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Der Pharma Chemica, 2013, 5(6):282-287  
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ISSN 0975-413X  
CODEN (USA): PCHHAX

## Ultrasonic studies on the stability constants of certain charge transfer complexes in solution

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### ABSTRACT

The present investigation aims at the comparative study of stability constants of the “Ketone-Amine” charge transfer complexes at various temperatures to gain a better understanding of the effect of temperature, and different structural aspects of acceptor-donor to the stability constants of charge transfer complexes under investigation. The density, speed of the sound and viscosity of the above mentioned charge transfer complexes were measured in n-hexane solvent at 293 K. A quantitative relationship has been established among the thermodynamic properties like acoustical impedance (Z), sound velocity (U), internal pressure ( $\pi$ ), Intermolecular free length (Lf) and adiabatic compressibility ( $\beta$ ) etc. The results obtained are much comparable and are in good agreement. A molecular interaction study has also been made successfully in the light of these acoustical properties.

**Keywords:** Charge Transfer Complexes, Stability Constants, Viscosity, Adiabatic Compressibility, Intermolecular free length

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### INTRODUCTION

Ultrasonic velocity measurement has been successfully employed to detect and assess weak and strong molecular interaction, present in binary [1] and ternary [2] liquid mixtures. Ultrasonic investigations find extensive applications in predicting the physico-chemical behaviors and molecular interactions occurring in a variety of liquid mixtures. In a chemical industry, these properties are very significant in design calculations, heat transfer and mass transfer etc. There has been an increasing interest in the study of molecular interaction between the component molecules and they find applications in several industrial and technological processes [3]. Ultrasonic is a non-destructive and quick method for the investigation of charge transfer complexes [4]. Further, such studies as a function of concentration are useful in gaining insight into the structure and bonding of associated molecular complexes and other molecular processes [5]. The carbonyl group has electron-deficient carbons which can function as electrophiles. Basic groups like amino groups can interact with this group to form a complex and influence the properties of such compounds [6]. These studies are made mainly to investigate the effect of structure of donor molecules and polarity of medium on the stability of this type of complexes and the factor which plays significant role in the complexation[7]. In this background, an attempt has been made to determine densities ( $\rho$ ), ultrasonic speeds (U) and viscosities ( $\eta$ ) of the ternary mixtures consists of Pyridine as donor with Cyclohexanone, Acetone, Acetophenone and Ethyl methyl ketone as acceptors separately in n-hexane solvent including pure liquids at

293K. From these experimental data, the acoustical impedance ( $Z$ ), internal pressure ( $\pi$ ), intermolecular free length ( $L_f$ ) and adiabatic compressibility ( $\beta$ ) have been calculated using standard method [8].

### MATERIALS AND METHODS

Cyclohexanone, Acetone, Acetophenone and Pyridine were Anal R grade. Densities, Viscosities and Ultrasonic Velocities were measured at 293K over a wide range of concentrations. The densities of pure compounds and their solutions were measured accurately using 10 ml specific gravity bottle in an electronic balance precisely and the accuracy in weighing is  $\pm 0.1$  mg. Viscosities of pure compounds and their mixtures were determined using Ostwald's Viscometer calibrated with double distilled water.

The ultrasonic velocity as measured by using variable path single crystal interferometer (Model F-81S, Mittal Enterprise, India) at fixed frequency 2 MHz with accuracy of 0.03%. The temperature was maintained with an accuracy of  $0.1^\circ\text{C}$ . Electronically digital operated constant temperature bath (Plasto Craft Industries) for low temperature bath Odel LTB-10 was used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature with accuracy in temperature measurement -  $10^\circ\text{C}$  to  $-90^\circ\text{C}$ . Acoustical parameters such as adiabatic compressibility ( $\beta$ ), free length ( $L_f$ ), internal pressure ( $\pi$ ), relaxation time ( $\tau$ ), stability constant ( $K$ ) and the free energy change ( $\Delta G_F^0$ ) were calculated using standard equations.

