



Ultrasonic Studies on Molecular Interaction of Aniline, N-Methyl Aniline, N, N-Dimethyl Aniline and Cinnamaldehyde in N-Hexane Solution at 303K

S. Srinivasan

Department of Chemistry, Presidency College, Chennai-600 005, Tamilnadu, India.

S. Chidambar
Avinayagam

Department of Chemistry, Presidency College, Chennai-600 005, Tamilnadu, India.

B. S. Santhi

Department of Chemistry, Presidency College, Chennai-600 005, Tamilnadu, India.

ABSTRACT

The ultrasonic velocity (v), density (ρ) and viscosity (η) of ternary liquid mixtures contain three aromatic amine compounds such as aniline, N-methyl aniline, N,N-dimethylaniline with cinnamaldehyde in n-hexane at 303K a wide range concentration ($1 \times 10^{-4}M$ to $1 \times 10^{-3}M$). From the experimental data of various acoustical parameters such as adiabatic compressibility (κ), free length (L_f), internal pressure (π), cohesive energy (CE), formation constant (K) have been computed using standard relation. The excess values of these parameters are also evaluated for aldehyde and amine in polar medium like n-hexane have been investigated by ultrasonic measured. The result is interpreted in terms of molecular interaction such as dipole – dipole interaction through hydrogen bonding between components of mixtures. These values indicate complex formation and ion-solvent interaction between aromatic amine compounds and cinnamaldehyde in n-hexane medium.

KEYWORDS : Ultrasonic velocity, ultrasonic density, molecular interaction, hydrogen bonding.

INTRODUCTION

The study of physicochemical behaviour and molecular interaction in liquid mixtures are of considerable importance and a number of experimental techniques have been used to investigate the interactions between the component of ternary liquid mixtures 1-5. In recent years, ultrasonic technique has become a powerful tool for studying the molecular behaviour of liquid mixtures. Ultrasonic waves have been used by many scientists to investigate the nature of molecular interaction and physicochemical behaviour of pure, binary and ternary liquid mixtures 5. Molecular interaction studies can be carried out by both spectroscopic and spectroscopic techniques 8-9. Many studies have been carried out in ternary solution, since the ultrasonic procedure favours for good yield, short reaction time, mild condition and higher purity of the product 2. Carbonyl compounds contain polar carbonyl group in which electron rich oxygen can function as electron donor. Amines behave as Lewis bases since they contain nitrogen as the basic centre with lone pair of electrons and has hydrogen as acceptor. Aromatic amine also contain electrons and hence they can function as both n and p electron donors. Thus donor – acceptor complexes will be formed between amine and aldehyde 1-5. It has been known that amine interact with aldehyde by dipole – dipole interaction formation of new hydrogen bonds or hetero-associates and dispersion forces 6-8. Ultrasonic investigations were carried out to detect charge transfer complexes between carbonyl compounds and chloroform the stability constants of these complexes were calculated using modified Bhat equation proposed by Kannappan 1-3. In the present investigation, ultrasonic velocity, density and viscosity for solutions containing equimolar concentrations of cinnamaldehyde (donor), three aromatic amine (acceptor) in n-hexane at 303K. The following three ternary systems and studied at 303K.

EXPERIMENTAL SECTION

Anal grade samples of aromatic amine compounds such as aniline, N-methyl aniline, N,N-dimethyl aniline and cinnamaldehyde were used. The solvent n-hexane was distilled before use. All solutions were prepared in distilled n-hexane 5-7. The ultrasonic velocities of the above liquids and their mixtures were measured using multi-frequency ultrasonic interferometer at a frequency of 2MHz. The accuracy in the measurement of ultrasonic velocity was with in ± 0.01 ms⁻¹. The densities of these solutions were determined accurately using 10ml specific gravity bottle and an electronic balance precisely with in ± 0.1 mg accuracy 8. Ostwald's viscometer was used to measure the viscosities of the solutions 1-3. The temperature was maintained constant at 303.0 ± 0.1 K. The acoustical parameters are calculated

from ultrasonic velocity, density and viscosity using following reaction.

