

## Ultrasonic and infrared study of molecular interactions in ternary mixtures of 1-naphthol and 2-naphthol with 2-propanone in benzene

ISHT VIBHU, AMIT MISRA, MANISHA GUPTA and J P SHUKLA\*

Department of Physics, University of Lucknow, Lucknow 226 007, India

\*Corresponding author

E-mail: guptagm@rediffmail.com

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**Abstract.** The measurements of ultrasonic velocity and density were made for the ternary mixtures of 1-naphthol/2-naphthol with 2-propanone in benzene at 20, 30 and 40°C in the mole fraction range of 0.00 to 0.05. Adiabatic compressibility and intermolecular free length have been evaluated using ultrasonic velocity data. The non-linear variation of ultrasonic velocity and allied parameters with mole fraction indicates solute–solute interactions through hydrogen bonding between unlike molecules. Results of ultrasonic velocity and density measurements are further supported by FT–IR spectra. The change in transmittance as well as the shift in the frequency of the representative peak of the OH stretching in FT–IR spectra give inferences about the complex formation.

**Keywords.** 1-naphthol; 2-naphthol; 2-propanone; hydrogen bonding; ultrasonic velocity.

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### 1. Introduction

Investigations of the physical properties of liquid mixtures with varying compositions and ambience give valuable insight into the microscopic structure of and interactions between the component liquid molecules and also provide experimental data useful for scrutinizing the validity of various theories for mixtures [1–4]. The measurement of sound velocity provides a convenient means for determining certain properties of fluids, which are not easy to measure using other methods [5]. This technique has been extensively used to study the physico-chemical behaviour of the pure liquids [6–8]. During the last two decades, there has been considerable upsurge in the experimental investigation of the nature of molecular interaction between the molecules in a medium through ultrasonic velocity measurement [9–12].

The OH–O bond complexes have been thoroughly investigated using infrared techniques [13–15]. The study of OH–O bond complexes between acetone and ethyl methyl ketone with phenol has also been reported using dielectric techniques

by our research group [4], where longer relaxation time and high value of distribution parameter have been explained on the basis of association forming a OH–O type hydrogen bond. As a continuation of our programme of research on the ongoing study of thermo-acoustical properties of ternary mixtures in non-polar solvent [16–18], we have reported here the study of OH–O bonded complexes by measuring the ultrasonic velocity ( $U$ ) (at a fixed frequency of 1 MHz) and density ( $\rho$ ) for two ternary mixtures, viz. 1-naphthol + 2-propanone + benzene mixture (mixture 1) and 2-naphthol + 2-propanone + benzene mixture (mixture 2) at 20, 30 and 40°C and at the atmospheric pressure. The molecular interactions through hydrogen bonding between the hydrogen atom of naphthol molecule and oxygen atom of propanone molecule have been examined. The results of ultrasonic velocity measurements were further examined using the FT–IR spectra for both the ternary mixtures at 30°C.

## 2. Experimental details

Ultrasonic velocity was measured using the ultrasonic interferometer (Model M83) provided by Mittal Enterprises, New Delhi. The instrument was calibrated by measuring the velocity in standard liquids, e.g. AR grade benzene and carbon tetrachloride ( $\text{CCl}_4$ ). Our measured values of  $U$  at 20, 25, 30, and 40°C for benzene and carbon tetrachloride agree closely with the literature values [19]. Maximum possible experimental error in  $U$  has been found to be  $\pm 0.08\%$ . The temperature was controlled by circulating water around the liquid cell from thermostatically controlled adequately stirred water bath (accuracy  $\pm 0.1^\circ\text{C}$ ). The density of various systems has been measured using a dilatometer as described earlier [18].

FT–IR spectrum was recorded using FT–IR spectrophotometer provided by Perkin&Elmer, at the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow.

The chemicals used were obtained from Ranbaxy Fine Chemicals Limited, Central Drug House (P) Limited, and E. Merk (India) Ltd., Mumbai. All the chemicals used were purified by standard procedures discussed by Perrin and Armarego [20].

Adiabatic compressibility ( $\beta$ ) and intermolecular free length ( $L_f$ ) [17] were calculated from the measured values of ultrasonic velocity ( $U$ ) and density ( $\rho$ ) using the following standard formulae:

$$\beta = \frac{1}{U^2 \rho},$$

$$L_f = K\beta^{1/2},$$

the values of  $K$  for different temperatures were taken from the work of Jacobson [21]. The respective percentage error in the estimation of  $\beta$  and  $L_f$  are 0.215% and 0.11%.

