Ultrasonic and Thermodynamical Parameters on Cinnamaldehyde with Ethylenediamine 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 ethylenediaminein n-hexane at 303K,308K and 313K.Acoustical parameters such as the adiabatic compressibility (β),acoustic impedance (Z),free length (L_f),free volume (V_f),internal pressure (π_i),cohesive energy (CE),Lenard Jones potential(LJP),formation constant (K),free energy of formation (ΔG),free energy activation ($\Delta G^{\#}$) and viscous relaxation time (ι) 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,Formationconstant, Hydrogen bond, Cinnamaldehyde, ethylenediamine

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 aliphatic amine with free $-NH_2$ groups.Hydrogen bond gives a very good strength of molecular interaction. In the present workcinnamaldehyde withethylenediamine 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 strongself 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 Details

The cinnamaldehyde was of spectrum purity supplied by SD Fine chemicals. Ethylenediamine and the n-hexane were used of AnalaR grade samples which were purified by standard methods. The ultrasonic velocity of liquid mixture have 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 $\pm 0.1 ms^{-1}$.A 10ml specific gravity bottle and a single pan digital balance of Shimadzu make with an accuracy of 0.1mg was 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 ±0.1K.

Results and discussion

Acoustical parameters

The ultrasonic velocity increases with in concentration at all temperatures.The bahaviour 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 ethylenediamine 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 a 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 explain 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 is 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 aliphatic amine.

Thermodynamical parameters

The higher values for cinnamaldehyde-ethylenediame complex suggest that the extension of conjucation in cinnamaldehyde.There is intramolecular hydrogen bond between carbonyl oxygen of the aldehyde and the nearer amine group[12].At all temperature the complex have negative free energy of formation(ΔG) indicating that the complex is thermodynamically stable.The intrinsic trend of the complex conformed due to the constant values of relaxation time(r) and free energy of activation($\Delta G^{\#}$) at all temperature. The aromatic aldehyde cinnamaldehyde has the highest K value showing that more stable complex at low temperature and at low concentration and the values are presented in Table 4 .It was also observed on the charge transfer complexes of carbonyl compounds and chloroform in n-hexane by Mahendran[13].Molecular interaction parameter(χ_u) are calculated and are presented in Table 5 at different temperature.This parameter can be analysed the strength of molecular interaction between aldehyde and amine in n-hexane.These values increase with concentration showing that the strength of complexation and concentration dependent.

Excess parameters

The existent of any intermolecular interaction was explained by using the excess values of the thermo dynamical parameters. The strength of interaction always depends upon the sign of excess values[14,15].The excess values are presented in Table 6.The excess ultrasonic velocity is negative at low concentration and it is positive at high concentration which can be concluded the high interaction at high

concentration. The negative values of excess adiabatic compressibility and excess free length indicating that the strong interaction in liquid mixtures.

Table 1 Thevalue of Ultrasonic velocity(U),Density(ρ),Viscosity(η), Adiabatic ompressibility(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 Ethylenediamine in n-hexane solution at 303K.

Conc x10^{-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	5.70	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 Ethylenediamine in n-hexane solution at 308K.

Conc x10^{-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

The negative sign of excess free length show a compactness due to molecular interaction through dipole-dipole interaction [16,17] indicating high compact structure making which enhances excess free length to have negative values. The positive value of excess impedance and excess velocity at high concentration suggests the presence of strong interaction the components mixture [18,19].The close packing proves the trend in excess free volume and excess internal pressure is opposite to each other. Excess free volume is negative and excess internal pressure is positive.

Table 3 Thevalue 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 Ethylenediamine in n-hexane solution at 313K.

Conc x10^{-4}	U	ρ	η	β	Z	L_f	V_f	AB.CO	LJP	π_i	V_a	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(K) **,Free energy of formation**(ΔG) **,Free energy of activation**($\Delta G^{\#}$) **and Viscous relaxation time**(r) **values of donor-acceptor complexes of Cinnamaldehyde with Ethylenediamine in n-hexane 303K,308K and 313K.**

Value	303K	308K	313K
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
$\Delta G^{\#}$/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 Molecular interaction parameter $\chi u/10^{-2}$ for Cinnamaldehyde with Ethylenediamine in n-hexane at 303K,308K and 313K.