ULTRASONIC VELOCITY (U)

The ultrasonic velocity can be determined by several methods. Among them, the interferometer method gives reliable and precise values. The expression used to determine the ultrasonic velocity is given by,

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

Where, f value is 2×10^6 Hertz

ADIABATIC COMPRESSIBILITY (κ)

Singh and Kalsh showed that the adiabatic compressibility should be independent of temperature and pressure for unassociated and weakly associated molecules. It also determines the orientation of the solvent molecules around the liquid molecules. This structural change of the molecule takes place due to the existence of electrostatic field between interacting molecules may affect the adiabatic compressibility which defined as,

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

ABSORPTION COEFFICIENT (α/f^2)

It can be calculated from the viscosity using the relation

$$\alpha/f^2 = 8\pi^2\eta/3\rho U^3 \text{ Nps}^2\text{m}^{-1}$$

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.

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

COHESIVE ENERGY (CE)

The concept of molar cohesive energy has been used by several researchers for comparing the interactions in liquid mixtures. It is usually given as a product of internal pressure and molar volume

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

MOLECULAR INTERACTION PARAMETER (χ_{12})

The molecular interaction parameter can be computed using the following formula

$$\chi_{12} = (U_{exp}/U_{ideal}) - 1$$

RESULTS AND DISCUSSION

The values of ultrasonic velocity (U), density (ρ), viscosity (η) at different concentration of cinnamaldehyde with aniline, N-methyl aniline, N,N- dimethyl aniline in n-hexane were measured at 303K. Acoustical parameters such as adiabatic compressibility, free length, internal pressure, cohesive energy, molecular interaction parameter and formation constant have been measured at 303K is given the table 1 to 3

TABLE 1.1
Acoustical parameters Values for Cinnamaldehyde -Aniline System

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

Concentration C/10-4M	Ultrasonic velocity	Density	Molecular interaction parameter	Adiabatic compressibility	Cohesive Energy	Free volume	Internal pressure	Acoustic impedance	Free length
1	1060.1	650.1	0.15	1.37	30.53	6.02	2273.1	6.89	7.28
2	1003.8	645.0	-10.1	1.54	31.13	5.72	2299.9	6.47	7.72
3	1060.0	637.7	-0.20	1.40	31.20	5.75	2278.8	6.76	7.35
4	1144.1	648.7	16.7	1.18	30.12	6.29	2237.7	7.42	6.75
5	1135.8	649.7	15.0	1.19	30.43	6.09	2263.6	7.38	6.79
6	1192.0	655.6	26.6	1.07	29.99	6.31	2250.9	7.81	6.45
7	1143.7	650.9	16.5	1.17	30.37	6.12	2263.1	7.44	6.74
8	1147.8	653.6	17.3	1.16	30.67	5.92	2241.8	7.50	6.70

TABLE 2.1
Acoustical parameters Values for Cinnamaldehyde - N-methylaniline system

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

Concentration C/10-4M	Ultrasonic velocity	Density	Molecular interaction parameter	Adiabatic compressibility	Cohesive Energy	Free volume	Internal pressure	Acoustic impedance	Free length
1	1127.9	654.2	6.56	1.20	30.23	6.16	2265.5	7.38	6.82
2	1124.1	650.9	1.27	1.22	30.42	6.08	2267.9	7.32	6.86
3	1052.0	644.9	-1.30	1.40	32.69	4.95	2413.7	6.78	7.36
4	1015.8	654.3	-8.02	1.48	34.09	4.30	2554.1	6.65	7.57
5	1060.0	668.4	0.13	1.33	30.89	5.65	2363.7	7.09	7.18
6	1035.9	647.6	-4.41	1.44	31.01	5.45	2343.6	6.71	7.40
7	1035.8	647.3	-4.47	1.44	31.57	5.47	2339.4	6.70	7.46
8	1064.0	648.8	0.76	1.36	31.67	5.41	2351.9	6.90	7.26

