

Acoustical and Thermodynamical Studies on Crotonaldehyde with o-Phenyldiamine in n-hexane at Different Temperature

Y Geetha^{#1} and Dr. S.ChidambaraVinayagam^{*2}

^{#1}*Department of Chemistry, Sree Sastha Institute of Engineering & Technology,
Chennai - 600 123, Tamil Nadu, India*

^{*2}*Postgraduate and Research, Department of Chemistry, Presidency College,
Chennai - 600 005, Tamil Nadu, India*

Abstract

The ultrasonic velocities (U), densities (ρ) and viscosities (η) have been measured in the ternary systems of o-phenyldiamine with aliphatic unsaturated aldehyde in n-hexane medium at different temperatures. Acoustical parameters such as adiabatic compressibility (β), free length (L_f), internal pressure (π_i), acoustic impedance (Z), free volume (V_f), molar volume (V_a), Lenard Jones Potential (LJP) and cohesive energy (CE) were calculated. Thermodynamic parameters such as formation constant (K), free energy (ΔG), free energy activation (ΔG^\ddagger) were also determined. The interactions were observed by using these parameters. The constant values of relaxation time (τ) and free energy of activation (ΔG^\ddagger) proved that the similar type of complexes in these system at all temperature.

Keywords: Crotonaldehyde, o-phenyldiamine, charge transfer complex, excess parameter.

INTRODUCTION

The study of physiochemical behavior and molecular interactions in ternary system is considerable importance and various techniques have been used to determine the mixture of components [1-5]. In recently, the ultrasonic velocity measurement has been evidenced in the behavior of charge transfer complex, the formation of stability complex and solute-solvent interaction [6-8]. V.Kannappan and N.Indra Gandhi [9]

studied the molecular interaction of various aromatic, aliphatic aldehyde with aromatic amine, in n-hexane at 303K and proved that the presence of strong interaction depends upon the structure of donor-acceptor. Rambabu et al. [10] discussed extensive application of isentropic compressibilities of ternary system in characterizing molecular association, dissociation and complex formation. Charge transfer interaction is very important role in various fields [11-13]. These interaction depends upon the polar group of aldehyde and amine in non polar medium. Carbonyl group which is a nucleophile and it conform strong hydrogen bond. The active hydrogen of aldehyde forms a strong complex with aromatic amine in n-hexane. It is reported that amine form the charge transfer complex with ketone in n-hexane [14,15,16]. The intermolecular interaction affect the structure of components and noticeable interaction to conform the complex formation. The strength of interaction was proved by using the simple ultrasonic method [17,18,19]. The present work proved that the strong intermolecular hydrogen bond was identified between aliphatic unsaturated aldehyde like crotonaldehyde with aromatic amine like o-phenyldiamine in n-hexane medium at various temperature. Thermodynamic parameter also proved the stable complex formation. The aromatic aldehydes form less stable complexes than the aliphatic aldehydes as evident from K values.

MATERIALS AND METHOD

AR grade chemical used for the measuring of various parameter in different concentrations. The ultrasonic velocity have been determined using ultrasonic interferometer (Mittal type :model:F81) working at 2MHZ frequency with overall accuracy of $0 \pm 0.1 \text{ms}^{-1}$. The density was measured using a Pycknometer with an accuracy of 0.1kgm^{-3} . The viscosity was measured by using Ostwald's viscometer with an accuracy of $0.0001 \text{mNm}^{-2}\text{S}$. The temperature was kept constant by constant temperature water bath with an accuracy of 0.1K

RESULTS AND DISCUSSION

Analysis of Acoustical parameter

The calculated values of ultrasonic velocity, density and viscosity of crotonaldehyde with o-phenyldiamine in n-hexane at 303K, 308K and 313K were given in table 1-3. Ultrasonic velocity increases with concentration and temperature also. Thus the strong complexation behavior was observed. The complex was concentration and temperature dependent. The increase in velocity may be attributed to strong solute-solute interactions. The mixing of crotonaldehyde with o-phenyldiamine was showed the formation of new intermolecular hydrogen bond [20]. Whenever, the interaction between the two components were based upon the nature of double bond present in solute due to unsaturation.

A decrease in adiabatic compressibility and intermolecular free length was showed the evidence for the existence of strong interactions in ternary system which indicate the increasing compactness of the system. The decrease trend in adiabatic

compressibility showed that the complex were tightly bound systems. The decrease trend in free length observed that the close packing of solute and solvent molecule in the ternary system [21]. The gradual changes (or) constant values of molar volume at all temperature proved that the mixture of components may be same size and also there is no any changes by mixture of solute with solvent in structural.

