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A comparative acoustics studies of some charge transfer complexes in predicting the acoustical and its allied properties at 303K

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ABSTRACT

The density, speed of the sound and viscosity were measured for solutions containing equimolar concentrations of the ternary mixtures consists of Pyridine as donor with Cyclohexanone, Acetone, Acetophenone and Ethyl methyl ketone as an acceptors separately in n-hexane solvent including pure liquids at 303K. Acoustical and thermodynamic parameters like acoustical impedance (Z), sound velocity (U), internal pressure (πi), Intermolecular free length (Lf) and adiabatic compressibility (ß), Formation Constant (K) have been evaluated. The constant values of free energy of formation ($\Delta G^{\#}$) and relaxation time (τ) indicates that the formation of similar type of complexes in these systems. The variation in free energy of formation (ΔG^{0}_{F}) values suggests that their thermodynamic stability depends on the structure of donor and acceptor.

Keywords: Speed of sound, Adiabatic Compressibility, Formation constant, Relaxation time, Thermodynamic Stability.

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. These studies can also be used to identify complexation and calculation of the stability constants of complexes, in particular the charge transfer complexes formed between organic compounds containing electron rich centers and electron deficient compounds. Chemical industry finds these properties are very significant in design calculations, heat transfer and mass transfer etc. Ultrasonic is a non- destructive and quick method for the investigation of charge transfer complexes [3]. 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 [4]. 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 factors, which plays significant role in the complexation. In this background, an attempt has been made to determine densities (ρ), ultrasonic speeds (U) and viscosities (η) of the ternary mixtures consists of Isopropyl amine as donor with Cyclohexanone, Acetone, Acetophenone and Ethyl methyl ketone as an acceptors separately in n-hexane solvent including pure liquids at 303K.

MATERIALS AND METHODS

Cyclohexanone, Acetone, Acetophenone and Pyridine were Anal R grade. Densities, Viscosities and Ultrasonic Velocities were measured at 303K 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 ± 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^{0}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^{0}C to -90^{0}C. Acoustical parameters such as adiabatic compressibility (ß), free length (Lf), internal pressure (πi), relaxation time (τ), stability constant (K) and the free energy change (ΔG^0_F) were calculated using standard equations.

RESULTS AND DISCUSSION

Optical and ultrasonic methods are essential tools to detect such Charge Transfer Complexes [5]. In this article, we employed an ultrasonic method to detect these complexes. Amines behave as Lewis bases since they contain nitrogen as the basic center with a lone pair of electrons. 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. 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. Isopropyl amine is used as a donor in the formation of these types of Charge Transfer Complexes.

The measured values of ultrasonic velocity, density and viscosity at equimolar concentrations of various Carbonyl compounds (Acceptors) and Isopropyl amine (donor) in n-hexane at 303 K are given in Tables 1–3

Table 1. Ultrasonic velocity (m s-1) values of ketones with Isopropyl Amine in n-hexane at 303 K

Equimolar Conc.	Cyclohexanone	Acetone	Acetophenone	Ethyl Methyl Ketone
0.02	1045.2	964.8	1050.8	1056.4
0.04	1046.0	964.4	1051.6	1055.6
0.06	1046.4	964.0	1053.2	1055.2
0.08	1047.2	963.9	1054.0	1054.4
0.10	1048.6	963.6	1054.4	1054.0
0.12	1049.0	962.8	1055.6	1052.8
0.14	1049.6	962.6	1056.0	1054.4
0.16	1050.0	961.4	1056.4	1055.2
0.18	1052.0	960.0	1057.2	1054.4
0.20	1053.1	958.8	1057.6	1053.6

Table 2. Density (Kg m-3) values of ketones with Isopropyl amine in n-hexane at 300 K

Equimolar Conc.	Cyclohexanone	Acetone	Acetophenone	Ethyl Methyl Ketone
0.02	636.1	634.1	665.5	661.7
0.04	635.8	634.7	666.9	662.8
0.06	636.4	634.9	669.4	664.4
0.08	637.0	634.8	670.1	669.9
0.10	635.9	634.1	671.8	670.8
0.12	635.6	635.0	673.2	672.1
0.14	636.3	634.9	675.2	673.5
0.16	635.9	635.7	679.0	674.2
0.18	636.7	635.4	679.9	681.8
0.20	636.8	635.1	681.4	682.7

