

## Excess transport properties of binary mixtures of methanol and pyridine through ultrasonic measurements at different temperatures

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The viscosities, densities and ultrasonic velocities of binary liquid mixtures of methanol with piperidine and morpholine and pyridine with piperidine and morpholine have been determined at 303.15 to 318.15K over the entire composition range. These data have been utilized to estimate the excess free volume, excess internal pressure, excess enthalpy, excess velocity, excess acoustic impedance and excess Gibb's free energy of activation of flow. The results obtained have been discussed in the light of existing theories of molecular interaction involved and chemical constitution of the liquid components. Analysis of these parameters indicates that there are intermolecular interactions among components of the binary mixtures that lead to possible hydrogen bond formation (of the type N...H-O) between unlike molecules.

Ultrasonic velocity measurements are useful when dealing with the problems of structure and molecular interactions in liquids because of their accuracy. Thermodynamic and ultrasonic sound measurements have been used to determine the internal pressure of liquids and also the effect of change in composition and temperature on excess free volume and internal pressure of binary mixtures by several workers<sup>1-4</sup>. It has been pointed out by several workers<sup>5-9</sup> that excess thermodynamic functions are dependent not only on the difference in intermolecular forces, but also on the difference in the size of molecules. The main advantage of considering internal pressure in calculating the transport properties lies in the fact that it may be obtained experimentally and also depends

on free volume and molar volume. Above all, internal pressure is closely related to the solubility parameter, which determines the way in which the interactions occur in the system.

For a detailed study of the interactions of the liquid mixtures of methanol with piperidine and morpholine and pyridine with piperidine and morpholine, it is necessary to know the behaviour of a comprehensive set of thermodynamic properties. In this work we report the experimental values of the density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity ( $U$ ) of the above binary mixtures at the temperatures 303.15, 308.15, 313.15 and 318.15K. These data have been used to compute the free volume ( $V_f$ ), internal pressure ( $\pi$ ), enthalpy ( $H$ ), specific acoustic impedance ( $Z$ ), excess free volume ( $V_f^E$ ), excess internal pressure ( $\pi^E$ ), excess enthalpy ( $H^E$ ), excess velocity ( $U^E$ ), excess specific acoustic impedance ( $Z^E$ ) and excess Gibb's free energy of activation of flow ( $G^E$ ).

### Experimental

Methanol, morpholine, pyridine and piperidine from Merck were purified using fractionating column<sup>10,11</sup> and the middle fractions were collected and stored over molecular sieves. The purity of samples was checked by density and viscosity measurements<sup>11</sup>. Job's method of continuous variation was used to prepare the mixtures of required proportions. The mixed liquid binary systems were preserved in well-stoppered conical flasks. After mixing the liquids thoroughly, the flasks were left undisturbed to allow them to attain thermal equilibrium.

The densities of pure liquids and liquids mixtures were measured by employing a specific gravity bottle. The accuracy in the measurement of density employing the specific gravity method is better than  $\pm 0.01\%$ . Weight measurements in the present study were made with an electronic balance capable of measuring up to 0.5mg. Viscosities were determined using Ubbelohde viscometer<sup>12, 13</sup>, which was calibrated with benzene and doubly distilled water at all four temperatures. The values are accurate to  $\pm 0.001$  cP. Velocities were determined<sup>14</sup> using single crystal ultrasonic pulse echo interferometer (model

M-82, Mittal Enterprises, India) working at 1 M Hz. The ultrasonic velocity had an accuracy of  $\pm 0.5$  m/s. The temperature of the solution was controlled by circulating water through the jacket of double walled cell. Measurements were made using constant temperature bath with in  $\pm 0.01$  K.

### Theory

On the basis of dimensional analysis, using free volume concept, the following expression can be used for calculating internal pressure

$$\pi = bRT/(K\eta/U)^{1/2} \rho^{2/3} M^{7/6} \quad \dots (1)$$

where 'b' is a packing factor, K is independent of temperature constant<sup>15,16</sup> having a value of  $4.28 \times 10^9$  and  $\eta$  is the viscosity. The other symbols have their usual meaning.

