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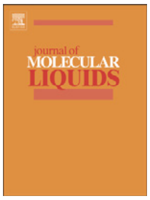

Spectroscopic and ultrasonic studies on the hydrogen bonded complexes of aromatic aldehydes with phenol in hexane medium

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ABSTRACT

The molecular interactions have been studied in the ternary systems of phenol with three structurally different aromatic aldehydes, viz., benzaldehyde, cinnamaldehyde and salicylaldehyde in n-hexane medium, through the behavior of measured ultrasonic velocity ‘u’, density ‘ρ’, dynamic viscosity ‘η’ and the calculated acoustic parameters at 303.15 K and at atmospheric pressure. Excess thermo acoustic parameters reveal the existence of hydrogen bonded complexes between aldehydes and phenol. The variation of the excess parameters both in sign and magnitude within the range of concentration investigated is also discussed in terms of structural aspect and functional groups of the components involved. The existence of solute interactions is also confirmed through electronic absorption spectra with Benesi–Hildebrand theory at 303.15 K. The formation constants of the donor and acceptor complexes determined both by spectroscopic and ultrasonic methods are comparable and follow similar trend. The trend in the formation constants is discussed based on structures of the component molecules in terms of field effects.

1. Introduction

Hydrogen bond plays an important role in chemical, physical and biological processes. Organic compounds containing electronegative groups can interact with compounds containing active hydrogen through hydrogen bond [1,2]. The interaction of hydroxyl group of alcohol with polar groups such as carbonyl group of aldehydes in non-polar environment is significant in practical applications. Carbonyl group is part of several biologically important molecules such as protein, lipids and hormones. The complexes formed between esters and amines, phenols, ethers and ketones, have been attributed to the hydrogen bonding between nucleophile carbonyl oxygen and active hydrogen. Higuchi and Lachman [3] have investigated the complex formation of caffeine with a number of acidic drugs. They attributed the interaction between caffeine and a drug to a dipole–dipole force or hydrogen bonding between the polarized carbonyl groups of caffeine and the hydrogen atom of the acid. Similarly, in the formation of 1:1 complex between p-benzoquinone and hydroquinone, hydrogen bonding occurs between the donor and acceptor components [4]. Recently, the ultrasonic and spectroscopic methods have been successfully employed to detect the formation of charge transfer complexes and the hydrogen bonded complexes [5–8]. The present investigation is aimed on the detection of the possibility of specific interaction between phenol with aromatic aldehydes in n-hexane medium through the acoustic and UV–vis spectroscopic methods.

2. Experimental

Phenol, benzaldehyde and the solvent n-hexane used were of AnalaR grade samples (MERCK) with the estimated purity of >99.8%. The cinnamaldehyde and salicylaldehyde were of spectrochem purity supplied by SD Fine Chemicals. The reagents were purified before use in accordance with the procedure described elsewhere [9,10]. A single crystal variable path ultrasonic interferometer (Model F81) operating at 2 MHz frequency supplied by Mittal Enterprises Pvt. Ltd. India was used to measure the ultrasonic velocities of liquid mixtures. The precision of the speed of sound measurements was estimated to be better than ±0.1 m/s. The estimated uncertainty is better than 0.5 m/s. The instrument was calibrated by measuring the velocity of triple distilled water, carbon tetrachloride and dimethyl sulfoxide and was compared with literature values. A 10 ml specific gravity bottle and a single pan digital balance of Shimadzu make with an accuracy of ±0.1 mg were used to determine the density of the solutions. Ostwald's viscometer was used to find the viscosity, in which the flow time for solutions was measured through a digital stop clock of accuracy ±0.01 s. In all cases, the experiments were performed generally at least in six replicates for each composition and the results were averaged. The reproducibility in mole fraction was within ±0.0002 units. The temperature of the samples was maintained constant to an accuracy of ±0.1 K by digitally controlled thermostatic water bath. UV–vis spectra were recorded on a Shimadzu UV-1650 model spectrophotometer

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Table 1
The values of ultrasonic velocity u, density ρ, viscosity η, free length L_f, molar volume V, Lenard Jones Potential LJP, internal pressure π_i and interaction parameter α of n-hexane solution containing equimolar concentration 'C' of cinnamaldehyde and phenol at 303.15 K.

C (mol dm^{-3})	u (ms^{-1})	ρ (kg m^{-3})	η (10^{-4}Nsm^{-2})	L_f (Å)	V (10^{-4}m^3 mol^{-1})	LJP (J mol^{-1})	π_i (10^{3}atm)	α
0.02	1065.9	670.1	3.606	0.725	1.288	4.974	2.558	0.0008
0.04	1068.3	673.2	3.621	0.722	1.284	5.055	2.564	0.0009
0.06	1068.2	673.6	3.631	0.721	1.286	5.05	2.564	−0.0037
0.08	1069.0	675.7	3.642	0.720	1.284	5.079	2.567	−0.0064
0.1	1070.1	676.8	3.662	0.718	1.284	5.117	2.571	−0.0085
0.12	1071.2	679.7	3.693	0.716	1.280	5.154	2.583	−0.0106
0.14	1071.1	679.9	3.725	0.716	1.282	5.151	2.591	−0.0149
0.16	1072.0	680.2	3.741	0.715	1.283	5.182	2.591	−0.0173
0.18	1071.4	680.3	3.755	0.716	1.285	5.161	2.593	−0.0223
0.2	1073.9	683.0	3.781	0.713	1.281	5.246	2.601	−0.0217

with quartz cell of 1 cm optical path length. The solvent (n-hexane) was used for baseline correction. The absorbance spectra were recorded in the wavelength region of 200–700 nm at a scanning rate of 0.2 nm/s and a slit width of 1 cm.

