

# Ultrasonic study on binary mixture containing dimethylformamide and methanol over the entire miscibility range ( $0 < x < 1$ ) at temperatures 303–323 K

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## ABSTRACT

The experimental density and speed of ultrasound measurements in connection with literature data have been measured for pure *N,N*-dimethylformamide (DMF), methanol and their binary mixtures over the whole miscibility range at different temperatures 303, 308, 313, 318 and 323 K. These parameters were used to determine the adiabatic compressibility, intermolecular free length, molar compressibility, molar sound velocity, acoustic impedance, relaxation strength and their excess values. The variation of these parameters with composition of mixture indicates the nature and extent of interaction between unlike molecules. The non-ideal behavior of the system studied was explained on the basis of the dipole-induced dipole interactions and hydrogen bonding. The complex formation through intermolecular hydrogen bonding was confirmed from the recorded FTIR spectra. Available thermal energy breaks the bonds between the associated molecules into their respective monomers on increasing the temperature.

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## 1. Introduction

The concentration and temperature dependence of acoustic properties has proved to be a significant observation of intermolecular interactions in liquids, liquid mixtures and solutions [1–4]. Since liquid mixtures have found applications in medicine, engineering, agriculture and other industrial applications, the study and understanding of thermodynamic and transport properties are more essential [5,6]. Intermolecular interactions in liquid mixtures modify the structural arrangements and hence change the shape of the molecule. The study of molecular interactions in the liquid mixtures is therefore important in elucidation of the structural properties of the molecules. Measurements of ultrasonic velocity and density have been used to calculate various parameters related to different types of molecular interactions in liquid mixtures. The compressibility behavior of solutes, which is the second derivative of the Gibbs energy, is a very sensitive indicator of

molecular interactions and can provide useful information about these phenomena [7–10]. The non-rectilinear behavior of ultrasonic velocity, compressibility and other thermodynamical parameters of liquid mixtures also reveal the strength of interactions. To get additional information about the nature and strength of molecular interactions, other related acoustical parameters such as free length, adiabatic compressibility, free volume, acoustic impedance and their excess parameters have been calculated in the liquid mixtures [11,12]. The excess thermodynamic functions are sensitive to the intermolecular forces as well as to the size of the molecules. In order to study all these molecular-kinetic properties of liquids and liquid mixtures, low amplitude ultrasonic wave is very valuable. Ultrasonic methods have established a permanent place in science and new applications and found for the solution of many theoretical and practical problems. Most important features of ultrasonic systems are robustness, non-invasiveness, precision, low cost, rapidity and easy automation.

Since acoustic parameters provide a better insight into molecular environments in liquid mixtures, it seems important to study molecular interactions in binary liquid mixtures. The present investigation is concerned with the study of *N,N*-dimethylformamide

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(DMF)–methanol mixtures covering the whole miscibility range. DMF is highly polar ( $\mu = 3.86$  D and  $\epsilon = 36.71$  at 298.15 K), yet is practically unassociated and behaves as a good solvent in chemical and technological process [13–15]. Moreover, DMF is reported to be a powerful breaker of polymerized structures of hydroxy compounds and the dipoles of DMF are randomly oriented [16]. Methanol is an interesting non-aqueous solvent, in particular because it is strongly self-associated through hydrogen bonding despite its low dipole moment and dielectric constant ( $\mu = 1.70$  D and  $\epsilon = 33$  at 298.15 K). Many researchers have studied the hydrogen bonding and volumetric behavior of amide–water [17,18], amide–alcohol [19,20] and ternary mixture containing amide and alcohol mixed with other organic liquids [21]. Most of the authors have studied the acoustic parameters only at a single temperature and therefore a clear understanding of the solution structure of DMF–methanol system is lacking.

In this report, we estimate densities, viscosities and ultrasonic velocities of mixtures of DMF with methanol at temperatures 303, 308, 313, 318 and 323 K covering the whole miscibility range expressed by the mole fraction 'x' of DMF ( $0 < x < 1$ ). These properties have been used to determine adiabatic compressibility, intermolecular free length, molar sound velocity, molar compressibility, acoustic impedance, etc. The significance of these parameters has been emphasized in understanding the intermolecular interaction between DMF and methanol molecules. The variation of these parameters with composition of mixture and temperature is useful in understanding the nature and extend of interaction between unlike molecules in the mixture. The excess parameters such as excess velocity ( $U^E$ ), excess adiabatic compressibility ( $\beta^E$ ), excess free length ( $L_f$ ), excess acoustic impedance ( $Z^E$ ) and excess free volume ( $V_f$ ) have significant role in determining the molecular interaction amongst the atoms of the liquid mixture. The presence of dispersion forces, dipole–dipole, dipole-induced dipole, charge transfer and hydrogen bonding interaction has been understood from the positive and negative values of the mixture. Based on the above facts, excess values are used to study the strength and nature of interaction namely strong, weak and complex formation.

## 2. Experimental details

Methanol and DMF used were of AnalaR grade samples and they were used after purification as mentioned in the literatures [22,23]. The estimated purity was >99.8%. The mixtures were prepared by mixing known volume of pure liquids in airtight-stopper bottles and adequate precautions were taken to minimize evaporation losses during the actual measurements. The reproducibility in mole fraction was within  $\pm 0.0002$  units. The density of pure solvent and of solutions was measured at the experimental temperatures by using a pycnometer with the uncertainties of 0.0001 g/ml. The ultrasonic velocities in pure liquids and their mixtures were measured using a single crystal variable path ultrasonic interferometer operating at 2 MHz supplied by Mittal Enterprises, Model F-81. The instrument was calibrated by measuring the velocity of benzene and carbon tetrachloride. Measured values were found to be in good agreement with their literature values of 1295 and 926 m/s, respectively, at 25 °C [24,25]. The temperature of the solution was maintained constant to an accuracy of  $\pm 0.05$  °C by circulating water through the brass jacket from a thermostatic water bath. The various acoustical parameters were calculated using Microsoft® Excel and plotted using Micro cal® Origin software. The hydrogen bonding in the binary solution mixture was confirmed through infrared spectrum recorded in the wavenumber range 4000–650  $\text{cm}^{-1}$ . Various acoustical parameters were calculated from the measured values of ultrasonic velocity 'U' and

density ' $\rho$ ' [26–28].