Table 3. Viscosity (10-4Ns m-2) values of ketones with Isopropyl Amine in n-hexane at 303 K

Equimolar Conc.	Cyclohexanone	Acetone	Acetophenone	Ethyl Methyl Ketone
0.02	3.201	3.106	3.243	3.678
0.04	3.451	3.116	3.289	3.701
0.06	3.564	3.125	3.453	3.734
0.08	3.764	3.133	3.498	3.759
0.10	3.769	3.141	3.562	3.801
0.12	3.801	3.152	3.569	3.808
0.14	3.805	3.161	3.599	3.901
0.16	3.910	3.169	3.763	3.943
0.18	3.923	3.177	3.871	3.987
0.20	3.987	3.189	3.900	4.203

The trend in the ultrasonic velocity with concentration in the case of systems containing ketones indicates that there are strong interactions between molecules of ketones and isopropyl amine .The ultrasonic velocity increases with an increase in the concentration of carbonyl compound and amine in the case of aromatic ketones,. 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 [6]. Cyclic ketones form more stable charge transfer complexes with Isopropyl ketone 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 isopropyl ketone is both concentration- and structure-dependent [7]. 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.

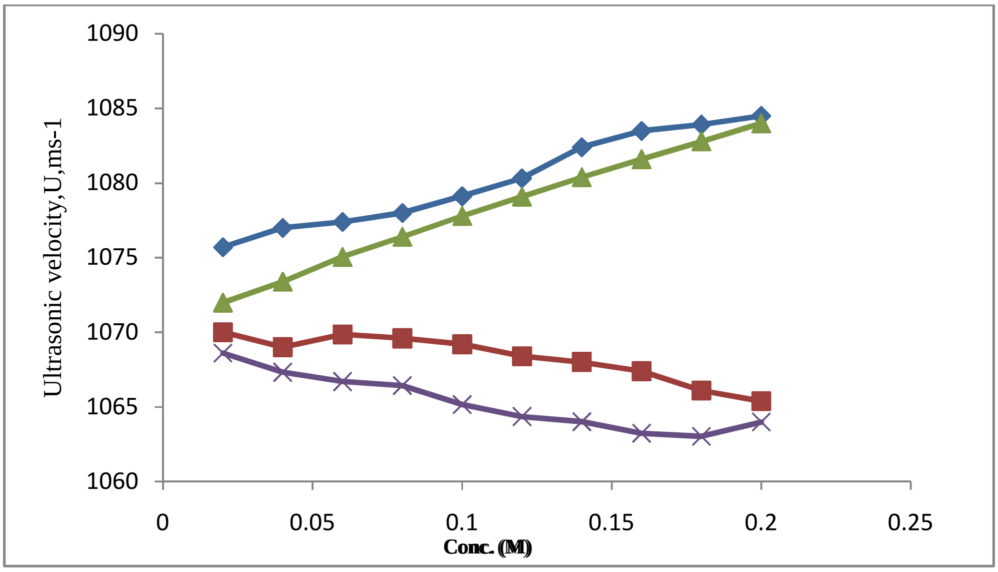

Figure 1. Plots of Ultrasonic velocity vs. Concentration of pyridine-ketones
(CHX= Cyclohexanone; ACT= Acetone; APH=Acetophenone; EMK= Ethyl methyl ketone)

Adiabatic compressibility (β) 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 ($10^{-9}Kg^{-1}\ ms^{2}$) values of ketones with Isopropyl Amine in n-hexane at 303 K

Equimolar Conc.	Cyclohexanone	Acetone	Acetophenone	Ethyl Methyl Ketone
0.02	1.346	1.356	1.306	1.356
0.04	1.344	1.343	1.303	1.341
0.06	1.343	1.341	1.297	1.340
0.08	1.342	1.339	1.293	1.334
0.10	1.342	1.329	1.287	1.325
0.12	1.343	1.320	1.282	1.256
0.14	1.342	1.312	1.275	1.213
0.16	1.342	1.306	1.270	1.198
0.18	1.343	1.305	1.267	1.194
0.20	1.343	1.265	1.263	1.193