### RESULTS AND DISCUSSION

Amines behave as Lewis bases by the virtue of presence of nitrogen as the basic centre with an unshared pair of electron. A carbonyl compound contains electron deficient carbon which can function as electron acceptor. Thus, donor-acceptor complexes can be formed between amine and carbonyl compounds. There are optical and ultrasonic methods to detect such complexes. In this article, we employed an ultrasonic method to detect these complexes. The stability constants ( $K$ ) are determined from ultrasonic velocities and the trend in  $K$  values is explained on the basis of the structure of the carbonyl compounds. Pyridine is used as a donor in the formation of these types of complexes. The measured values of ultrasonic velocity, density and viscosity at equimolar concentrations of various Carbonyl compounds (Acceptors) and Pyridine (donor) in n-hexane at 293 K are given in Tables 1–3

**Table 1. Ultrasonic velocity ( $\text{m s}^{-1}$ ) values of ketones with Pyridine in n-hexane at 293 K**

Equimolar Conc.	Cyclohexanone	Acetone	Acetophenone	Ethyl Methyl Ketone
0.02	1075.70	1070.00	1072.00	1068.60
0.04	1076.13	1069.00	1073.40	1067.32
0.06	1077.40	1069.86	1075.06	1066.70
0.08	1078.00	1069.60	1076.40	1066.44
0.10	1079.12	1069.20	1077.80	1065.16
0.12	1080.32	1068.40	1079.10	1064.36
0.14	1082.40	1068.01	1080.40	1064.01
0.16	1083.50	1067.40	1081.60	1063.24
0.18	1083.92	1066.10	1082.80	1063.04
0.20	1084.50	1065.40	1084.00	1062.20

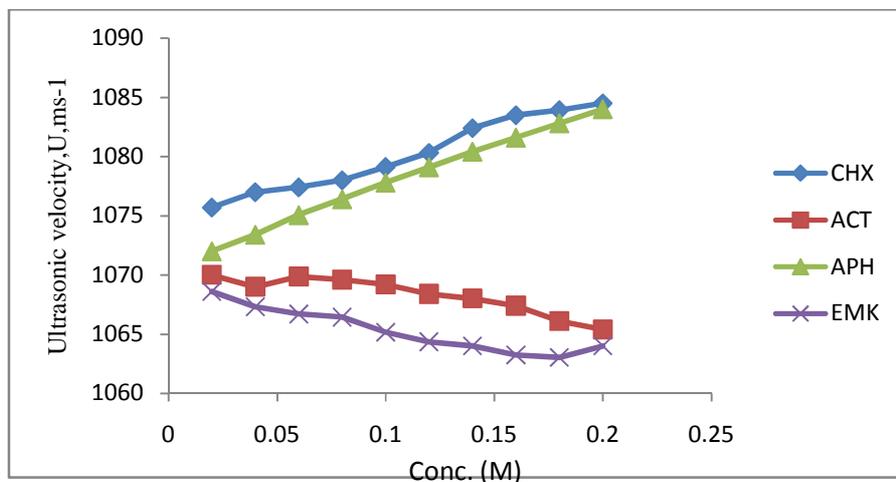
**Table 2. Density ( $\text{Kg m}^{-3}$ ) values of ketones with Pyridine in n-hexane at 293 K**

Equimolar Conc.	Cyclohexanone	Acetone	Acetophenone	Ethyl Methyl Ketone
0.02	654.3	661.5	660.8	663.7
0.04	655.2	663.9	662.6	665.2
0.06	656.0	667.4	664.5	666.8
0.08	656.6	669.1	667.9	668.5
0.10	657.1	671.8	670.2	670.0
0.12	657.6	673.8	672.8	673.0
0.14	658.1	676.6	673.3	674.6
0.16	659.2	678.0	674.7	675.3
0.18	660.5	679.4	675.8	677.0
0.20	661.5	680.6	677.5	682.1

**Table 3.** Viscosity ( $10^{-4}\text{Ns m}^{-2}$ ) values of ketones with Pyridine in n-hexane at 293 K

Equimolar Conc.	Cyclohexanone	Acetone	Acetophenone	Ethyl Methyl Ketone
0.02	3.181	3.065	3.190	3.106
0.04	3.197	3.079	3.202	3.116
0.06	3.208	3.094	3.214	3.125
0.08	3.227	3.106	3.227	3.133
0.10	3.244	3.120	3.238	3.141
0.12	3.264	3.132	3.248	3.152
0.14	3.275	3.145	3.260	3.161
0.16	3.289	3.156	3.270	3.169
0.18	3.302	3.163	3.278	3.177
0.20	3.319	3.176	3.291	3.189