The free volume of liquid mixtures behaves exactly in a reverse trend as that of internal pressure values. There is a relationship between the internal pressure ( $\pi$ ), the external pressure ( $p$ ) and the free volume ( $V_f$ ) of a liquid

$$V_f = KRT/[(\pi+p)(p+V_f^{1/3}/K)^2] \quad \dots (2)$$

This relationship is very important since it shows that free volume of a molecule at a particular temperature and pressure depends only on the internal pressure of the liquid in which it is immersed. The free volumes of the binary mixtures have been computed using its relationship with the ultrasonic velocity and viscosity as follows

$$V_f = (MU/K\eta)^{3/2} \quad \dots (3)$$

where  $K$  is a proportionality constant, which is sensitive to molecular phenomena.

The strength of interaction between the component molecules of binary mixtures is well reflected in the deviation of the excess functions from ideality. Thermodynamic excess functions are found to be very sensitive towards mutual interactions between component molecules of liquid mixtures. The sign and extent of deviation of these functions from ideality depends on the strength of interaction between unlike molecules<sup>17</sup>.

The excess properties such as  $V_f^E$ ,  $\pi^E$ ,  $Z^E$ , and  $H^E$  have been calculated using the equation

$$Y^E = Y_{\text{mix}} - [X_1 Y_1 + X_2 Y_2] \quad \dots (4)$$

where  $Y^E$  is  $V_f^E$  or  $\pi^E$  or  $H^E$  or  $G^E$  and  $X$  represent mole fraction of the component and subscript 1 and 2 stand

for the components 1 and 2. These excess functions were fitted to Redlich-Kister type polynomial equation.

$$Y_{\text{cal}}^E = \left[ X_1 X_2 \sum_{j=1}^N \{a_{j-1} (X_2 - X_1)\} \right]^{j-1} \quad \dots (5)$$

The values of coefficient  $a_{j-1}$  evaluated by the method of least squares with all points weighed equally with the standard deviations are listed in Table 1 and are calculated as

$$\sigma(Y^E) = ([Y_{\text{ob}}^E - Y_{\text{cal}}^E]^2 / m - n)^{1/2} \quad \dots (6)$$

where  $m$  is the number of experimental data points and  $n$  is the number of coefficients considered ( $n=3$  in the present calculation).

### Results and discussion

It is observed that as the concentration of methanol and pyridine increases, free volume decreases whereas the internal pressure increases. This suggests close packing of the molecules inside the shield, which may be brought about by the increasing magnitude of interactions<sup>2,18,19</sup>. It is to be noticed that the variation in the internal pressure values shows exactly in a reverse trend as that of free volume<sup>20</sup>.

In order to substantiate the presence of interaction between molecules, it is essential to study the excess parameters like free volume ( $V_f^E$ ), internal pressure ( $\pi^E$ ), enthalpy ( $H^E$ ), and acoustic impedance ( $Z^E$ ). The variation of the excess parameters in all the four systems with the composition of methanol or pyridine are represented in Figs 1-4. The deviation of physical property of the liquids mixtures from the ideal behavior is a measure of the interaction between the molecules, which is attributed to either adhesive or cohesive forces<sup>21</sup>.

In the present study, methanol and pyridine are polar components having self-association character. When piperidine and morpholine are added to methanol and pyridine, it results in considerable decrease in intermolecular spaces between the molecules as suggested by Jacobson<sup>22</sup>. This contributes to decrease in free volume and hence its increase in the internal pressure giving rises to negative  $V_f^E$  and positive  $\pi^E$  values. The negative values of  $V_f^E$  decrease with increase in the concentrations of methanol and pyridine attaining a minimum value at about 0.6 mole fraction, indicating the presence of strong molecular interaction<sup>23,24</sup>. These observations support the view that the mixtures

Table 1—Values of the coefficients of Eq. 5 and standard deviation ( $\sigma$ ) for the studied systems

