Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2013, 5(1):283-289

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Ultrasonic studies on molecular interaction of benzaldehyde, cinnamaldehyde, 4-methoxy benzaldehyde and diethylamine in n-hexane solutions at 303K

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ABSTRACT

Ultrasonic velocities(U), Densities(ρ), Viscosities(η), are measured for three different aromatic carbonyl compounds (Benzaldehyde, Cinnamaldehyde, 4-methoxy benzaldehyde) and Diethylamine in n-hexane solutions containing equimolar concentrations ($1x10^{-4}$M to $1x10^{-3}$M) at 303K. The interaction between solvent molecules and Carbonyl compounds - Diethyl amine complexes are observed. Acoustical parameters such as adiabatic compressibility (κ), free length (L_f), internal pressure(π_i), cohesive energy(CE), formation constant(K) values are also calculated. These values indicate complex formation and ion-solvent interaction between aromatic carbonyl compounds and diethylamine in n-hexane medium.

INTRODUCTION

Carbonyl group is a functional group of several biologically important molecules such as protein and hormones. Carbonyl compounds contain polar carbonyl group in which electron rich oxygen can function as electron donor. Basic group like amino group can interact with this group to form a complex and influence the properties of such compounds [1]. Amines behave as Lewis bases since they contain nitrogen as the basic centre with lone pair of electrons and has hydrogen as acceptors. Aromatic amines also contain π-electrons and hence they can function as both n and π-electron donors. Thus donor-acceptor complexes can be formed between amines and aldehydes. Ultrasonic investigations were carried out to detect charge-transfer complexes between certain carbonyl compounds and chloroform, the stability constants of these complexes were calculated using modified Bhat equation proposed by Kannappan [2-6]. Ultrasonic velocity measurements have been successfully employed to detect the nature of interactions between certain aldehydes and amines in polar-medium like n-hexane. Calculations of adiabatic compressibility (κ), free length (L_f), internal pressure(π_i), cohesive energy(CE), formation constant(K) values can be used to investigate interaction of these aromatic carbonyl compounds-diethylamine complexes.

EXPERIMENTAL SECTION

Analar grade samples of aromatic carbonyl compounds such as benzaldehyde, cinnamaldehyde, 4-methoxy benzaldehyde and aliphatic amine like diethyl amine were used. All solutions were prepared in distilled n-hexane. The ultrasonic velocities of aqueous solutions were measured using ultrasonic interferometer (model F81) supplied by Mittal Enterprises, New Delhi operating at the frequency of 2MHZ with the accuracy of ±0.01 ms-1. The densities(ρ) of solutions were determined using specific gravity bottles of capacity 10ml. The viscosities(η) of the solutions are measured using Oswald's viscometer. The temperature was maintained at 303 ± 0.1K during the measurement of ultrasonic velocity, density, and viscosity values. The acoustical parameters are calculated from U, ρ, and η [7-10] using following relation.

1. Ultrasonic Velocity (U)

The relation used to determine the ultrasonic velocity is given by,

$$U = f\lambda \ ms^{-1}$$

Where, f - Frequency of ultrasonic waves λ - Wave length

2. Adiabatic compressibility (κ)

The intermolecular association or dissociation leads to structural arrangement of the constituent particles. This structural change of the molecule takes place due to the existence of electrostatic field between interacting molecules may affect the adiabatic compressibility which is defined as

$$\kappa = (1/U^2 \rho) \quad kg^{-1} \ ms^2$$

Where

U – Ultrasonic velocity ρ – Density of the solution.

3. Internal pressure (π_i)

On the basis of statistical thermodynamics, Suryanarayana derived an expression for the determination of internal pressure through use of concept of free volum

$$\pi_i = bRT (k\eta/U)^{1/2} (\rho^{2/3}/M_{eff})^{7/6}$$

Where
T – Absolute temperature, ρ- Density, and R is the gas constant, M_{eff} – effective molecular weight.

