

## Ultrasonic studies on charge transfer complexes of certain aldehydes with benzylamine and cyclohexylamine as donors in *n*-hexane at 303K

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The ultrasonic velocities ( $U$ ), densities ( $\rho$ ), and viscosities ( $\eta$ ) were measured for solutions containing equimolar concentrations of eight aldehydes namely, benzaldehyde, *o*-chlorobenzaldehyde, anisaldehyde, *p*-tolualdehyde, cinnamaldehyde, crotonaldehyde, propionaldehyde, and valeraldehyde as acceptors, benzylamine and cyclohexylamine as donors in *n*-hexane at 303K. Acoustical parameters such as adiabatic compressibility ( $\beta$ ), free length ( $L_f$ ), viscous relaxation time ( $\tau$ ), molecular interaction parameter ( $\chi_u$ ) have been computed. These values indicate the formation of charge transfer complexes between aldehydes and amines. Formation constant ( $K$ ) values of the complexes have been evaluated using a modified Bhat equation proposed by Kannappan. The constant values of free energy of activation ( $\Delta G^\ddagger$ ) and relaxation time indicate the formation of similar type of complexes in these systems. However, the variation in free energy of formation ( $\Delta G$ ) values suggests that their thermodynamic stability depends on the structure of donor and acceptor.

**Keywords:** Charge transfer complexes, Aldehydes, Primary amines, Stability constant, Ultrasonic method

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### 1 Introduction

Carbonyl group is a part of several biologically important molecules such as proteins, lipids and hormones. This group can interact with basic group like amino group to form a complex and influence the properties of such compounds<sup>1</sup>. Ultrasonic velocity measurements have been successfully employed to detect and assess weak and strong molecular interactions present in binary<sup>2,3</sup> and ternary<sup>4,5</sup> liquid mixtures. These studies can also be used to determine the extent of complexation and calculate the stability constants of such complexes<sup>6,7</sup>. The formation constant values of charge transfer complexes of eight aldehydes(acceptors) and two primary amines, benzylamine and cyclohexylamine (donors) in *n*-hexane at 303K, have been determined.

### 2 Experimental Details

The acceptors, benzaldehyde (b.pt 178°C), *o*-chlorobenzaldehyde (b.pt 209°C), anisaldehyde(b.pt 248°C), *p*-tolualdehyde (b.pt 202°C), cinnamaldehyde (b.pt 76.1°C), crotonaldehyde (b.pt 104°C), propionaldehyde (b.pt 49°C), valeraldehyde (b.pt 103°C) and the two amines benzylamine (b.pt 185°C) and cyclohexylamine (b.pt 135°C) were AnalaR samples. The solvent *n*-hexane (b.pt 69°C) was laboratory reagent

and was purified by distillation before use. It was dried over sodium wire and stored in air tight amber coloured dry bottle. The ultrasonic velocities of pure liquids and their mixtures were measured by using ultrasonic interferometer working at a frequency of 2 MHz (Mittal enterprises model F-81) (Accuracy  $\pm 0.1 \text{ ms}^{-1}$ ). The densities ( $\rho$ ) of these solutions were determined by using specific gravity bottles of capacity 10 mL. For viscosity measurements, Ostwald's viscometer was employed. The accuracy in the measurement of density was of the order of  $\pm 0.1 \text{ kgm}^{-3}$  and of viscosity was 0.1%. Acoustical parameters such as adiabatic compressibility ( $\beta$ ), free length ( $L_f$ ), viscous relaxation time ( $\tau$ ) and molecular interaction parameter ( $\chi_u$ ) were calculated using standard equations<sup>2,8-11</sup>. The formation constant values are calculated using modified Bhat equation proposed by Kannappan<sup>12,13</sup>.

$$K = Y/(b-y)^2$$

where  $Y = (a-k^{1/2} b) / (k-k^{1/2})$  in which  $k = x/y$ ,  $K$  is the formation constant;  $x$  the difference between  $U_{\text{cal}}$  and  $U_{\text{obs}}$  at lower concentration  $a$ ;  $y$  the difference between  $U_{\text{cal}}$  and  $U_{\text{obs}}$  at higher concentration  $b$  and  $U_{\text{cal}}$  is the ultrasonic velocity of the mixture calculated from the

mole fraction of the components using additive principle.

