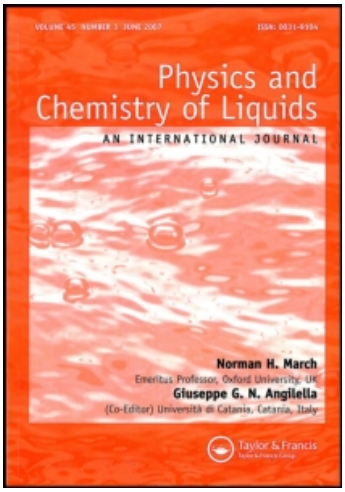

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Ultrasonic method of determination of stability constants of charge transfer complexes of certain carbonyl compounds and diethylamine in n-hexane

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Ultrasonic method of determination of stability constants of charge transfer complexes of certain carbonyl compounds and diethylamine in *n*-hexane

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The ultrasonic velocities (U), densities (ρ) and viscosities (η) were measured for solutions containing equimolar concentrations of diethylamine (donor), nine aldehydes and nine ketones (acceptors) in *n*-hexane at 303 K. Acoustical parameters such as adiabatic compressibility (β), free length (L_f), viscous relaxation time (τ), and molecular interaction parameter (χ_U) have been computed. These values indicate the formation of charge transfer complexes between carbonyl compounds and amine. Formation constant (K) values of the complexes have been evaluated using the equation proposed by Kannappan. The constant values of free energy of activation (ΔG) and relaxation time indicate the formation of similar charge transfer complexes in these systems. However, the variation in free energy of formation (ΔG°_{F}) values suggests that their thermodynamic stability depends on the structure of donor and acceptor.

Keywords: charge transfer complexes; carbonyl compounds; diethylamine; stability constant; ultrasonic method

1. Introduction

The carbonyl group is part of several biologically important molecules such as proteins, lipids and hormones. It 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 [1]. Ultrasonic velocity measurement has been successfully employed to detect and assess weak and strong molecular interactions present in binary [2,3] and ternary [4–7] liquid mixtures. These studies can also be used to determine the extent of complexation and to calculate the formation constant values of charge transfer complexes [8,9]. In this background, an attempt has been made to determine the formation constant values of charge transfer complexes of nine aldehydes and nine ketones (acceptors) and diethylamine (donor) in *n*-hexane at 303 K by ultrasonic method.

2. Experimental details

Benzaldehyde, *o*-chlorobenzaldehyde, anisaldehyde, *p*-tolualdehyde, cinnammaldehyde, β-phenylpropionaldehyde, crotonaldehyde, propionaldehyde, valeraldehyde, acetone,

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ethyl methyl ketone, acetophenone, *p*-methylacetophenone, *p*-chloroacetophenone, cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone, and the donor diethylamine were AnalaR samples. The solvent *n*-hexane (Laboratory Reagent) was purified by distillation (b.p. 69°C) before use. It was dried over sodium wire and stored in an amber coloured dry bottle. The ultrasonic velocities of pure liquids and mixtures were measured in an ultrasonic interferometer operating at a frequency of 2 MHz (Mittal Enterprises, model F-81, New Delhi) with an accuracy of $\pm 0.1\ m\ s^{-1}$. The densities of these solutions were calculated by determining the weight of liquids in 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 $\pm 0.1\ kg\ m^{-3}$ and the accuracy in the measurement of viscosity measured was 0.1%. Acoustical parameters such as adiabatic compressibility (β), free length (L_f) viscous relaxation time (τ) and molecular interaction parameter (χ_U) were calculated using standard equations [2,10–13].

3. Results and discussion

Amines behave as Lewis bases since they contain nitrogen as the basic centre with a lone pair of electrons. Carbonyl compounds contain a polar group in which electron deficient carbon 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. Diethylamine 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 acceptors and diethylamine (donor) in *n*-hexane at 303 K are given in Tables 1–6.

Plots of ultrasonic velocity *versus* concentration for the nine aldehyde-diethylamine systems are presented in Figure 1. Figure 2 contains similar plots for nine ketones and diethylamine systems.

Table 1. Ultrasonic velocity ($m\ s^{-1}$) values of aldehydes with diethylamine in *n*-hexane at 303 K.