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

$$\text{Intermolecular free length } (L_f) = (K\beta)^{1/2} \quad (2)$$

where  $K$  is a temperature dependent constant taken from the work of Jacobson [29].

$$\text{Molar sound velocity } (R) = U^{1/3} V \quad (3)$$

where  $V$  is the molar volume.

$$\text{Molar compressibility } (B) = \frac{M}{\rho} \beta^{-1/7} \quad (4)$$

where  $M$  is the molecular weight.

$$\text{Acoustic impedance } (Z) = \rho U \quad (5)$$

$$\text{Excess ultrasonic velocity } (U^E) = U - \bar{U} \quad (6)$$

$$\text{Excess adiabatic compressibility } (\beta^E) = \beta - \bar{\beta} \quad (7)$$

$$\text{Excess intermolecular free length } (L_f^E) = L_f - \bar{L}_f \quad (8)$$

$$\text{Excess molar compressibility } (B^E) = B - \bar{B} \quad (9)$$

where  $\bar{U}$ ,  $\bar{\beta}$ ,  $\bar{L}_f$  and  $\bar{B}$  are respective values defined under the volume additive rule.

$$\text{Relaxation strength } (r) = 1 - \left( \frac{U}{U_\infty} \right)^{1/2} \quad (10)$$

where  $U_\infty = 1.6 \times 10^5 \text{ cm}^2/\text{s}$ .

## 3. Results and discussion

Acoustical parameters such as adiabatic compressibility, intermolecular free length, molar sound velocity, molar compressibility and acoustic impedance were calculated from the measured ultrasonic velocity and density values at temperatures 303, 308, 313 and 323 K have been tabulated in Table 1 for various mole fractions of DMF. In order to understand the reaction kinetics of the binary liquid, tabulated values of the acoustic parameters are graphically displayed. The linear and nonlinear behavior of the curve reveals the respective tendency of the molecular interactions.

Fig. 1 shows the variation of ultrasonic velocity with the entire miscibility range of *N,N*-dimethylformamide in methanol at different temperatures. Obtained values of ultrasonic velocity for pure DMF and methanol are in agreement with the reported values

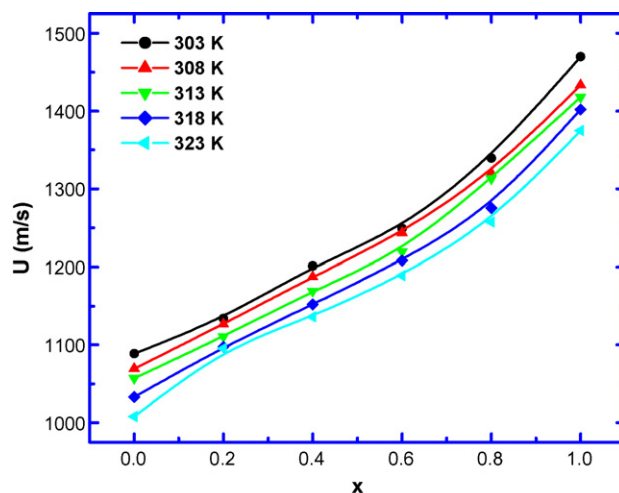


Fig. 1. Ultrasound velocity ( $U$ ) with mole fraction ( $x$ ) of DMF at different temperatures.

**Table 1**Values of  $U$ ,  $\rho$ ,  $\beta$ ,  $L_f$ ,  $V$ ,  $R$ ,  $B$  and  $Z$  values of DMF in methanol for various mole fractions ( $x$ ).

Temperature (K)	$x$	$U$ (m/s)	$\rho$ (kg/m <sup>3</sup> )	$\beta \times 10^{-10}$ (N <sup>-1</sup> m <sup>2</sup> )	$L_f \times 10^{-11}$ (m)	$V \times 10^{-5}$ (mol m <sup>-3</sup> )	$R \times 10^{-3}$ (m <sup>3</sup> mol <sup>-1</sup> (m s <sup>-1</sup> ) <sup>1/3</sup> )	$B \times 10^{-3}$ (m <sup>3</sup> mol <sup>-1</sup> (N <sup>-1</sup> m <sup>3</sup> ) <sup>-1/7</sup> )	$Z \times 10^5$ (kg m <sup>-2</sup> s <sup>-1</sup> )
303	0.0	1089.0	771.90	10.924	6.858	4.150	0.427	0.791	8.406
	0.2	1133.8	818.70	9.501	6.396	4.916	0.512	0.956	9.282
	0.4	1201.2	801.17	8.650	6.103	6.048	0.643	1.192	9.623
	0.6	1249.2	853.80	7.505	5.684	6.637	0.714	1.335	10.665
	0.8	1339.4	888.88	6.270	5.196	7.299	0.804	1.506	11.905
	1.0	1469.8	953.21	4.856	4.572	7.667	0.871	1.641	14.010
308	0.0	1069.6	764.70	11.430	7.079	4.189	0.428	0.794	8.179
	0.2	1126.8	811.76	9.702	6.522	4.958	0.516	0.961	9.146
	0.4	1187.4	794.11	8.931	6.257	6.102	0.646	1.197	9.429
	0.6	1243.4	852.94	7.583	5.766	6.644	0.714	1.334	10.605
	0.8	1320.0	888.23	6.461	5.322	7.304	0.801	1.501	11.724
	1.0	1433.2	952.94	5.109	4.732	7.669	0.864	1.630	13.657
313	0.0	1057.2	757.40	11.810	7.260	4.230	0.431	0.797	8.007
	0.2	1110.8	798.81	10.150	6.728	5.038	0.522	0.970	8.873
	0.4	1169.2	786.98	9.295	6.440	6.157	0.649	1.201	9.201
	0.6	1219.4	846.15	7.948	5.955	6.697	0.716	1.336	10.318
	0.8	1313.2	881.65	6.577	5.417	7.358	0.806	1.508	11.577
	1.0	1418.0	952.66	5.220	4.826	7.672	0.862	1.625	13.508
318	0.0	1033.2	750.00	12.490	7.532	4.272	0.432	0.799	7.749
	0.2	1097.7	785.71	10.562	6.926	5.123	0.528	0.981	8.624
	0.4	1152.0	773.80	9.737	6.650	6.263	0.657	1.213	8.914
	0.6	1208.0	833.33	8.223	6.111	6.800	0.724	1.350	10.066
	0.8	1275.4	875.00	7.025	5.649	7.415	0.804	1.505	11.159
	1.0	1402.2	952.38	5.340	4.925	7.674	0.859	1.620	13.354
323	0.0	1008.0	718.60	13.695	7.956	4.458	0.447	0.823	7.243
	0.2	1095.4	778.44	10.706	7.034	5.170	0.533	0.989	8.527
	0.4	1136.0	754.49	10.270	6.890	6.422	0.670	1.235	8.571
	0.6	1189.0	803.35	8.804	6.379	7.054	0.747	1.387	9.551
	0.8	1257.2	868.26	7.286	5.803	7.472	0.806	1.509	10.915
	1.0	1374.8	952.09	5.557	5.068	7.676	0.854	1.612	13.089