## 3. Results and discussion

Ultrasonic velocity ( $U$ ) and density ( $\rho$ ) for mixtures 1 and 2 have been listed in table 1. The representative graphs of  $\beta$  and  $L_f$  as a function of mole fraction for

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**Table 1.** Ultrasonic velocity ( $U$ ) and density ( $\rho$ ) for 1-naphthol + 2-propanone + benzene (mixture 1) and 2-naphthol + 2-propanone + benzene (mixture 2) mixtures.

$X^*$	Mole ratio**	$t = 20^\circ\text{C}$		$t = 30^\circ\text{C}$		$t = 40^\circ\text{C}$	
		$U$ ( $\text{m s}^{-1}$ )	$\rho$ ( $\text{kg m}^{-3}$ )	$U$ ( $\text{m s}^{-1}$ )	$\rho$ ( $\text{kg m}^{-3}$ )	$U$ ( $\text{m s}^{-1}$ )	$\rho$ ( $\text{kg m}^{-3}$ )
Mixture 1							
0.0000	–	1316	877.2	1273	869.1	1223	857.1
0.0054	0.187	1317	877.7	1273	869.6	1226	859.1
0.0109	0.377	1318	878.3	1275	870.1	1228	861.0
0.0163	0.572	1320	881.1	1279	873.8	1230	863.2
0.0193	0.677	1323	882.6	1280	875.0	1240	864.0
0.0219 <sup>c</sup>	0.783 <sup>c</sup>	1324	884.0	1286	875.9	1249	866.1
0.0247	0.874	1325	885.9	1292	877.7	1246	866.9
0.0275	0.975	1329	887.4	1294	878.6	1245	868.1
0.0303	1.083	1330	887.8	1299	879.0	1245	868.7
0.0331 <sup>b</sup>	1.186 <sup>b</sup>	1332	889.3	1301	880.3	1244	870.6
0.0360	1.291	1333	891.2	1294	881.7	1243	871.2
0.0389	1.383	1334	891.7	1293	882.9	1243	872.6
0.0446	1.607	1339	894.1	1290	886.6	1240	874.0
0.0479 <sup>a</sup>	1.763 <sup>a</sup>	1349	894.8	1289	887.0	1236	876.5
0.0504	1.813	1342	896.6	1288	887.7	1234	877.6
0.0534	1.935	1331	897.5	1281	889.2	1233	879.4
0.0563	2.055	1328	898.3	1279	890.2	1233	880.0
Mixture 2							
0.0000	–	1316	877.2	1273	869.1	1223	857.1
0.0054	0.1836	1319	878.2	1278	869.7	1231	858.5
0.0108	0.3748	1322	880.3	1282	871.6	1235	862.0
0.0164	0.5714	1323	883.6	1284	874.2	1236	864.4
0.0219	0.7672	1324	885.0	1285	876.9	1238	866.3
0.0275	0.9932	1325	886.7	1286	878.0	1241	868.7
0.0330	1.1970	1326	889.2	1289	880.4	1245	870.4
0.0360	1.2952	1327	889.9	1290	881.3	1248	870.9
0.0387 <sup>c</sup>	1.4008 <sup>c</sup>	1329	890.9	1294	882.1	1250	872.3
0.0417	1.5105	1330	891.7	1295	884.1	1248	874.8
0.0446 <sup>b</sup>	1.6491 <sup>b</sup>	1334	892.8	1299	886.2	1248	876.8
0.0475	1.7418	1340	893.8	1297	886.9	1246	877.3
0.0504	1.8373	1349	894.6	1296	887.8	1244	877.7