The variation of internal pressure with concentration was also noticed. The internal pressure increases with change of concentration. It revealed that the interaction between the system was confirmed by the association of molecule. The magnitude of free volume decreases with concentration. It also suggest that the solute-solvent was bounded strongly. It can be seen in table 1-3. So the free volume parameter also supports the solute-solvent interaction and tightly bounded inside the molecule. LJP value is almost constant at all temperature. It provide that the presence of strong intermolecular interaction in the ternary system. The magnitude of CE value is constant for all temperature. It is the evidence of strong dipole-dipole interaction and strong intermolecular hydrogen bond between crotonaldehyde with o-phenyldiamine in n-hexane medium. The CE value is noticed by using graph also to show the small variation and low value. It is also confirmed by relatively flexible chains in the molecules. The negative value of excess ultrasonic velocity and the positive value of other parameter in Table [5], also proved that the strong intermolecular interaction in the ternary system.

Analysis of Thermodynamic parameter

The determination of stability constant of these complexes between aliphatic unsaturated aldehyde with aromatic amine conformed the stability of donor-acceptor complex. As the complexation occurs between carbonyl oxygen of aldehyde and hydrogen of imino group in o-phenyldiamine, the stability of the complex is affected on the availability of electrons carbonyl oxygen and nitrogen of amino group. The interaction and stability of the complexes increases with rise in temperature. It can be seen in table 4. The constant value of relaxation time (τ) was also observed from table 4. It suggest that the same type of complexes at all temperature. The free energy activation was also confirmed that the same type of complexes formed at all temperature. The negative value of free energy formation showed that the charge transfer interaction is exothermic and also confirmed the formation of stable complex between the system.

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 crotonaldehyde-ortho phenyldiamine in n-hexane solution at 303K.

Conc $\times 10^{-4}$	U	ρ	η	β	Z	Lf	Vf	AB.CO	LJP	π_i	Va	CE
1	1072.5	659.5	0.278	1.32	7.07	7.14	2.17	8.98	5.2	7.042	4.31	9.2
2	1073.2	660.3	0.28	1.31	7.09	7.13	2.15	9.02	5.22	7.069	4.3	9.2
3	1074.7	661.8	0.282	1.31	7.11	7.12	2.13	9.03	5.27	7.097	4.28	9.2
4	1075.6	662.4	0.284	1.3	7.12	7.11	2.11	9.06	5.3	7.122	4.27	9.3
5	1076.3	663.7	0.286	1.3	7.14	7.09	2.09	9.09	5.31	7.151	4.26	9.3
6	1077.6	664.6	0.288	1.3	7.16	7.08	2.07	9.11	5.38	7.176	4.24	9.3
7	1078.4	665.9	0.311	1.29	7.18	7.07	1.85	9.79	5.39	7.462	4.23	9.6
8	1079.1	666.9	0.324	1.29	7.2	7.06	1.74	1.02	5.41	7.619	4.22	9.8

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 crotonaldehyde-ortho phenyldiamine in n-hexane solution at 308K.

Conc $\times 10^{-4}$	U	ρ	η	B	Z	Lf	Vf	AB.CO	LJP	π_i	Va	CE
1	1075.4	655.4	0.267	1.32	7.05	7.15	2.31	8.61	5.31	6.863	4.31	9.02
2	1076.6	656.3	0.268	1.31	7.07	7.13	2.3	8.6	5.33	6.877	4.3	9.03
3	1077.8	657.9	0.269	1.31	7.09	7.12	2.29	8.59	5.38	6.895	4.28	9.03
4	1078.3	658.1	0.27	1.31	7.1	7.11	2.28	8.6	5.42	6.905	4.27	9.05
5	1079.5	659.3	0.271	1.3	7.12	7.1	2.28	8.59	5.44	6.92	4.26	9.05
6	1080.2	660.3	0.272	1.3	7.13	7.09	2.27	8.59	5.46	6.936	4.25	9.06
7	1081.7	661.3	0.273	1.29	7.15	7.07	2.26	8.58	5.52	6.949	4.23	9.07
8	1082.9	662.7	0.274	1.29	7.18	7.06	2.25	8.56	5.57	6.965	4.21	9.08

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 crotonaldehyde-ortho phenyldiamine in n-hexane solution at 313K.