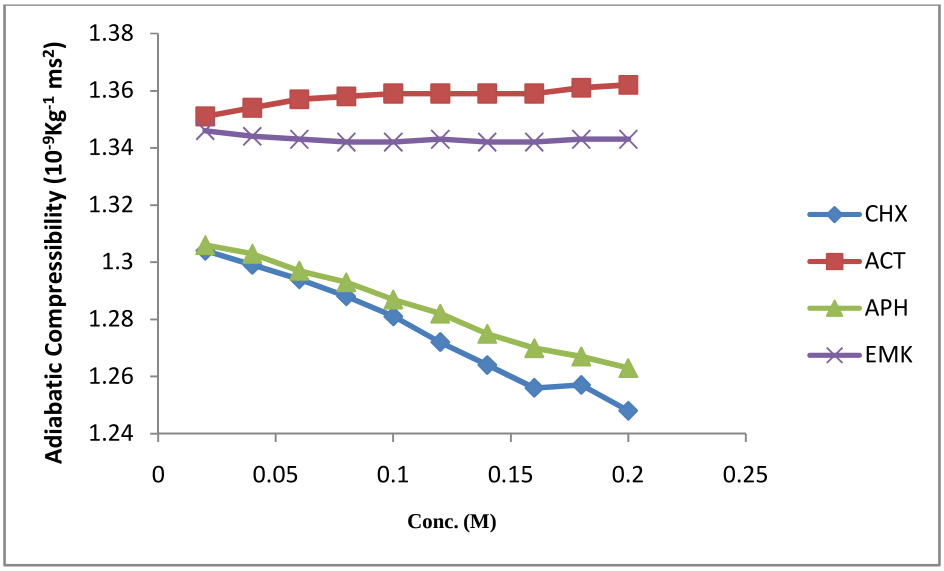

Figure 2. Plots of Adiabatic Compressibility vs. Concentration of Isopropyl amine-ketones
(CHX= Cyclohexanone; ACT= Acetone; APH=Acetophenone; EMK= Ethyl methyl ketone)

Table 5. Intermolecular free length (pm) values of ketones with Isopropyl amine in n-hexane at 303 K

Equimolar Conc.	Cyclohexanone	Acetone	Acetophenone	Ethyl Methyl Ketone
0.02	75.236	71.717	72.807	73.238
0.04	72.876	71.629	72.756	72.478
0.06	71.479	71.480	72.732	72.895
0.08	70.237	71.365	72.722	72.345
0.10	70.145	71.205	72.710	72.120
0.12	70.143	71.062	72.720	71.458
0.14	70.142	70.857	72.701	70.231
0.16	69.657	70.716	72.705	70.457
0.18	69.543	70.636	72.743	70.129
0.20	68.230	70.530	72.722	69.781

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 [8].

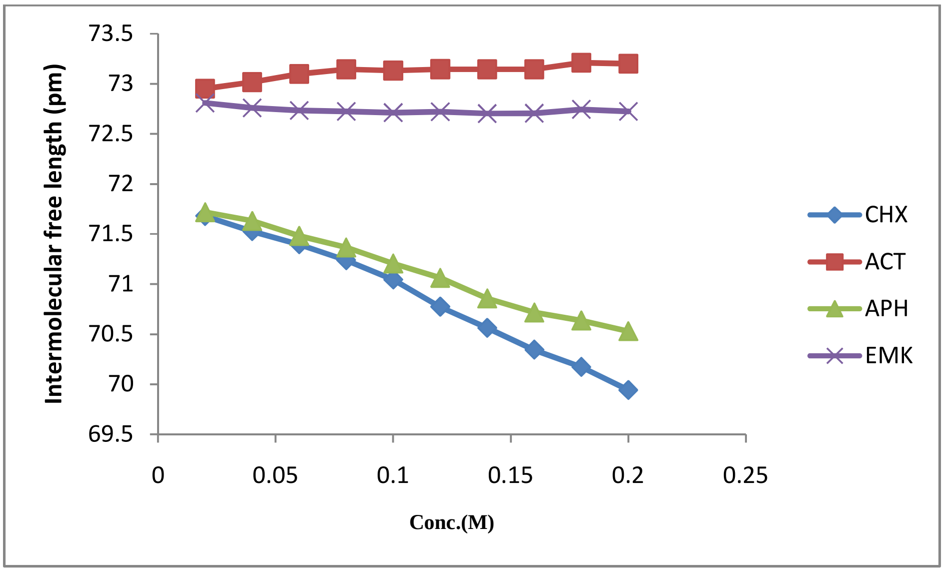

Figure 3. Plots of Intermolecular free length vs. Concentration of pyridine-ketones
(CHX= Cyclohexanone; ACT= Acetone; APH=Acetophenone; EMK= Ethyl methyl ketone)