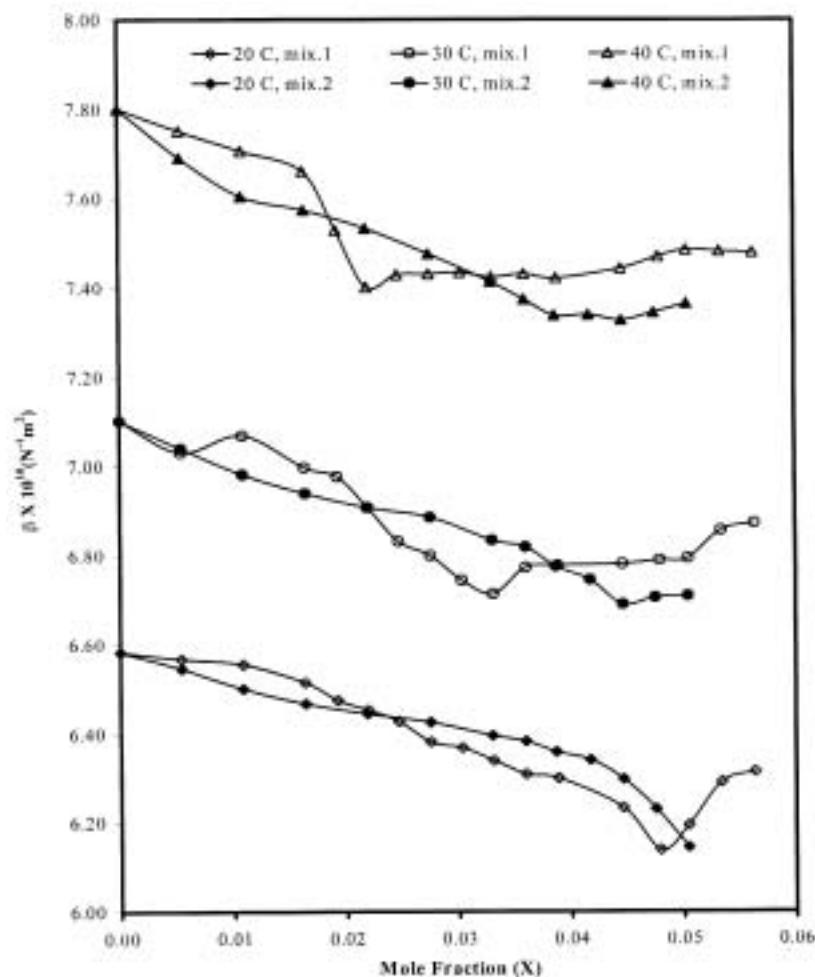
\*Mole fraction of 1-naphthol for mixture 1 and 2-naphthol for mixture 2.

\*\*Mole ratio =  $n_{1\text{-naphthol}}/n_{2\text{-propanone}}$  for mixture 1 and  $n_{2\text{-naphthol}}/n_{2\text{-propanone}}$  for mixture 2.

<sup>a</sup>Position of velocity maximum at  $20^\circ\text{C}$ .

<sup>b</sup>Position of velocity maximum at  $30^\circ\text{C}$ .

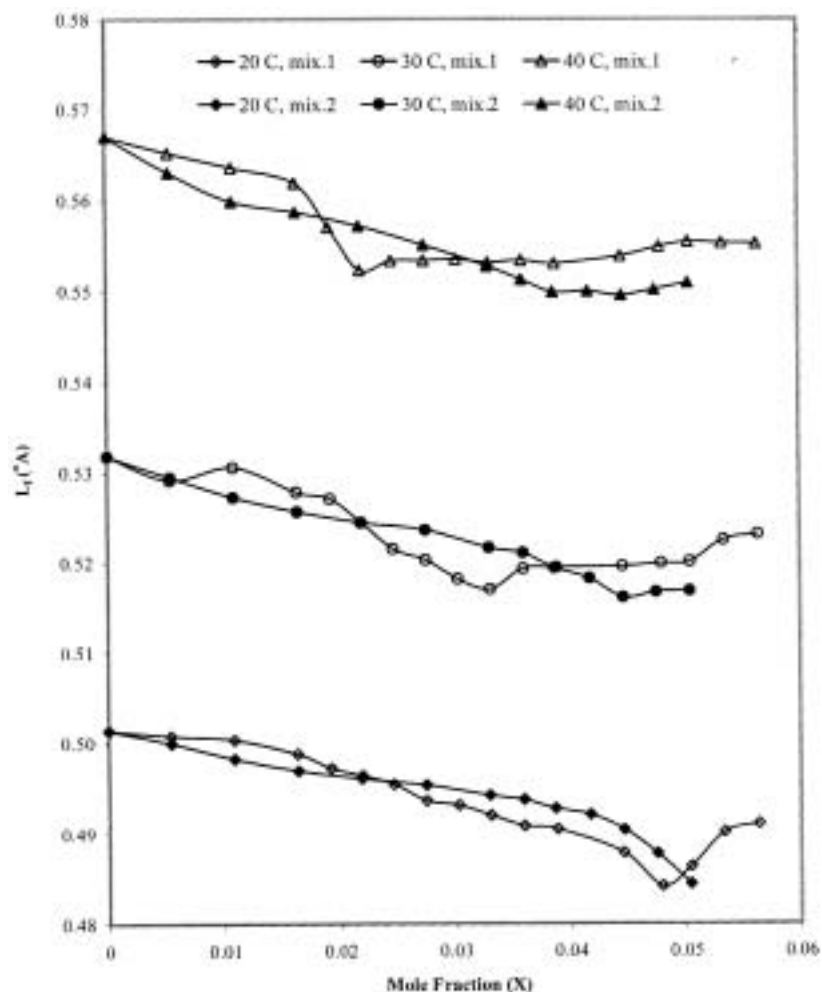
<sup>c</sup>Position of velocity maximum at  $40^\circ\text{C}$ .