4. Free Length (L_f)

Jacobson introduced the concept of the free length in liquids. He suggested the following relation to calculate the intermolecular free length.

$$L_f = (K/U \rho^{1/2}) \ m$$

Where U – Ultrasonic velocity of liquid, ρ – Density of liquid, K – Jacobson temperature dependent constant defined as

$$K = (93.875 + 0.345T) X 10^{-8}$$

5. Cohesive energy (CE)

It is usually given as a product of internal pressure (π_i) and molar volume (V_m).

$$CE = \pi_i V_m \ kJ \ mol^{-1}$$

6. Formation constant (K)

The Formation constant is calculated using the relation

$$K = Y/ (b-y)^2 \ dm^3mol^{-1}$$

Where $\mathbf{Y = (a - k^{1/2}b)/ (k - k^{1/2}); k = x/y.}$

x = difference between U_{cal} and U_{obs} at lower concentration ‘a’, y = difference between U_{cal} and U_{obs} at higher concentration ‘b’ and U_{cal} = the ultrasonic velocity of the mixture calculated from the mole fractions of the components using additive principle.

This equation can be used to calculate stability constant values for different combination of concentration 'a' and 'b'

RESULTS AND DISCUSSION

The measured ultrasonic velocities (U), densities (ρ), viscosities (η) and other acoustical parameters such as adiabatic compressibility (κ), free length (L_f), internal pressure(π_i), cohesive energy(CE), formation constant(K) values at 303K is given in the table-1 to 3.

Table-1. Acoustical parameters Values for Benzaldehyde-Diethylamine system

$C/10^{-4}M$	U/ms^{-1}	$\rho/\ kgm^{-3}$	$\eta/10^{-4}\ Nsm^{-2}$	$\kappa/10^{-9}\ kg^{-1}\ ms^{-2}$	π_i atm	L_f , pm	CE, KJ/mole	K/m^{-1}
1	1073.0	641.0	3.9081	1.355	2557.6	72.4	34.8	7.7
2	1053.0	638.6	3.3373	1.412	2379.7	73.9	32.5	8.1
3	1035.0	639.5	4.4560	1.459	2776.1	75.2	37.9	6.3
4	1017.0	640.6	5.0216	1.509	2976.3	76.4	40.6	7.0
5	1083.0	641.8	3.3540	1.328	2360.1	71.7	32.1	7.5
6	1040.0	634.8	3.8703	1.456	2568.0	75.1	35.3	6.7
7	1035.0	630.3	4.9409	1.481	2894.8	75.7	40.1	8.2
8	1040.0	633.4	4.4135	1.459	2738.2	75.2	37.7	8.0
9	1044.0	636.3	3.3253	1.442	2379.5	74.7	32.6	7.8
10	1032.0	634.3	3.3142	1.480	2384.2	75.7	32.8	7.6

Solvent: n-Hexane [Benzaldehyde] = [Diethylamine] Temp: 303K

Table-2. Acoustical parameters Values for Cinnamaldehyde-Diethylamine System

$C/10^{-4}M$	U/ms^{-1}	$\rho/\ kgm^{-3}$	$\eta/10^{-4}\ Nsm^{-2}$	$\kappa/10^{-9}\ kg^{-1}\ ms^{-2}$	π_i atm	L_f , pm	CE, KJ/mole	K/m^{-1}
1	1044.8	641.2	3.9093	1.428	2592.7	74.4	35.3	48.2
2	1032.8	639.2	4.4539	1.467	2777.7	75.3	37.9	49.4
3	1036.8	641.4	3.3519	1.450	2410.5	74.9	32.8	50.2
4	1037.2	633.5	3.8624	1.467	2565.7	75.4	35.4	48.4
5	1044.0	641.1	2.7919	1.431	2191.5	74.4	29.8	49.3
6	1062.0	641.8	4.4720	1.382	2751.9	73.1	37.4	47.6
7	1044.0	638.5	2.7806	1.437	2181.0	74.6	29.8	46.5
8	1032.4	640.9	3.3493	1.464	2413.0	75.3	32.8	46.3
9	1021.2	635.9	4.4309	1.508	2776.0	76.4	38.1	47.2
10	.1036.4	635.7	4.5062	1.465	2778.2	75.3	38.2	48.0