Temp. (K)	$A_0$	$A_1$	$A_2$	$\sigma$	Temp. (K)	$A_0$	$A_1$	$A_2$	$\sigma$
<i>Methanol + piperidine</i>					<i>Pyridine + piperidine system</i>				
		$V_f^E$					$V_f^E$		
303.15	-2.7781	2.6584	-1.3157	0.0810	303.15	-6.5227	-3.5658	1.0968	0.0786
308.15	-3.8650	-0.2997	1.7019	0.0381	308.15	-5.0775	-0.9793	1.6839	0.1061
313.15	-2.7903	-2.7903	-0.0356	0.0197	313.15	-6.8026	-0.5114	3.7582	0.1097
318.15	-2.2923	-1.9981	-0.6723	0.1343	318.15	-6.7166	0.1140	4.5181	0.0784
		$\pi^E$					$\pi^E$		
303.15	-3369.16	-1998.36	-738.29	17.61	303.15	1052.48	160.38	-319.70	7.3896
308.15	-3148.34	-1137.78	-1353.07	13.65	308.15	837.87	-120.97	-254.43	9.4088
313.15	-3488.48	-435.42	-102.90	6.90	313.15	1020.04	-177.24	-425.95	8.6418
318.15	-3908.26	-826.57	109.30	46.46	318.15	947.08	-220.84	-351.29	4.7543
		$H^E$					$H^E$		
303.15	92947	-29225	26723	1863	303.15	45184	36238	-27688	1228
308.15	107143	29974	-33059	618	308.15	24605	11173	-22388	1307
313.15	73660	63886	16400	396	313.15	37101	6163	-41489	1137
318.15	48519	43304	24259	2257	318.15	28757	3475	-44211	538
		$G^E$					$G^E$		
303.15	761.56	162.81	214.89	5.3401	303.15	182.37	134.55	-58.08	5.2932
308.15	753.49	329.52	162.17	4.6537	308.15	142.86	105.95	-9.96	3.3265
313.15	700.72	377.81	238.72	3.1152	313.15	136.86	59.15	-105.42	3.7377
318.15	687.94	345.42	110.72	2.5844	318.15	110.44	35.48	-105.24	3.315
<i>Methanol+ morpholine system</i>					<i>Pyridine + morpholine system</i>				
		$V_f^E$					$V_f^E$		
303.15	-1.2747	-12.3532	-30.0521	0.2207	303.15	-10.5140	-5.3082	-1.4376	0.0381
308.15	-4.2631	-8.6978	-16.1085	0.2755	308.15	-10.0971	-4.7521	-1.1509	0.0346
313.15	-7.7655	-5.8685	-6.6702	0.1094	313.15	-10.1208	-4.6994	-1.1001	0.0398
318.15	-8.4492	-6.0369	-7.0150	0.1653	318.15	-10.7155	-4.7531	-1.3100	0.0321
		$\pi^E$					$\pi^E$		
303.15	-1693.2	8407.2	19551	33.24	303.15	935.46	146.00	-205.61	7.0208
308.15	171.14	5556.6	9376.4	80.09	308.15	831.06	108.92	-169.81	6.0379
313.15	1784.2	3858.72	3219.51	53.61	313.15	750.59	115.32	-130.60	6.7084
318.15	1736.06	3703.08	2781.58	40.19	318.15	725.70	77.13	-99.34	3.8736
		$H^E$					$H^E$		
303.15	110763	314328	726877	2332	303.15	65779	14157	-17588	574
308.15	182742	194221	285120	4685	308.15	56838	11593	-14260	443
313.15	259485	112482	27253	3105	313.15	48845	12613	-12344	562
318.15	250758	119700	44946	1794	318.15	45150	8991	-6011	276
		$G^E$					$G^E$		
303.15	778.9	1083.2	2110.4	51.92	303.15	271.41	70.59	-26.78	1.0993
308.15	968.27	812.06	1056.77	16.92	308.15	236.97	61.46	-23.59	0.8535
313.15	1179.23	593.74	424.22	5.22	313.15	212.61	60.58	-15.57	1.3498
318.15	1158.3	64.9	525.43	13.45	318.15	195.22	63.24	0.8833	0.6148