**Figure 1.** Adiabatic compressibility ( $\beta$ ) against mole fraction ( $X$ ) of naphthols for 1-naphtol + 2-propanone + benzene (mixture 1) and 2-naphtol + 2-propanone + benzene (mixture 2).

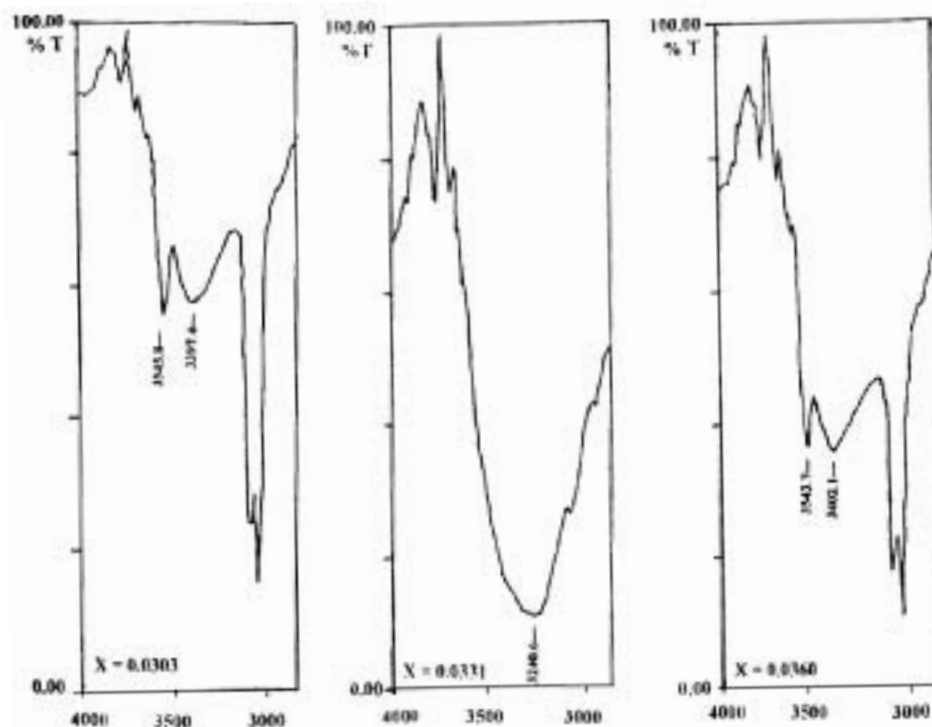
both the mixtures have been presented in figures 1 and 2. The measured values of standard deviation of velocities (at the peak) have been found to be lesser than 0.12 m/s for the mixtures studied at various temperatures for 20 measurements. The infrared spectra for mixture 1 and mixture 2 in the region of OH stretching have been presented in figures 3 and 4 respectively.