Solvent: n-Hexane [Cinnamaldehyde] = [Diethylamine] Temp: 303K

Table-3. Acoustical parameters Values for 4-methoxy benzaldehyde-Diethylamine System

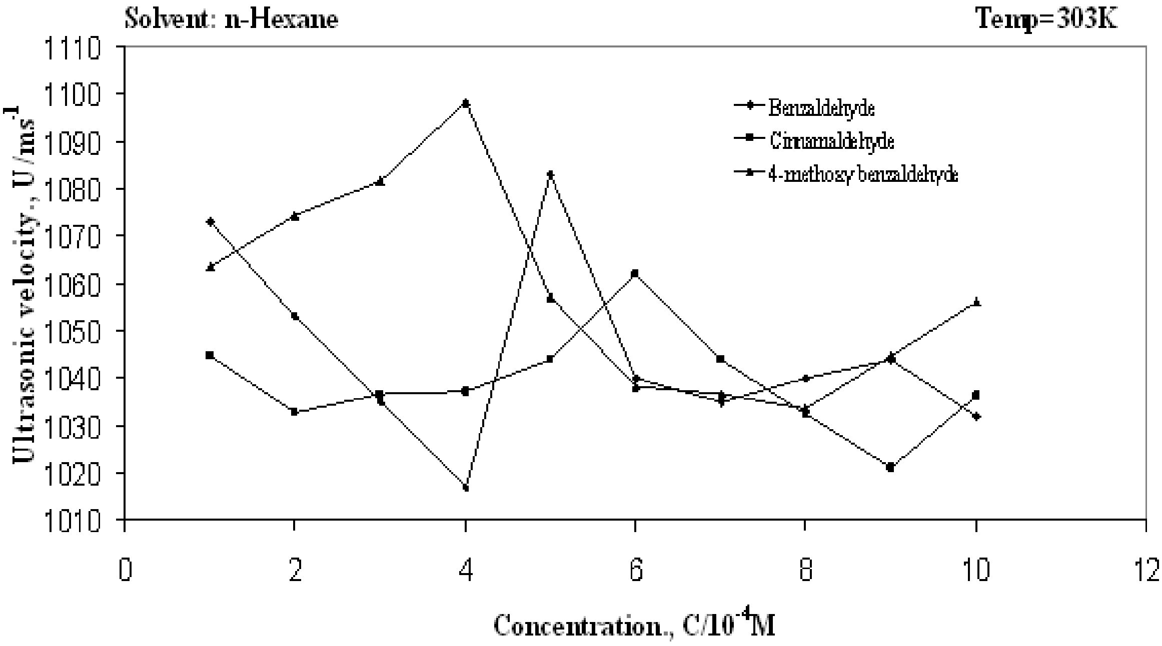
$C/10^{-4}M$	U/ms^{-1}	$\rho/\ kgm^{-3}$	$\eta/10^{-4}\ Nsm^{-2}$	$\kappa/10^{-9}\ kg^{-1}\ ms^{-2}$	π_i atm	L_f , pm	CE, KJ/mole	K/m^{-1}
1	1063.6	640.7	2.7902	1.379	2169.9	73.1	29.5	20.2
2	1074.4	644.3	3.9282	1.344	2571.2	72.1	34.8	21.2
3	1081.6	644.0	3.3655	1.327	2371.2	71.7	32.1	20.6
4	1098.4	639.6	2.7854	1.295	2130.7	70.8	29.0	20.4
5	1057.4	647.8	2.8211	1.381	2204.4	73.1	29.7	21.4
6	1038.4	638.7	3.3378	1.452	2396.6	75.0	32.7	21.6
7	1036.8	641.0	3.9081	1.451	2601.4	74.9	35.4	24.2
8	1033.6	642.0	3.3550	1.458	2416.4	75.1	32.8	20.2
9	1044.8	641.8	2.7950	1.427	2193.2	74.3	29.8	22.2
10	1056.0	646.7	4.5062	1.386	2783.9	73.3	37.5	25.2

Solvent: n-Hexane [4-methoxy benzaldehyde] = [Diethylamine] Temp: 303K

Ultrasonic velocity versus Concentration

The values of ultrasonic velocities for three systems are given in the tables- 1 to 3. Plots of ultrasonic velocity versus concentration for different aldehyde-amine systems are presented in fig .1. It is clearly shows Ultrasonic velocity increases with increase in concentration for all these systems indicates stronger interaction between these aldehydes and amine.