Conc. (M)*	BEA	OCA	ANA	TUA	CNA	PPA	CRA	PRA	VLA
0.03	1071.20	1072.00	1072.40	1073.20	1076.24	1069.60	1068.20	1070.13	1071.10
0.06	1071.60	1072.40	1073.50	1073.40	1076.80	1070.40	1068.40	1070.20	1072.73
0.09	1072.00	1072.80	1074.70	1073.76	1077.12	1071.60	1068.60	1070.40	1073.04
0.12	1072.80	1073.84	1076.00	1074.10	1078.40	1073.00	1069.00	1070.56	1073.33
0.15	1073.80	1074.88	1077.40	1074.32	1079.60	1074.60	1069.60	1070.80	1073.44
0.18	1075.00	1076.16	1078.20	1074.72	1080.20	1076.20	1070.40	1070.96	1073.60
0.21	1076.20	1077.60	1079.00	1075.40	1081.53	1078.72	1071.20	1071.12	1073.80
0.24	1077.60	1078.27	1080.24	1076.60	1082.40	1080.80	1072.00	1071.30	1074.20
0.27	1078.80	1079.60	1081.20	1078.40	1084.10	1083.00	1073.00	1071.50	1075.12
0.30	1080.20	1080.27	1082.67	1079.20	1086.20	1085.40	1074.20	1071.80	1075.44

BEA = Benzaldehyde; OCA = *o*-Chlorobenzaldehyde; ANA = Anisaldehyde;
TUA = *p*-Tolualdehyde; CNA = Cinnammaldehyde; PPA = β-Phenylpropionaldehyde;
CRA = Crotonaldehyde; PRA = Propionaldeyde; VLA = Valeraldehyde.
*Equimolar concentration of donor and acceptor.

Table 2. Ultrasonic velocity ($m\,s^{-1}$) values of ketones with diethylamine in *n*-hexane at 303 K.

Conc. (M)*	ACT	EMK	ACP	PMA	PCA	CPN	CHX	CHP	COT
0.05	1071.20	1070.00	1075.70	1072.60	1072.00	1071.60	1074.40	1072.40	1076.00
0.10	1069.60	1070.00	1076.13	1074.00	1073.40	1072.32	1075.06	1072.80	1077.30
0.15	1067.73	1069.86	1077.40	1076.40	1075.06	1073.70	1075.92	1073.04	1078.60
0.20	1066.40	1069.60	1078.00	1078.00	1076.40	1075.44	1076.60	1073.40	1080.00
0.25	1065.60	1069.20	1079.12	1080.00	1077.80	1076.16	1078.40	1074.88	1082.40
0.30	1064.64	1068.40	1080.32	1081.80	1079.10	1077.36	1080.60	1075.20	1084.80
0.35	1064.00	1068.00	1082.40	1083.60	1080.40	1078.70	1082.80	1075.80	1086.00
0.40	1063.60	1067.40	1083.50	1086.60	1081.60	1080.24	1085.10	1076.80	1087.20
0.45	1062.40	1066.10	1083.92	1089.20	1082.80	1081.40	1087.50	1078.10	1088.50
0.50	1061.60	1065.60	1084.50	1092.00	1084.00	1082.20	1090.00	1080.20	1092.00

ACT = Acetone; EMK = Ethyl methyl ketone; ACP = Acetophenone;
PMA = *p*-Methylacetophenone; PCA = *p*-Chloroacetophenone; CPN = Cyclopentanone;
CHX = Cyclohexanone; CHP = Cycloheptanone; COT = Cyclooctanone.
*Equimolar concentration of donor and acceptor.

Table 3. Density ($kg\,m^{-3}$) values of aldehydes with diethylamine in *n*-hexane at 303 K.

Conc. (M)*	BEA	OCA	ANA	TUA	CNA	PPA	CRA	PRA	VLA
0.03	654.3	661.5	660.8	663.5	663.7	667.5	649.9	636.2	648.8
0.06	655.2	663.9	662.6	664.2	665.2	668.2	650.6	638.3	649.3
0.09	656.0	667.4	664.5	665.8	666.8	669.3	651.2	640.5	650.4
0.12	656.6	669.1	667.9	666.8	668.5	670.8	652.3	641.8	651.4
0.15	657.1	671.8	670.2	669.0	670.0	672.2	653.4	642.9	652.4
0.18	657.6	673.8	672.8	670.2	673.0	673.5	654.3	643.3	653.2
0.21	658.1	676.6	673.3	671.1	674.6	674.7	655.1	643.6	654.0
0.24	659.2	678.0	674.7	672.0	675.3	676.5	656.6	643.9	654.9
0.27	660.5	679.4	675.8	672.5	677.0	678.5	657.7	644.2	656.1
0.30	661.5	680.6	677.5	673.6	682.1	680.3	659.9	644.7	657.7

BEA = Benzaldehyde; OCA = *o*-Chlorobenzaldehyde; ANA = Anisaldehyde;
TUA = *p*-Tolualdehyde; CNA = Cinnammaldehyde; PPA = β-Phenylpropionaldehyde;
CRA = Crotonaldehyde; PRA = Propionaldeyde; VLA = Valeraldehyde.
*Equimolar concentration of donor and acceptor.