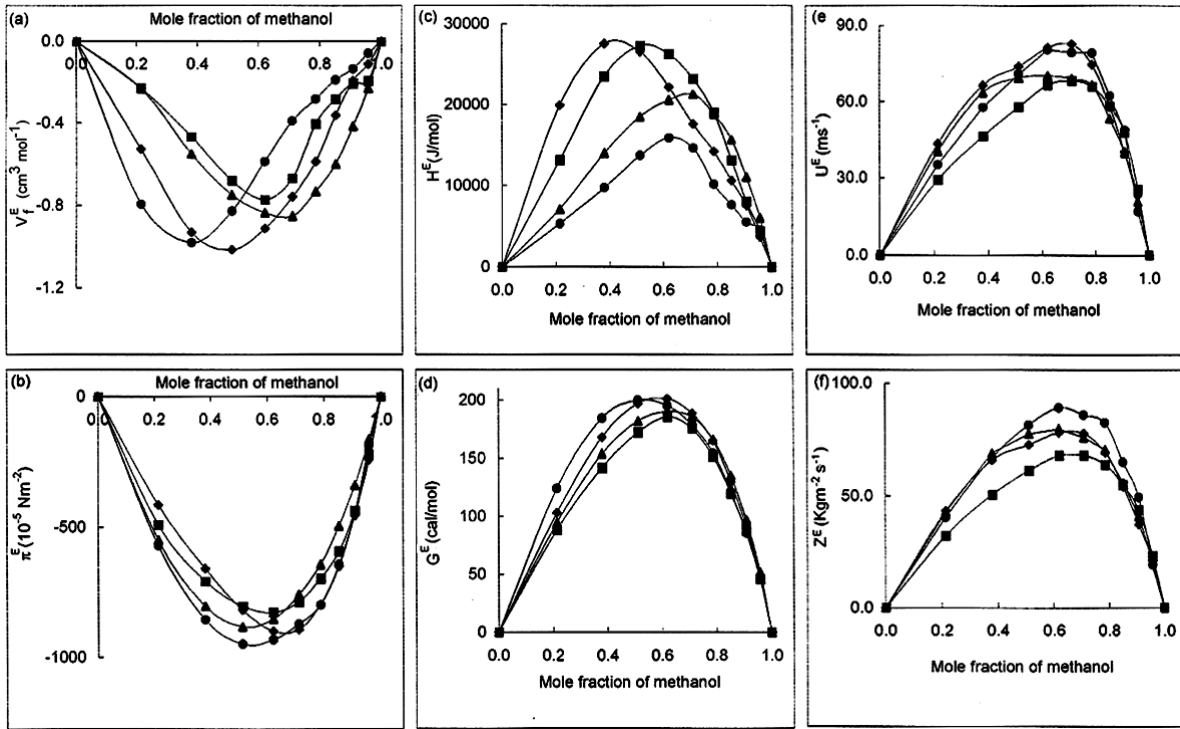


Fig. 1—Variation of excess properties with mole fraction of methanol for methanol + piperidine system. [a, excess free volume; b, excess internal pressure; c, excess enthalpy; d, excess Gibb's free energy; e, excess velocity; f, excess acoustic impedance. —○—, 303.15K; —◆—, 308.15K; —▲—, 313.15K; —■—].

