Journal of Molecular Liquids 188 (2013) 120–125

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Ultrasonic and spectroscopic investigations of hydrogen bonded complexes of aromatic aldehydes with aniline in n-Hexane at 303.15 K

B.S. Santhi [a], D. Krishnamurthy [b], V. Kannappan [a], R. Kumar [c,*]

[a] Department of Chemistry, Presidency College, Chennai 600 005, India
[b] Department of Physics, D.G. Vaishnav College, Chennai 600 106, India
[c] Department of Physics, The New College, Chennai 600 014, India

ARTICLE INFO

Article history:
Received 14 June 2013
Received in revised form 16 September 2013
Accepted 28 September 2013
Available online 16 October 2013

Keywords:
Aromatic aldehyde
Aniline
H-bonded complex
Acoustic parameter
Benesi–Hildebrand theory
Formation constant

ABSTRACT

Acoustical properties are computed for three ternary systems of aniline (ANI) and structurally different aromatic aldehydes, benzaldehyde (BA), cinnamaldehyde (CA) and salicylaldehyde (SA) in n-hexane medium from the measured ultrasonic velocity, density and dynamic viscosity at 303.15 K and at atmospheric pressure. The trend in the acoustical parameters in the concentration range investigated confirmed complex formation through intermolecular hydrogen bonding between aldehyde and aniline. The formation constants (K) of the hydrogen bonded complexes are determined by ultrasonic method. The existence of strong aldehyde–amine interaction is also confirmed through electronic absorption spectra and the formation constants of these complexes are determined using Benesi–Hildebrand method at 303.15 K. The values of K determined by ultrasonic and optical methods are comparable and follow similar trend. The trend in the formation constants is discussed based on structures of the component molecules and correlated with computed molecular properties.

1. Introduction

In recent years, the ultrasonic technique is widely employed in the detection of charge transfer complexes [1,2] and in the determination of stability constants and thermodynamic properties of the complexes [3–5]. Hydrogen bond plays important role in strengthening of molecular interactions and stabilizing supra-molecular complexes. Study of hydrogen bonded systems is important and useful since 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 [6]. This type of hydrogen bond plays important role in the stability of biologically important molecules [7]. Carbonyl group is part of several biologically important molecules such as protein, lipids and hormones. Amines in pure state are self-associated through intermolecular hydrogen bonds. They are both π- as well as n-electron donors which allow them to have specific interactions with other electron deficient molecules. The complexes formed between esters and amines, phenols, ethers and ketones have been attributed to the hydrogen bonding between nucleophilic carbonyl oxygen and active hydrogen. Higuchi and his coworkers [8] have investigated the complex formation of caffeine with a number of acidic drugs. They attributed the interaction between caffeine and 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 bond exists between the donor and acceptor components [9]. The present investigation is aimed on the detection of the possibility of specific interaction between aniline with aromatic aldehydes in n-hexane medium through ultrasonic and UV–Visible spectroscopic techniques.

2. Experimental

Aniline, benzaldehyde and the solvent n-hexane used were AnalaR grade samples (MERCK) with the estimated purity of >99.8%. Cinnamaldehyde and salicylaldehyde were of spectrochem purity supplied by SD fine Chemicals, India. The reagents were purified before use in accordance with the procedure described elsewhere [10,11] and the boiling points of the four compounds agreed well with the literature values. A single crystal variable path ultrasonic interferometer (Model F81) operating at 2 MHz frequency supplied by Mittal Enterprises, India was used in the measurement of ultrasonic velocity 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 0.2 m/s. The instrument was calibrated by measuring the velocity of triple distilled water, carbon tetrachloride at 298.15 K and dimethyl sulfoxide at 303.15 K and these values are comparable with literature values [12–14]. 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 determine the viscosity, in which the flow

---

* Corresponding author. Tel.: +91 9444297498 (mobile).
E-mail address: kumss73@gmail.com (R. Kumar).

0167-7322/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molliq.2013.09.029

Table 1
Ultrasonic velocity u, density ρ, viscosity η, adiabatic compressibility κ, acoustic impedance Z, free length L_f, internal pressure π_i free volume V_f, cohesive energy CE and interaction parameter χ_U vales for solutions containing equimolar concentration of benzaldehyde and aniline at 303.15 K.

Solvent: n-hexane									T = 303.15 K
Conc.,*/10^{-4} M	u m s^{-1}	ρ kg m^{-3}	η/10^{-4} Nsm^{-2}	κ/10^{-9} kg^{-1} ms^{-2}	Z/10^5 kg m^{-2} s^{-1}	$L_{f\ A^\circ}$	π/atm	CE kJ mol^{-1}	$\chi_U/10^{-2}$
1	1044.8	661.5	3.66	1.38	6.91	0.738	2477	32.7	−2.27
2	1045.2	662.1	3.68	1.38	6.92	0.738	2483	32.7	−2.19
3	1045.6	663.4	3.69	1.38	6.94	0.737	2490	32.8	−2.11
4	1046.0	664.9	3.70	1.37	6.95	0.736	2498	32.8	−2.03
5	1046.8	665.5	3.72	1.37	6.97	0.735	2504	32.8	−1.88
6	1047.6	665.8	3.72	1.37	6.97	0.734	2505	32.8	−1.72
7	1048.0	666.3	3.73	1.37	6.98	0.733	2507	32.8	−1.64
8	1048.4	668.8	3.74	1.36	6.99	0.733	2511	32.9	−1.57
9	1048.8	666.9	3.74	1.36	6.99	0.733	2512	32.9	−1.49
10	1049.6	669.1	3.76	1.36	7.02	0.731	2522	32.9	−1.33