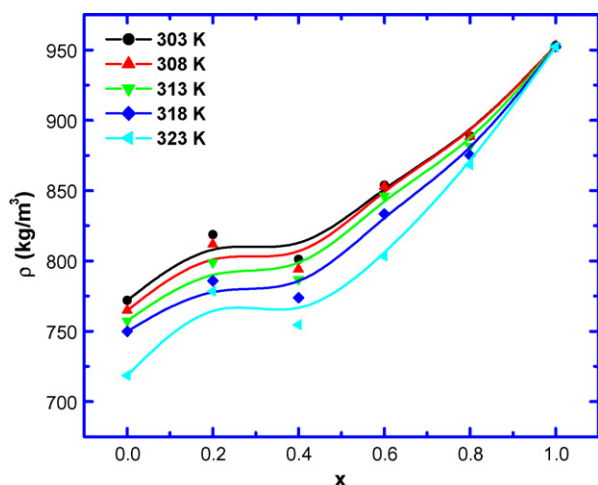


Fig. 2. Density ( $\rho$ ) in binary mixture of DMF with methanol for various mole fractions ( $x$ ) at different temperatures.

[30]. In all the measurement temperatures and concentrations, the plot comprises two linear portions with different slopes. These slopes show a break at the mole fraction of 0.6 of DMF/methanol. This nonlinear behavior of velocity with concentration indicates the deviation from ideal mixing behavior, similar to the previous reports of the water/ether system [31,32]. Even though the ultrasonic velocity increases with ' $x$ ', there are no maxima or minima. The linear behavior with increase in velocity with concentration indicates the interactions between unlike molecules through hydrogen bonding (OH–O) which in turn produces displacement of electron and nuclei [33–35]. Also it is noted that the velocity of ultrasonic wave decreases with temperature. At 303 K, the velocity of DMF is 1469.8 m/s and it is decreased to 1374.8 m/s when the temperature is increased to 323 K. As the temperature is increased, available thermal energy facilitates the breaking of the bonds between the associated molecules into their monomers. Moreover, increase of thermal energy weakens the molecular forces which tend to decrease the ultrasonic velocity as expected [36].

The experimental results of density measurements of binary mixtures of DMF with methanol over the whole composition range expressed in mole fraction  $x$  of DMF ( $0 < x < 1$ ) at different temperatures is shown in Fig. 2 and are in agreement with the reported values [37]. Large dispersion in densities with temperature is seen at lower values of mole fractions. However, dispersion in density gradually decreases on increasing the mole fractions and the dispersions decreases almost to zero at  $x = 1$ . This indicates the dominant character of *N,N*-dimethylformamide over methanol, that binds the molecules together and therefore the density variation with temperature is less at higher values of ' $x$ '.

Fig. 3 illustrates the variation of the adiabatic compressibility for various mole fraction of DMF in forming solution with methanol. The nature of variation indicates the possible interaction among molecules. The adiabatic compressibility gradually decreases with increasing the concentration of DMF in the mixture. The reverse behavior of adiabatic compressibility occurs because of structural changes present in the mixture that brings the molecules to a closer packing. Also, it reveals negative deviation with temperature, when compared with ultrasonic velocity. These deviations can be explained in terms of the dispersion forces that increase the intermolecular path lengths as described by Jacobson [38,39]. Decrease of the intermolecular path lengths on the other hand leads to a positive deviation in sound velocity and negative deviation in the compressibility. In our observation it seems that the negative

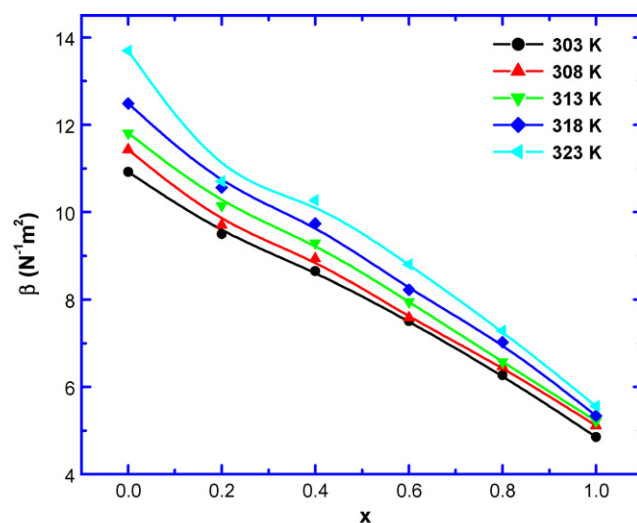


Fig. 3. Adiabatic compressibility ( $\beta$ ) versus mole fraction ( $x$ ) for DMF.

deviation in compressibility at higher mole fractions of DMF is due to the presence of dipole-induced dipole interactions. DMF being dipolar molecules induces dipole moment in methanol, causing dipole-induced dipole interactions to operate. These findings are in accordance with the previously reported results of Yadava and Yadav [40].