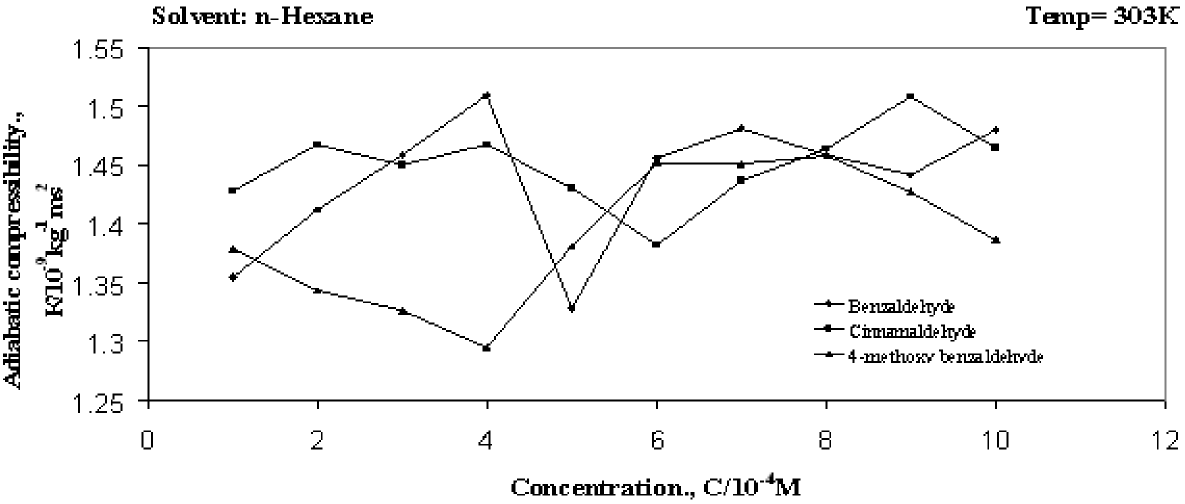
Fig. 1 Plots of Ultrasonic velocity versus Concentration



Adiabatic compressibility versus Concentration

The values of adiabatic compressibility for three systems are given in the tables- 1 to 3. Plots of adiabatic compressibility versus concentration for different aldehyde-amine systems are presented in fig .2. It shows adiabatic compressibility decreases with increase in concentration which a reverse trend to that of ultrasonic velocity. The decrease in adiabatic compressibility suggests that the three aldehyde form donor-acceptor complexes with the amine.

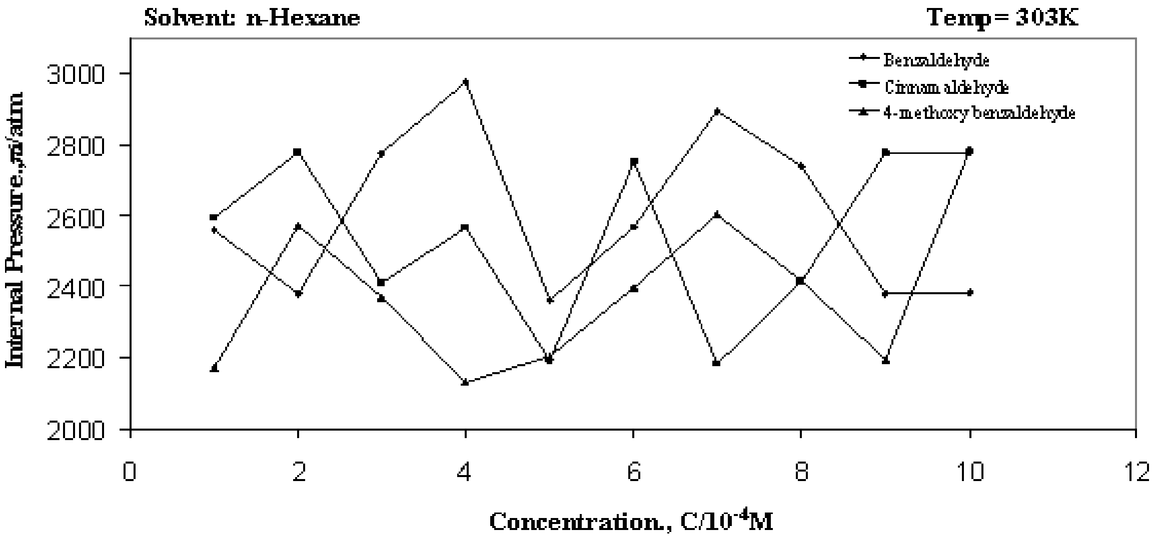
Fig. 2 Plots of adiabatic compressibility versus concentration