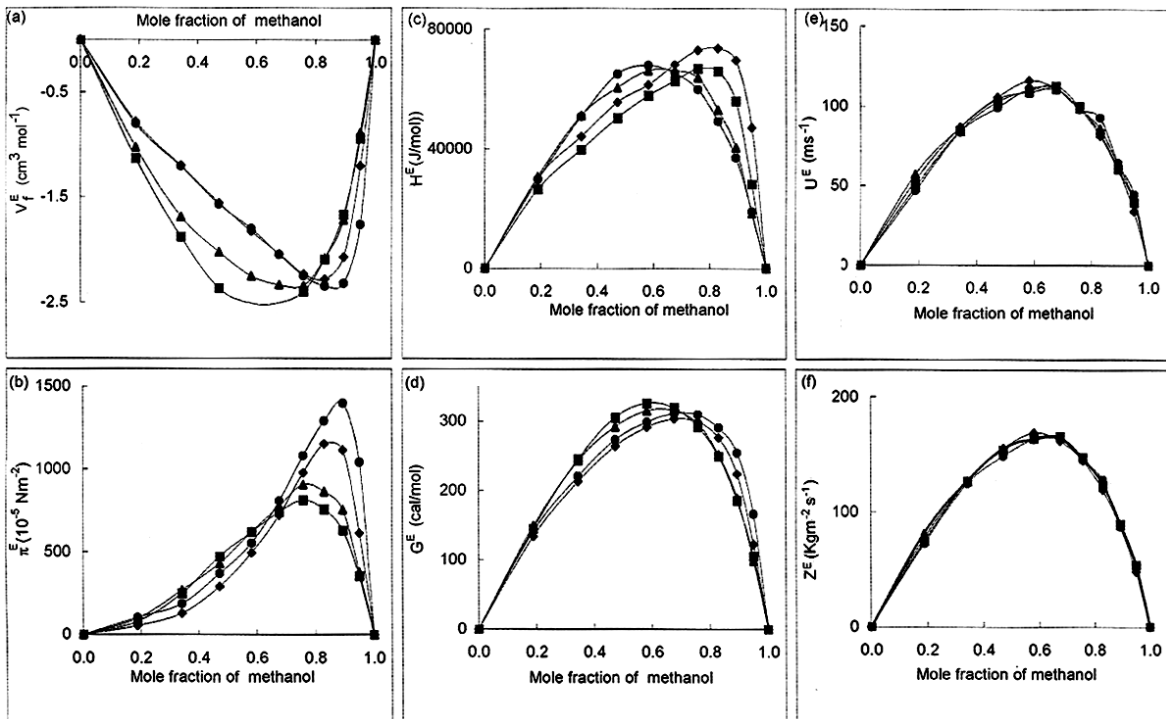


Fig. 2—Variation of excess properties with mole fraction of methanol for methanol + morpholine system. [a, excess free volume; b, excess internal pressure; c, excess enthalpy; d, excess Gibb's free energy; e, excess velocity; f, excess acoustic impedance. —○—, 303.15K; —◆—, 308.15K; —▲—, 313.15K; —■—].