Conc x10 ⁻⁴	U	ρ	η	β	Z	Lf	Vf	AB.CO	LJP	π_i	Va	CE
1	1079.1	650.4	0.262	1.32	7.02	7.15	2.47	8.43	5.45	6.753	4.31	8.5
2	1083.5	651.4	0.263	1.31	7.06	7.11	2.42	8.35	5.6	6.757	4.27	8.7
3	1087.9	652.6	0.264	1.29	7.1	7.08	2.39	8.26	5.75	6.762	4.23	8.8
4	1091.3	653.9	0.265	1.28	7.14	7.05	2.39	8.2	5.89	6.771	4.19	8.8
5	1095.9	654.7	0.266	1.27	7.17	7.02	2.39	8.12	6.06	6.773	4.15	8.9
6	1099.4	655.3	0.267	1.26	7.2	6.99	2.39	8.06	6.18	6.777	4.12	8.9
7	1130.7	656.8	0.268	1.23	7.29	6.91	2.39	7.83	6.62	6.764	4.02	8.9
8	1179.4	657.1	0.269	1.19	7.42	6.79	2.39	7.47	7.38	6.72	3.87	8.9

Table: 4

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

	303K	308K	313K
K/mol	492.2	442.9	418.6
	384.4	357.1	355.8
	344.4	336.4	309.7
	292.7	316	287.9
	275.3	288	226.7
	260.8	253	184.8
	234.9	198	169
$\Delta G/kJmol$	-3.4	-3.4	-3.4
$\Delta G\#/kmol$	2.22	2.21	2.2
	2.22	2.21	2.2
	2.22	2.21	2.2

	2.22	2.21	2.2
	2.22	2.21	2.19
	2.22	2.21	2.19
	2.24	2.21	2.17
	2.25	2.21	2.15
$r \times 10^{-13} s$	4.89	4.7	4.61
	4.91	4.7	4.56
	4.92	4.69	4.51
	4.94	4.7	4.48
	4.96	4.7	4.43
	4.98	4.71	4.39
	5.35	4.7	4.13
	5.56	4.7	3.79

Table : 5

Excess velocity (u_{excess}) excess adiabatic compressibility (β_{excess}), excess internal pressure (π_{excess}), excess acoustic impedance (Z_{excess}) and excess free volume (V_{excess}) of crotonaldehyde with phenyl hydrazine in n-hexane at 303K.

Conc $\times 10^{-4}$	u	β	π	z	v
1	-130.81	1.26	2.84	7.8	0.16
2	-123.2	1.78	3.41	7	0.67
3	-118.12	1.8	3.28	6.3	1.5
4	-114.13	2.46	3.17	5.6	2.6
5	109.42	2.64	3.02	4.9	4.1
6	-108.28	2.97	2.98	4.3	6.3
7	-105.38	3.54	2.84	3.8	8.2
8	-102.6	4.16	2.71	3.3	10.7

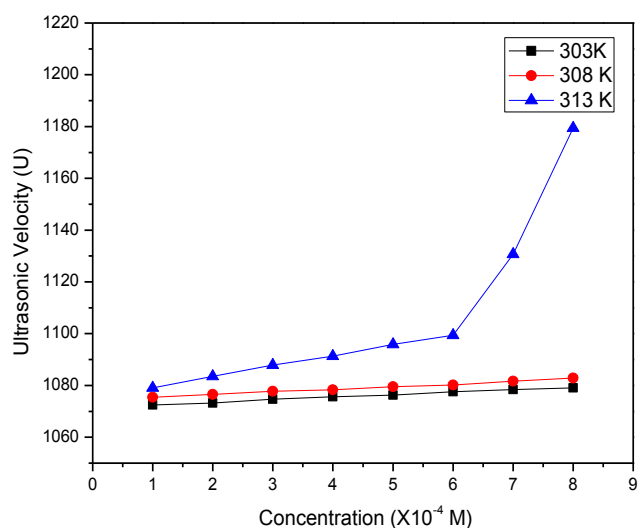


Figure 1. Plots of ultrasonic velocity vs various concentration of crotonaldehyde-ortho phenyldiamine in n-hexane at 303K 308K & 313K.

