Ultrasonic and spectral studies on charge transfer complexes of anisole and certain aromatic amines

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ARTICLE INFO

ABSTRACT

Stability constants of two complexes of anisole with aniline and N-methylaniline (NMA) are determined from the measured ultrasonic velocity in n-hexane medium at four different temperatures. Acoustic and excess thermo acoustic parameters [excess ultrasonic velocity (u^E), excess molar volume (V^E), excess internal pressure (π_i^E)] are reported for these systems at four different temperatures. The trend in acoustic and excess parameters with concentration in the two systems establishes the formation of hydrogen bonded complexes between anisole and the two amines. Thermodynamic properties are computed for the two complexes from the variation in K with temperature. The formation of these complexes is also established by UV spectral method and their spectral characteristics and stability constants are determined. K values of these complexes obtained by ultrasonic and UV spectroscopic techniques agree well. Aniline forms more stable complex than N-methylaniline with anisole in n-hexane medium.

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1. Introduction

Ultrasonic technique is widely employed in the study of intermolecular interaction and helpful in the development of molecular sciences. The intermolecular interaction changes the structural arrangement of the molecules [1,2]. The study of weak interactions in liquid mixtures is helpful in understanding physical properties [3–6]. The strength of these weak interactions can be assessed in terms of the association constant and other thermodynamic parameters. The determination of equilibrium constant of weak interacting systems and influence of temperature on such systems was studied by ultrasonic method by several investigators [7–10] to evaluate thermodynamic parameters. Hydrogen bond plays important role in strengthening of molecular interactions and stabilizing supra-molecular complexes and such systems [11–13] play a vital role in chemical, physical and biological processes.

Amines in pure state are self-associated through inter molecular 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 and ketones have been attributed to the hydrogen bonding between electron-rich carbonyl oxygen and active hydrogen.

Higuchi and his coworkers [14] have investigated the complex formation of caffeine with a number of acidic drugs. They attributed the interaction between caffeine and drug to 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 [15].

Recently, we determined the equilibrium constants for the protonation of N,N-dimethylaniline with three isomeric cresols by ultrasonic method and correlated the hydrogen bond stabilized protonated species with the molecular properties of proton donors [16]. In this paper, the results obtained in the study of molecular interaction between anisole with two amines namely aniline and N-methylaniline in n-hexane medium are presented. Acoustic parameters such as intermolecular free length (L_f), adiabatic compressibility (κ), internal pressure (π), free volume (V_f), molar volume (V_m), molecular cohesive energy (MCE) are computed for the three ternary systems at four different temperatures (293.15, 298.15, 303.15, 308.15 K) in n-hexane medium from the measured ultrasound velocity, density and viscosity values. Excess properties (u^E, κ^E, L_f^E, π_i^E, V_f^E and V_m^E) are reported and discussed. The formation constants and thermodynamic properties are also reported for the two complexes. The formation of hydrogen bonded complexes in the two systems is confirmed by UV spectral investigation.

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2. Experimental

Merck samples of anisole, aniline and N-methylaniline, were purified by distillation before use. The solvent n-hexane used was spectral grade Aldrich sample. The purity of these chemicals was ascertained by comparing the measured densities and ultrasonic velocity (Table 1) at the investigated temperatures with the reported literature values [17–31]. The liquid mixtures of required concentrations were prepared by weighing appropriate amounts of pure liquids and mixed in airtight stopper bottles to minimize evaporation losses. The density of the pure liquids and their ternary systems were found by using a 10 ml specific gravity bottle. All the weighings were made with a digital balance (Shimadzu, Japan) of accuracy ±0.1 mg. The ultrasonic velocities of pure liquids and ternary liquid mixtures were measured using a single crystal variable path ultrasonic interferometer operating at 2 MHz frequency supplied by Mittal Enterprises, Model F81. The accuracy in the measurement of ultrasonic velocity was ±0.2 ms^{-1}. Viscosity measurements were made with an Ostwald's viscometer in which the flow time for solutions was measured through a digital stop clock of accuracy ±0.01 s. The temperature of the samples was maintained constant to an accuracy of ±0.1 K by digitally controlled thermostatic water bath. The results of u, ρ and η summarized in Table 2 represent the average of at least five independent measurements for each composition of the ternary liquid mixtures. 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 as reported in the literature [7–10].