The trend in the ultrasonic velocity with concentration in the case of systems containing ketones also suggests that there are strong interactions between molecules of ketones and pyridine. In the case of aromatic ketones, the ultrasonic velocity increases with an increase in the concentration of carbonyl compound and amine. But, the reverse trend is observed in the case of the aliphatic ketone–amine system. Generally, aromatic ketones have higher ultrasonic velocity values than aliphatic ketones. With an increase in the concentration of carbonyl compounds, the concentration of free carbonyl compounds also increases, and this may be the reason for the reversal in the trend. A similar observation was made by Mahendran in the study of donor–acceptor complexes between carbonyl compounds and chloroform [9]. Cyclic ketones form more stable charge transfer complexes with Pyridine than aromatic and acyclic ketones. This is indicated by the steeper curves obtained in the plot of ultrasonic velocity against concentration for these systems. Thus, the donor–acceptor complex formation between carbonyl compounds and diethylamine is both concentration- and structure-dependent. The viscosities are determined for these systems at various concentrations of the donor-acceptor mixtures (Table 3). The increase in viscosity with concentration in all these systems suggests that the extent of complexation increases with the increase in concentration.

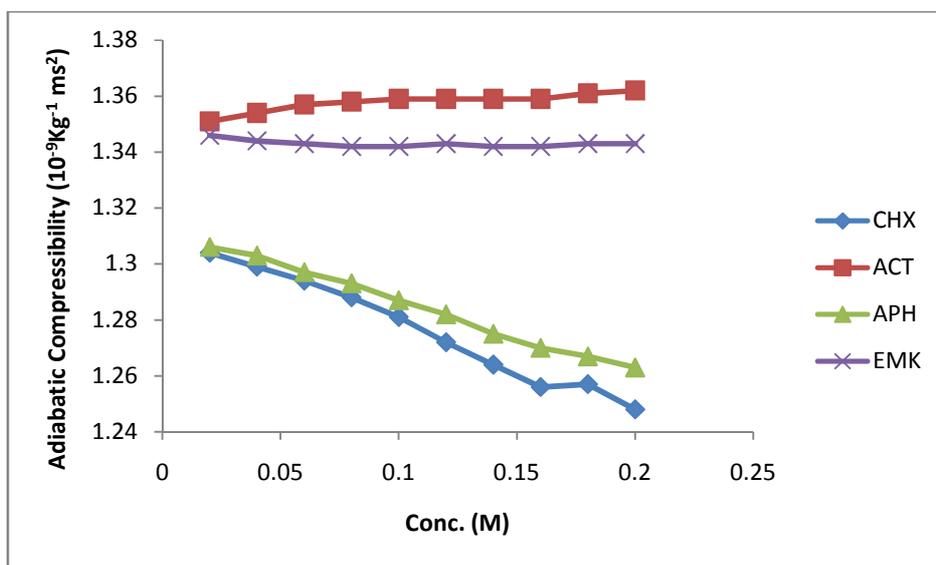


**Figure 1.** Plots of Ultrasonic velocity vs. Concentration of pyridine-ketones  
(CHX= Cyclohexanone; ACT= Acetone; APH=Acetophenone; EMK= Ethyl methyl ketone)

Adiabatic compressibility ( $\beta$ ) values were calculated for all corresponding systems and listed in Table 4. Adiabatic compressibility exhibits a reverse trend to that of ultrasonic velocity. It is the indication of the fact that complexation between the donor-acceptor is concentration dependent. This is also supported by the gradual decrease in free length (Table 5) of the corresponding systems.

