Ultrasonic and Thermodynamical Parameters on Cinnamaldehyde with O-Phenyldiamine in n-Hexane at Different Temperature

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ABSTRACT

Ultrasonic velocity (U), Density (ρ), and Viscosity (η) have been measured for unsaturated aromatic aldehyde with o-phenyldiamine in n-hexane at 303 K, 308 K and 313 K. Acoustical parameters such as the adiabatic compressibility (β), acoustic impedance (Z), free length (Lf), free volume (Vf), internal pressure (πi), cohesive energy (CE), Lenard Jones potential(LJP), formation constant (K), free energy of formation (ΔG), free energy activation (ΔG) and viscous relaxation time (τ) are also calculated. The variation of parameter with different temperature is also discussed in terms of unsaturated and mechanism of reaction. The thermodynamic parameter is also conformed strong charge transfer complex. Excess thermo acoustic parameters conclude the existence of hydrogen bonded complexes between cinnamaldehyde and amine.

Keywords: Acoustical parameter; Formation constant; Hydrogen bond; Cinnamaldehyde; O-phenyldiamine
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INTRODUCTION

The ultrasonic technique is used to conform the charge transfer complexes [1,2] and calculation of some acoustical parameters also. The present investigation is proved the specific hydrogen bond between unsaturated aromatic aldehyde and aromatic amine with free $-NH_2$ groups. Hydrogen bond gives a very good strength of molecular interaction. In the present work cinnamaldehyde with o-phenyidiamine in n-hexane has been reported. Carbonyl groups like aldehyde, ketone are biologically important and also electron deficient molecules [3,4]. Carbonyl compounds are weakly polar compounds and they are less associated liquids in pure state. But amines are strong self-associated through intermolecular hydrogen bonds. They are both π-electron as well as n-electron donors. They interact with electron acceptor like carbonyl compounds [5,6]. Extension of conjucation in the aldehyde proved the strong charge transfer complex may be due to availability of π-electrons [7,8].

EXPERIMENTAL SECTION

The cinnamaldehyde was of spectrum purity supplied by SD Fine chemicals. O-phenyldiamine and the n-hexane were used of Analar grade samples which were purified by standard methods. The ultrasonic velocity of liquid mixture has been measured using an Ultrasonic interferometer (Model F 81) operating at 2 MHZ frequency supplied by Mittal Enterprises Pvt. Ltd. The measurement was estimated with an overall accuracy of ±0.1 ms^{-1}. 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 solutions. Ostwal's viscometer was used to determine the viscosity, in which the flow time for solutions was measured through a digital stop clock of accuracy ±0.1 K.

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RESULTS AND DISCUSSION

Acoustical Parameters

The ultrasonic velocity increases with in concentration at all temperatures. The behavior of increasing tendency showed the strong solute-solute interactions. It was proved that the molecular interaction strong in liquid mixtures becomes high where the velocity maximum occurs [9]. The successive increase in ultrasonic velocity which conformed the stronger molecular interactions such as dipole-dipole or charge transfer complex formation through intermolecular hydrogen bond [10]. Adiabatic compressibility is used to determine the intermolecular association or dissociation. The behaviour of adiabatic compressibility and free length decreases with concentration. It revealed that the existence of strong interactions between o-phenyldiamine and cinnamaldehyde in the liquid mixtures. It is also supported for the structural arrangements of atoms in the compound. The decrease of β shows the formation of large number tightly bound systems. From the β values indicates a close packing and compactness. This result shows a decrease of free length with concentration [11]. The measurement of internal pressure explains the force of attraction and the force of repulsion in liquid mixtures. It is also used to identify the intermolecular interaction. The internal pressure increases with the concentration at all temperature. The measurement of free volume (V_f) shows the strong molecular interaction and suggests the tightly bound system within the molecule. The V_f decreases, while the concentration was increasing. It also proved that the strong intermolecular hydrogen bonds between aldehyde and amine. The steep variation of CE showed that there is no flexibity in the chains. CE values are very high at all temperature. It suggests that the intermolecular forces are also high. The constant values of molar volume observed that there are no any structural changes between solute and solvent. The value of LJP slightly varied with concentration and temperature. It supports the presence of strong intermolecular hydrogen bonding between unsaturated aldehyde and aromatic amine (Tables 1-5 and Figures 1-5).

