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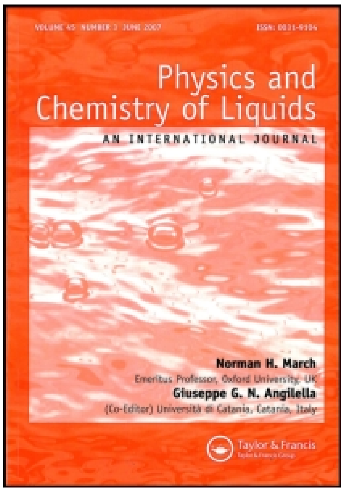

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Madhu Rastogi[a]; Aashees Awasthi[a]; J. P. Shukla[a]
[a] Department of Physics, University of Lucknow, Lucknow - 226 007, U.P., India

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ULTRASONIC AND IR INVESTIGATIONS OF N–H BOND COMPLEXES

MADHU RASTOGI, AASHEES AWASTHI* and J.P. SHUKLA

Department of Physics, University of Lucknow, Lucknow – 226 007, U.P., India

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Complex formation of 1 : 1 mixtures of naphthols, viz. (α-naphthol and β-naphthol) with triethylamine in benzene have been studied at a frequency of 2 MHz in the concentration range of 0.010–0.090 and at varying temperatures of 30, 40 and 50°C. Using the measured ultrasonic velocity, the thermoacoustical parameters such as adiabatic compressibility, intermolecular free length, molar sound velocity, molar compressibility and acoustic impedance have been calculated. The ultrasonic velocity shows a maxima and adiabatic compressibility shows a corresponding minima as a function of concentration for these mixtures. These, in turn, are used to study the solute–solute interaction and the possibility of complex formation between unlike molecules of naphthols and triethylamine through intermolecular hydrogen bonding. The hydrogen bond is formed between hydrogen atom of naphthols and nitrogen atom of triethylamine molecule. The result obtained using infrared spectroscopy for both the systems also supports the existence of complex formation through intermolecular hydrogen bonding.

Keywords: Ultrasonic velocity; Hydrogen bonding; Infrared spectrum

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INTRODUCTION

The study of molecular interaction in the liquid mixtures is of considerable importance in obtaining fundamental information regarding the structural arrangement along with the shape of molecules [1–3].

In recent years ultrasonic velocity technique has been found to be a powerful tool to study the nature of molecular interactions in liquid mixtures [4–7]. Ultrasonic waves with low amplitude have been used by many scientists to investigate the structural and physicochemical behaviour of liquid mixtures as ultrasonic energy is found useful in studying the chemical processes, playing a major role in synthesis of chemical substances.

Lagemann and Dunbar [8] were the first to point out the sound velocity approach for quantitative determination of the degree of association in liquids. A survey of the literature indicates the ultrasonic velocity and other acoustical parameters calculated are useful in understanding the solute–solute interaction between unlike molecules.

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*Corresponding author. E-mail: aasheesawasthi@rediffmail.com

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Recently, ultrasonic investigation of molecular association in ternary liquid mixtures of amides with ethanol in benzene has been carried out at various temperatures by our research group [12].

Since the N–HO bonding has direct relevance to biochemical processes, Misra *et al.* [9] have studied the dielectric properties such as dipole moment and association equilibrium constant for liquid mixtures of phenols with triethylamine in a polar solvent cyclohexane in which triethylamine is a proton acceptor and others are proton donors to study the molecular association among the molecules through hydrogen bonding between hydrogen atom of acids and nitrogen atom of amine. The complex formation has been interpreted in terms of association equilibrium constant.

Since acoustic parameters provide better insight into molecular environments in liquid mixtures, it was considered desirable to investigate the molecular association in ternary liquid mixtures of triethylamine with α-naphthol and β-naphthol in a non-polar solvent benzene using ultrasonic technique. Apart from ultrasonic velocity other thermoacoustical parameters such as adiabatic compressibility, intermolecular free length, molar sound velocity, molar compressibility and acoustic impedance for these ternary liquid mixtures have been evaluated at temperatures 30, 40 and 50°C, respectively.

Infrared spectrum is an important record which gives sufficient information about the structure of a compound. Therefore the infrared spectrum for both the systems have been recorded to study and verify the molecular association occurring in liquid mixtures through hydrogen bonding.