3. Results and discussion

Hydrogen bonded complexes formed between a proton donor molecule and a base (containing nitrogen or oxygen lone-pair donors) play vital role in biological systems. The partial charge-transfer nature of such bonds is the reason for the stability of these complexes [32]. Chowdhury investigated aniline–diethyl ether and aniline–tetrahydrofuran complexes using one-color-resonant two-photon ionization spectroscopy in combination with infrared depletion spectroscopy and concluded that hydrogen bonded complexes are formed in these systems [33]. They found that fast vibrational relaxation occurs in the hydrogen-bonded aniline–tetrahydrofuran complex. Here, we used anisole, aromatic ether in the complex formation with two aromatic primary and secondary that can form hydrogen bond with ethereal oxygen of anisole.

3.1. Acoustical parameters

The values of ultrasonic velocity (u), density (ρ) and viscosity (η) for the two ternary systems at various concentrations and at four different temperatures are given in Table 2. Plots of ultrasonic velocity versus concentration for the two ternary systems are depicted in Fig. 1(a) and (b). Plots of 'u' versus concentration are similar in the two ternary systems indicating the presence of similar type of interaction in both the systems. It is observed that the ultrasonic velocity increases with increase in concentration in both the systems. However, the variation is not perfectly linear. This non-linear variation in 'u' with concentration suggests that there are specific solute–solute interactions in the two systems as the solute–solvent interaction in these ternary systems is less prominent due to chemical inertness and non-polar nature of n-hexane [34]. This strong solute–solute interaction of unlike molecules may be attributed to the formation of hydrogen bonded complex between anisole and amine [35]. The formation of complex is also supported by the significant increase in density and the viscosity with concentration. It is found that the ultrasonic velocity decreases with increase in temperature in a system at a given concentration. This may be due to thermal agitation which affects the intermolecular interaction [36]. The increase in density and viscosity with concentration in both the systems suggests that the extent of complex formation increases with the increase in concentration.

The complex formation can be established by the variation in the adiabatic compressibility of ternary liquid mixtures. It is observed that isentropic compressibility 'κs' decreases with increasing concentration (Table 3) in the two systems. It is primarily the compressibility that changes with structure which leads to a change in ultrasonic velocity. The decrease in isentropic compressibility (κs) in liquid mixtures indicates that there is a definite contraction on mixing and the significant variation is attributed to H-bonded complex formation [37]. Intermolecular free length (L_f) reflects similar behaviour as isentropic compressibility. The decrease in compressibility brings the molecules to close packing, resulting in the decrease of intermolecular free length. There is regular decrease in L_f with increase in concentration (Table 3) in both the systems at a given temperature. This indicates that the molecules are closer in the system due to strong interaction between solute molecules in the ternary mixtures. The disruption of molecular interactions with rise in temperature makes the molecules to

Table 1
Ultrasonic velocity and density values of pure components at different temperatures.

Components	Temp (K)	Velocity (ms^{-1})		Density (kg m^{-3})	
		Experimental value	Literature value	Experimental value	Literature value
n-hexane	293	1099.6	1100[a]	0.6603	0.6597[a]
					0.6593[b]
	298	1076.2	1077[c]	0.6549	0.6551[c]
			1075.8[d]		0.6552[a]
			1077[e]		0.6548[d]
	303	1058.1	1058.3[f]	0.6508	0.6506[a]
			1055[a]		0.6505[b]
	308	1039	1032[a]	0.6457	0.6460[a]
Anisole	293	1424.8	–	0.9922	–
	298	1408.1	1408[g]	0.9882	0.9891[g]
			1407[h]		0.9891[h]
					0.9889[i]
	303	1390.6	–	0.9846	–
	308	1376.1	–	0.9798	–
Aniline	293	1650.6	1651.3[j]	1.0190	1.0217[k]
	298	1639.2	1638.6[k]	1.0169	1.0174[k]
			1635[l]		1.0172[l]
	303	1624.8	1619.2[k]	1.0138	1.0130[k]
					1.0129[m]
	308	1606.6	1595.1[j]	1.0089	–
N-methyl aniline	293	1584.0	1582.5[n]	0.9865	0.9862[n]
	298	1564.1	1563.9[n]	0.9819	0.9822[n]
	303	1547.2	1546.0[o]	0.9767	0.9782[o]
	308	1532.8	–	0.9703	–

[a] Ref. [17].
[b] Ref. [18].
[c] Ref. [19].
[d] Ref. [20].
[e] Ref. [21].
[f] Ref. [22].
[g] Ref. [23].
[h] Ref. [24].
[i] Ref. [25].
[j] Ref. [26].
[k] Ref. [27].
[l] Ref. [28].
[m] Ref. [29].
[n] Ref. [30].
[o] Ref. [31].