Thermodynamical Parameter

The higher values for cinnamaldehyde-ortho phenyldiamine complex suggest that the extension of conjucation in cinnamaldehyde. The electron release from the aromatic aldehyde by resonance effect is supported by the double bond aldehyde group and benzene ring. Similar reports have been proved in the study of hydrogen bonded complexes between carbonyl compounds and chloroform by Mahendran [12]. There is intramolecular hydrogen bond between carbonyl oxygen of the aldehyde and the nearer amine group [13]. At all temperature the complex has negative free energy of formation indicating that the complex is thermodynamically stable. The intrinsic trend of the complex conformed due to the constant values of relaxation time (r) at all temperature.

Table 1: The value of ultrasonic velocity(U), density(ρ), viscosity(η), Adiabatic compressibility (β), Acoustical impedance (Z), free length (L_f), free volume (V_f), Absorbtion coefficient, Lenard Jones Potential(LJP), Internal pressure (π_i), Molar volume (V_a) and cohesive energy of n-hexane solution at 303 K

Conc × 10^{-4}	U	ρ	η	β	Z	L_f	V_f	AB.CO	LJP	π_i	V_a	CE
1	1041.9	645	3.728	1.43	6.72	7.43	4.22	1.34	5.12	2.578	4.66	31
2	1048.7	646.4	3.871	1.41	6.78	7.38	4.03	1.37	5.13	2.621	4.6	31
3	1052.4	647.3	3.962	1.39	6.81	7.35	3.92	1.38	5.32	2.649	4.56	32
4	1056.1	648.9	4.083	1.38	6.85	7.31	3.76	1.4	5.34	2.688	4.52	32
5	1060.9	649.8	4.173	1.37	6.89	7.27	3.67	1.41	5.52	2.713	4.47	33
6	1064.6	650.2	4.283	1.36	6.92	7.25	3.55	1.44	5.55	2.744	4.44	33
7	1068.6	651.5	4.389	1.34	6.96	7.21	3.44	1.45	5.67	2.775	4.4	34
8	1072.7	652.4	4.471	1.33	7	7.18	3.37	1.46	5.7	2.797	4.36	35

Table 2: The value of ultrasonic velocity (U),density (ρ),viscosity (η), Adiabatic compressibility (β),Acoustical impedance (Z), free length (L_f), free volume (V_f), Absorbtion coefficient, Lenard Jones Potential (LJP), Internal pressure (π_i), Molar volume (V_a) and cohesive energy of cinnamaldehyde with o-phenyldiamine in n-hexane solution at 308 K

Conc × 10^{-4}	U	ρ	η	β	Z	L_f	V_f	AB.CO	LJP	π_i	V_a	CE
1	1034.6	643.8	3.601	1.45	6.66	7.49	4.4	1.33	3.98	2.539	4.73	34
2	1039.9	644.1	3.726	1.44	6.7	7.45	4.22	1.35	4.13	2.576	4.69	34
3	1043.8	645.3	3.835	1.42	6.74	7.42	4.06	1.37	4.25	2.611	4.65	35
4	1048.6	646.8	3.968	1.4	6.78	7.38	3.89	1.4	4.4	2.654	4.6	35
5	1055.2	647.3	4.073	1.39	6.83	7.33	3.78	1.41	4.62	2.681	4.54	36
6	1061.4	648.5	4.153	1.37	6.88	7.28	3.7	1.41	4.83	2.701	4.48	36
7	1068.6	649.1	4.295	1.35	6.94	7.23	3.56	1.43	5.06	2.739	4.42	36
8	1073.3	650.2	4.388	1.34	6.98	7.19	3.47	1.44	5.24	2.764	4.37	37

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Table 3: The value of ultrasonic velocity (U),density (ρ),viscosity (η), Adiabatic compressibility (β), Acoustical impedance (Z), free length (L$_f$), free volume (V$_f$), Absorbtion coefficient, Lenard Jones Potential (LJP), Internal pressure (π$_i$), Molar volume (V$_a$) and cohesive energy of cinnamaldehyde with o-phenyldiamine in n-hexane solution at 313 K