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EXPERIMENTAL DETAILS

The ultrasonic velocity of the mixtures was measured using the continuous wave (low amplitude) variable path ultrasonic interferometer, supplied by Mittal Enterprises, New Delhi (Model M 81), with an accuracy of 0.01%. The temperatures were controlled by circulating water around the liquid cell from thermostatically controlled water bath (accuracy ±0.1°C). The temperature of the cell as measured using a thermocouple (at the crystal) was found to be accurate to ±0.25°C.

The chemicals used were of AR/BDH quality. The solvent benzene was distilled before use. All other chemicals were used as such.

The density of various systems at different temperatures 30, 40 and 50°C have been measured using a pyknometer of capacity of 5 ml and accuracy of 0.5 kg/m^3.

THEORY

Various physical parameters were calculated using the measured values of ultrasonic velocity (u) and density (ρ) using the following formulae:

$$\text{Adiabatic compressibility } (\beta) = 1/(u^2\rho) \tag{1}$$

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

where values of K were taken from the work of Jacobson [10]

$$\text{Molar sound velocity } (R) = u^{1/3}\, V \tag{3}$$

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

where V and M are the molar volume and molecular weight, respectively.

$$\text{Acoustic impedance } (Z) = \rho u \tag{5}$$

RESULTS

Ultrasonic velocity, molar sound velocity, molar compressibility and acoustic impedance for each system have been reported in Tables I and II. Representative graphs of ultrasonic velocity, adiabatic compressibility and intermolecular free length as a function of concentration have been presented in Figs. 1–3, respectively.

The measured values of standard deviation of velocities (at the peak) have been found to be lesser than 0.11 m/s for the mixtures under study at various temperature for 20 measurements.

The infrared spectra for α-naphthol–TEA and β-naphthol–TEA systems have been reported in Figs. 4 and 5, respectively.

DISCUSSION

It is seen from Fig. 1 that in α-naphthol–TEA and β-naphthol–TEA systems ultrasonic velocity increases as a function of concentration for each temperature of the solution, attains a maximum value and then decreases. As the temperature increases, the velocity maxima shifts towards lower concentration in each system. The non-linear variation of ultrasonic velocity with concentration indicates the occurrence of complex formation between unlike molecules. The complex formation in the molecular association becomes maximum at those concentrations where velocity maxima occur. This behaviour which is different from an ideal mixture behaviour may be interpreted due to the formation of strong hydrogen bonding resulting into complex formation producing displacement of electrons and nuclei. The chemical interaction involves dipole–dipole interaction due to the charge transfer complexes [5].

The occurrence of maximum velocity at 0.050 and 0.070 concentration for α-naphthol–TEA and β-naphthol–TEA systems, respectively and then further decrease in velocity with increasing concentration may be explained as follows:

At 0.050 and 0.070 weight fraction for these systems, the maximum hydrogen bond formation appears to take place between the hydrogen atom of naphthols and nitrogen atom of triethylamine. On further increasing the concentration, the velocity decreases due to some structural changes occurring in the mixture, resulting in weakening of intermolecular forces.

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TABLE I Ultrasonic velocity and related parameters for α-naphthol–TEA in benzene

T (°C)	X (wt. fraction)	ρ (gm cm^{-3})	U ($\times 10^4$) (cm s^{-1})	R ($\times 10^3$) (cm^3 mol^{-1}) (cm s^{-1})$^{1/3}$	B ($\times 10^3$) (cm^3 mol^{-1}) (dyne^{-1} cm^2)$^{-1/7}$	Z ($\times 10^4$) (gm cm^{-2} s^{-1})
30	0.010	1.452	12.751	5.309	3.194	18.514
	0.015	1.452	12.784	5.289	3.187	18.569
	0.020	1.453	12.800	5.273	3.177	18.598
	0.025	1.453	12.840	5.262	3.167	18.662
	0.030	1.454	12.874	5.249	3.162	18.719
	0.035	1.454	12.903	5.236	3.154	18.764
	0.040	1.455	12.936	5.224	3.147	18.822
	0.045	1.456	12.948	5.207	3.137	18.852
	0.050	1.457	12.989	5.193	3.128	18.925
	0.055	1.458	12.953	5.172	3.116	18.880
	0.060	1.458	12.938	5.155	3.106	18.864
	0.070	1.459	12.904	5.117	3.084	18.827
	0.080	1.461	12.851	5.075	3.060	18.775
	0.090	1.463	12.822	5.036	3.037	18.759
40	0.010	1.437	12.555	5.329	3.209	18.042
	0.015	1.438	12.572	5.313	3.199	18.079
	0.020	1.439	12.591	5.295	3.189	18.118
	0.025	1.439	12.600	5.280	3.179	18.114
	0.030	1.440	12.610	5.264	3.170	18.158
	0.035	1.441	12.720	5.262	3.167	18.324
	0.040	1.441	12.715	5.245	3.157	18.322
	0.045	1.442	12.690	5.222	3.145	18.299
	0.050	1.444	12.682	5.198	3.131	18.313
	0.055	1.444	12.675	5.182	3.121	18.309
	0.060	1.445	12.671	5.165	3.111	18.310
	0.070	1.446	12.620	5.125	3.088	18.248
	0.080	1.448	12.596	5.086	3.065	18.239
	0.090	1.450	12.505	5.039	3.038	18.132
50	0.010	1.422	12.173	5.330	3.209	17.310
	0.015	1.422	12.257	5.325	3.206	17.436
	0.020	1.423	12.374	5.324	3.020	17.608
	0.025	1.423	12.300	5.296	3.188	17.509
	0.030	1.424	12.210	5.266	3.171	17.387
	0.035	1.424	12.205	5.248	3.161	17.386
	0.040	1.425	12.200	5.231	3.150	17.385
	0.045	1.425	12.193	5.213	3.140	17.381
	0.050	1.426	12.190	5.195	3.129	17.383
	0.055	1.427	12.184	5.194	3.119	17.382
	0.060	1.427	12.180	5.162	3.109	17.381
	0.070	1.429	12.127	5.118	3.084	17.389
	0.080	1.433	12.066	5.066	3.055	17.291
	0.090	1.435	12.035	5.027	3.032	17.270