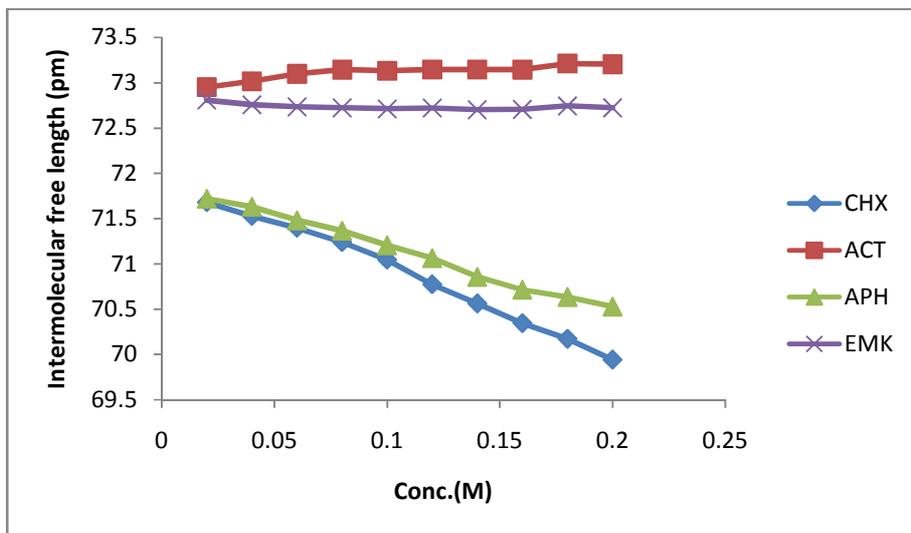
**Table 4.** Adiabatic Compressibility ( $10^{-9}\text{Kg}^{-1}\text{ms}^2$ ) values of ketones with Pyridine in n-hexane at 293 K

Equimolar Conc.	Cyclohexanone	Acetone	Acetophenone	Ethyl Methyl Ketone
0.02	1.304	1.351	1.306	1.346
0.04	1.299	1.354	1.303	1.344
0.06	1.294	1.357	1.297	1.343
0.08	1.288	1.358	1.293	1.342
0.10	1.281	1.359	1.287	1.342
0.12	1.272	1.359	1.282	1.343
0.14	1.264	1.359	1.275	1.342
0.16	1.256	1.359	1.270	1.342
0.18	1.257	1.361	1.267	1.343
0.20	1.248	1.362	1.263	1.343

**Figure 2.** Plots of Adiabatic Compressibility vs. Concentration of pyridine-ketones (CHX= Cyclohexanone; ACT= Acetone; APH=Acetophenone; EMK= Ethyl methyl ketone)**Table 5.** Intermolecular free length (pm) values of ketones with Pyridine in n-hexane at 293 K.

Equimolar Conc.	Cyclohexanone	Acetone	Acetophenone	Ethyl Methyl Ketone
0.02	71.679	72.950	71.717	72.807
0.04	71.528	73.015	71.629	72.756
0.06	71.396	73.097	71.480	72.732
0.08	71.238	73.143	71.365	72.722
0.10	71.045	73.130	71.205	72.710
0.12	70.774	73.145	71.062	72.720
0.14	70.562	73.144	70.857	72.701
0.16	70.345	73.143	70.716	72.705
0.18	70.173	73.209	70.636	72.743
0.20	69.942	73.201	70.530	72.722

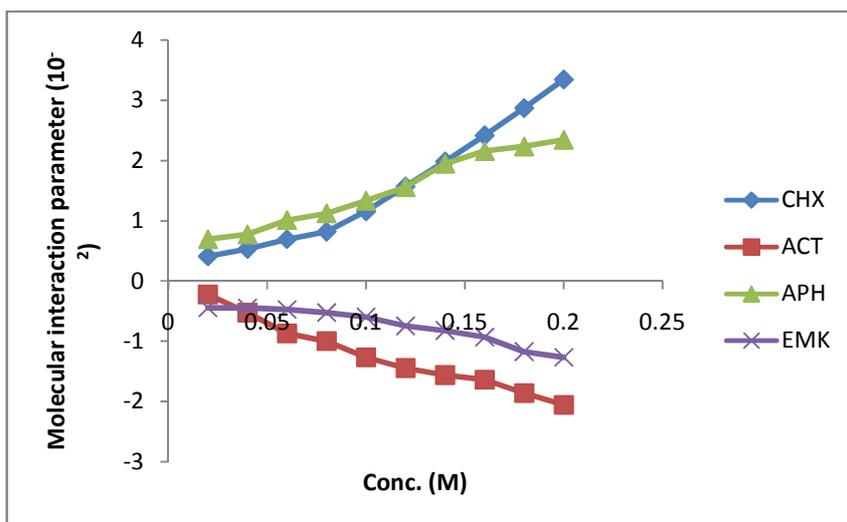
Molecular interaction parameter may be used to investigate the extent of deviation from ideal behaviour caused by complexation. It is a useful tool to measure the strength of molecular interaction between the donor and acceptor in non-polar medium. Both positive and negative is indicative of positive as well as negative deviation from ideal behaviour.