Conc × 10^{-4}	U	ρ	η	β	Z	Lf	Vf	AB.CO	LJP	π$_i$	Va	CE
1	1028.3	641.5	3.567	1.47	6.6	7.55	4.42	1.34	3.8	2.529	4.8	33.98
2	1032.5	642.8	3.623	1.46	6.64	7.51	4.35	1.35	3.91	2.546	4.76	34.15
3	1036.5	643.6	3.768	1.45	6.67	7.48	4.13	1.38	4.04	2.593	4.72	34.75
4	1040.9	644.1	3.891	1.43	6.7	7.45	3.96	1.41	4.17	2.63	4.68	35.23
5	1046.4	645.9	3.936	1.41	6.76	7.4	3.92	1.4	4.35	2.642	4.62	35.3
6	1051.4	646.8	4.092	1.4	6.8	7.36	3.73	1.43	4.48	2.689	4.58	35.89
7	1055.6	647.9	4.156	1.39	6.84	7.32	3.67	1.43	4.65	2.707	4.53	36.07
8	1059.2	648.7	4.275	1.37	6.87	7.29	3.53	1.46	4.75	2.742	4.5	36.48

Table 4: The formation constant, free energy of formation, free energy of activation and viscous relaxation time values of donor-acceptor complexes of cinnamaldehyde with o-phenyldiamine in n-hexane 303 K, 308 K and 313 K

Value	303 K	308 K	313 K
K/mol	629.5	454.7	336.1
	392.2	344.8	311.4
	372.6	375.7	319.7
	395.9	407.4	344.6
	335.8	369.6	311.1
	324	349.2	279.3
	302.1	306.9	252.9
ΔG/kJmol	-3.4	-3.4	-3.4
ΔG$^{#}$/kmol	2.96	2.95	2.95
	2.96	2.96	2.96
	2.97	2.96	2.96
	2.97	2.97	2.97
	2.98	2.97	2.97
	2.98	2.98	2.98
	2.99	2.98	2.98
	2.99	2.98	2.99
rx10^{-13}s	7.1	6.97	7.01
	7.26	7.13	7.05
	7.37	7.27	7.27
	7.52	7.44	7.43
	7.61	7.53	7.42
	7.75	7.58	7.63
	7.87	7.73	7.68
	7.94	7.81	7.83

Table 5: Excess velocity (u$_{excess}$) excess adiabatic compressibility (β$_{excess}$), excess internal pressure (π$_{i\ excess}$), excess acoustic impedance (Z$_{excess}$) and excess free volme (V$_{excess}$) of cinnamaldehyde with phenyl hydrazine in n-hexane at 303 K

Conc × 10^{-4}	u	β	π$_i$	z	v
1	-145.25	1.37	2.84	7.8	-8.7
2	-139.2	1.88	3.4	6.9	-8.4
3	-138.03	1.9	3.25	6.1	-7.4
4	-137.97	2.56	3.12	5.2	-6.8
5	-136.21	2.75	2.93	4.5	-6.4
6	-135.74	3.08	2.86	3.7	-4.3
7	-134.75	3.66	2.68	3.03	-3.8
8	-131.03	4.29	2.51	2.2	-1.1

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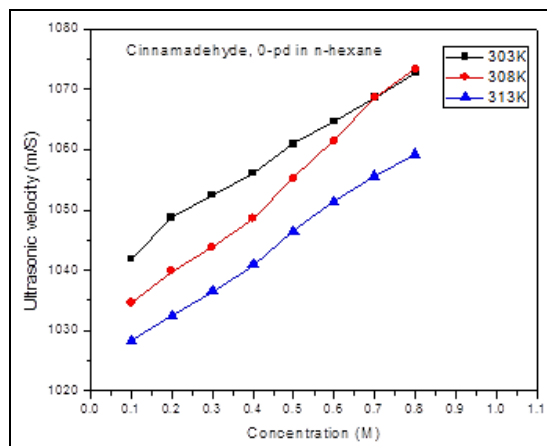*J. Chem. Pharm. Res., 2017, 9(5):271-276*

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Figure 1: Plots of ultrasonic velocity vs various concentration of cinnamaldehyde-o- phenyldiamine in n- hexane at 303 K, 308 K and 313 K
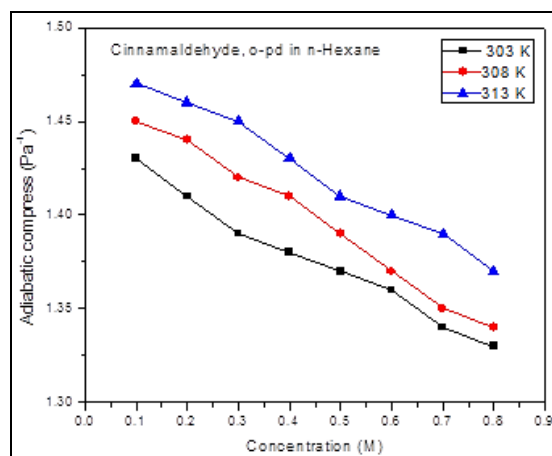