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 o ±0.1 K by digitally controlled thermostatic water bath. UV–Visible spectra were recorded in a Shimadzu UV – 1650 model spectrophotometer with quartz cell of 1 cm optical path length. The solvent n-hexane was used for the base line correction. The absorbance spectra were recorded in the wavelength region of 200–700 nm at the 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 parameters were calculated using the standard equations reported in the literature [12]. The stability constants of the complexes using 'u' values by employing Kannappan equation and using the absorbance values of UV–Visible spectra by employing Benesi–Hildebrand equation and the other thermodynamic parameters were computed as reported in our earlier work [15].

Molecular orbital calculations are carried out for compounds to determine the complexation site and to correlate formation constants with the molecular projection. MNDO method gives better electronic charge distribution. The gross atomic charge on the donor atom of different donor molecules is calculated by MNDO/3 method. The optimization of the molecular geometry has been done using GAMMESS software. The other molecular properties dipole moment and ionization potential values are also computed by MNDO/3 method.

3. Results and discussion

3.1. Acoustical parameters

The measured properties, ultrasonic velocity (u), density (ρ), and viscosity (η) and the calculated acoustical parameters for the three ternary systems at 303.15 K are summarized in Tables 1–3. The graphical representation for the variations of ultrasonic velocity (u) and free volume (V_f) for solutions containing equimolar concentration of solutes are depicted in Figs. 1 & 2. An inspection of the acoustical parameters in Tables 1–3 reveals that the ultrasonic velocity increases with increase in concentration in the three ternary systems. The trend in the ultrasonic velocity is depicted in Fig. 1 which shows that the variation 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 high where the velocity maximum occurs [16]. The highly polar nature of the carbonyl group of aldehyde may disrupt the dipolar association in pure ANI 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 complex formation through intermolecular hydrogen bond [17].

Adiabatic compressibility (κ) is a measure of intermolecular association or dissociation. The structural arrangement of the molecule affects the adiabatic compressibility. The trend in adiabatic compressibility and free length with concentration shows a reverse trend as that of 'u' and 'ρ'. A continuous decrease in adiabatic compressibility (κ) and intermolecular free length (L_f) is supporting the existence of strong interactions between ANI and aldehyde in the liquid mixtures which lead to the increasing compactness of the systems. The rapid decrease of 'κ' indicates the formation of a large number of tightly bound systems. Such a reduction in 'κ' brings the molecules to a close packing, resulting in a decrease of free length 'L_f' [18].

Internal pressure (π_i) is a significant parameter in the study of the thermodynamic properties of liquid mixtures. The internal pressure is a measure of the resultant force of attraction and force of repulsion between the interacting components in the mixture. The internal pressure is a measure of the resultant force of attraction between the

Table 2
Ultrasonic velocity u, density ρ, viscosity η, adiabatic compressibility κ, acoustic impedance Z, free length L_f, internal pressure π_i free volume V_f, cohesive energy CE and interaction parameter χ_U values for solutions containing equimolar concentration of cinnamaldehyde and aniline at 303.15 K.

Solvent: n-hexane									T = 303.15 K
Conc.,*/10^{-4} M	u m s^{-1}	ρ kg m^{-3}	η/10^{-4} Nsm^{-2}	κ/10^{-9} kg^{-1} ms^{-2}	Z/10^5 kg m^{-2} s^{-1}	$L_{f\ A^\circ}$	π_i/ atm	CE kJ $mole^{-1}$	$\chi_U/10^{-2}$
1	1045.2	646.6	3.35	1.42	6.76	0.747	2331	31.5	−2.20
2	1045.6	647.7	3.36	1.41	6.77	0.746	2338	31.5	−2.13
3	1046.4	648.4	3.37	1.41	6.78	0.745	234.2	31.5	−1.98
4	1046.8	649.1	3.39	1.41	6.79	0.744	2350	31.6	−1.91
5	1047.2	649.5	3.40	1.40	6.80	0.743	2356	31.7	−1.84
6	1048.0	650.3	3.41	1.40	6.81	0.742	2358	31.7	−1.69
7	1048.8	650.4	3.43	1.40	6.82	0.742	2365	31.7	−1.54
8	1049.6	651.0	3.44	1.39	6.83	0.741	2368	31.7	−1.40
9	1050.0	652.3	3.47	1.39	6.85	0.740	2381	31.9	−1.32
10	1051.2	659.3	3.53	1.37	6.93	0.735	2418	32.0	−1.10