It is seen from table 1 for mixture 1 that, at 20°C, ultrasonic velocity increases with increasing concentration and attains a maximum at 0.0479 mole fraction. On further increasing the concentration the velocity decreases. A shift in velocity maxima from 0.0479 to 0.0331 and 0.0219 mole fractions with increase in temperature from 20°C to 30°C and then to 40°C respectively, is observed in mixture 1. In the



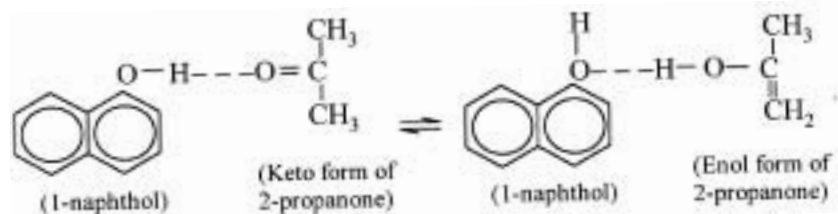
**Figure 2.** Intermolecular free length ( $L_f$ ) against mole fraction ( $X$ ) of naphthols for 1-naphthol + 2-propanone + benzene (mixture 1) and 2-naphthol + 2-propanone + benzene (mixture 2).

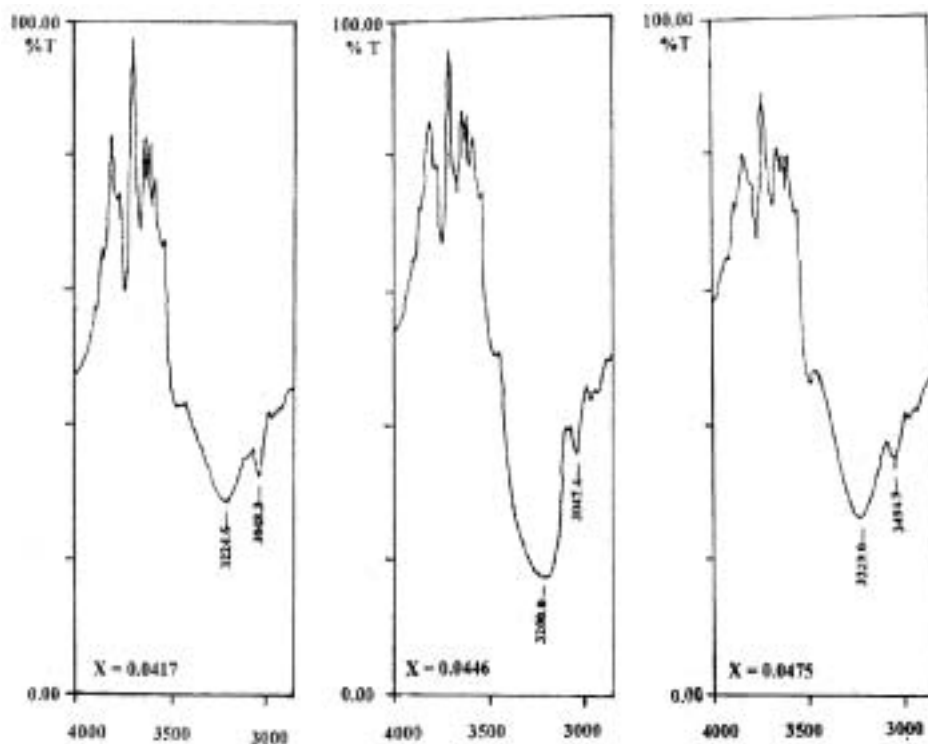
case of mixture 2, velocity increases with increasing mole fraction at 20°C without exhibiting any velocity peak. It appears that velocity maximum at 20°C for mixture 2 may occur at some higher mole fraction but mixtures of mole fraction higher than 0.0504 could not be prepared because 2-naphthol is not completely soluble in benzene at room temperature beyond this mole fraction. However, a velocity maximum does occur for this mixture at 0.0446 mole fraction at 30°C, which shifts to 0.0387 mole fraction when temperature is raised to 40°C. The non-linear variation of ultrasonic velocity with concentration indicates the occurrence of complex formation between unlike molecules [17,22]. The strength of the molecular interaction in liquid mixture becomes maximum at those mole fractions where the



**Figure 3.** Observed OH stretching bands in IR spectrum of mixture 1 (1-naphthol + 2-propanone + benzene) at various concentrations.

velocity maxima occur. 2-Propanone exists in two tautomeric forms: one is keto form  $[H_3C-C(=O)-CH_3]$  and the other is enol form  $[H_2C=C(-OH)-CH_3]$ . The variation of ultrasonic velocity may be explained on the basis of the fact that the hydrogen bonds are formed between the free hydrogen attached to the oxygen atom in the molecule of 1-naphthol or 2-naphthol and the oxygen atom of the carbonyl group in the molecule of 2-propanone. Besides, complex formation through hydrogen bonding is also possible between the hydrogen atom of the hydroxyl group in the enol form of 2-propanone and oxygen atom of hydroxyl group of 1-naphthol/2-naphthol molecule. The complex formation can be illustrated through the molecular structure shown below:





**Figure 4.** Observed OH stretching bands in IR spectrum of mixture 2 (2-naphthol+2-propanone + benzene) at various concentrations.