Intermolecular free length is an important parameter that has association with adiabatic compressibility. Fig. 4 shows the variation of free length with mole fractions. It is clear that the intermolecular free length shows a similar behavior as reflected by ' $\beta$ '. The decreased compressibility brings the molecules to a closer packing resulting a decrease in intermolecular free length. Moreover, free length is a predominant factor in determining the variation of ultrasonic velocity in solutions. The inter dependence of ' $L_f$ ' and ' $U$ ' has been evolved from a model for sound propagation proposed by Eyring and Kincaid [41]. According to the proposed theory, the decrease in the value of ' $\beta$ ' and ' $L_f$ ' with increase in ultrasonic velocity further strengthens the process of complex formation between the solute molecules through hydrogen bonding due to which structural arrangement is considerably altered. In the present study also, there is a possibility of complex formation due to interactions as revealed by the nonlinear variation of ultrasonic

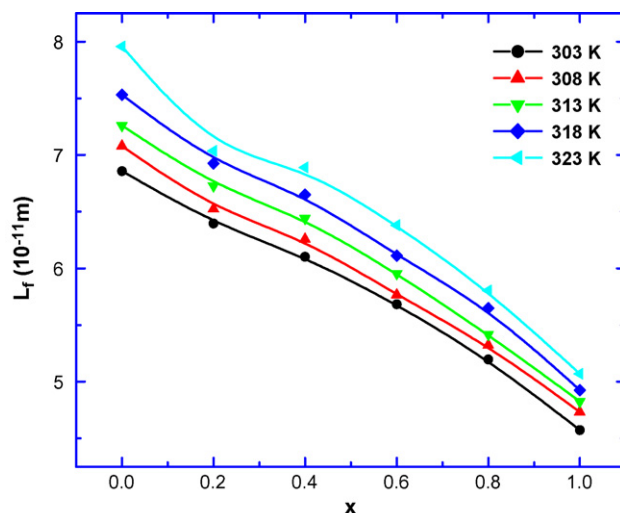


Fig. 4. Intermolecular free length ( $L_f$ ) versus mole fraction ( $x$ ) for DMF.

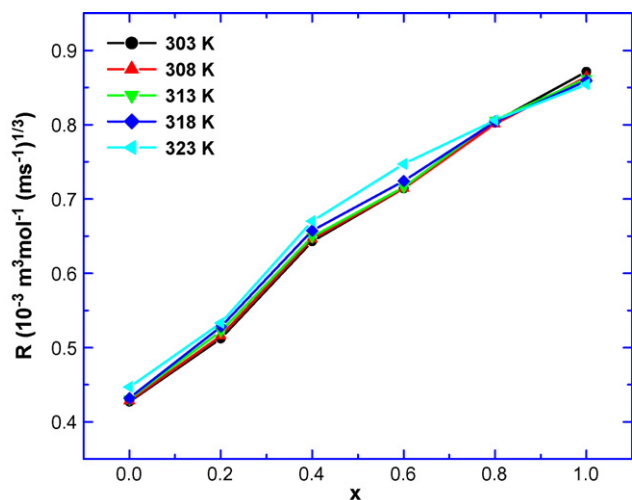


Fig. 5. Variation of molar sound velocity ( $R$ ) with mole fraction of DMF ( $x$ ) at different temperatures.

velocity and their related parameters due to strong interaction of forces [42,43].

The variation in molar sound velocity with mole fraction measured at various temperatures is represented in Fig. 5. Observed variation is almost linear; however, in the range of mole fractions 0.4–0.6, deviation is more from linearity. This indicates that the molecular interaction is comparatively higher in that region. The variation of molar compressibility is also similar to the molar sound velocity (Fig. 6). Since interaction is less at lower and higher mole fractions of DMF, temperature effect on molar compressibility is very less in those compositions. However, for the mole fraction of 0.4–0.6, variation of molar sound velocity with temperature is prominent. At these mole fractions, complex formation is initiated and therefore thermal energy is utilized for breaking of bonds between the associated molecules, resulting into creation of their monomers [44].

When an acoustic wave travels in a medium, there is a variation of pressure from particle to particle. When a plane ultrasonic wave is set up in a liquid, then the pressure and hence density and refractive index of the liquid show a periodic variation with distance from the source along the direction of propagation. If there is stationary ultrasonic pattern in the liquid, the density will be greater in the

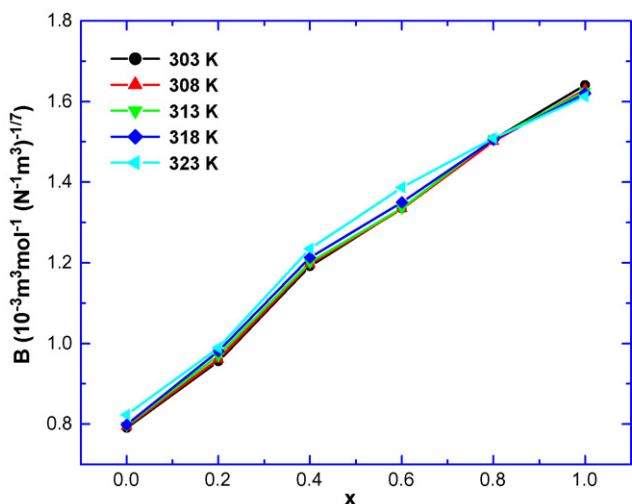


Fig. 6. Molar compressibility ( $B$ ) variation with concentration of DMF ( $x$ ) at different temperatures.

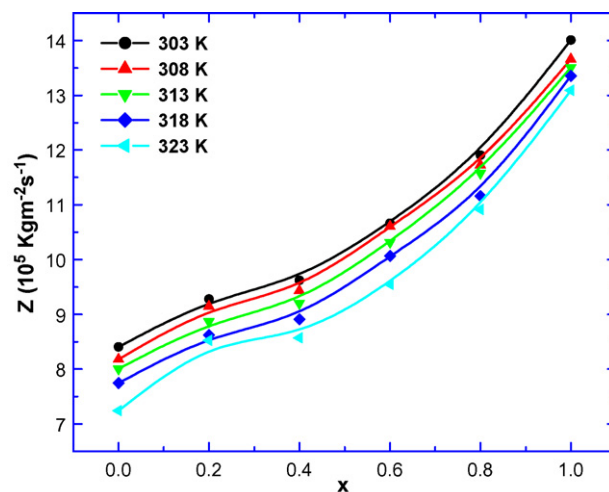


Fig. 7. Variation of acoustic impedance ( $Z$ ) with concentration of DMF ( $x$ ).

nodal plane. The acoustic impedance is the parameter related to the elastic properties of the medium. Therefore, it is important to examine specific acoustic impedance in relation to concentration and temperature. Fig. 7 shows the variation of acoustic impedance with mole fraction and temperature. Acoustic impedance exhibits a nonlinear variation with concentration at  $x = 0.4$ – $0.6$ . The nonlinear behavior further supports the possibility of molecular interactions due to the H bonding [45,46].