### 3 Results and Discussion

Amines behave as Lewis bases since they contain nitrogen as the basic centre with lone pair of electrons. Aromatic amines also contain  $\pi$ -electrons and hence they can function as both  $n$  and  $\pi$ -electron donors. Carbonyl compounds contain polar group in which electron deficient carbon can function as electrophile. Thus, donor-acceptor complexes are expected between amines and aldehydes. There are optical and ultrasonic methods to detect such complexes. In this paper, we refer the ultrasonic method to detect these complexes. The stability constants ( $K$ ) are determined from ultrasonic velocities and the trend in  $K$  values is explained based on the structure of the carbonyl compounds. Two structurally different donors are used to study the influence of donor structure on the formation of this type of complexes.

The measured values of ultrasonic velocity, density and viscosity at equimolar concentration of aldehydes (acceptors) and benzylamine and cyclohexylamine (donors) in *n*-hexane at 303 K are given in Tables 1-3. It is seen from the Table 1 that ultrasonic velocity increases with the concentrations of both amine and aldehyde for all the sixteen systems. The trend in ultrasonic velocity values in these systems indicates stronger interactions between aromatic aldehydes and amines. Thus, the complexation is concentration dependent. The viscosities are determined for these systems at various concentrations of the donor-acceptor mixtures (Table 3). Increase in viscosity with concentration in all the systems suggests that the extent of complexation increases with increase in concentration.

Adiabatic compressibility ( $\beta$ ) values are calculated and Figs 1 and 2 contain plots of adiabatic compressibility versus concentration for the sixteen systems. Adiabatic compressibility exhibits reverse trend to that of ultrasonic velocity. The decrease in adiabatic compressibility with concentration suggests that the interaction between the donor and acceptor is concentration dependent. This is also evidenced by the gradual decrease in free length (Figs 3 and 4) with concentration in these systems.

Molecular interaction parameter ( $\chi_u$ ) are calculated and presented in Figs (5 and 6). Molecular interaction parameter ( $\chi_u$ ) is indicative of the extent of deviation

from ideal behaviour due to complexation. This parameter can be used to assess the strength of molecular attraction between the donor and acceptor in non-polar medium. These values increase with concentration indicating that extent of complexation is concentration dependant and it increases with concentration. The formation constant ( $K$ ) can be used to compare stabilities of the charge transfer complexes<sup>12,13</sup>. The formation constant values are calculated using modified Bhat equation proposed by Kannappan and the values are presented in Table 4.

The trend in the values of  $K$  indicates that the stability of aldehyde-amine complex depends on the micro structure of donor and acceptor. Generally, the aromatic aldehydes form less stable complexes than aliphatic aldehydes as evident from the  $K$  values. Thus, the presence of phenyl ring in the aldehyde decreases the positive charge on carbonyl carbon due to mesomeric effect. Among the aromatic aldehydes, cinnamaldehyde has the highest  $K$  value indicating that cinnamaldehyde forms relatively more stable complex with amines than other aromatic aldehydes. Similar trend was also observed on the charge transfer complexes of carbonyl compounds and chloroform in *n*-hexane by Mahendran.<sup>13</sup> In the case of aromatic aldehydes, the stability of aldehyde amine complex increases in the order

Cinnamaldehyde > anisaldehyde > *p*-tolualdehyde > *o*-chlorobenzaldehyde > benzaldehyde

This trend in  $K$  values is of the same order as the electron releasing capacity of substituent in aromatic aldehydes. It may be pointed out that methoxy group releases electron better than methyl group. In the case of *o*-chlorobenzaldehyde, the chloro substituent exerts both mesomeric and inductive effects in opposite directions. However, mesomeric effect dominates over inductive effect. Therefore, it forms a more stable complex with amine donor than benzaldehyde but less stable complex than those of anisaldehyde and *p*-tolualdehyde. In the case of aliphatic aldehydes the  $K$  value is maximum in crotonaldehyde due to the extension of conjugation in the molecule. Among saturated aliphatic aldehydes, the stability increases with increase in length of the alkyl chain. Thus, valeraldehyde forms more stable complex with amine than propionaldehyde.