It is noteworthy that the hydrogen bonded complex in both the cases is of the type OH-O and probably would not make much difference in the observed velocity values.

A close perusal of table 1 reveals that as the temperature increases, the position of velocity maximum shifts towards lower mole fraction as well as lower mole ratio. Stoichiometry of the complex, as represented by mole ratio ( $n_{\text{naphthol}}/n_{\text{propanone}}$ ) suggests that at a higher temperature, lesser number of 1-naphthol (or 2-naphthol) molecules are forming complex with one molecule of 2-propanone. This may be due to increased randomness induced by the rise in temperature. Further, it is evident from table 1 that in the case of mixture 2, the velocity peak obtained at a specific temperature exists at a higher mole fraction as compared to mixture 1. This may be due to the fact that 1-naphthol is more acidic than 2-naphthol, the dissociation constant of 1-naphthol ( $pK_a = 9.30$ ) being less than that of 2-naphthol ( $pK_a = 9.57$ ) [19].

Since the adiabatic compressibility ( $\beta$ ) has an inverse relationship with the velocity, it decreases as the concentration of solute increases and reaches a minimum and then again increases. As expected, the mixtures studied here show compressibility minima in the same region of concentration where the velocity maxima occur (figure 1). The hydrogen bond formation strengthens the intermolecular forces re-

sulting in a decrease in  $\beta$  and an increase in  $U$  at or very near those concentrations where complex formation occurs. In case of liquid mixtures showing minima in  $\beta$ , there is a definite contraction on mixing and the variation observed is due to complex formation. Similar results were reported by Awasthi *et al* [17] and Babu *et al* [23]. The inverse dependence of intermolecular free length ( $L_f$ ) and ultrasonic velocity has been evolved from a model for sound propagation proposed by Eyring and Kincaid [24]. Distinct changes observed in the form of the minimum of  $L_f$  (figure 2) in the same region of concentration where compressibility minimum and velocity maximum occur, indicate that there is a significant interaction between the two solute molecules due to which structural arrangement is considerably affected [25].

In order to examine molecular association in these systems further, Fourier transform-infrared spectra (FT-IR) were recorded at room temperature (30°C) at three concentrations each (at and near the ultrasonic velocity peaks) for both mixture 1 and mixture 2.

It is a well-established fact that the formation of hydrogen bonding lowers the frequency of OH stretching and a broad band appears at a lower frequency as compared to free OH group, which gives a sharp band in the frequency range of 3650–3590  $\text{cm}^{-1}$  [26].

Figures 3 and 4 clearly indicate that in mixture 1, the O–H band appears at frequency 3240.6  $\text{cm}^{-1}$  for 0.0331 mole fraction and in mixture 2, the band appears at frequency 3200.0 for 0.0446 mole fraction but with further increase or decrease in concentration in these mixtures, O–H band shifts toward higher frequency which indicates the weakening of molecular association through intermolecular hydrogen bonding. It is also seen from these figures that at mole fractions where velocity maximum occurs, viz. 0.0331 for mixture 1 and 0.0446 for mixture 2, transmittance at O–H broad band is minimum as compared to that at other two concentrations (0.0303 and 0.0360 mole fractions for mixture 1 and 0.0417 and 0.0475 mole fraction for mixture 2) in both the cases. This further indicates that a maximum number of molecular absorbers are present at this frequency and concentration. This reduces the intensity of transmitted light at the frequency where the strength of complex formation through hydrogen bonding is strong.

Thus the pattern, position and transmittance of the O–H band as per infrared data strongly support the conclusion drawn from the ultrasonic data that the molecular interaction is taking place through hydrogen bonding between the oxygen atom of 2-propanone molecule and the hydrogen atom of 1-naphthol/2-naphthol molecule. It may be concluded that ultrasonic studies supported with IR studies provide for a comprehensive investigation of complex formation in ternary mixtures.

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