Concx10^{-4}	303K	308K	313K
1	-0.0054	0.0015	-0.006
2	-0.0226	-0.0059	-0.0142
3	-0.0287	-0.0126	-0.0139
4	-0.0342	-0.0203	-0.0146
5	-0.0418	-0.0314	-0.0166
6	-0.047	-0.0412	-0.0188
7	-0.0528	-0.0528	-0.0242
8	-0.0571	-0.0582	-0.0261

Table 6 Excess values Ultrasonic velocity(U^E),Excess Adiabatic compressibility(β^E),Excess Free length(L_f^E),Excess Acoustical impedance(Z^E),Excess Free Volume(V_f^E) and Excess Internal pressure(π_i^E) for Cinnamaldehyde with Ethylenediamine in n-hexane medium at 303K.

Concx10^{-4}	U^E	β^E	L_f^E	Z^E	V_f^E	π_i^E
1	-90.2	-0.922	-13.3	867133.3	2	2.97
2	-67.81	-0.934	-3.51	861115.3	-6.4	3.71
3	-27.86	-0.946	-1.1	865098.9	-6.8	3.72
4	-13.41	-0.959	-0.639	861083.9	-8.44	3.73
5	23.47	-0.971	-0.306	863070.1	-4.3	3.7

6	46.86	-0.983	-0.158	860057.4	-1.55	3.77
7	68.97	-0.996	0.0932	865045.6	-6.6	3.73
8	88.09	-1.008	-0.512	862031.6	-2	3.7

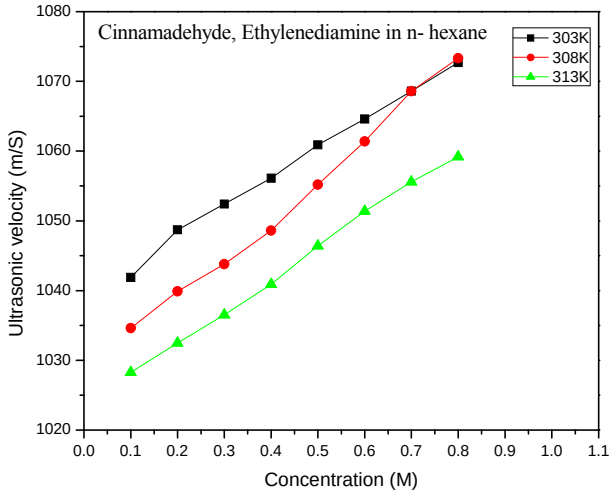

Figure 1 Plots of Ultrasonic velocity Vs Various Concentration of Cinnamaldehy de-Ethylenediamine in n- hexane at 303K, 308K and 313K.

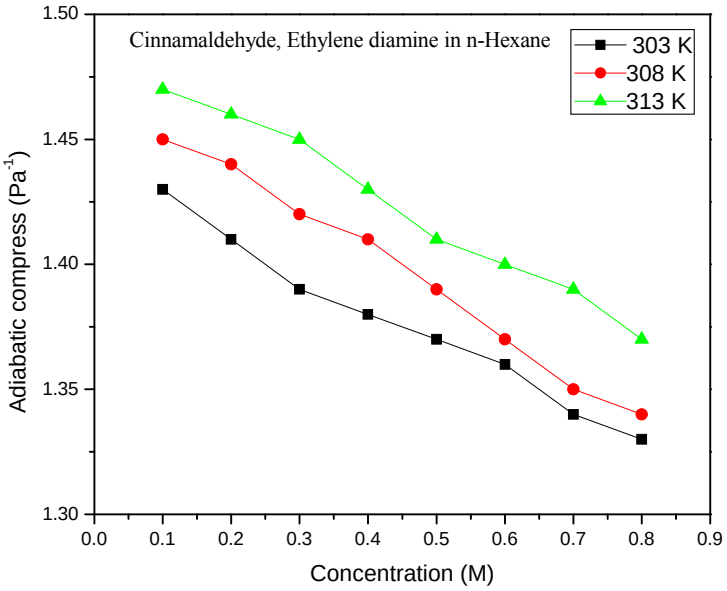

Figure 2 Plots of Adiabatic compressibility Vs Various Concentration of Cinnamaldehyde-Ethylenediamine in n-hexane at 303K, 308K and 313K