**Figure 3. Plots of Intermolecular free length vs. Concentration of pyridine-ketones**  
(CHX= Cyclohexanone; ACT= Acetone; APH=Acetophenone; EMK= Ethyl methyl ketone)

**Table 5. Molecular interaction parameter ( $10^{-2}$ ) values of ketones with Pyridine in n-hexane at 293 K**

Equimolar Conc.	Cyclohexanone	Acetone	Acetophenone	Ethyl Methyl Ketone
0.02	0.411	-0.224	0.692	-0.447
0.04	0.533	-0.522	0.772	-0.448
0.06	0.694	-0.869	1.009	-0.473
0.08	0.820	-1.116	1.121	-0.522
0.10	1.156	-1.265	1.331	-0.596
0.12	1.570	-1.444	1.556	-0.745
0.14	1.983	-1.561	1.947	-0.820
0.16	2.417	-1.636	2.154	-0.931
0.18	2.870	-1.858	2.233	-1.171
0.20	3.342	-2.005	2.342	-1.265



**Figure 4. Plots of Molecular interaction parameter vs. Concentration of pyridine-ketones**  
(CHX= Cyclohexanone; ACT= Acetone; APH=Acetophenone; EMK= Ethyl methyl ketone)

Generally, the aromatic aldehydes and ketones form comparatively less stable complexes than aliphatic counterparts. Mesomeric effect due to presence of aromatic group enhances the partial negative charge on carbonyl carbon and hence reduces the extent of complexation with electronically rich various amines. This explanation is evidenced by smaller K Value of Acetophenone, an aromatic ketone in comparison with both aliphatic carbonyls, Acetone and Ethyl methyl ketone respectively.

Cyclic ketones generally form more stable complexes with pyridine than acyclic ketone. From the values of formation constant, stability of the charge transfer complexes among ketones are as follows:

Cyclohexanone > Ethyl methyl ketone > Acetone > Acetophenone

The negative free energy of formation ( $\Delta G^0_F$ ) value for all complexes indicates that the donor-acceptor complexes formed between ketones and amines are thermodynamically stable.  $\Delta G^\ddagger$  and  $\tau$ , two inherent parameters have approximately constant value which indicates that similar type of complex are formed between the corresponding ketones and amines.

**Table 6. Formation constant, free energy of formation, mean free energy of activation and mean viscous relaxation time values of donor-acceptor complexes of certain ketones with Pyridine in n-hexane at 293 K**

Acceptor	K (M <sup>-1</sup> )	$\Delta G^0_F$ (kJ mol <sup>-1</sup> )	$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )	$\tau$ (10 <sup>-13</sup> ) s
Cyclohexanone	180.50	-12.64	3.8	5.9
Acetone	8.30	-4.9	3.7	5.8
Acetophenone	7.75	-4.8	3.8	5.8
Ethyl methyl ketone	10.34	-5.4	3.8	5.7

## CONCLUSION

Ketones with electron-deficient carbonyl carbon form thermodynamically stable charge transfer complexes with electron donor amines. The complexation between ketones and amine can be detected by ultrasonic method. The stabilities of these complexes depend on the structure of acceptor molecule and concentration of the donor-acceptors.

## Acknowledgement

One of the authors (SH) is grateful to The Director, P.G & Research Dept. of Chemistry, Hislop College, Nagpur for providing laboratory facilities.

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