The free energy of formation ( $\Delta G$ ), free energy of activation ( $\Delta G^\ddagger$ ) and relaxation time ( $\tau$ ) values are computed for all the charge transfer complexes

Table 1—Ultrasonic velocity values ( $\text{ms}^{-1}$ ) of aldehydes with benzylamine and cyclohexylamine in *n*-hexane at 303 K

S. No	Donor Conc. (M)*	Benzylamine						Cyclohexylamine									
		BEA	OCA	ANA	TUA	CNA	CRA	PRA	VLA	BEA	OCA	ANA	TUA	CNA	CRA	PRA	VLA
1	0.03	1071.26	1077.20	1078.67	1080.80	1078.90	1072.47	1069.44	1077.30	1078.13	1070.93	1074.80	1072.40	1078.33	1086.53	1066.40	1080.40
2	0.06	1072.24	1078.26	1079.60	1081.04	1079.80	1073.92	1070.24	1078.30	1079.60	1071.92	1076.16	1074.40	1079.33	1087.20	1066.88	1081.30
3	0.09	1074.67	1079.44	1081.60	1082.00	1079.76	1074.96	1071.80	1078.70	1081.90	1073.20	1079.70	1076.20	1081.87	1088.32	1067.40	1082.20
4	0.12	1075.80	1080.50	1082.72	1083.84	1080.27	1076.00	1072.64	1079.52	1082.40	1075.68	1081.60	1078.20	1084.08	1088.80	1068.93	1084.08
5	0.15	1080.40	1082.13	1086.08	1084.50	1087.20	1076.70	1073.44	1080.24	1083.60	1077.60	1082.67	1080.00	1084.53	1089.80	1069.84	1084.32
6	0.18	1082.24	1084.56	1090.24	1085.80	1090.08	1077.90	1074.52	1082.88	1085.60	1079.00	1086.08	1083.00	1086.50	1091.76	1070.60	1085.92
7	0.21	1084.08	1086.80	1091.84	1087.60	1092.00	1078.80	1076.16	1085.70	1086.96	1080.66	1088.16	1086.60	1092.40	1092.20	1071.70	1087.40
8	0.24	1085.60	1089.70	1094.64	1089.04	1093.53	1080.80	1078.10	1086.93	1088.96	1081.60	1090.56	1089.60	1094.00	1094.40	1072.80	1087.93
9	0.27	1089.46	1092.08	1096.96	1090.00	1095.76	1082.00	1080.00	1087.08	1091.36	1082.80	1091.93	1093.30	1095.27	1095.46	1073.50	1090.40
10	0.3	1093.00	1096.88	1100.00	1093.00	1098.20	1086.16	1082.00	1088.92	1095.20	1085.50	1093.52	1096.00	1097.52	1096.70	1074.70	1091.84

BEA=benzaldehyde; OCA=o-chlorobenzaldehyde; ANA=anisaldehyde; TUA=p-tolualdehyde; CNA=cinnamaldehyde; CRA=crotonaldehyde; PRA=propionaldehyde; VLA=valeraldehyde  
 \*Equimolar conc of donor and acceptor

Table 2—Density values ( $\text{kg m}^{-3}$ ) of aldehydes with benzylamine and cyclohexylamine in *n*-hexane at 303 K

S. No.	Conc. (M)	Benzylamine						Cyclohexylamine									
		BEA	OCA	ANA	TUA	CNA	CRA	PRA	VLA	BEA	OCA	ANA	TUA	CNA	CRA	PRA	VLA
1	0.03	665.6	635.3	654.7	647.6	666.3	665.4	643.8	652.1	657.3	634.8	665.4	651.4	655.8	642.4	644.9	654.4
2	0.06	667.1	639.2	656.2	650.4	668.1	666.0	646.5	653.3	658.7	637.9	667.8	654.0	657.1	643.7	646.0	656.2
3	0.09	669.6	643.4	658.5	652.9	670.3	668.5	649.6	654.4	659.8	640.8	670.3	656.0	658.0	646.0	647.0	658.4
4	0.12	671.5	646.1	661.6	654.3	672.1	669.9	652.3	655.3	660.8	643.3	672.2	659.0	661.4	648.7	648.0	660.0
5	0.15	673.8	648.9	663.9	655.7	675.1	671.2	654.5	656.1	662.8	646.1	674.9	661.8	662.7	651.3	649.1	661.7
6	0.18	675.9	653.7	666.3	657.1	678.2	673.2	656.2	657.3	664.7	649.2	676.7	664.2	664.3	654.0	650.3	663.8
7	0.21	678.1	655.9	668.0	658.9	682.0	674.9	657.6	658.2	666.8	652.3	679.5	667.3	665.8	656.1	651.6	665.0
8	0.24	681.2	659.1	671.4	660.2	685.1	676.2	659.0	659.3	668.6	655.2	683.5	669.5	667.1	659.2	653.4	667.0
9	0.27	684.1	661.5	673.7	662.4	688.6	678.8	660.8	660.4	671.1	658.2	686.2	671.4	668.6	661.5	655.0	669.1
10	0.3	687.1	663.9	676.1	664.1	690.3	680.8	662.9	661.7	674.0	662.0	689.1	673.7	670.3	663.7	656.4	672.0