Further, it may be seen from Fig. 1 that in α-naphthol–TEA system, the velocity peak obtained at specific temperatures exists at lower concentration as compared to β-naphthol–TEA system. This may arise due to the fact that α-naphthol is more acidic in nature as is evident from pK_α value 9.30 compared to β-naphthol with pK_α value 9.57 (K_α is acidity constant). The smaller the p$K\alpha$ value, the stronger the acid. Triethylamine is a stronger base. It is obvious that it will react more readily with α-naphthol as compared to β-naphthol.

There may be another reason that α-naphthol is more acidic in character as α-naphthoxide ion is stabilised to a greater extent through resonance as compared to

TABLE II Ultrasonic velocity and related parameters for β-naphthol–TEA in benzene

T (°C)	X (wt. fraction)	ρ (gm cm^{-3})	U ($\times 10^4$) (cm s^{-1})	R ($\times 10^3$) (cm^3 mol^{-1}) (cm s^{-1})$^{1/3}$	B ($\times 10^3$) (cm^3 mol^{-1}) (dyne^{-1} cm^2)$^{-1/7}$	Z ($\times 10^4$) (gm cm^{-2} s^{-1})
30	0.010	1.452	12.741	5.299	3.193	18.500
	0.020	1.453	12.752	5.187	3.126	18.529
	0.030	1.454	12.773	5.122	3.087	18.572
	0.035	1.454	12.810	5.224	3.148	18.632
	0.040	1.455	12.840	5.211	3.140	18.682
	0.045	1.456	12.864	5.196	3.131	18.730
	0.050	1.457	12.886	5.180	3.122	18.775
	0.055	1.458	12.896	5.163	3.112	18.802
	0.060	1.459	12.910	5.147	3.101	18.836
	0.065	1.459	12.977	5.140	3.097	18.940
	0.070	1.460	13.064	5.135	3.093	19.073
	0.075	1.461	12.992	5.108	3.078	18.981
	0.080	1.462	12.864	5.073	3.059	18.807
	0.090	1.463	12.776	5.028	3.033	18.677
40	0.010	1.436	12.293	5.295	3.191	17.653
	0.020	1.437	12.309	5.180	3.122	17.688
	0.030	1.438	12.392	5.127	3.089	17.820
	0.035	1.439	12.412	5.225	3.148	17.861
	0.040	1.440	12.431	5.209	3.139	17.901
	0.045	1.441	12.522	5.203	3.135	18.044
	0.050	1.442	12.621	5.198	3.131	18.199
	0.055	1.443	12.677	5.187	3.124	18.293
	0.060	1.444	12.643	5.164	3.111	18.256
	0.065	1.444	12.613	5.144	3.099	18.219
	0.070	1.445	12.569	5.122	3.086	18.162
	0.075	1.445	12.560	5.105	3.076	18.155
	0.080	1.446	12.554	5.088	3.066	18.153
	0.090	1.467	12.482	5.046	3.042	18.061
50	0.010	1.422	12.018	5.307	3.197	17.090
	0.020	1.424	12.063	5.192	3.128	17.178
	0.030	1.425	12.108	5.134	3.093	17.254
	0.035	1.426	12.120	5.231	3.152	17.283
	0.040	1.427	12.151	5.217	3.143	17.339
	0.045	1.427	12.108	5.194	3.130	17.284
	0.050	1.428	11.992	5.160	3.111	17.125
	0.055	1.428	11.897	5.130	3.095	16.995
	0.060	1.429	11.805	5.101	3.078	16.869
	0.065	1.430	11.772	5.078	3.065	16.834
	0.070	1.431	11.757	5.058	3.053	16.824
	0.075	1.432	11.740	5.038	3.042	16.812
	0.080	1.433	11.736	5.020	3.031	16.818
	0.090	1.434	11.612	4.971	3.003	16.652