In addition to above observations, the nature and strength of molecular associations in the present system (DMF–methanol) have been studied from excess acoustic parameters such as excess velocity ( $U^E$ ), excess adiabatic compressibility ( $\beta^E$ ), excess acoustic impedance ( $Z^E$ ), excess free length ( $L_f^E$ ) and excess molar compressibility ( $B^E$ ) (Table 2). It is expected that the dispersion forces should make positive contributions to excess values while dipole–dipole, dipole-induced dipole, charge-transfer interaction and hydrogen bonding between unlike components should make negative contributions [42]. Fig. 8 shows the variation of excess velocity of the solution for different mole fractions of DMF at five different temperatures. For the whole composition range, the excess velocity becomes increasingly negative with increasing strength of interaction between the component molecules. As seen, at 303 K, the excess velocity increases in the negative side up to the mole frac-

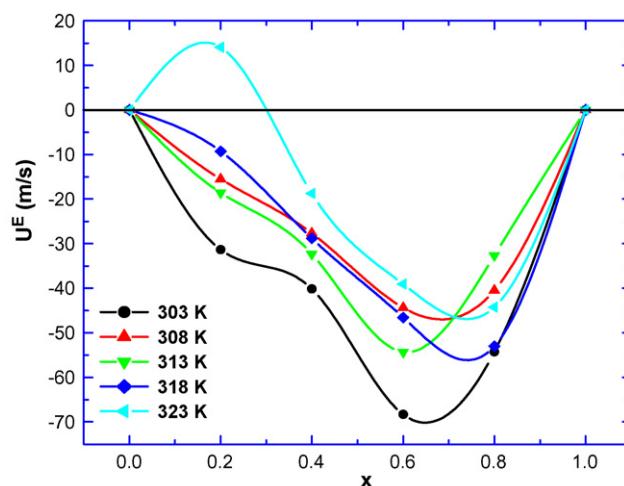


Fig. 8. Excess ultrasound velocity ( $U^E$ ) with various concentrations of DMF ( $x$ ) at different temperatures.



**Table 2**Variation of excess parameters,  $U^E$ ,  $\beta^E$ ,  $Z^E$ ,  $L_f^E$ ,  $B^E$  and  $r$  with mole fraction ( $x$ ) of DMF in methanol at different temperatures ( $T$ ).

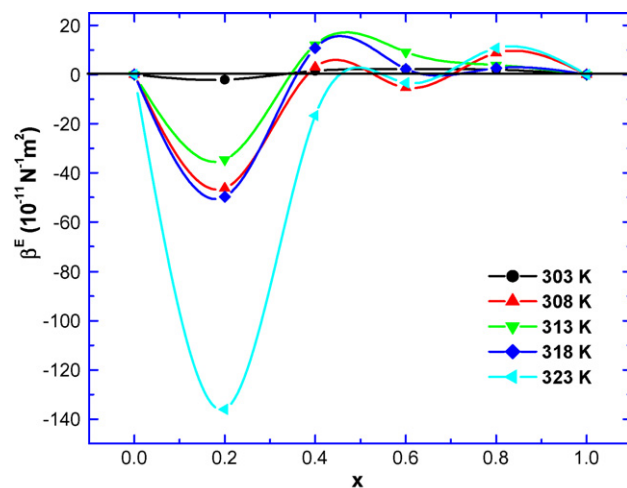
$T$ (K)	$x$	$U^E$ (m/s)	$\beta^E \times 10^{-11}$ ( $N^{-1} m^2$ )	$Z^E \times 10^5$ ( $kg m^{-2} s^{-1}$ )	$L_f^E \times 10^{-12}$ (m)	$B^E$ ( $m^3 mol^{-1} (N^{-1} m^2)^{-1/7}$ )	$r$
303	0.0	0	0	0	0	0	0.536
	0.2	-31.36	-2.087	-0.244	-0.049	-0.960	0.497
	0.4	-40.12	1.536	-1.024	1.589	-1.130	0.436
	0.6	-68.28	2.221	-1.102	1.978	-1.300	0.390
	0.8	-54.24	2.012	-0.983	1.664	-1.469	0.299
	1.0	0	0	0	0	0	0.156
308	0.0	0	0	0	0	0	0.553
	0.2	-15.52	-46.300	-0.128	-8.780	-0.960	0.504
	0.4	-27.64	2.984	-0.941	11.710	-1.127	0.449
	0.6	-44.36	-5.410	-0.860	9.494	-1.294	0.396
	0.8	-40.48	8.816	-0.837	12.070	-1.461	0.319
	1.0	0	0	0	0	0	0.197
313	0.0	0	0	0	0	0	0.563
	0.2	-18.56	-34.620	-0.234	-4.50	-0.962	0.518
	0.4	-32.32	12.118	-1.006	15.35	-1.127	0.466
	0.6	-54.28	9.201	-0.990	15.53	-1.292	0.419
	0.8	-32.64	3.916	-0.830	10.42	-1.458	0.326
	1.0	0	0	0	0	0	0.214
318	0.0	0	0	0	0	0	0.583
	0.2	-9.28	-49.803	-0.245	-8.42	-0.962	0.529
	0.4	-28.80	10.766	-1.076	16.13	-1.126	0.481
	0.6	-46.60	2.306	-1.045	14.37	-1.290	0.429
	0.8	-53.00	2.555	-1.073	20.26	-1.454	0.364
	1.0	0	0	0	0	0	0.231
323	0.0	0	0	0	0	0	0.603
	0.2	14.04	-136.070	0.114	-34.42	-0.979	0.531
	0.4	-18.72	-16.709	-1.010	8.88	-1.137	0.495
	0.6	-39.08	-3.393	-1.199	15.60	-1.294	0.447
	0.8	-44.24	10.767	-1.004	15.77	-1.452	0.382
	1.0	0	0	0	0	0	0.261

tion  $x=0.6$  of DMF and then begins to rise up towards positive values. Since dimethylformamide it is a dipolar aprotic liquid with large dipole moment, mixing of DMF with methanol will induce the mutual destruction of dipolar structure of the component liquids releasing free dipoles. As a result, strong dipolar interactions between DMF and methanol are expected. The observed negative values of velocity ( $U^E$ ) over the complete range of composition of dimethylformamide–methanol binary mixture support the above view. Negative deviation decrease and the velocity maximum point shifts towards higher ' $x$ ' values on increasing the temperature. This clearly indicates the presence of strong hydrogen bonding which becomes maximum where the minima occur.