Ultrasonic velocity increases with the increase in concentration of donor and acceptor in the aldehyde–amine system. Generally, aldehydes are non-associated liquids and in the amine–aldehyde mixtures, the intermolecular attraction is strong and this is indicated by the increase in ultrasonic velocity. It is seen in Figure 1 that the curve is steeper in the case of the β-phenylpropionaldehyde-diethylamine system and this suggests that stronger molecular interactions are present in this system. Weak interactions exist in the aliphatic aldehyde-diethylamine mixture. It may be pointed out that the presence of unsaturation in the aldehyde molecule enhances the interaction. 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 diethylamine. However, these systems exhibit two types of variation of ultrasonic velocity with concentration. In the case of aromatic ketones, the ultrasonic velocity increases with an increase in the concentration of carbonyl compound/amine. But, the reverse trend is observed in the case of the aliphatic

Table 4. Density ($kg\,m^{-3}$) values of ketones with diethylamine in *n*-hexane at 303 K.

Conc. (M)*	ACT	EMK	ACP	PMA	PCA	CPN	CHX	CHP	COT
0.05	645.0	649.0	661.8	654.3	656.9	651.5	664.1	651.2	661.3
0.10	645.8	649.9	662.9	657.3	660.2	653.7	666.1	652.4	664.0
0.15	646.6	650.5	664.1	660.6	663.2	655.4	667.5	653.0	667.9
0.20	647.4	651.0	665.5	663.3	666.5	657.6	669.6	654.1	669.4
0.25	648.6	651.7	667.1	666.2	669.4	659.4	671.0	655.2	671.4
0.30	649.5	652.5	668.3	669.7	672.4	661.9	673.4	656.3	673.0
0.35	650.3	653.3	669.6	672.9	675.7	664.7	674.7	657.3	675.1
0.40	650.8	654.0	670.9	675.1	679.0	666.9	676.0	658.6	677.2
0.45	651.1	654.9	671.9	677.7	682.2	668.9	677.6	661.0	678.9
0.50	651.5	655.9	673.2	680.2	685.2	670.8	679.6	664.3	681.1

ACT = Acetone; EMK = Ethyl methyl ketone; ACP = Acetophenone;
PMA = *p*-Methylacetophenone; PCA = *p*-Chloroacetophenone; CPN = Cyclopentanone;
CHX = Cyclohexanone; CHP = Cycloheptanone; COT = Cyclooctanone.
*Equimolar concentration of donor and acceptor.

Table 5. Viscosity ($10^{-4}\,Ns\,m^{-2}$) values of aldehydes with diethylamine in *n*-hexane at 303 K.

Conc. (M)*	BEA	OCA	ANA	TUA	CNA	PPA	CRA	PRA	VLA
0.03	3.148	3.151	3.152	3.265	3.145	3.186	3.212	3.023	3.085
0.06	3.161	3.172	3.169	3.270	3.165	3.194	3.222	3.036	3.097
0.09	3.17	3.196	3.185	3.282	3.182	3.206	3.231	3.049	3.111
0.12	3.179	3.213	3.212	3.291	3.199	3.219	3.244	3.058	3.126
0.15	3.188	3.236	3.229	3.316	3.219	3.229	3.258	3.066	3.138
0.18	3.197	3.251	3.245	3.328	3.242	3.240	3.271	3.072	3.148
0.21	3.208	3.272	3.255	3.337	3.258	3.251	3.282	3.077	3.157
0.24	3.223	3.288	3.272	3.346	3.268	3.268	3.295	3.081	3.166
0.27	3.238	3.304	3.285	3.358	3.282	3.287	3.307	3.087	3.177
0.30	3.255	3.316	3.326	3.370	3.315	3.309	3.329	3.098	3.190

BEA = Benzaldehyde; OCA = *o*-Chlorobenzaldehyde; ANA = Anisaldehyde;
TUA = *p*-Tolualdehyde; CNA = Cinnammaldehyde; PPA = *β*-Phenylpropionaldehyde;
CRA = Crotonaldehyde; PRA = Propionaldeyde; VLA = Valeraldehyde.
*Equimolar concentration of donor and acceptor.

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 [14]. Cyclic ketones form more stable charge transfer complexes with diethylamine 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 (Tables 5 and 6).

The increase in viscosity with concentration in all these systems suggests that the extent of complexation increases with the increase in concentration.

Table 6. Viscosity (10^{-4} Ns m^{-2}) values of ketones with diethylamine in *n*-hexane at 303 K.