β-naphthoxide ion. Therefore, the interaction between triethylamine and α-naphthol will be stronger and will take place earlier than TEA–β-naphthol system.

Adiabatic compressibility for both systems show an inverse behaviour. The adiabatic compressibility shows a minimum at corresponding concentration in each system and then increases with increase in concentration. This again is happening because of the change in structure, as there is a definite contraction on mixing and variation is due to complex formation. Occurrence of velocity maxima and compressibility minima at the same concentration further strengthens the maximum complex formation

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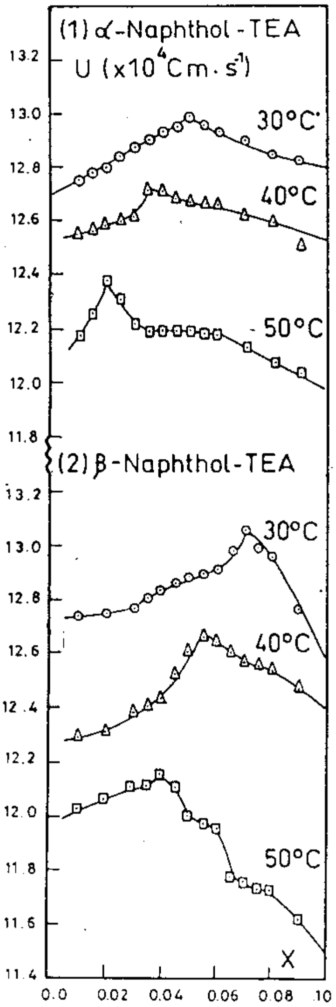

FIGURE 1 Ultrasonic velocity (U) *versus* concentration (X) for α-naphthol–TEA and β-naphthol–TEA system.

due to hydrogen bonding to 0.050 and 0.070 weight fractions for each system respectively. Similar results were also reported by other workers [7,12].

Intermolecular free length exhibits similar behaviour as that of adiabatic compressibility. The variation in ultrasonic velocity in a solution depends upon the intermolecular free length on mixing. According to sound propagation model of Erying and Kincaid [11], ultrasonic velocity decreases with increase in intermolecular free length and vice-versa. Here, in this case intermolecular forces are increasing on increasing the concentration resulting in a decrease in intermolecular free length and hence an increase in ultrasonic velocity is expected. The decrease in the value of intermolecular free length with an increase in ultrasonic velocity again supports the molecular interaction taking place between solute molecules in both system [14].

It may be seen from Tables I and II that molar sound velocity, molar compressibility and acoustic impedance for each system show a non-linear behaviour which again

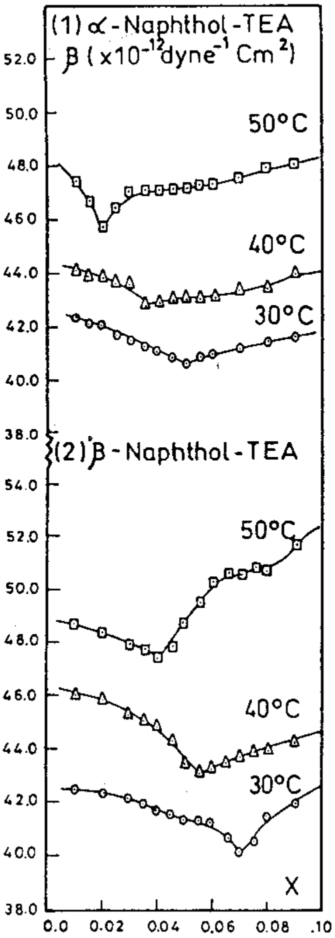

FIGURE 2 Adiabatic compressibility (β) *versus* concentrtion (X) for α-naphthol–TEA and β-naphthol–TEA system.

supports the possibility of complex formation through hydrogen bonding as well as through charge transfer complexes [15].

