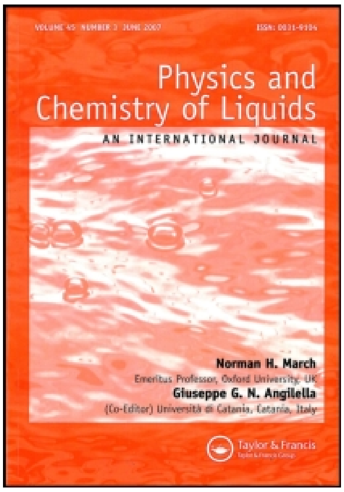

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ULTRASONIC STUDIES ON CHARGE TRANSFER COMPLEXES OF CYCLO ALKANONES WITH CHLOROFORM IN *n*-HEXANE SOLUTIONS

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The ultrasonic velocity (U), density (ρ) and viscosity (η) of solutions containing equimolar concentration of four cycloalkanones (cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone) and chloroform in *n*-hexane solutions have been measured in the temperature range 293–313 K. Acoustical parameters such as adiabatic compressibility (β), Rao constant (R), absorption coefficient (α/f^2), free energy of activation (ΔG^*), internal pressure (π_i) cohesive energy (CE), free volume (V_f), interaction parameters with respect to ultrasonic velocity (X_u), density (X_ρ), and viscosity (X_η) were calculated from the experimental data. These investigations indicate the formation of charge transfer complexes between cyclic ketones and chloroform in *n*-hexane medium. Formation constant values of the complexes have been evaluated using a newly proposed equation. Thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) for the formation of these complexes are computed from the variation of formation constant values with temperature. The stability constants of the charge transfer complexes formed between four cyclic ketones and chloroform correlate satisfactorily with polarisability (α), and ionization potential (IP) values of the ketones computed by semi empirical molecular orbital calculations.

Keywords: Ultrasonic velocity; Thermodynamic parameters; Charge transfer complexes; Cyclo alkanones; Chloroform

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1. INTRODUCTION

Aldehydes and ketones are polar compounds. They can form charge transfer complexes with polar compounds like chloroform through inter molecular hydrogen bonding [1]. The formation of such complexes between aliphatic ketones and chloroform has been detected by spectral methods [2,3]. Recently, ultrasonic measurements have been employed to detect the charge transfer complexes between ketones and chloroform in this laboratory and we have calculated the formation constants of these complexes using a new equation [4]. The stability constants are correlated with the total charge density on the carbonyl oxygen of the alkyl and aryl ketones. Proteins contain carbonyl group as a part of peptide linkage [5] and the study of the interaction between carbonyl group and chloroform will be helpful in understanding the role of chloroform as an anaesthetic. Several biologically important compounds contain carbonyl group in the ring [6] and this prompted us to investigate the molecular interaction between cyclic ketones and chloroform in a non-polar medium like *n*-hexane. In this paper, we report the ultrasonic velocities, densities and viscosities for *n*-hexane solutions containing equimolar concentration of cyclic ketones and chloroform. The stability constants (K) are calculated for the charge transfer complexes formed between chloroform and four cyclic ketones, namely, cyclopentanone, cyclohexanone, cycloheptanone, and cyclooctanone at 293, 298, 303, 308 and 313 K. Acoustical parameters such as adiabatic compressibility (β), Rao constant (R), absorption coefficient (α/f^2), free energy of activation (ΔG^*), internal pressure (π_i), cohesive energy (CE), molecular interaction parameters with respect to ultrasonic velocity (X_u), density (X_ρ), and viscosity (X_η) are also reported in this paper. The thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) are determined from the stability constant values at different temperatures.

2. EXPERIMENTAL

The donors used in the present study are cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone. Laboratory Reagent grade samples of these liquids were purified by usual method [7,8]. The boiling points of these liquids agree with the literature values indicating that the liquids used in the present study are of high purity. The boiling points are listed below:

Compound	*Boiling point* °C
Cyclopentanone	130
Cyclohexanone	155
Cycloheptanone	179
Cyclooctanone	196
Chloroform	61.2
n-Hexane	69

These liquids are stored in air tight amber colored bottles to minimize the absorption of moisture. Solutions containing equimolar quantities of cyclic ketones and chloroform in *n*-hexane were prepared fresh and thermostated before taking ultrasonic velocity, density and viscosity measurements.

The ultrasonic velocities of pure components and *n*-hexane solutions containing cyclic ketones and chloroform were measured in a multifrequency ultrasonic interferometer at 2 MHz (MITTAL ENTERPRISES New Delhi, Model F-81). The temperature of the liquid was maintained constant to an accuracy of ± 0.1°C in an electronically controlled thermostat. Densities of pure components and solutions were measured accurately using specific gravity bottles of 10 ml capacity. These bottles were calibrated before use with doubly distilled water. Weighings were done in an electronic balance with an accuracy of 0.1 mg. Viscosities of the liquids were measured in an Ostwald's viscometer, which was previously calibrated. The viscometer containing the samples was kept for 5 min in an electronically controlled thermostat to attain equilibrium. The accuracy in the measurement of density and viscosity of the liquids are of the order of ± 1 part in 10^3 parts and 0.1%, respectively. The ultrasonic velocity, density and viscosity measurements were made at 293, 298, 303, 308 and 313 K, respectively.