Table 3—Viscosity values (cP) of aldehydes with benzylamine and cyclohexylamine in *n*-hexane at 303 K

S. No	Conc. (M)	Benzylamine						Cyclohexylamine									
		BEA	OCA	ANA	TUA	CNA	CRA	PRA	VLA	BEA	OCA	ANA	TUA	CNA	CRA	PRA	VLA
1	0.03	0.317	0.303	0.312	0.311	0.316	0.323	0.306	0.312	0.314	0.305	0.315	0.310	0.315	0.306	0.307	0.313
2	0.06	0.318	0.306	0.314	0.313	0.318	0.324	0.308	0.314	0.317	0.307	0.317	0.312	0.317	0.308	0.308	0.314
3	0.09	0.320	0.308	0.316	0.315	0.320	0.325	0.310	0.316	0.319	0.309	0.319	0.314	0.319	0.310	0.309	0.316
4	0.12	0.322	0.310	0.317	0.316	0.322	0.327	0.312	0.317	0.319	0.311	0.321	0.316	0.321	0.312	0.310	0.318
5	0.15	0.324	0.312	0.317	0.318	0.325	0.329	0.314	0.317	0.321	0.313	0.323	0.318	0.322	0.314	0.312	0.320
6	0.18	0.326	0.315	0.318	0.319	0.327	0.332	0.317	0.318	0.322	0.315	0.325	0.320	0.323	0.317	0.313	0.322
7	0.21	0.328	0.317	0.320	0.321	0.330	0.334	0.318	0.320	0.324	0.317	0.328	0.323	0.325	0.318	0.315	0.323
8	0.24	0.330	0.319	0.321	0.322	0.332	0.335	0.320	0.321	0.325	0.319	0.331	0.325	0.326	0.321	0.316	0.325
9	0.27	0.332	0.321	0.322	0.324	0.334	0.337	0.322	0.322	0.327	0.321	0.333	0.327	0.327	0.323	0.318	0.327
10	0.3	0.334	0.323	0.323	0.326	0.336	0.339	0.324	0.323	0.329	0.324	0.336	0.329	0.328	0.324	0.319	0.329

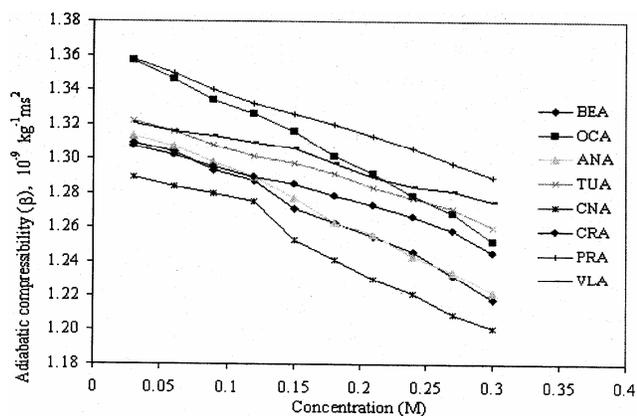


Fig. 1—Plots of adiabatic compressibility versus concentration of aldehydes-benzylamine

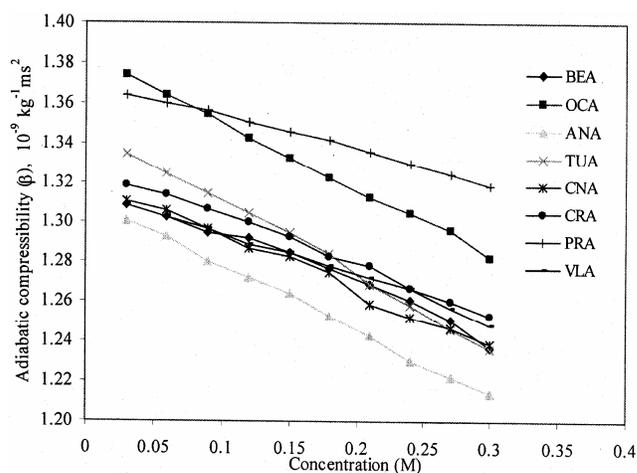


Fig. 2—Plots of adiabatic compressibility versus concentration of aldehydes-cyclohexylamine