On increasing the temperature the velocity peak shifts towards lower concentration. This may be due to the fact that thermal energy enhances the activation energy of the molecules which would also increase the rate of association of unlike molecules through hydrogen bonding. Hence maximum complex formation will occur earlier. As is observed, the ultrasonic velocity decreases with increase in temperature. This may probably be due to the reason that an increase in thermal energy weakens the molecular forces [7,12,13,16,17] thus decreasing the ultrasonic velocity.

INFRARED SPECTRUM

In order to investigate the presence of N–HO bond complexes and the strength of molecular association at specific concentrations in these systems further, infrared

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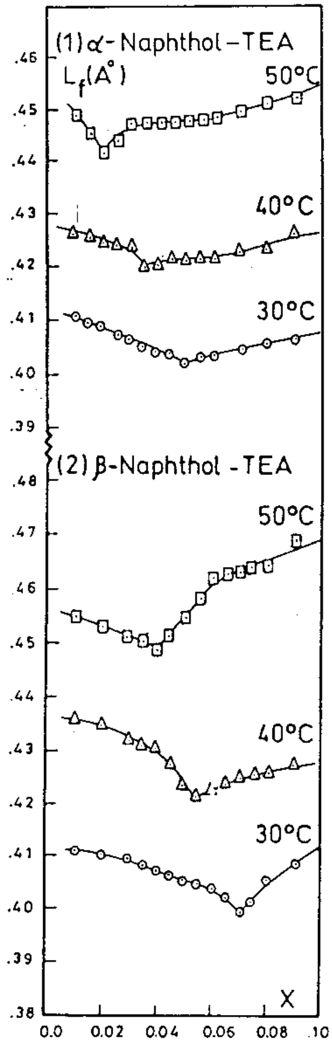

FIGURE 3 Intermolecular free length (L_f) *versus* concentration (X) for α-naphthol–TEA and β-naphthol–TEA system.

spectra of both systems (α-naphthol–TEA and β-naphthol–TEA) were recorded for various concentrations at room temperature (30°C). It is seen from the IR spectrum that for α-naphthol–TEA system two sharp bands appear at frequencies 3285.7 cm^{-1}, 3235.7 cm^{-1} for 0.045 weight fraction, 3270.4 cm^{-1}, 3218.6 cm^{-1} for 0.050 weight fraction and 3282.0 cm^{-1}, 3233.8 cm^{-1} for 0.55 weight fractions, respectively (Fig. 4) and for β-naphthol–TEA systems the bands appear at frequencies 3283.8 cm^{-1}, 3232.7 cm^{-1} for 0.065 weight fraction, 3257.1 cm^{-1}, 3211.4 cm^{-1} for 0.070 weight fraction and 3285.9 cm^{-1}, 3235.7 cm^{-1} for 0.075 weight fractions, respectively (Fig. 5). It is well known that free N–H stretching appears as two sharp bands at higher frequency range of 3500–3400 cm^{-1}, but N–H stretching due to hydrogen bonding appears in the range of 3350–3180 cm^{-1} [18].

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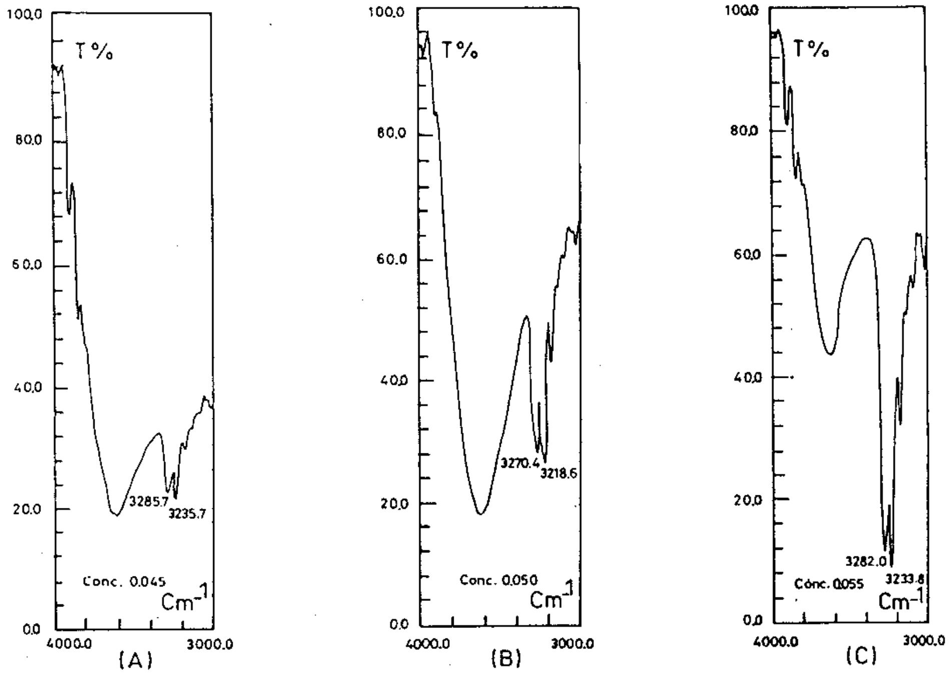