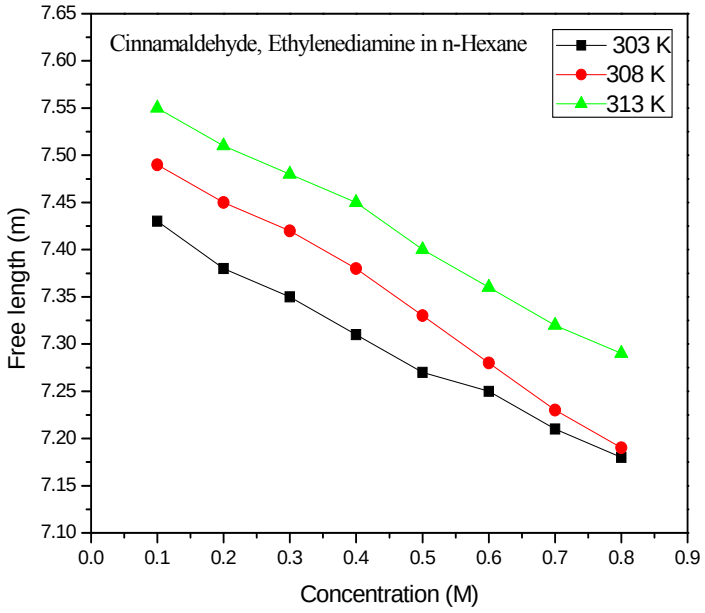

Figure 3 Plots of Free length Vs Various Concentration of Cinnamaldehyde-Ethylenediamine in n-hexane at 303K, 308K and 313K.

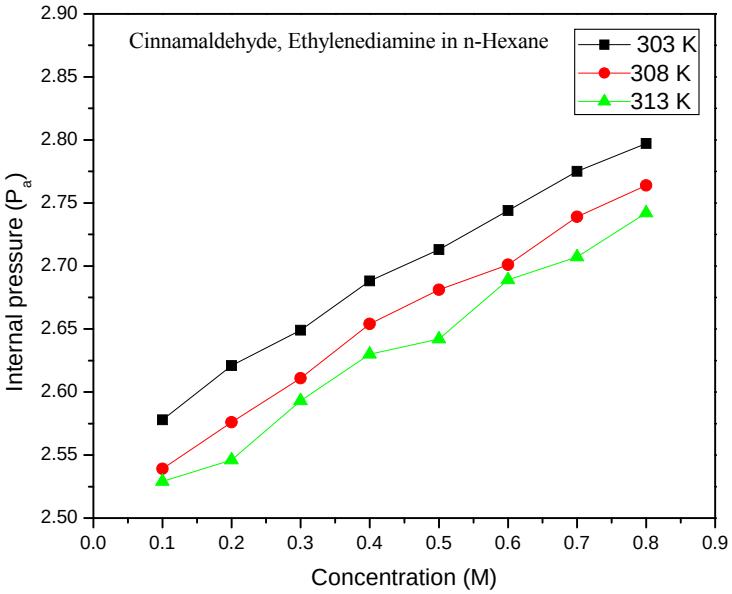

Figure 4 Plots of Internal pressure Vs Concentration of Cinnamaldehyde-Ethylenediamine in n-hexane at 303K, 308K and 313K.

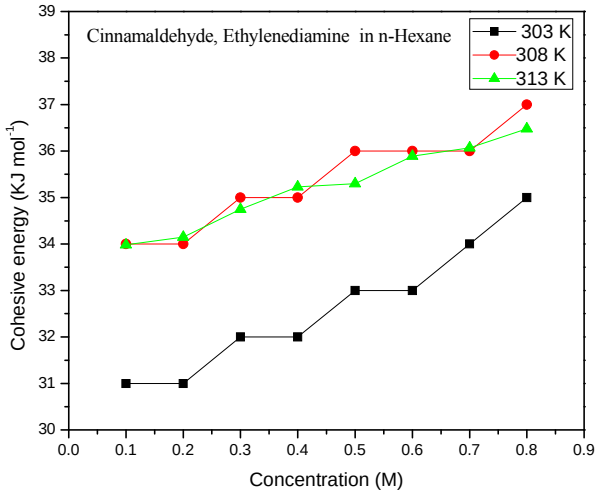

Figure 5 Plots of Cohesive energy Vs Various Concentration of Cinnamaldehyde-Ethylenediamine with n-hexane at 303K, 308K and 313K.

Conclusion

The formation of intermolecular and intramolecular hydrogen bonded between ethylenediamine and cinnamaldehyde is calculated by using ultrasonic method. Acoustical parameters are determined for the system which proved the strong inter and intramolecular hydrogen bond between cinnamaldehyde and ethylenediamine. The stability constant is very high for this system because of π-electrons and n-eletrons of ethylenediamine. 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-ethylenediamine. Molecular interaction parameter has a strong evidence for the formation complex between aldehyde and amine.The excess parameter is also helpful for the strong interaction in liquid components.

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