From the measured values of ultrasonic velocity (u), density (ρ) and viscosity (η), various acoustical and excess thermo acoustical parameters were calculated using the standard formulae reported in the literature [5,11–13]. The stability constants of the complexes using 'u' values by employing Kannappan [29] equation and using the absorbance values of UV–vis spectra by employing Benesi–Hildebrand equation and the other thermodynamic parameters were computed as reported in our earlier works [5,14].

3. Results and discussion

3.1. Acoustical parameters

The values of measured parameters of ultrasonic velocity (u), density (ρ), and viscosity (η) and the calculated acoustical and excess thermo acoustical parameters for the three ternary systems at temperature 303.15 K are summarized in Tables 1–6. The graphical representation for the variations of ultrasonic velocity (u), adiabatic compressibility (κ), free volume (V_f), excess free length (κ^E), and excess internal pressure (π_i^E), for equimolar concentration of solute molecules are depicted in Figs. 1–5. An inspection of the acoustical parameters in Tables 1–3 reveals that the measured properties for the three ternary systems increase with an increase in concentration. The trend in the ultrasonic velocity (Fig. 1) is similar in all the systems. The increase in velocity may be attributed to strong solute–solute interactions. It was reported that the strength of molecular interactions in liquid mixtures becomes maximum where the velocity maximum occurs [15]. The strong polar nature of the carbonyl group of aldehyde may disrupt the dipolar association in pure phenol leading to the possibility of unlike molecular attraction. The steep increase in the ultrasonic velocity may be an indication of stronger molecular interactions such as dipole–dipole or hydrogen bonding. The increasing trend of internal pressure with concentration supports the existing interaction between aldehyde and phenol [16]. The variation of Lenard Jones Potential (LJP) is similar for all the three systems. The magnitude and the gradual increasing trend of LJP indicate the presence of complex formation or hydrogen bonding type of interactions in the ternary systems. The decreasing trend of adiabatic compressibility (κ), free volume (V_f) and free length (L_f) (Tables 1–3 and Figs. 2–3) with concentration of aldehyde and phenol reveals the compactness of the system due to the existence of the specific interactions [17].

The close observation of data presented in Tables 4–6 and plots in Figs. 4–5 reveals that almost all the excess parameters show growing negative deviation for all the systems. The negative values of excess parameters reflect the possible interactions as commented earlier [18–21]. The negative deviations in ultrasonic velocity explain the non-ideal nature of these three ternary liquid mixtures. Further, larger deviations suggest stronger intermolecular interactions such as hydrogen bonding and charge transfer complexes between the component molecules. The degree of compactness is increasing as observed by increasingly negative values of κ^E. It was reported that the domination of strong dipole–dipole interactions over that of disruption of associated structure may result in negative κ^E [22]. The behavior of L_f^E also supports this observation. Further the negative excess values of κ^E, L_f^E and V_f^E indicate the possibility of interstitial accommodation of unlike molecules [23]. The change of sign from positive to negative in excess internal pressure is an indication of stronger adhesion between the components in the mixture.

3.2. Analysis of UV spectra

The recorded UV–vis spectra of pure benzaldehyde shows one broad absorption band at 240.8 nm, whereas in cinnamaldehyde the maximum absorption is observed at 275.2 nm and there are two more weak absorptions at 224.0 and 218.4 nm. Salicylaldehyde

Table 2
The values of ultrasonic velocity u, density ρ, viscosity η, free length L_f, molar volume V, Lenard Jones Potential LJP, internal pressure π_i and interaction parameter α of n-hexane solution containing equimolar concentration 'C' of benzaldehyde and phenol at 303.15 K.

C (mol dm^{-3})	u (ms^{-1})	ρ (kg m^{-3})	η (10^{-4}Nsm^{-2})	L_f (Å)	V (10^{-4}m^3 mol^{-1})	LJP (J mol^{-1})	π_i (10^{3}atm)	α
0.02	1064.6	670.3	3.669	0.726	1.287	4.929	2.585	−0.0012
0.04	1065.2	671.6	3.682	0.725	1.285	4.951	2.590	−0.0039
0.06	1065.8	672.6	3.694	0.724	1.285	4.971	2.593	−0.0066
0.08	1066.6	674.8	3.712	0.722	1.281	4.998	2.602	−0.0089
0.1	1067.6	675.6	3.722	0.721	1.281	5.032	2.604	−0.0107
0.12	1068.2	679.1	3.727	0.719	1.275	5.052	2.611	−0.0133
0.14	1069.1	680.0	3.736	0.717	1.275	5.083	2.613	−0.0153
0.16	1070.3	681.6	3.752	0.716	1.273	5.122	2.619	−0.0167
0.18	1071.3	682.0	3.761	0.715	1.273	5.158	2.620	−0.0183
0.2	1071.7	682.4	3.780	0.714	1.273	5.171	2.624	−0.0211