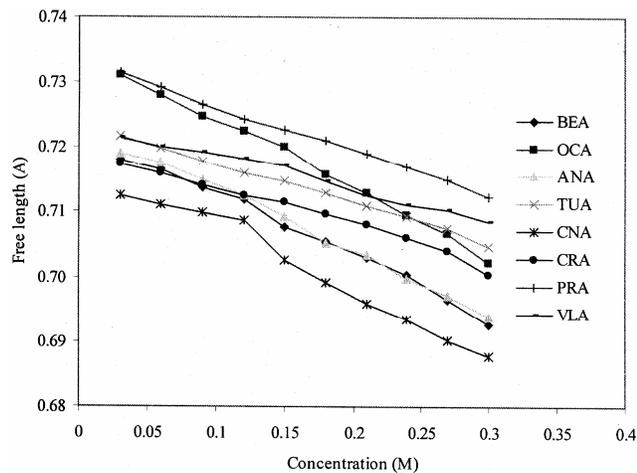


Fig. 3—Plots of free length versus concentration of aldehydes-benzylamine

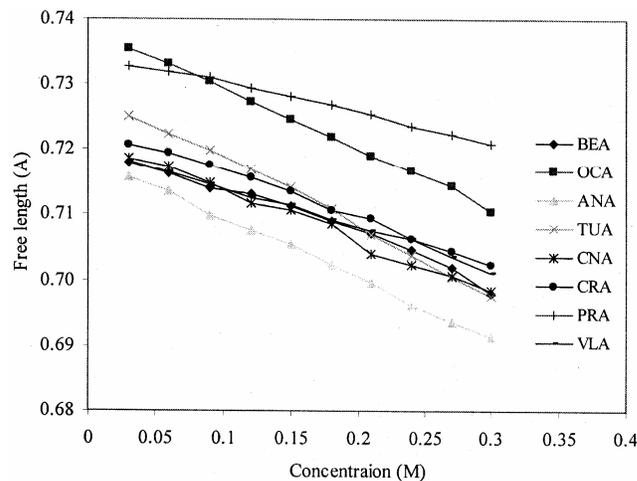


Fig. 4—Plots of free length versus concentration of aldehydes-cyclohexylamine

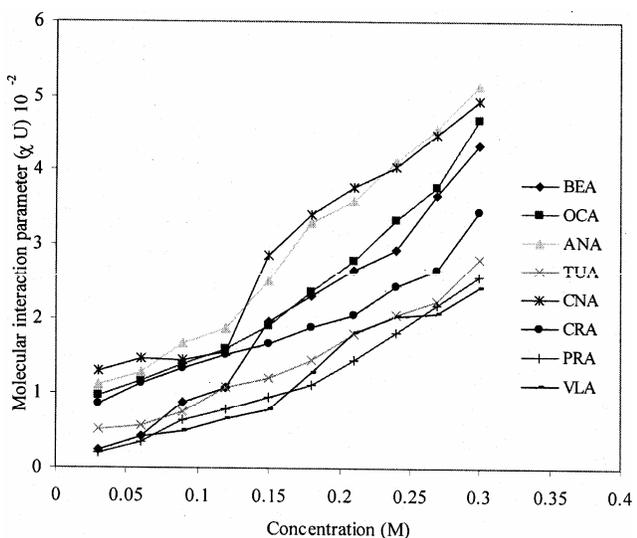


Fig. 5—Plots of molecular interaction parameter versus concentration of aldehydes-benzylamine