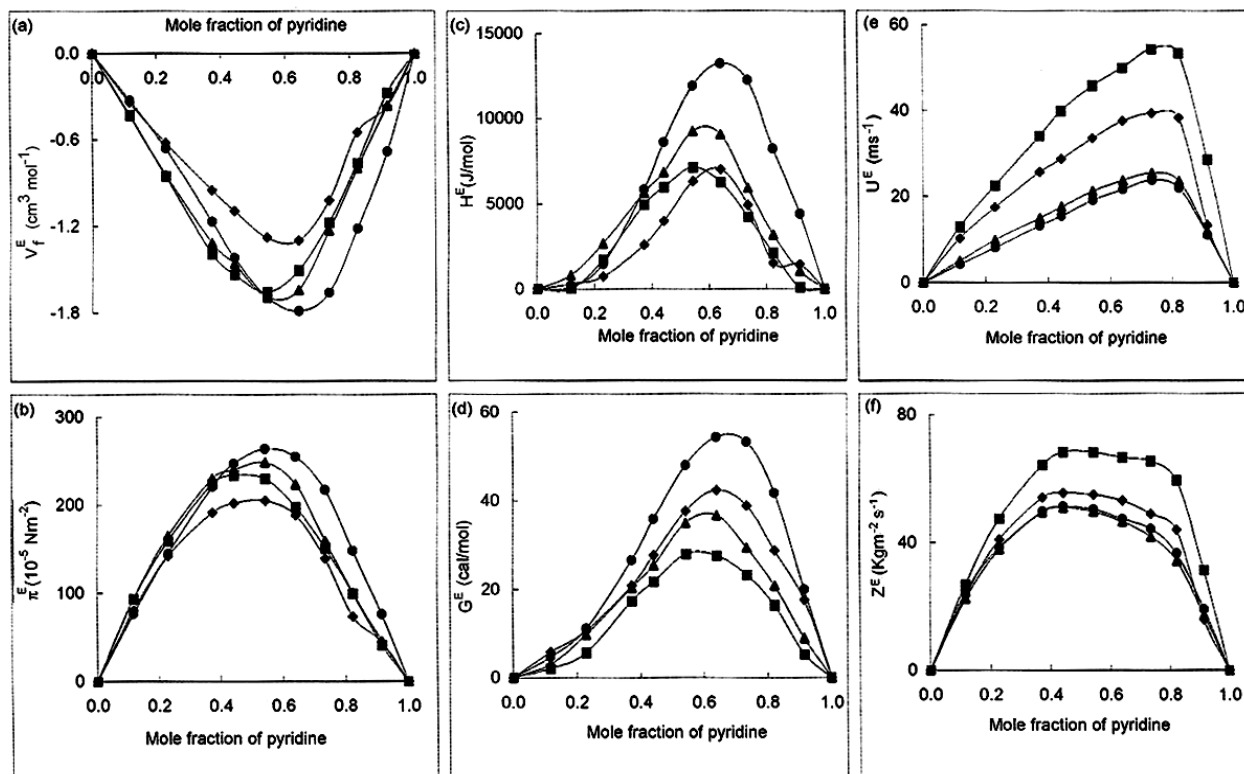


Fig. 3—Variation of excess properties with mole fraction of methanol for pyridine + piperidine system. [a, excess free volume; b, excess internal pressure; c, excess enthalpy; d, excess Gibb's free energy; e, excess velocity; f, excess acoustic impedance. —○—, 303.15K; —◆—, 308.15K; —▲—, 313.15K; —■—].