Internal pressure versus Concentration

Internal pressure (π_i) values are also presented for three systems in Tables- 1 to 3. Fig. 3 contain plots of internal pressure versus concentration. It may be referred that internal pressure increases with increase in concentration indicating that extent of complexation increases with concentration.

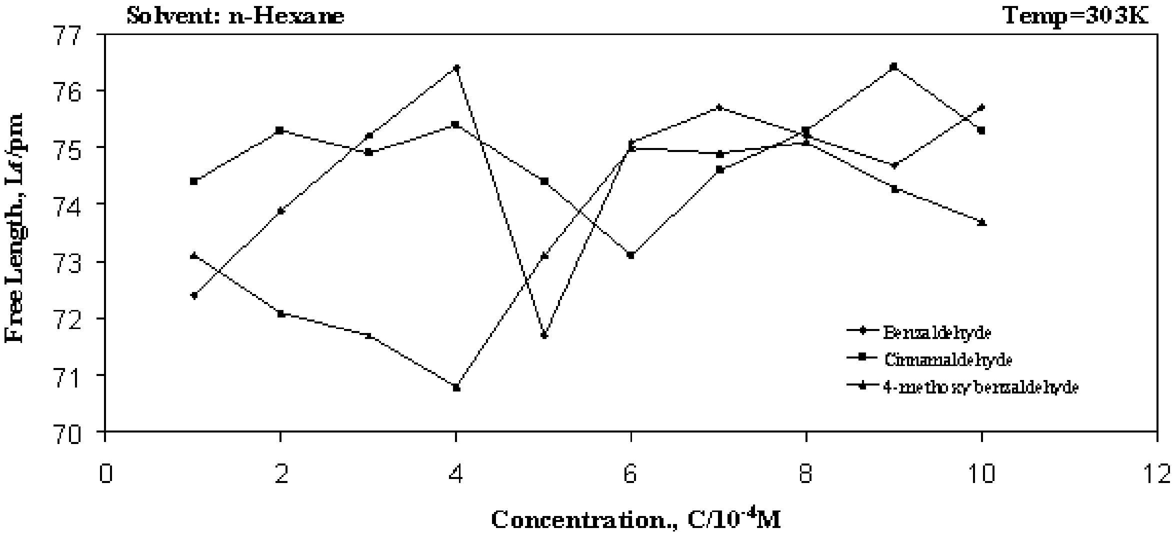
Fig. 3 plots of internal pressure versus concentration



Free length versus concentration

The values of Free length for three systems are given in the tables- 1 to 3. Plots of adiabatic compressibility versus concentration for different aldehyde-amine systems are presented in fig .4. It shows gradual decrease in free length with increase in concentration.