Conc. (M)*	ACT	EMK	ACP	PMA	PCA	CPN	CHX	CHP	COT
0.05	3.065	3.106	3.190	3.121	3.128	3.107	3.181	3.123	3.219
0.10	3.079	3.116	3.202	3.141	3.149	3.123	3.197	3.137	3.240
0.15	3.094	3.125	3.214	3.163	3.169	3.141	3.208	3.150	3.270
0.20	3.106	3.133	3.227	3.183	3.192	3.159	3.227	3.163	3.284
0.25	3.120	3.141	3.238	3.204	3.213	3.173	3.244	3.174	3.301
0.30	3.132	3.152	3.248	3.229	3.236	3.191	3.264	3.188	3.319
0.35	3.145	3.161	3.260	3.255	3.258	3.208	3.275	3.198	3.338
0.40	3.156	3.169	3.270	3.275	3.283	3.223	3.289	3.209	3.354
0.45	3.163	3.177	3.278	3.296	3.308	3.240	3.302	3.228	3.367
0.50	3.176	3.189	3.291	3.317	3.333	3.256	3.319	3.253	3.385

ACT = Acetone; EMK = Ethyl methyl ketone; ACP = Acetophenone;
PMA = *p*-Methylacetophenone; PCA = *p*-Chloroacetophenone; CPN = Cyclopentanone;
CHX = Cyclohexanone; CHP = Cycloheptanone; COT = Cyclooctanone.
*Equimolar concentration of donor and acceptor.

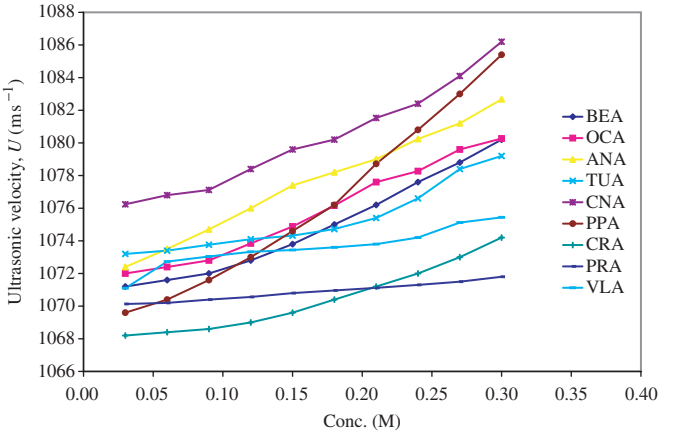

Figure 1. Plots of ultrasonic velocity *vs.* concentration of diethylamine–aldehydes.

Adiabatic compressibility (β) values are calculated for the 18 systems and presented in Tables 7 and 8.

Figures 3 and 4 contain plots of adiabatic compressibility *versus* concentration for these systems.

Adiabatic compressibility exhibits a 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 (Tables 9 and 10) with concentration in these systems.

Molecular interaction parameter (χ_U) values are calculated and presented in Tables 11 and 12.

Figures 5 and 6 contain plots of (χ_U) *versus* concentration. The molecular interaction parameter is indicative of the extent of deviation from ideal behaviour which may be due to complexation. It can be used to assess the strength of molecular attraction between the

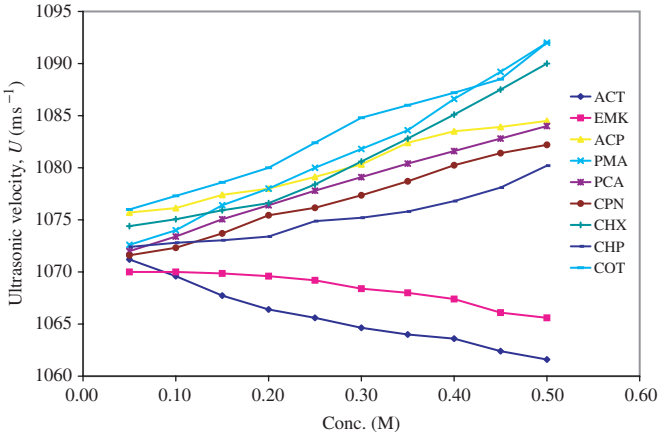

Figure 2. Plots of ultrasonic velocity *vs*. concentration of diethylamine–ketones.

Table 7. Adiabatic compressibility (10^{-9} $kg^{-1}ms^2$) values of aldehydes with diethylamine in *n*-hexane at 303 K.

Conc. (M)*	BEA	OCA	ANA	TUA	CNA	PPA	CRA	PRA	VLA
0.03	1.332	1.315	1.316	1.309	1.301	1.310	1.348	1.373	1.343
0.06	1.329	1.310	1.310	1.307	1.297	1.306	1.347	1.368	1.338
0.09	1.326	1.302	1.303	1.303	1.293	1.301	1.345	1.363	1.335
0.12	1.323	1.296	1.293	1.300	1.286	1.295	1.342	1.359	1.333
0.15	1.32	1.288	1.285	1.295	1.281	1.288	1.338	1.357	1.330
0.18	1.316	1.281	1.279	1.292	1.273	1.282	1.334	1.355	1.328
0.21	1.312	1.273	1.276	1.288	1.267	1.274	1.330	1.354	1.326
0.24	1.306	1.269	1.270	1.284	1.264	1.265	1.325	1.353	1.323
0.27	1.301	1.263	1.266	1.279	1.257	1.257	1.321	1.352	1.319
0.30	1.296	1.259	1.259	1.275	1.243	1.248	1.313	1.350	1.315