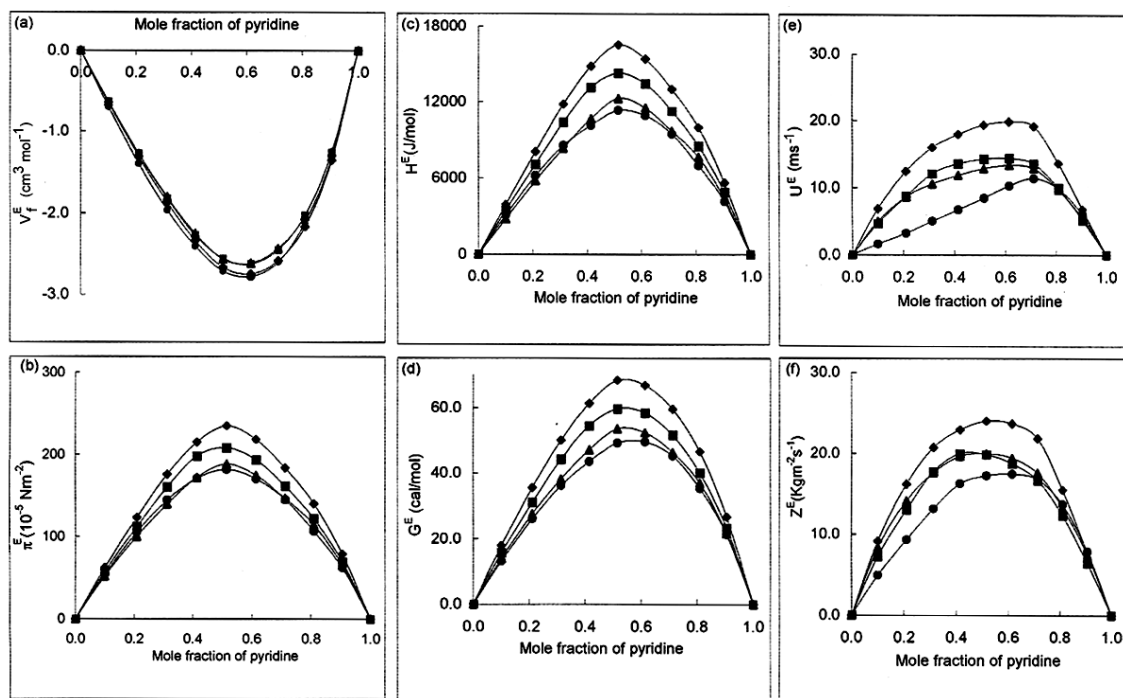


Fig. 4—Variation of excess properties with mole fraction of methanol for pyridine + morpholine system. [a, excess free volume; b, excess internal pressure; c, excess enthalpy; d, excess Gibb's free energy; e, excess velocity; f, excess acoustic impedance. —○—, 303.15K; —◆—, 308.15K; —▲—, 313.15K; —■—].

have a tendency for closer packing and that there is a decrease in free volume in intermediate composition due to strong hetero molecular interactions. This conclusion is further substantiated by the values of excess Gibb's free energy of activation ( $G^E$ ). However, the excess internal pressure for methanol and piperidine system show negative values indicating that the interactions are not as strong as in the case of methanol and morpholine system. The internal pressure is the result of the forces of attraction and repulsion between the molecules in a liquid. The  $\pi$  values of the liquid mixtures decrease and  $V_f$  values increase with the increase in temperature. At low temperatures, Brownian moment is less. However,  $\pi$  decreases and  $V_f$  increases due to the destruction of association at higher temperatures. Since cohesive forces get loosened due to thermal energy at higher temperatures, the  $\pi$  values decrease while  $V_f$  values increase. The positive values of  $G^E$  in all the systems show strong interaction through the formation of hydrogen bonding between the components.<sup>25-28</sup>

It is noticed that  $H^E$  values are positive for binary liquid mixtures of methanol with piperidine and morpholine and pyridine with piperidine and morpholine suggesting the strong nature of interactions between the unlike molecules<sup>29,30</sup>.

From Figs 1-4, It is clear that  $U^E$  and  $Z^E$  values are positive for all the systems at all the temperatures over the entire range of mole fraction. Positive deviations indicate the increasing strength of interaction between component molecules of a binary liquid mixture as suggested by Tiwari *et al*<sup>31-33</sup>. The above trends are in support of the findings for variation of  $\beta_{ad}^E$  and  $L_f^E$  with composition. The speed of sound ( $U$ ) is related to adiabatic compressibility and the density. Thus, a change in the structure resulting from mixing, affects the compressibility or the density, which in turn influences the speed of sound. Thus, the compactation or the expansion effects will have more influence on the values of the speed of sound. Thus, if strong interactions arise among the components of a mixture leading to the formation of molecular aggregates and more compact structures, sound will travel faster through the mixture by means of longitudinal waves and the speed of sound deviations with respect to a linear behavior will be positive. On the other hand, if the predominant effect in the mixture is structure – breaking resulting in expansion, the opposite will occur and the speed of

sound through the mixture will be slower and the deviation will be negative<sup>34</sup>. In the present study the excess ultrasonic velocity of all binary mixtures are positive, which indicates that structure making effect is predominant.

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### Corrigendum

In the paper entitled, "Prediction of new organo-noble gas compounds by *ab initio* quantum chemical calculations", *Indian J Chem*, 46A October 2007, pp. 1565 – 1572:

Equation 1 should read as:

$$U(\mathbf{r}) = \sum_A Z_A / |\mathbf{R}_A - \mathbf{r}| - \int [\rho(\mathbf{r}') / |\mathbf{r}' - \mathbf{r}|] d\mathbf{r}' \quad \dots (1)$$