.250	0.691	1.415	2.309
0.351	6.067	6.318	6.788	4.915	5.015	5.175	6.899	5.940	5.176	0.617	1.260	2.090
0.447	6.352	6.678	7.184	5.029	5.156	5.348	6.706	5.869	5.122	0.567	1.132	1.852
0.548	6.614	7.048	7.638	5.131	5.267	5.478	6.576	5.788	5.090	0.506	1.019	1.611
0.654	6.991	7.385	8.063	5.276	5.409	5.626	6.431	5.693	5.025	0.451	0.877	1.369
0.764	7.330	7.795	8.507	5.402	5.542	5.759	6.360	5.642	4.970	0.390	0.715	1.119
0.879	7.877	8.297	8.996	5.600	5.716	5.934	6.256	5.682	4.973	0.351	0.561	0.853
1.000	8.583	8.866	9.511	5.846	5.941	6.154	6.257	5.783	5.305	0.312	0.393	0.557

Excess adiabatic compressibility (β^E) is plotted against mole fraction of 1-PrOH and is shown in Figure 3. β^E values are found negative over the entire composition range at all the three temperatures. The negative β^E suggests that the mixture is less compressible than the corresponding ideal mixture. This is in accordance with the view proposed by Fort and Moore [14] according to which liquids of different molecular size usually mix with decrease in volume yielding negative β^E values.
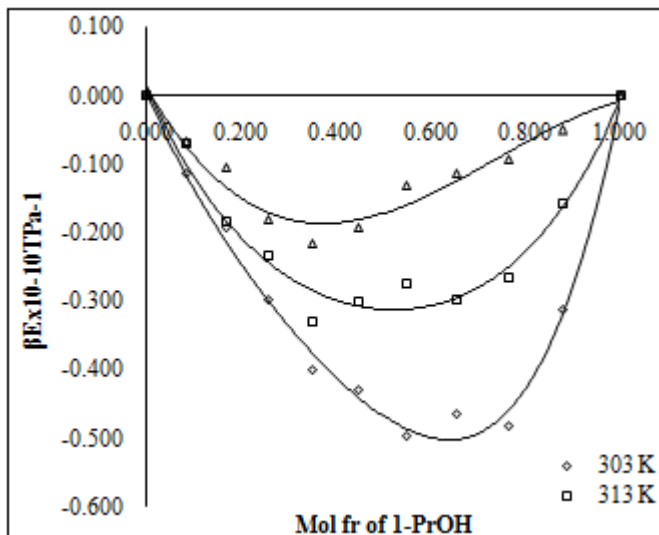
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Figure 3: Plot of excess adiabatic compressibility (β^E) against mole fraction of 1-PrOH. (−) shows the fitted line of Redlich-Kister equation

Plot of excess intermolecular free length against mole fraction of 1-PrOH is shown in Figure 4.
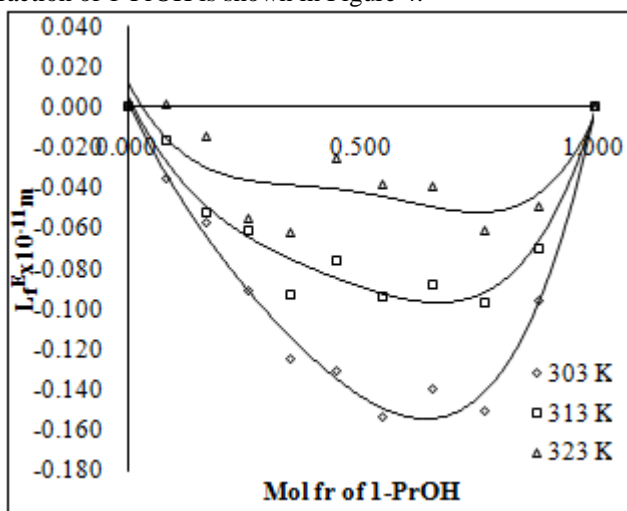

Figure 4: Plot of excess free length (L_f) against mole fraction of 1-PrOH. (−) shows the fitted line of Redlich-Kister equation.

From Figure it can be observed that L_f^E values for the binary mixtures Pyridine + 1-PrOH are negative over entire composition range. Negative L_f^E values suggest the existence of dispersive forces and intermolecular interaction between unlike molecules. This result is similar in

accordance with the result obtained by Singh et al[17] for binary mixture of tetrahydrofuras with 1-propanol.

The excess internal pressure π_i^E against mole fraction of 1-PrOH is plotted in Figure 5. From the Figure it can be seen that the excess internal pressure is negative and increases with rising of temperature. The negative value of π_i^E indicate that only dipolar forces are operating between the unlike molecules. This further supports that dispersive forces are stronger in Pyridine + 1-PrOH system as indicated by values of η^E. Similar trend in excess internal pressure π_i^E is found by Gupta et al [15] for binary mixture of tetrahydrofuran with 1-propanol and 2-propanol.
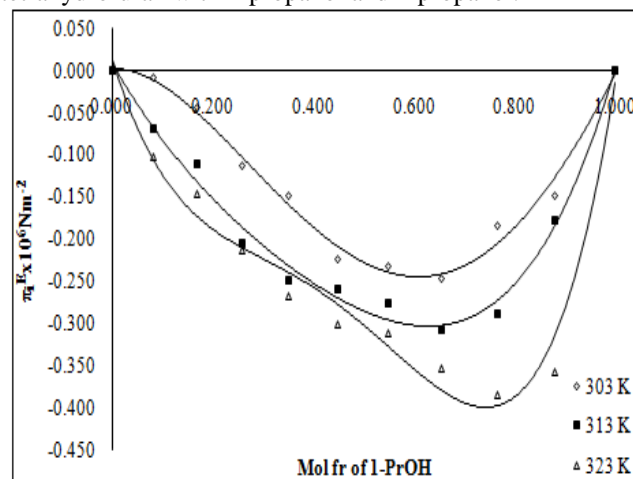