BEA = Benzaldehyde; OCA = *o*-Chlorobenzaldehyde; ANA = Anisaldehyde;
TUA = *p*-Tolualdehyde; CNA = Cinnammaldehyde; PPA = *β*-Phenylpropionaldehyde;
CRA = Crotonaldehyde; PRA = Propionaldeyde; VLA = Valeraldehyde.
*Equimolar concentration of donor and acceptor.

donor and acceptor in non-polar medium. These values increase with concentration indicating that the extent of complexation is concentration dependent and it increases with concentration. Both positive and negative values are obtained for these systems suggesting that some systems exhibit positive deviation, while others negative deviation, from ideal behaviour.

The formation constant (K) can be used to compare stabilities of the charge transfer complexes [6,14]. The formation constant values are calculated from the ultrasonic velocities using the equation proposed by Kannappan and the K values are presented in Table 13.

The trend in the values of K indicates that the stability of carbonyl compound–amine complexes depend on the microstructure of acceptor. Generally, the aromatic aldehydes and aromatic ketones form less stable complexes than aliphatic carbonyl compounds,

Table 8. Adiabatic compressibility ($10^{-9}\,kg^{-1}\,m\,s^2$) values of ketones with diethylamine in *n*-hexane at 303 K.

Conc. (M)*	ACT	EMK	ACP	PMA	PCA	CPN	CHX	CHP	COT
0.05	1.351	1.346	1.306	1.328	1.325	1.337	1.304	1.335	1.306
0.10	1.354	1.344	1.303	1.319	1.315	1.330	1.299	1.332	1.297
0.15	1.357	1.343	1.297	1.307	1.305	1.324	1.294	1.330	1.287
0.20	1.358	1.343	1.293	1.297	1.295	1.315	1.288	1.327	1.281
0.25	1.358	1.342	1.287	1.287	1.286	1.309	1.281	1.321	1.268
0.30	1.358	1.343	1.282	1.276	1.277	1.302	1.272	1.318	1.262
0.35	1.358	1.342	1.275	1.266	1.268	1.293	1.264	1.315	1.256
0.40	1.358	1.342	1.270	1.255	1.259	1.285	1.256	1.310	1.249
0.45	1.361	1.343	1.267	1.244	1.250	1.278	1.248	1.302	1.243
0.50	1.362	1.343	1.263	1.233	1.242	1.273	1.238	1.290	1.231

ACT = Acetone; EMK = Ethyl methyl ketone; ACP = Acetophenone;
PMA = *p*-Methylacetophenone; PCA = *p*-Chloroacetophenone; CPN = Cyclopentanone;
CHX = Cyclohexanone; CHP = Cycloheptanone; COT = Cyclooctanone.
*Equimolar concentration of donor and acceptor.

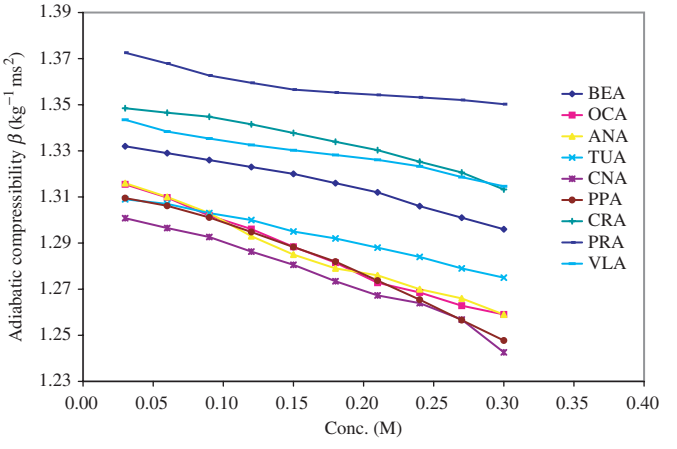

Figure 3. Plots of adiabatic compressibility *vs*. concentration of diethylamine–aldehydes.

as evident from their smaller *K* values. Thus, the presence of phenyl ring in the aldehyde or ketone decreases the positive charge on the carbonyl carbon due to the mesomeric effect and reduces the electrophilic character of carbonyl compounds. Among the aromatic aldehydes, cinnammaldehyde has higher *K* value, indicting that cinnamaldehyde forms a relatively more stable complex with amines than other aromatic aldehydes. A similar trend was also observed on the charge transfer complexes of carbonyl compounds and chloroform in *n*-hexane by Mahendran [14]. In the case of aromatic aldehydes, the stability of aldehyde-amine complex decreases in the order:

Cinnamaldehyde > Anisaldehyde > *p*-Tolualdehyde > *o*-Chlorobenzaldehyde
$\approx$ *β*-phenylpropionaldehyde > Benzaldehyde