The variation of adiabatic compressibility ( $\beta^E$ ) with mole fraction of DMF in the binary solution (DMF + methanol) is represented in Fig. 9. The values of excess adiabatic compressibility is found to be the negative over the mole fraction of 0–0.4 DMF indicating the presence of interactions between the molecules. The strength of the interaction between the components increases when excess values tend to become increasingly negative. This may be qualitatively interpreted in terms of closer approach of unlike molecules leading to reductions in compressibility and volume [40,42]. This type of interactions for the binary mixture DMF–toluene [47], DMF–water [48] has been already reported. The pronounced compressibility minimum at  $x=0.2$  may be attributed to strong molecular interaction which eventually results in complexation [48]. The excess properties are found to decrease with increasing temperature which is in agreement with the previously reported result [49].

Fig. 10 indicates the variation of excess free length for the entire composition of the DMF–methanol binary system. In this system, the negative values of ( $L_f^E$ ) tend to increase in the lower mole fractions of DMF  $x=0-0.2$  indicating strong interactions between the unlike molecules. The change from negative to positive  $L_f^E$  values indicating greater be the dissociation between the components

and may be quantitatively interpreted in terms of detachment of unlike molecules leading to increase in compressibility and volume. The  $\beta^E$  and  $L_f^E$  minima occur at the same concentrations further strengthens the occurrence of molecular associations. The positive contribution is mainly to the dispersion forces and this type of variation of  $L_f^E$  has also been reported for binary mixtures [50,51]. At low composition of DMF, the strong hydrogen bonding between DMF and methanol molecules may be attributed to the presence of two unshared electron pairs on the oxygen atom of the C=O group of DMF represented by the two  $Sp^2$ -hybridized orbital. If one of these orbital may be considered to be collinear with the  $-OH \cdots O$  axis, there is maximum interaction between  $-OH$  group of



**Fig. 9.** Excess adiabatic compressibility ( $\beta^E$ ) with various concentrations of DMF ( $x$ ) at different temperatures.

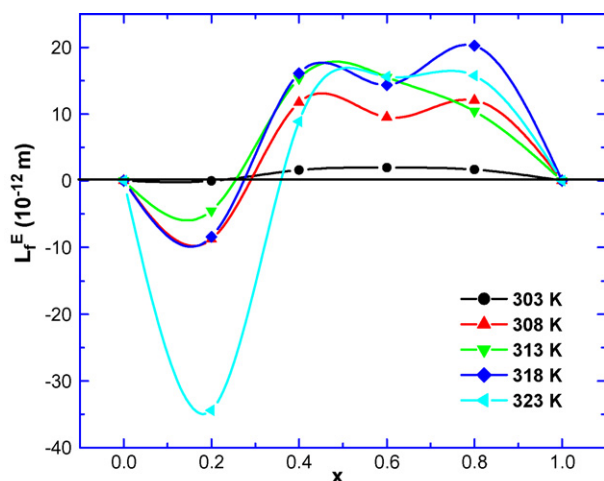


Fig. 10. Excess molecular free length ( $L_f^E$ ) with various concentrations of DMF ( $x$ ) at different temperatures.

methanol and oxygen atom of the carbonyl group. This is because, the dipole moment of the DMF–methanol complex thus formed would be enhanced due to a moment induced by the –OH bond in the highly polarizable lone pair. The strength of hydrogen bonding ( $C=O \cdots HO-$ ) between oxygen atom of the carbonyl group is strong. This is because, the dipole moment of the DMF–methanol complex thus formed would be enhanced due to a moment induced by the –OH bond in the highly polarizable lone pair. The strength of hydrogen bonding ( $C=O \cdots HO-$ ) between the oxygen atom of the DMF and methanol may be further enhanced by the nitrogen atom of the DMF molecule. For higher mole fractions of DMF, available methanol molecules are less and therefore hydrogen bonding saturates leading to initiate association of two types of molecules. Therefore the compressibility increases and shifts the excess free length to the positive side.

The excess acoustic impedance variation is shown in Fig. 11. Over the mole fraction range 0–0.2 of the investigated system, the interaction between unlike molecules are quite obvious. In the higher compositions  $x = 0.2$ –0.8, excess impedance value is more in the negative side and this indicates the dissociation reaction between the molecules as revealed in the excess adiabatic compressibility and free length variations [52]. Dielectric studies of polar molecules and non-polar solvent using ultrasonic method have been widely

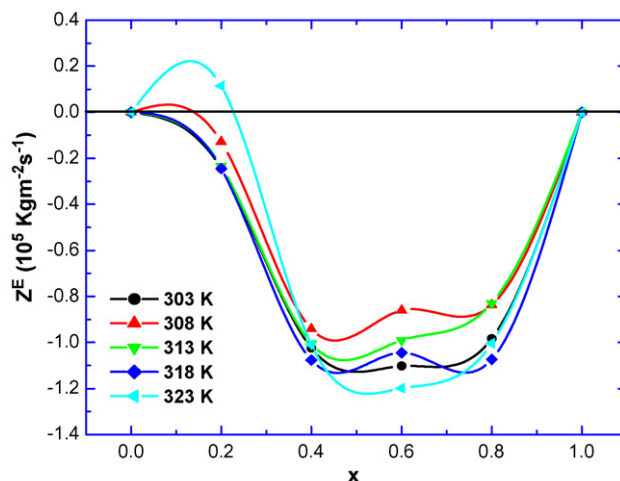


Fig. 11. Variation of excess acoustic impedance ( $Z^E$ ) with mole fraction of DMF ( $x$ ).

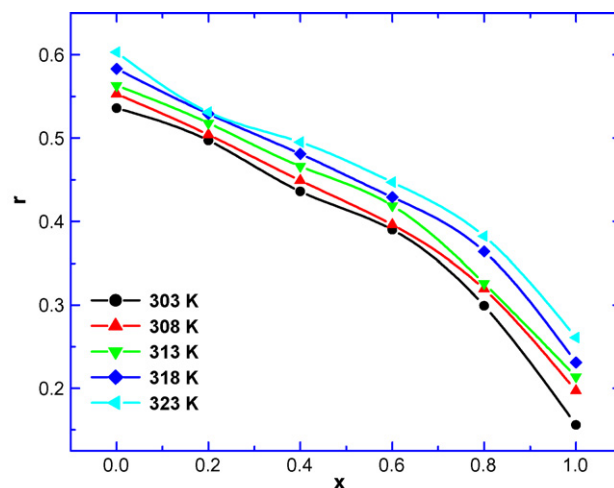


Fig. 12. Variation of relaxation strength ( $r$ ) with mole fractions of DMF ( $x$ ).