FIGURE 4 Observed N–H stretching bands in infrared spectrum of α-naphthol–TEA system at various concentrations.

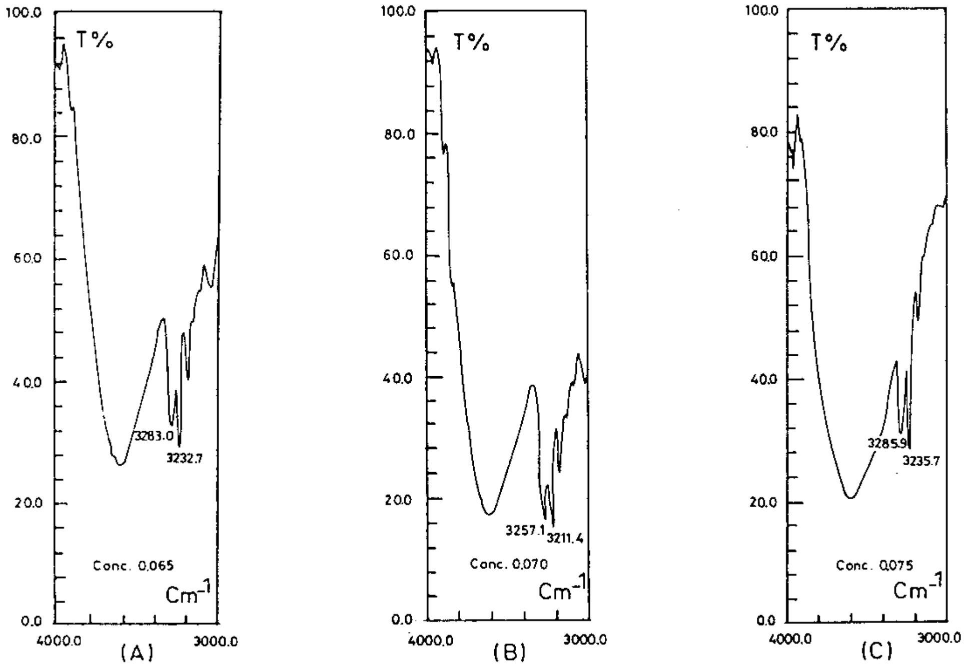

FIGURE 5 Observed N–H stretching bands in infrared spectrum of β-naphthol–TEA system at various concentrations.

It is seen from Figs. 4 and 5 that in α-naphthol–TEA system the N–H band appears at frequencies 3270.4 cm^{-1} and 3218.6 cm^{-1} for 0.050 weight fraction and in β-naphthol–TEA system the N–H band appears at frequencies 3257.1 cm^{-1} and 3211.4 cm^{-1} for 0.070 weight fraction. But with further increase or decrease of concentration in both the systems the N–H band shifts towards higher frequency which indicates the weakening of molecular association through intermolecular hydrogen bonding [12,16,17]. Thus, the study of infrared shows the complex formation becomes maximum at 0.050 weight fraction for α-naphthol–TEA system and at 0.070 weight fraction for β-naphthol–TEA system which are indicated by the peaks of ultrasonic velocities as discussed.

Further, the infrared spectrum shows a broad band near 3613 cm^{-1} which corresponds to the free O–H stretching of the individual α or β-naphthols, which are left out in the process of complex formation through hydrogen bonding.

The results drawn from infrared data strongly supports the conclusions drawn from ultrasonic data that complex formation is maximum at those concentrations where the velocity maxima occur.

It may thus be concluded that the ultrasonic and IR study provide useful information related to the molecular association between naphthols and triethylamine molecules through hydrogen bonding.

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