3. COMPUTATIONAL METHODS

Adiabatic compressibility, Rao constant, absorption coefficient, internal pressure and the interaction parameters were calculated from the ultrasonic velocity, density and viscosity using standard equations [9–12]. Marwein and Bhat [13] have proposed an equation used to calculate the stability constants of donor–acceptor complexes in binary liquids. Their equation generally gives concentration dependent formation constant values in binary liquid mixtures. Recently, we have proposed an equation to calculate the formation constant values of the charge transfer complexes, applicable to weak complexes and in dilute solutions [4]. It can be represented as

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

where

$$Y = (a - k^{1/2}b)/(k - k^{1/2}),$$

in which $k = x/y$, x = difference between U_{cal} and U_{obs} at lower concentration 'a', y = difference between U_{cal} and U_{obs} at higher concentration 'b' and U_{cal} = the ultrasonic velocity of the mixture calculated from the mole fraction of the components using additive principle

4. RESULTS AND DISCUSSION

Carbonyl compounds such as aldehydes and ketones form charge transfer complexes with electrophilic accepter molecules through electron deficient atoms. It has been found that aliphatic and aromatic ketones form stable complexes with chloroform through strong interaction between carbonyl group of ketone and hydrogen of chloroform [4]. The stability of these complexes are attributed to intermolecular hydrogen bond. Earlier workers in this laboratory have found that aliphatic and aromatic aldehydes and ketones form complexes with chloroform and they correlated the total electronic charge density on the carbonyl oxygen with the stability constants. In this paper, we report the ultrasonic velocity, density and viscosity values of solutions containing equimolar amount of four cyclic ketones and chloroform in *n*-hexane.

Table I contains ultrasonic velocity, density, and viscosity values of such solutions at 303 K and at different concentrations. The ultrasonic velocity decreases with increase in concentration, reaches minimum at a characteristic concentration, thereafter increases. Plots of ultrasonic velocity *versus* concentration for the four systems are given in Fig. 1. These plots suggest that the interaction between cyclic ketones and chloroform is maximum at a particular concentration, which depends on the structure of ketone.

Figure 2 contains the plots of viscosity against concentration for the four mixtures of cyclic ketones and chloroform at 303 K. The non-linear variation in viscosity is indicative of formation of charge transfer complexes between cyclic ketones (donor) and chloroform (acceptor). In order to assess the intermolecular attraction between the four cyclic ketones and chloroform, adiabatic compressibility values are calculated from the ultrasonic velocity and density values. These values are plotted against concentration (Fig. 3). It is evident from these plots that at any concentration the compressibility factor for cyclopentanone–chloroform system is the highest while that of cyclooctanone–chloroform is the lowest at 303 K. This trend indicates that there are stronger molecular interaction between cyclooctanone and chloroform and the interaction is weak in the case of cyclopentanone and chloroform. It may also be noted that the compressibility factor remains almost constant at the lower concentration in the three of the four cyclic ketones investigated, but in the case of cyclopentanone adiabatic compressibility decreases with increase in concentration and increases at higher concentration. These observations suggest that the complexation between cycloheptanone and chloroform is concentration dependent while it is almost independent of concentration at low concentration of other cyclic ketones.

The linear free length, Rao constant, and absorption coefficient values at 303 K are given in Table II. It may be noted that there is no significant change in linear free length values with concentration in all the four systems. However, there is non-linear variation in Rao constant and the absorption coefficient values indicating the formation of charge transfer complexes in the four systems.

Cohesive energy in a liquid mixture is a measure of potential energy of attraction between the molecules of the components. It can also be used to compare the interaction between the molecules in binary

TABLE I Ultrasonic velocity, density and viscosity values of cyclic ketones with chloroform in *n*-hexane Solutions at 303 K

*Conc.,**/ M × 10^{-5}	*Ultrasonic velocity* (*U*) ms^{-1}				*Density* (ρ) $kg\,m^{-3}$				*Viscosity* (η) × 10^{-3} $N\,s\,m^{-2}$			
	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$
1.0	1044.4	1045	1045.9	1045.9	643.52	644.06	645.44	646.74	0.295	0.288	0.282	0.260
2.5	1044	1044.5	1045.6	1045.4	644.45	645.89	646.82	647.44	0.288	0.282	0.283	0.253
5.0	1043.1	1043.6	1044.9	1044.5	645.24	646.97	647.71	648.51	0.282	0.283	0.276	0.254
7.5	1042.4	1042.8	1044.3	1043.7	646.78	647.24	648.71	649.58	0.276	0.276	0.270	0.248
10	1041.7	1042	1043.7	1042.9	648.34	648.17	649.22	650.68	0.277	0.270	0.263	0.242
25	1043.8	1038.6	1042.6	1041.9	640.74	650.62	650.7	651.91	0.267	0.271	0.257	0.242
50	1042.6	1036.1	1044.4	1040.8	643.49	651.47	644.36	652.63	0.281	0.264	0.268	0.236
75	1041.4	1044.1	1043.6	1044.3	645.07	647.23	645.28	647.31	0.275	0.283	0.268	0.247
100	1040.2	1042.3	1042.8	1043.5	646.94	648.32	646.72	648.47	0.269	0.276	0.262	0.241
500	1039.1	1041.4	1041.4	1042.4	649.39	649.72	647.88	649.69	0.263	0.270	0.256	0.241

*Ketone = Chloroform.