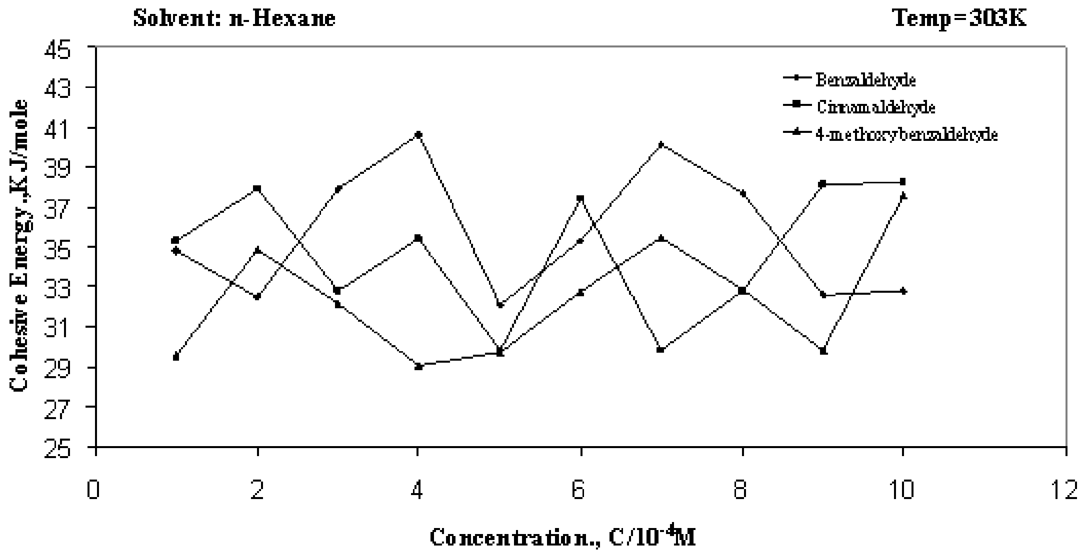
Fig. 4 plots of free length versus concentration



Cohesive energy versus concentration

Cohesive energy (CE) in a liquid mixture is a measure of interaction between the molecules. Cohesive energy values are given in tables- 1 to 3. Fig. 5 shows the plot of cohesive energy against various concentrations. The variations in cohesive energy values with increase in concentration suggest that stronger molecular interactions are present in these systems.

Fig. 5 Plots of cohesive energy versus concentration



Formation constant

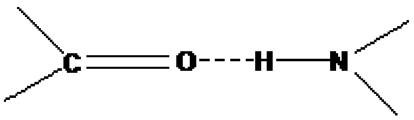
The formation constant values are tabulated in Tables 1,2 and 3. The formation constant (K) can be used to compare the stability of the charge transfer complexes. The mean values of formation constants are given in Table 4.

Table- 4

System	Mean K value
Benzaldehyde - diethylamine	7.5
Cinnamaldehyde - diethylamine	43.1
4-methoxy benzaldehyde - diethylamine	21.7

The trend in the values of K indicates that the stability of aldehyde - amine complex depends on the structure of acceptors as well as donors. Fig. 6 shows the oxygen atom may form charge transfer complex with amine through strong intermolecular hydrogen bond.

Fig. 6



If the complexation is through oxygen, then electron releasing group in the phenyl ring of aromatic aldehyde would favour the complex formation and electron withdrawing substituent would retard the complex formation. The mean value of formation constant of cinnamaldehyde is greater than benzaldehye. Cinnamaldehyde forms relatively more stable complex with diethylamine than benzaldehyde. This is due to extension of conjugation with carbonyl double bond. This trend in K values is in the same order as the electron releasing capacity of substituent in aromatic aldehyde. It may be pointed that methoxy group releases electrons by mesomeric effect and hence 4-methoxy benzaldehyde forms more stable complex than benzaldehyde.

CONCLUSION

The results establish that aldehyde molecule forms donor - acceptor complex with diethylamine. The formation constants of these complexes indicate the presence of electron releasing group in donor molecule increases the tendency of complex formation. Thus, the formation constant value of benzaldehyde -

diethylamine complex is less than that of 4-methoxy benzaldehyde - diethylamine complex. Due to the extension of conjugation with carbonyl double bond, the cinnamaldehyde1 - diethylamine complex has higher formation constant than 4-methoxy benzaldehyde - diethylamine and benzaldehyde-diethylamine complex.

Acknowledgement
Author is thankful to Department of chemistry, Presidency college for encouraging the work.

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