It may be pointed out that methoxy group releases electrons by the mesomeric effect and hence anisaldehyde forms a more stable complex than benzaldehyde. In the case of

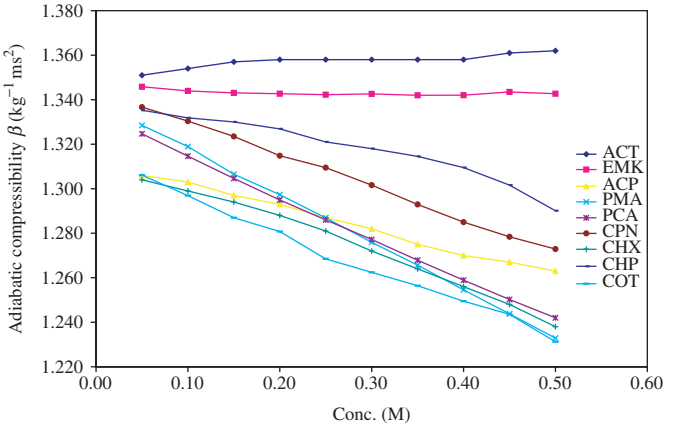

Figure 4. Plots of adiabatic compressibility *vs*. concentration of diethylamine–ketones.

Table 9. Intermolecular free length (pm) values of aldehydes with diethylamine in *n*-hexane at 303 K.

Conc. (M)*	BEA	OCA	ANA	TUA	CNA	PPA	CRA	PRA	VLA
0.03	72.430	71.981	71.992	71.792	71.578	71.817	72.879	73.526	72.743
0.06	72.353	71.824	71.821	71.741	71.460	71.726	72.826	73.401	72.605
0.09	72.282	71.609	71.638	71.630	71.353	71.587	72.779	73.261	72.522
0.12	72.195	71.448	71.369	71.554	71.178	71.414	72.690	73.176	72.447
0.15	72.100	71.236	71.154	71.422	71.019	71.233	72.588	73.097	72.384
0.18	71.993	71.045	70.963	71.331	70.821	71.058	72.484	73.063	72.329
0.21	71.885	70.803	70.884	71.238	70.650	70.829	72.386	73.035	72.271
0.24	71.732	70.686	70.730	71.111	70.557	70.599	72.249	73.006	72.195
0.27	71.581	70.526	70.609	70.966	70.358	70.352	72.121	72.975	72.067
0.30	71.434	70.420	70.425	70.856	69.959	70.103	71.920	72.926	71.958

BEA = Benzaldehyde; OCA = *o*-Chlorobenzaldehyde; ANA = Anisaldehyde;
TUA = *p*-Tolualdehyde; CNA = Cinnammaldehyde; PPA = *β*-Phenylpropionaldehyde;
CRA = Crotonaldehyde; PRA = Propionaldeyde; VLA = Valeraldehyde.
*Equimolar concentration of donor and acceptor.

o-chlorobenzaldehyde, the chloro substituent exerts both mesomeric and inductive effects but in opposite directions. Therefore, it forms a more stable complex with amine than benzaldehyde, but a less stable complex than those of anisaldehyde and *p*-tolualdehyde. Among the aliphatic aldehydes the *K* value is maximum in crotonaldehyde due to extension of conjugation in the molecule. Among the saturated aliphatic aldehydes the stabililty increases with increase in length of the alkyl chain. Thus, valeraldehyde forms a more stable complex with amine than propionaldehyde.

Among aromatic ketones, *p*-methylacetophenone has the highest *K* value, indicating that *p*-methylacetophenone forms a relatively more stable complex with amine than other ketones. Among aromatic ketones the stability constant is in the order:

p-Methylacetohenone > *p*-Chloroacetophenone > Acetophenone.

Table 10. Intermolecular free length (pm) values of ketones with diethylamine in *n*-hexane at 303 K.

Conc. (M)*	ACT	EMK	ACP	PMA	PCA	CPN	CHX	CHP	COT
0.05	72.950	72.807	71.717	72.335	72.232	72.558	71.679	72.521	71.724
0.10	73.014	72.756	71.629	72.076	71.958	72.387	71.528	72.427	71.492
0.15	73.097	72.732	71.480	71.735	71.684	72.201	71.396	72.378	71.197
0.20	73.143	72.722	71.365	71.483	71.417	71.963	71.238	72.292	71.025
0.25	73.130	72.710	71.205	71.195	71.170	71.817	71.045	72.132	70.762
0.30	73.145	72.720	71.062	70.891	70.925	71.601	70.774	72.050	70.521
0.35	73.144	72.702	70.857	70.605	70.667	71.361	70.562	71.955	70.334
0.40	73.143	72.704	70.716	70.295	70.417	71.142	70.345	71.818	70.147
0.45	73.209	72.743	70.636	69.992	70.173	70.959	70.107	71.601	69.975
0.50	73.242	72.722	70.530	69.684	69.942	70.806	69.843	71.284	69.638

ACT = Acetone; EMK = Ethyl methyl ketone; ACP = Acetophenone;
PMA = *p*-Methylacetophenone; PCA = *p*-Chloroacetophenone; CPN = Cyclopentanone;
CHX = Cyclohexanone; CHP = Cycloheptanone; COT = Cyclooctanone.
*Equimolar concentration of donor and acceptor.