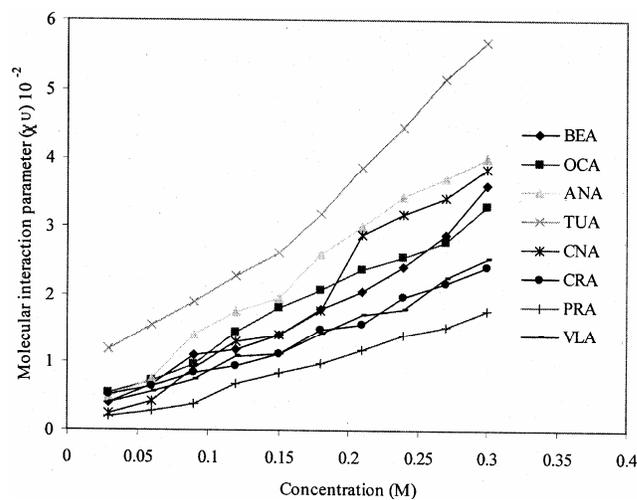


Fig. 6—Plots of molecular interaction parameter versus concentration of aldehydes-cyclohexylamine

Table 4—Formation constant, free energy of formation, free energy of activation, viscous relaxation time values of donor acceptor complexes of certain aldehydes with benzylamine and cyclohexylamine in *n*-hexane at 303K

Acceptor	Donor							
	Benzylamine				Cyclohexylamine			
	K/M <sup>-1</sup>	$\Delta G/\text{kJmol}^{-1}$	$\Delta G^\#/\text{kJmol}^{-1}$	$\tau/10^{-13}$ s	K/M <sup>-1</sup>	$\Delta G/\text{kJmol}^{-1}$	$\Delta G^\#/\text{kJmol}^{-1}$	$\tau/10^{-13}$ s
Benzaldehyde	3.75	-3.3	3.4	5.5	5.96	-4.5	3.4	5.5
<i>o</i> -Chlorobenzaldehyde	10.01	-5.8	3.4	5.5	15.42	-6.9	3.4	5.6
Anisaldehyde	19.55	-7.2	3.4	5.4	21.13	-7.7	3.4	5.4
<i>p</i> -Tolualdehyde	12.46	-6.4	3.4	5.5	17.47	-7.2	3.4	5.5
Cinnamaldehyde	33.53	-8.9	3.4	5.4	45.38	-9.6	3.4	5.5
Crotonaldehyde	65.12	-10.5	3.5	5.6	80.13	-11.0	3.4	5.4
Propionaldehyde	18.49	-7.4	3.4	5.6	24.38	-8.1	3.4	5.6
Valeraldehyde	20.76	-7.6	3.4	5.3	37.05	-9.1	3.4	5.5

investigated (Table 4). The negative free energy of formation values indicate that the donor acceptor complexes formed between aldehydes and amines are thermodynamically stable. The constant values of  $\Delta G^\#$  and  $\tau$  suggest that similar type of complexes are formed between aldehydes and amines as these two parameters are intrinsic properties of charge transfer complexes.

#### 4 Conclusion

Aldehydes with electron deficient carbonyl carbon form thermodynamically stable charge transfer complexes with primary amines such as benzylamine and cyclohexylamine. The complexation between aldehydes and amines can be detected by ultrasonic method. Stability constants are determined for such complexes at 303K. The stabilities of these complexes depend on the structure of donor and acceptor.

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#### References

- Graham Solomons T W, *Organic chemistry*, V edition, John Wiley, 1992, 1044.
- Jayakumar S, Karunanithi N & Kannappan V, *Indian J Pure & Appl Phys*, 34 (1996) 761.
- Prasad N, Singh. R, Prakash O & Prakash S, *Indian J Pure & Appl Phys*, 14 (1976) 676.
- Marwein. B L & Bhat. S N, *Acoustica*, 58 (1985) 243.
- Cater S, *J Chem Soc A*, 404 (1968).
- Prakash S, Sivanarayana K S & Prakash. O, *Can J Chem*, 58 (1980) 942.
- Shahid Pervez, Saaib Ali & Atchar Yaseen Khan, *Polish J Chem*, 64 (1990) 489.
- Bajan Dass, Prakash K, Muhari & Dilip K, Hazra, *Acoust Lett*, 18 (40) (1994) 69.
- Jacobson B, *Acta Chemica Scand*, 5 (1951) 1214.
- Jacobson B, *J Chem Phys*, 20 (1952) 927.
- Subhi Kemel Hassun, *Acoust Lett*, 11 (10) (1998) 195.
- Kannappan V, Jaya Shanthi R & Malar E J P, *Phys Chem Liq*, 40 (4) (2002) 507.
- Mahendran S, Ph.D Thesis, University of Madras, July (2002).