TABLE 3.1
Acoustical parameters Values for Cinnamaldehyde -N, N-Dimethylaniline system

Solvent: n-Hexane
[Cinnamaldehyde] = [N,N-Dimethylaniline]
Temp: 303K

Concentration C/10-4M	Ultrasonic velocity	Density	Molecular interaction parameter	Adiabatic compressibility	Cohesive Energy	Free volume	Internal pressure	Acoustic impedance	Free length
1	1028.1	646.8	-2.87	1.46	33.87	4.43	2509.2	6.65	7.52
2	1088.1	639.0	-5.63	1.32	30.91	5.90	2261.9	6.95	7.15
3	1032.1	647.9	-5.00	1.45	33.81	4.45	2508.6	6.69	7.49
4	1035.9	655.3	-4.34	1.42	32.27	5.06	2420.9	6.79	7.42
5	1084.0	647.9	-4.71	1.31	31.36	5.58	2326.1	7.02	7.13
6	1040.3	650.8	-3.60	1.42	32.16	5.15	2395.8	6.77	7.41
7	1068.2	647.7	-1.60	1.35	31.18	5.68	2311.1	6.92	7.24
8	1048.0	648.5	-2.24	1.40	31.61	5.44	2345.7	6.80	7.37

Ultrasonic velocity Vs concentration

The values of ultrasonic velocity for three systems are given in the tables 1.1, 2.1 and 3.1. Plots of ultrasonic velocity versus concentration for cinnamaldehyde-aniline systems are presented in fig 1. Ultrasonic velocity increases with increase in concentration for all these systems indicates stronger interaction between these aldehyde and amines.

Adiabatic compressibility Vs concentration

Adiabatic compressibility (κ) values were calculated for three systems and presented in tables 1.1, 2.1 and 3.1.

Plots of adiabatic compressibility versus concentration for different aldehyde and amine systems are presented in fig 2. Adiabatic compressibility decreases with increase in concentration which a reverse trend to that of ultrasonic velocity. The decrease in adiabatic compressibility suggests that aldehyde forms donor-acceptor complexes with the amines.

Internal pressure Vs concentration

Internal pressure (π) values are also presented for three systems in tables 1.1, 2.1, 3.1. Figs 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.

Free length Vs concentration

The values of free length for three systems are given in the table 1.1, 2.1, 3.1. Plots of free length versus concentration for different aldehyde - amine systems are presented in fig 4. It shows gradual decrease in free length with increase.

Cohesive energy Vs concentration

Cohesive energy (CE) in a liquid mixture is a measure of interaction between the molecules. Cohesive energy values are given in tables 1.1, 2.1 and 3.1. 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.