Table 11. Molecular interaction parameter (10^{-2}) values of aldehydes with diethylamine in *n*-hexane at 303 K.

Conc. (M)*	BEA	OCA	ANA	TUA	CNA	PPA	CRA	PRA	VLA
0.03	0.525	0.750	0.788	1.584	1.359	0.112	0.602	0.024	0.206
0.06	0.599	0.825	0.994	1.621	1.464	0.261	0.639	0.037	0.511
0.09	0.674	0.900	1.220	1.689	1.524	0.486	0.676	0.074	0.568
0.12	0.824	1.095	1.464	1.753	1.765	0.748	0.751	0.104	0.623
0.15	1.012	1.291	1.728	1.794	1.991	1.048	0.864	0.149	0.643
0.18	1.237	1.532	1.879	1.870	2.104	1.349	1.015	0.178	0.673
0.21	1.463	1.804	2.030	1.998	2.355	1.824	1.166	0.208	0.710
0.24	1.727	1.930	2.264	2.226	2.519	2.217	1.316	0.242	0.785
0.27	1.953	2.181	2.445	2.568	2.841	2.633	1.505	0.279	0.957
0.30	2.218	2.308	2.723	2.719	3.240	3.088	1.732	0.335	1.017

BEA = Benzaldehyde; OCA = *o*-Chlorobenzaldehyde; ANA = Anisaldehyde;
TUA = *p*-Tolualdehyde; CNA = Cinnammaldehyde; PPA = *β*-Phenylpropionaldehyde;
CRA = Crotonaldehyde; PRA = Propionaldeyde; VLA = Valeraldehyde.
*Equimolar concentration of donor and acceptor.

Cyclic ketones generally form more stable complexes with diethylamine than acyclic ketones. From the values of formation constant, it is found that the stability of the charge transfer complexes among cyclic ketones is in the order:

Cyclooctanone > Cyclohexanone > Cyclopentanone > Cycloheptanone

A similar trend was also observed on the charge transfer complexes of cyclic ketones and tetrachloroethylene in *n*-hexane by Jayashanthi [7]. This trend in K values is in the same order as the electron releasing capacity of substituents in aromatic aldehydes. In the case of *p*-chloroacetophenone, the chloro substituent exerts both mesomeric and inductive effects but in opposite directions. However, mesomeric effect dominates over inductive effect. Therefore, it forms a more stable complex with amine donor than acetophenone but

Table 12. Molecular interaction parameter (10^{-2}) values of ketones with diethylamine in *n*-hexane at 303 K.

Conc. (M)*	ACT	EMK	ACP	PMA	PCA	CPN	CHX	CHP	COT
0.05	−0.224	−0.447	0.691	1.211	0.374	0.186	0.410	0.111	0.916
0.10	−0.522	−0.447	0.771	1.475	0.636	0.321	0.533	0.186	1.160
0.15	−0.869	−0.473	1.009	1.928	0.947	0.579	0.694	0.230	1.404
0.20	−1.116	−0.522	1.121	2.231	1.198	0.904	0.820	0.297	1.666
0.25	−1.265	−0.596	1.331	2.61	1.461	1.039	1.157	0.573	2.118
0.30	−1.443	−0.745	1.556	2.952	1.705	1.264	1.570	0.632	2.571
0.35	−1.561	−0.820	1.947	3.294	1.95	1.515	1.983	0.744	2.797
0.40	−1.636	−0.931	2.154	3.866	2.176	1.805	2.417	0.931	3.024
0.45	−1.858	−1.172	2.233	4.363	2.402	2.023	2.870	1.174	3.269
0.50	−2.005	−1.265	2.342	4.899	2.629	2.174	3.343	1.568	3.934

ACT = Acetone; EMK = Ethyl methyl ketone; ACP = Acetophenone;
PMA = *p*-Methylacetophenone; PCA = *p*-Chloroacetophenone; CPN = Cyclopentanone;
CHX = Cyclohexanone; CHP = Cycloheptanone; COT = Cyclooctanone.
*Equimolar concentration of donor and acceptor.