used to study the molecular structures including the molecular interactions in the liquid mixtures [53,54]. The variation of relaxation strength is shown in Fig. 12. Relaxation strength is found to decrease with increase in concentration of dimethylformamide. At

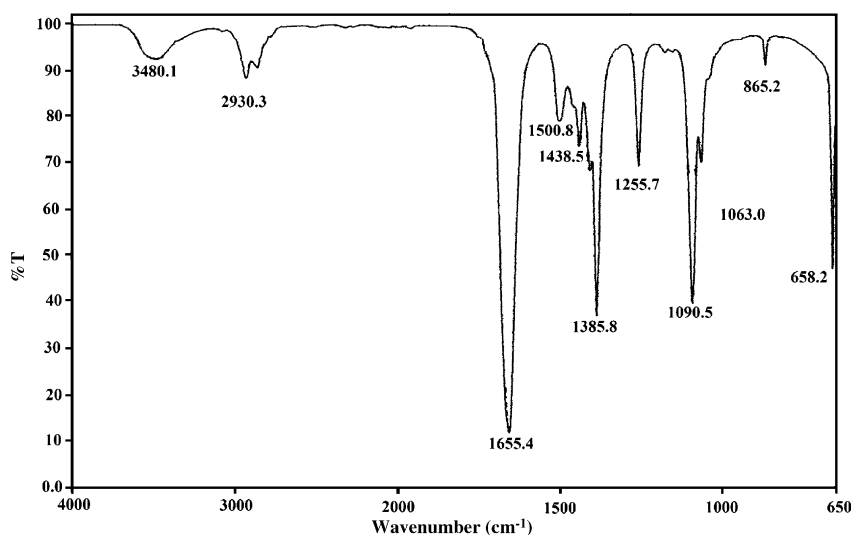


Fig. 13. FTIR spectrum of DMF.

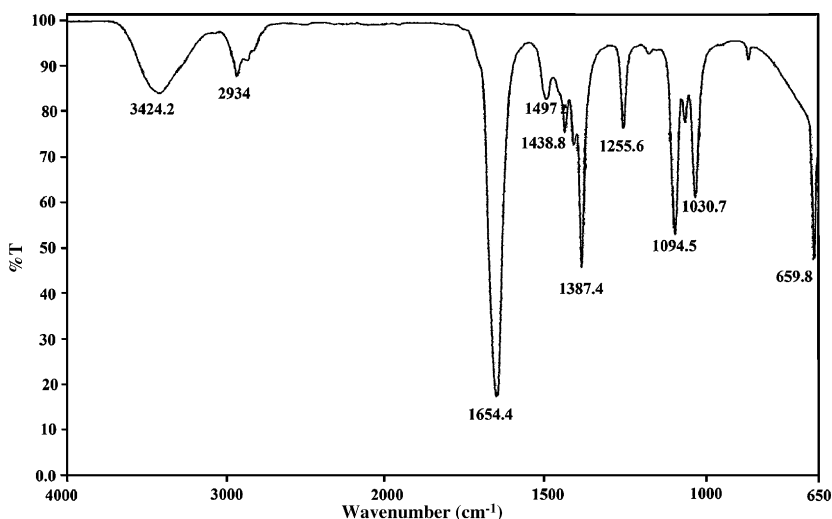


Fig. 14. FTIR spectrum of DMF–methanol binary mixture for mole fraction  $x = 0.6$  of DMF.

a fixed concentration, it increases with temperature. In the present case, at lower mole fractions the relaxation strength is predominant than those on higher mole fractions. The increase in ' $r$ ' suggests the predominance of molecular interactions [55].

In order to investigate the presence of hydrogen bonding and the strength of molecular association between the oxygen atom of the DMF and methanol at a specific composition, FTIR spectra were recorded for the DMF (Fig. 13), and DMF–methanol binary system (Fig. 14) for the composition  $x = 0.6$  of DMF at RT. It is observed that the broad band observed at 3480.1 and 3424.1  $\text{cm}^{-1}$  are corresponds to DMF and DMF–methanol binary solution, respectively. It was well established that for less extensive hydrogen bonding absorption band is observed at higher wavenumber region and for extensive hydrogen bonding, a broad band appears at a lower frequency [56]. The O–H bond stretching due to the free O and H group appears as a band at higher frequency range of 3480.1  $\text{cm}^{-1}$ , but the O–H stretching due to intermolecular hydrogen bonding which broadens the band and shifts its position to lower frequencies (3424.1  $\text{cm}^{-1}$ ). The IR study thus shows the complex formation at this mole fraction, which is also indicated through peaks of ultrasonic excess parameters. Thus the pattern, position and intensity of the O–H band as per infrared data strongly supports the conclusions drawn from the ultrasonic data that molecular association through hydrogen bonding is maximum at this concentrations where ultrasonic velocity maxima occurs [57]. The variation of acoustic parameters with mole fractions and the IR data strongly support the molecular association in binary liquid mixture DMF–methanol.

#### 4. Conclusions

The concentration dependencies of ultrasonic velocity and density of *N,N*-dimethylformamide–methanol binary system have been measured at different temperatures. The nonlinear variation of the related parameters such as adiabatic compressibility, intermolecular free length, molar compressibility, molar sound velocity, acoustic impedance and relaxation strength were elaborated to understand the molecular interactions that leads to the process of complex formation between the solute molecules through hydrogen bonding. The positive and negative variations of the excess values with concentration and temperature of the same acoustic parameters supported the presence of interaction between unlike molecules. The dominant character of *N,N*-dimethylformamide

over methanol was identified from its binding character of molecules together through the infrared spectral analysis.