Figure 2: Plots of adiabatic compressibility vs. various concentration of cinnamaldehyde-o- phenyldiamine in n-hexane at 303 K, 308 K and 313 K
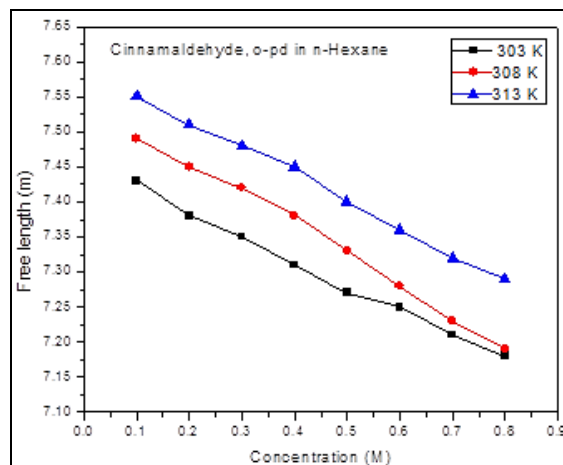

Figure 3: Plots of free length vs. various concentration of cinnamaldehyde-o-phenyldiamine in n-hexane at 303 K, 308 K and 313 K
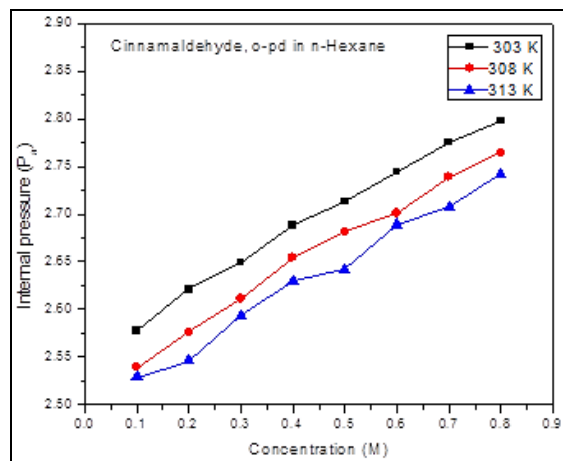
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Figure 4: Plots of internal pressure vs. concentration of cinnamaldehyde-o-phenyldiamine in n-hexane at 303 K, 308 K and 313 K
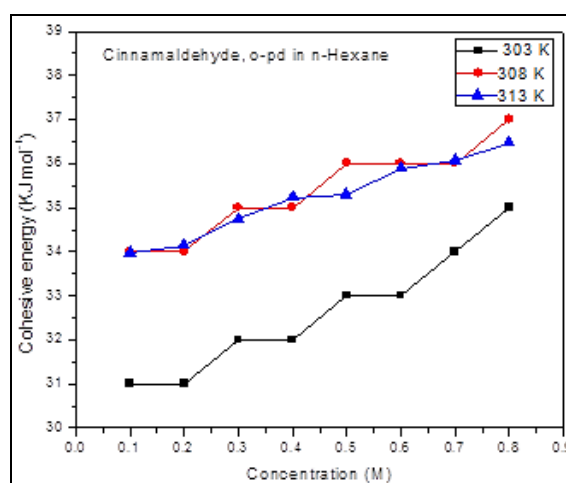

Figure 5: Plots of cohesive energy vs. various concentration of cinnamaldehyde-o- phenyldiamine with n-hexane at 303 K, 308 K and

313 K

CONCLUSION

The formation of intermolecular and intramolecular hydrogen bonded between o-phenyldiamine and cinnamaldehyde is calculated by using ultrasonic and spectral studies. Acoustical parameters are determined for the system which proved the strong inter and intramolecular hydrogen bond between cinnamaldehyde and o-phenyldiamine. The stability constant is very high for this system because of resonance effect and n-eletrons of o-phenyldiamine. The negative free energy formation is also proved thermodynamically stable complex. The free energy activation decreases, when the temperature increased. It also confirmed the formation of charge transfer complex. The formation of CE increases with the increase of temperature. It is also evidence for strong intramolecular hydrogen bond between cinnamaldehyde and o-phenyldiamine.

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