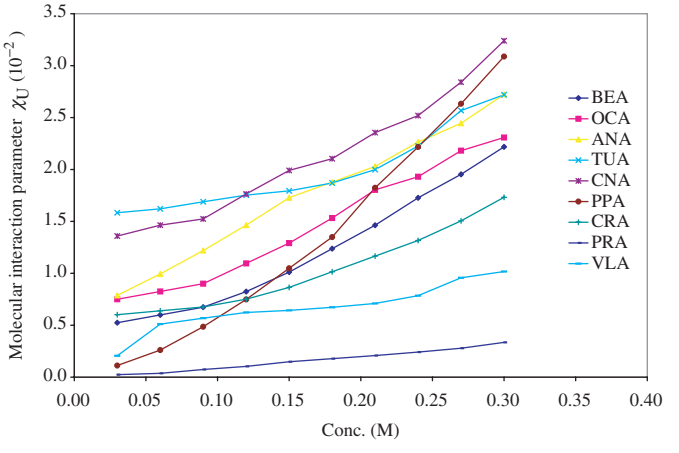

Figure 5. Plots of molecular interaction parameter *vs*. concentration of diethylamine–aldehydes.

a less stable complex than those of *p*-methylacetophenone in which case the methyl group releases electron. It is observed that the presence of an electron releasing group at para position in acetophenone favours complexation. Among the aliphatic ketones the stability increases with the increase in length of the alkyl chain on either side of the carbonyl group. Thus, ethyl methyl ketone forms a more stable complex with amine than acetone.

The free energy of formation (ΔG°_{F}), free energy of activation ($\Delta G^{\#}$), and relaxation time (τ) values are computed for all the charge transfer complexes investigated (Table 13). The negative free energy of formation values for all the eighteen complexes suggests that the donor–acceptor complexes formed between ketones and amines are thermodynamically stable. The nearly constant value of ($\Delta G^{\#}$) and (τ) for these systems suggests that a similar type of complexes are formed between carbonyl compounds and amines, as these two parameters are intrinsic properties of a charge transfer complex.

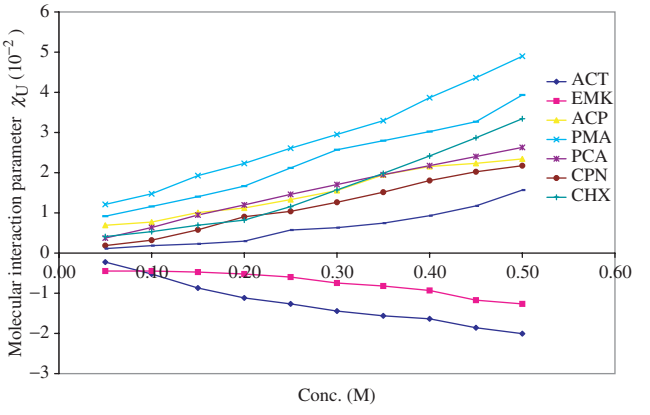

Figure 6. Plots of molecular interaction parameter *vs*. concentration of diethylamine–ketones.

Table 13. Formation constant, free energy of formation, mean free energy of activation and mean viscous relaxation time values of donor acceptor complexes of certain aldehydes and ketones with diethylamine in *n*-hexane at 303 K.

Acceptor	Donor-diethylamine			
	K (M^{-1})	ΔG°_F (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	τ (10^{-13}) s
Benzaldehyde	7.73	−5.2	3.5	5.6
o-Chlorobenzaldehyde	20.42	−7.6	3.5	5.6
Anisaldehyde	29.91	−8.6	3.5	5.5
p-Tolualdehyde	23.91	−8.0	3.5	5.7
Cinnammaldehyde	71.79	−10.8	3.4	5.5
β-Phenylpropionaldehyde	20.67	−7.6	3.5	5.5
Crotonaldehyde	113.48	−11.9	3.6	5.8
Propionaldeyde	27.79	−8.4	3.5	5.6
Valeraldehyde	44.16	−9.5	3.5	5.6
Acetone	9.51	−5.7	3.5	5.7
Ethyl methyl ketone	11.74	−6.2	3.5	5.6
Acetophenone	8.81	−5.5	3.5	5.6
p-Methylacetophenone	29.16	−8.5	3.4	5.5
p-Chlorolacetophenone	21.70	−7.8	3.4	5.5
Cyclopentanone	117.09	−12.0	3.5	5.5
Cyclohexanone	188.38	−13.2	3.5	5.5
Cycloheptanone	93.75	−11.4	3.5	5.6
Cyclooctanone	246.54	−13.9	3.5	5.6

4. Conclusion

Aldehydes and ketones with electron-deficient carbonyl carbon form thermodynamically stable charge transfer complexes with secondary amine-like diethylamine. The complexation between ketones and amine can be detected by ultrasonic method. Stability constants are determined for such complexes in *n*-hexane at 303 K. The stabilities of these complexes depend on the structure of acceptor molecule. The complex formation may be a prelude to

the formation of Schiffs base type condensation products between carbonyl compounds and secondary amine.

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