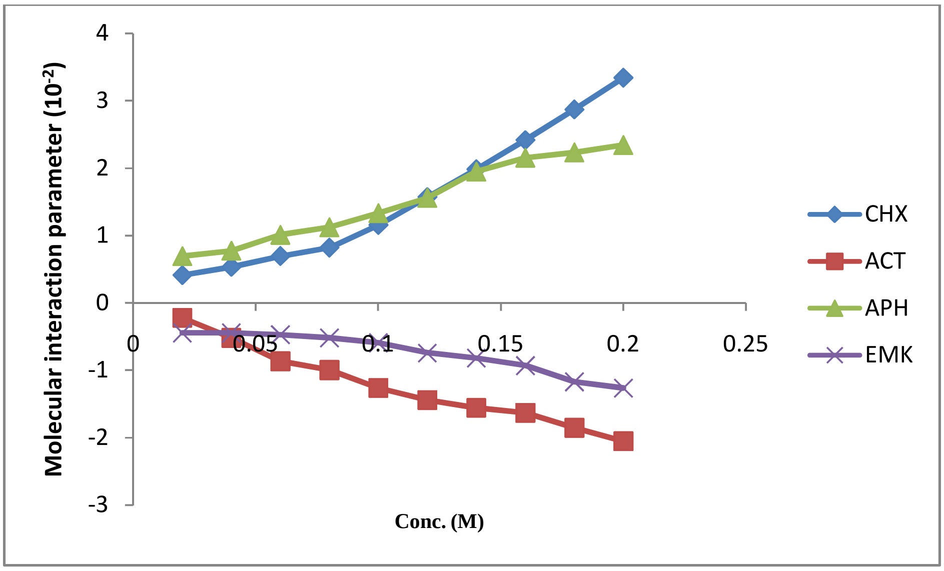

Figure 4. Plots of Molecular interaction parameter vs. Concentration of pyridine-ketones
(CHX= Cyclohexanone; ACT= Acetone; APH=Acetophenone; EMK= Ethyl methyl ketone)

Table 5. Molecular interaction parameter (10^{-2}) values of ketones with Isopropyl amine in n-hexane at 303 K

Equimolar Conc.	Cyclohexanone	Acetone	Acetophenone	Ethyl Methyl Ketone
0.02	0.692	-0.201	0.567	-0.561
0.04	0.772	-0.349	0.983	-0.598
0.06	1.009	-0.387	1.032	-0.763
0.08	1.121	-1.564	1.259	-0.799
0.10	1.331	-1.569	1.335	-0.980
0.12	1.556	-1.589	1.459	-0.991
0.14	1.947	-1.591	1.590	-1.456
0.16	2.154	-1.765	2.721	-1.490
0.18	2.233	-1.786	2.981	-1.213
0.20	2.342	-2.498	2.999	-1.368

Generally, the aromatic aldehydes and ketones form comparatively less stable complexs 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 reach various amines. These explanation is evidenced by smaller K Value of Acetophenone , an aromatic ketone in comparision 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 (ΔG^0_F) value for all complexes indicates that the donor-acceptor complexes formed between ketones and amines are thermodynamically stable. $\Delta G^\#$ and τ ,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 Isopropyl amine in n-hexane at 303 K

Acceptor	K (M^{-1})	ΔG^0_F (kJ mol^{-1})	$\Delta G^\#$ (kJ mol^{-1})	τ (10^{-13}) s
Cyclohexanone	165.98	-11.65	2.1	4.1
Acetone	5.51	-3.2	2.3	3.8
Acetophenone	3.12	-3.1	2.2	3.7
Ethyl methyl ketone	9.23	-4.5	2.4	2.1

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.

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