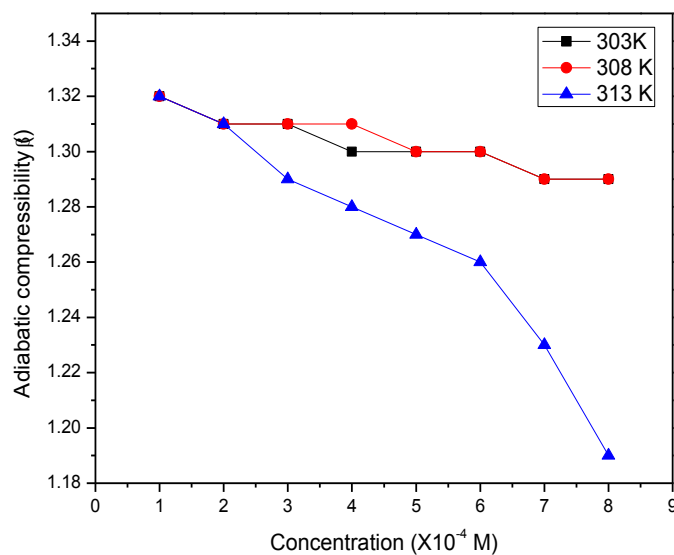


Figure 2. Plots of adiabatic compressibility vs various concentration of crotonaldehyde-ortho phenyldiamine in n-hexane at 303K 308K & 313K.

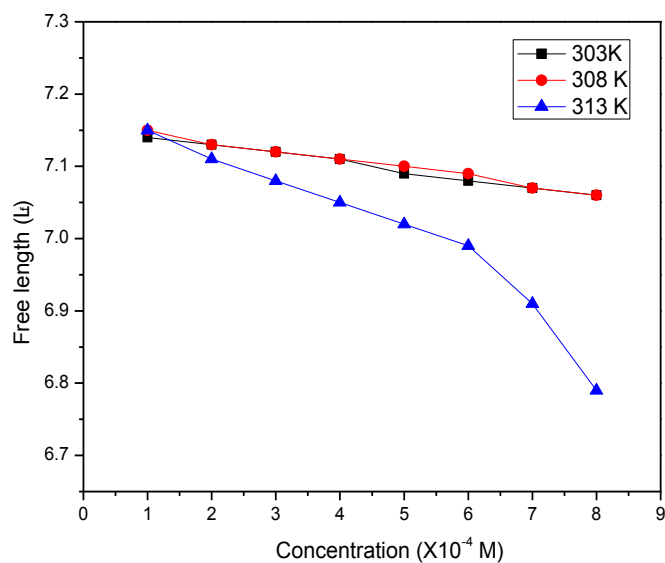


Figure 3. Plots of free length vs various concentration of crotonaldehyde –ortho phenyldiamine in n-hexane. 303K 308K & 313K.

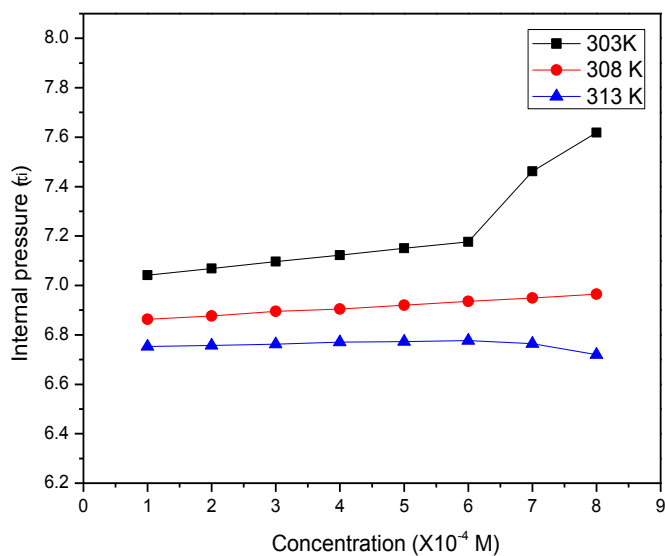


Figure 4. Plots of internal pressure vs concentration of crotonaldehyde-ortho phenyldiamine in n-hexane at 303K,308K & 313K.