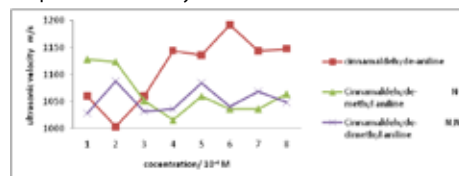


Fig 1 Ultrasonic velocity Vs Concentration

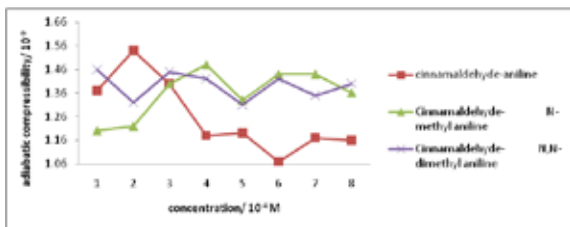


Fig 2 Plot of Adiabatic compressibility vs Concentration

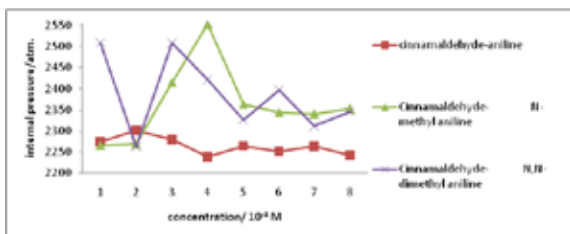


Fig 3 Plot of Internal Pressure vs Concentration

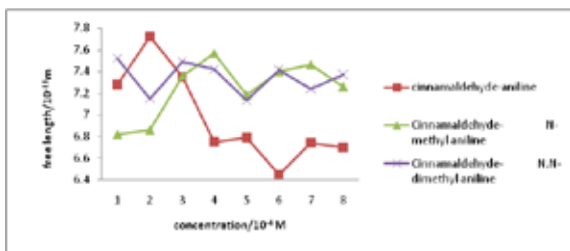


Fig 4 Plot of free length Vs concentration

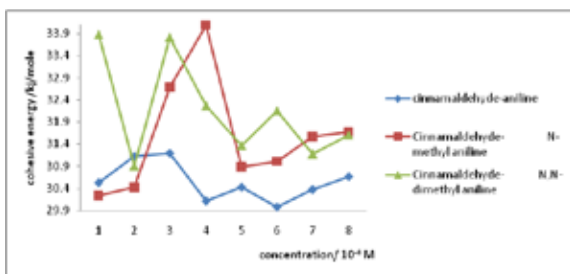


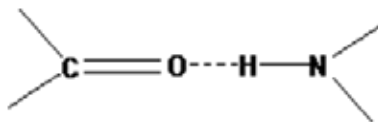
Fig 5 Plot of Cohesive energy Vs Concentration

Formation constant

The formation constant values are tabulated in Tables 1.1, 2.1 and 3.1. 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
Cinnamaldehyde - N-methyl aniline	196.3
Cinnamaldehyde- aniline	207.2
Cinnamaldehyde - N,N-dimethylaniline	286.7



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.

If the complexation is through oxygen, the 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 for N,N-dimethylaniline. Cinnamaldehyde forms relatively more stable complex with N,N-dimethylaniline. Due to the electron releasing methyl groups in N,N-dimethyl aniline, the complex formed by cinnamaldehyde – N,N- dimethyl aniline has a higher formation constant.

Conclusion

The result establish that amine molecule forms donor – acceptor complex with cinnamaldehyde. The formation constants of these complexes indicate the presence of electron releasing group in acceptor molecules increases the tendency of complex formation. Thus, the formation constant value of cinnamaldehyde – N-methyl aniline complex is less than that of cinnamaldehyde – aniline complex. Also, the formation constant value of cinnamaldehyde – N,N- dimethyl aniline complex is higher than that of cinnamaldehyde – aniline complex. Due to the electron releasing methyl groups in N,N- dimethyl aniline, the complex formed by cinnamaldehyde – N,N-dimethyl aniline has a higher formation constant than cinnamaldehyde – aniline and cinnamaldehyde – N-methyl aniline complex.

REFERENCES

1.Jayakumar,S,Karunanidhi. N &kannappan. V indian Jpure&Applphy ,34 (1996) 761. | 2.Marwein .B.L and Bhatt.S.N., Acustica , 58, 1985, 243. | 3.V.Kannappan ; S Xavier Jesu Raja ; and R.Jayasanthi Ind. Journal of Pure Applied Physics, (2003), 41, 690. | 4 .S.chidambaravinayagam, Ph.DThesis , University of madras, India , 2007 | 5. B SSanthi, Ph.D. Thesis, University of madras , India , 2008. | 6 .V.Kannappan and R.Jayasanthi. J.Acoust.soc.Ind., 2001, 29,192. | 7 .S.Rajesh, S.Chidambaravinayagam, B S Santhi, | J.Chem. Pharm . Res., 2013, 5 (1); 283-289. | 8 .D.Ubagaramary ,P.Neeraja Issn : 2278-5736 volume 2 issue 5 (Nov , Dec.2012) | 9 .B.L.Marwein; and S N Bhatt, ThermodynamicaActa., 1987,118,277. | 10 .V.kannappan ;R.jayasanthi ; EJP Malar .JPhyChem Liq. 2000, 40, 133.