Figure 5: Plot of excess internal pressure (π_i^E) against mole fraction of 1-PrOH. (−) shows the fitted line of Redlich-Kister equation

Excess free volume V_f^E is plotted against mole fraction of 1-PrOH and is shown in Figure 6. From the figure it can be seen that the excess free volume is negative over entire composition range. The sign of V_f^E depends upon the relative strength between the contractive forces and expansive forces [18]. The negative part of V_f^E curves of the system suggests that the combined effect of the factors responsible for volume contraction overweigh the combined effect of the factors causing volume expansion and vice-versa. Thirumarn et al.[19] showed negative value of V_f^E, indicating closely packed molecules which account for existence of strong intermolecular interaction and positive excess values of weak intermolecular interaction between unlike molecules.
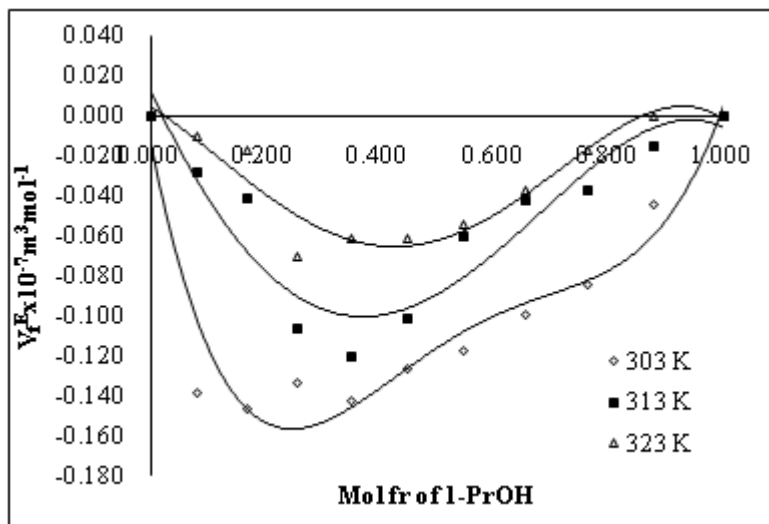
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Figure 6: Plot of excess free volume (V_f^E) against mole fraction of 1-PrOH. (−) shows the fitted line of Redlich-Kister equation

The adjustable parameters a_r, determined by least square fitting methods, fitting the experimental values of all the excess properties under study, to eq 15 are given in Table 4.

The standard deviations (σ) calculated using eq 15 is also presented in the same Table.

Table 4: Parameters of Redlich -Kister Equation for the Mathematical Representation of Deviation in Excess Functions for Pyridine +1-PrOH.

Excess Properties	Temp (K)	a_0	a_1	a_2	a_3	a_4	σ
$\beta^E/(\times 10^{-10}\ Tpa^{-1})$	303	-1.857	0.768	-0.708	0.5500	0.1466	0.0214
	313	-1.185	-0.116	-1.332	0.6723	1.9740	0.0203
	323	-0.667	-0.754	-0.280	1.0056	0.5107	0.0154
$L_f^E/(\times 10^{-11}m)$	303	-0.568	0.231	-0.221	0.1942	0.0453	0.0081
	313	-0.343	0.050	-0.460	0.3446	0.3957	0.0078
	323	-0.132	-0.144	-0.916	0.7308	1.1997	0.0094
$\pi_i^E/(\times 10^6 Nm^{-2})$	303	-0.927	0.4635	0.7269	0.4686	-0.814	0.0131
	313	-1.095	0.469	-1.134	0.1663	1.4725	0.0133
	323	-1.243	0.4884	-0.886	1.6875	-1.580	0.0082
$V_f^E/(\times 10^{-7} m^3 mol^{-1})$	303	-0.503	-0.101	-0.041	-0.905	-1.214	0.0087
	313	-0.336	-0.589	-0.163	0.8719	0.530	0.0119
	323	-0.236	-0.238	0.025	0.2432	0.4621	0.0086
$\eta^E(Nsm^{-2})$	303	-0.364	0.3637	-0.117	0.1653	-0.182	0.0030
	313	-0.389	0.3803	-0.353	0.1217	-0.200	0.0021
	323	-0.407	0.3300	-0.327	0.3705	-0.537	0.0011

5. Conclusion

This paper reports experimental data for density, viscosity and ultrasonic velocity for binary mixture of Pyridine + 1-PrOH at 303, 313 and 323 K temperatures. The observed decrease of ultrasonic velocity indicates the solute – solvent interaction. The behaviour of excess viscosity reveal that weak molecular interaction that exists in the Pyridine + 1-PrOH mixtures which may be due to the dominance of dispersion forces and dipolar interaction between unlike molecules. The adiabatic compressibility (β) and free length (L_f) show an opposite trend to that of ultrasonic velocity. Increase of β and L_f with temperature for all compositions suggests breaking of hetero and homo- association of molecules at higher temperature. Negative L_f^E values suggest the existence of dispersive forces and intermolecular interaction between unlike molecules. There is an intermolecular interaction of the component of binary mixture leading to possible hydrogen bond formation of type N···H─O between unlike molecules confirming hydrogen bond formation between Pyridine and 1-PrOH.

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