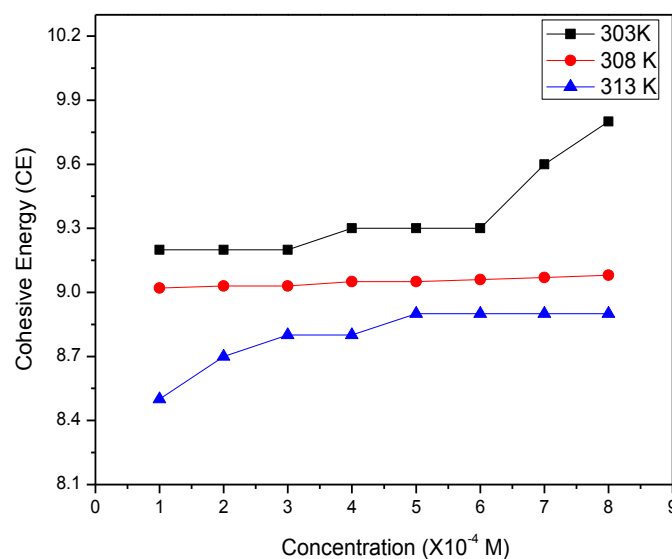


Figure 5. Plots of various cohesive energy vs concentration of crotonaldehyde-ortho phenyldiamine in n-hexane at 303K,308K & 313K.

CONCLUSION :

Acoustical parameters are evaluated through ultrasonic and thermodynamic studies. The formation of intermolecular hydrogen bond is strong by using these studies. Because of the unsaturation and extension of conjugation with carbonyl compound. The complexes are thermodynamically stable from the evidence of negative free energy of formation. Crotonaldehyde have showed that the similar relaxation time. From these values, there is no any structural changes in the complexes.

REFERENCES

- [1] K.Rambabu, P.Venkateswaralu and G.K Raman, *Acoustic Lett.* 13, **1989**, 87.
- [2] J.Govindappa, K.Rambabu, P.Venkateswaralu and G.K.Raman, *Indian J.Pure Appl.Phys.* 28, **1990**, 145.
- [3] U Srinivaslu and P.R.Naidu, *Indian J.Pure Appl.Phys.* 29, **1990**, 576.
- [4] T S Prasad and P.Venkateswaralu, *Acoustics Lett.* 18, **1994**, 5.
- [5] S.Jeyakumar, N.Karunanidhi and V.Kannappan, *Indian J.Pure Appl.Phys.* 34, **1996**, 761.
- [6] S.Prakash, J.Singh and S.Srivastava, *Acoustica* 65, **1988**, 263.

- [7] C.Chennarayappa,K.Ramababu,P.Venkateswaralu and G.K.Raman, *Acoutics Lett.*15,**1991**,83.
- [8] C.Padmasree and K.Ravindradas,*Indian J.Pure Appl.Phys.*32,**1994**,954.
- [9] V.Kannappan and N.Indra Gandhi,*Indian Journal of Pure and Applied Physics*,45,**2007**, 221-225.
- [10] K.Rambabu,P.Venkateswaralu and G.K.Raman,*Acoustics Lett.*13,**1989**,87.
- [11] S.Sadeghi,K.Karimi,*Chem.Pharm.Bull.*54,**2006**,1107-1112.
- [12] H.Kusma,H.Sugirtha,*J.Photochem.Photobiol.*,A181,**2006**,268-273.
- [13] K.Bradley,M.Briman,A.Star,G.Gruner,*Nano Lett.*4,**2004**,253-256.
- [14] R.Kumar,N.Swarnalatha,R.Mahesh,B.Shamugpriyan,V.Kannappan, *J.Mol.Liq.*163,**2011**, 57-63.
- [15] V.Kannappan,N.Indra Gandhi,*Phys.Chem.Liq.*46,**2008**,510-521.
- [16] V.Kannappan,S.J.Askar Ali,P.A.Abdul Mahaboob,*Indian J.Pure Appl.Phys.*47,**2009**, 97-102.
- [17] V.E.Borisenko,S.A.Krekov,M.Yu.Fomenko,A.Koll,P.Lipkovski, *J.Mol.Struct.*882,**2008**, 9-23.
- [18] M.Sethu Raman, V.Ponnuswamy, P.Kolandaivel, K.Perumal, *J.Mol.Liq.*142, **2008**, 10-16.
- [19] R.Kumar,V.Ulagendran,V.Kannappan,S.Jayakumar,*Fluid Phase Equilibria* 307,**2011**, 113-125.
- [20] V.Ulagendran,R.Kumar,S.Jeyakumar,V.Kannappan,*J.Mol.Liq.*148,**2009**,67-72.
- [21] V.Kannappan,S.J.Askar Ali,P.A.Abdul Mahaboob, *Indian J.Pure Appl.Phys.*47, **2009**, 97-102.