#### References

- [1] K. Tamura, T. Sonada, S. Murakami, J. Solution Chem. 28 (1999) 777.
- [2] B. Garcia, R. Alcalde, J.M. Leal, J.S. Matos, J. Chem. Soc., Faraday Trans. 93 (1997) 1115.
- [3] S.L. Oswal, P. Oswal, R.D. Phalak, J. Solution Chem. 27 (1998) 507.
- [4] M. Jorg, A. Ghoneim, G. Turky, M. Stockhausen, Phys. Chem. Liq. 29 (1995) 263.
- [5] S.K. Chauhan, V.R. Singh, Indian J. Pure Appl. Phys. 31 (1993) 635.
- [6] R.L. Blokhra, A. Nag, Indian J. Pure Appl. Phys. 29 (1991) 756.
- [7] B. Das, P.K. Muhuri, D.K. Hazra, Acoust. Lett. 18 (1994) 69.
- [8] P.K. Muhuri, B. Das, D.K. Hazra, Indian J. Chem. 35A (1996) 288.
- [9] P.J. Victor, P.K. Muhuri, B. Das, D.K. Hazra, J. Phys. Chem. B 103 (1999) 11227.
- [10] P.J. Victor, B. Das, D.K. Hazra, J. Solution Chem. 30 (2001) 435.
- [11] M. Gupta, J.P. Shukla, Indian J. Pure Appl. Phys. 34 (1996) 769.
- [12] A.N. Kannappan, R. Palani, Indian J. Phys. 70B (1) (1996) 59.
- [13] J.A. Dean, Lange's Handbook of Chemistry, McGraw-Hill, New York, 1956.
- [14] G.A. Krestov, Thermodynamics of Solvents, Ellis Horwood Limited, England, 1991.
- [15] L.S. Kovalenko, E.F. Evanova, A.P. Kransnoperova, Russ. J. Phys. Chem. 57 (1983) 1790.
- [16] K. Tamura, S. Murakami, Y. Akagi, M. Fukumori, Y. Kawasaki, J. Solution Chem. 23 (1994) 263.
- [17] P. Rajasekhar, K.S. Reddy, Thermochim. Acta 117 (1987) 379.
- [18] K. Subbarangiah, N.M. Murtfay, S.V. Subrahmanyam, Acustica 55 (1985) 105.
- [19] O. Kiyohara, G.C. Benson, J. Solution Chem. 10 (1981) 281.
- [20] M.V. Kualgud, K.S. Mohan Rao, J. Chem. Soc., Faraday Trans. 1 (75) (1979) 2237.
- [21] J.S. Sandhu, A.K. Sharma, R.K. Wadi, J. Chem. Eng. Data 31 (1986) 152.
- [22] K.P. Rao, K.S. Reddy, Thermochim. Acta 91 (1985) 321.
- [23] A. Weissberger, F.S. Prokaiser, J.A. Riddick, E.E. Toops, Techniques of Organic Chemistry, vol. VII, Organic Solvents, Interscience, New York, 1955.
- [24] J.A. Riddick, W.B. Bunger, T. Sakano, Organic Solvents: Physical Properties and Methods of Purification, 4th ed., Wiley Interscience, New York, 1986.
- [25] J. Timmermans, Physicochemical Constants of Pure Organic Compounds, Elsevier, Amsterdam, 1950.
- [26] K. Tiwari, C. Patra, V. Chakravorthy, Acoust. Lett. 19 (1995) 53.
- [27] B.K. Rout, V. Chakravorthy, K. Samal, Acoust. Lett. 10 (1994) 203.
- [28] S. Velmourougane, T.K. Nambinarayanan, A.S. Rao, B. Krishnan, Indian J. Phys. 61B (1987) 105.
- [29] B. Jacobson, J. Chem. Phys. 6 (1952) 927.
- [30] H.C. Ecstrom, D.-G. Oei, L.R. Dawson, J. Phys. Chem. 67 (1963) 2804.
- [31] Pankaj, C. Sharma, Ultrasonics 29 (1991) 344.
- [32] P. Babu, G. Chandra Sakhar, N. Prahakara Rao, Indian J. Pure Appl. Phys. 38 (2000) 88.
- [33] M. Rastogi, A. Awasthi, M. Gupta, J.P. Shukla, J. Mol. Liq. 107 (2003) 185.
- [34] O. Nomoto, J. Phys. Soc. Jpn. 8 (1953) 553.
- [35] M. Rastogi, A. Awasthi, M. Gupta, J.P. Shukla, Asian J. Phys. 7 (1998) 739.
- [36] S. Velmourougane, J.K. Nambinarayanan, A.S. Rao, B. Krishnan, Indian J. Phys. 61B (1987) 105.
- [37] M.E. Friedman, H.A. Scheraga, J. Phys. Chem. 69 (1965) 3795.
- [38] A. Krishnaiah, D.N. Rao, P.R. Naidu, Indian J. Chem. 21A (1982) 290.
- [39] B. Jacobson, Acta Chem. Scand. 6 (1952) 1485.
- [40] S.S. Yadava, A. Yadav, Ultrasonics 43 (2005) 732.



- [41] H. Eyring, J.F. Kincaid, J. Chem. Phys. 6 (1938) 620.
- [42] R.J. Fort, W.R. Moore, Trans. Faraday Soc. 61 (1965) 2102.
- [43] V.K. Syal, U. Kumari, S. Chauhan, M.S. Chauhan, Indian. J. Pure Appl. Phys. 25 (1987) 180.
- [44] P.S. Nikam, A.R. Hiray, Indian J. Pure Appl. Phys. 29 (1991) 601.
- [45] D. Ambanathan, Indian J. pure Appl. Phys. 16 (1978) 713.
- [46] A.N. Kannappan, V. Rajendran, Indian J. Pure Appl. Phys. 30 (1992) 240.
- [47] T.M. Aminabhavi, S.S. Joshi, R.H. Balundgi, Can. J. Chem. 69 (1990) 1028.
- [48] K. Subarangaiah, N.M. Murthy, S.V. Subrahmanyam, Acustica 55 (1985) 105.
- [49] S.N. Gour, J.S. Tomar, R.P. Varma, Indian J. Pure Appl. Phys. 24 (1986) 602.
- [50] M.R. Islam, S.K. Quadri, Acoust. Lett. 8 (1985) 166.
- [51] P.S. Nikam, A.R. Hiray, Indian J. Pure Appl. Phys. 29 (1991) 601.
- [52] A.R. Giaquisto, R.E. Lindstrom, J. Swarbrick, A. Losurdo, J. Sol. Chem. 6 (1977) 687.
- [53] P.J. Singh, K.S. Sharma, Pramana 46 (1996) 259.
- [54] M. Jorg, A. Ghouim, G. Turkey, M. Stookhausen, Phys. Chem. Liq. 29 (1995) 263.
- [55] S. Baluja, S. Oza, Fluid Phase Equilib. 200 (2002) 11.
- [56] J.R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, fourth ed., Prentice-Hall of India, New Delhi, 1978.
- [57] A. Awasthi, M. Rastogi, M. Gupta, J.P. Shukla, J. Mol. Liq. (Netherlands) 80 (1) (1999) 77.