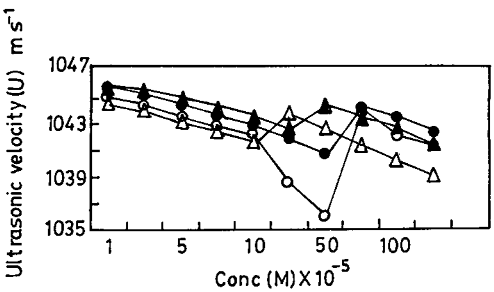

FIGURE 1 Plot of ultrasonic velocity *versus* concentration of cyclic ketones with chloroform in *n*-hexane solutions at 303 K.

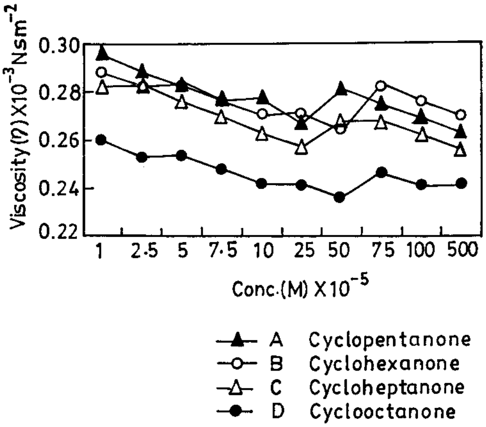

FIGURE 2 Plot of viscosity *versus* concentration of cyclic ketones with chloroform in *n*-hexane solutions at 303 K.

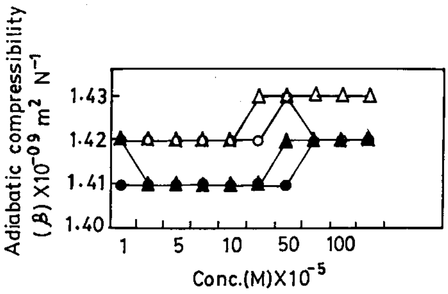

FIGURE 3 Plot of adiabatic compressibility *versus* concentration of cyclic ketones with chloroform *n*-hexane solutions at 303 K.

TABLE II Linear free length, Rao constant and absorption coefficient values of cyclic ketones with chloroform in *n*-hexane solutions at 303 K

Conc.,*/ M × 10^{-5}	*Linear free length* (L_f) Å				*Rao constant* (R) × 10^{-2}				*Absorption coefficient* (α/f^2) × 10^{-15} $N_p\,m^{-1}\,s^2$			
	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$
1.0	0.742	0.742	0.740	0.740	0.1838	0.1836	0.1833	0.1829	10.6	10.3	10.0	9.81
2.5	0.742	0.741	0.740	0.740	0.1857	0.1854	0.1852	0.185	10.3	10.1	10.1	9.81
5.0	0.742	0.741	0.740	0.740	0.1864	0.1859	0.1858	0.1855	10.1	10.1	9.82	9.61
7.5	0.742	0.742	0.740	0.740	0.1862	0.186	0.1857	0.1854	9.91	9.89	9.61	9.61
10	0.741	0.742	0.740	0.739	0.1858	0.1859	0.1857	0.1852	9.94	9.68	9.37	9.40
25	0.744	0.743	0.740	0.739	0.1884	0.1852	0.1854	0.185	9.63	9.78	9.16	9.20
50	0.743	0.744	0.742	0.740	0.1876	0.1849	0.1875	0.1849	10.1	9.58	9.60	8.97
75	0.743	0.741	0.742	0.740	0.1871	0.1866	0.1872	0.1866	9.92	10.1	9.61	9.59
100	0.743	0.741	0.742	0.740	0.1865	0.1862	0.1867	0.1863	9.71	9.88	9.39	9.38
500	0.742	0.741	0.742	0.740	0.1858	0.1858	0.1863	0.1859	9.49	9.67	9.20	9.18

*Ketone = Chloroform.

and ternary mixtures. Cohesive energy, free volume and free energy of activation values are computed for the four system from the measured ultrasonic velocities and viscosities are presented in Table III. The decrease in cohesive energy values with increase in concentration in all the four systems suggests that stronger molecular interactions are present in these systems. This is also supported by slight increase in free volume with concentration at 303 K. The free energy of activation obtained from the viscosity values is almost constant, since free energy of activation is intrinsic property of the charge transfer complexes. As the four cyclic ketones form similar complexes with chloroform, free energy of activation values for the four systems are always constant.

Internal pressure in a liquid system is directly related to the intermolecular attraction. The values of internal pressure at various concentrations of the donor and acceptor in *n*-hexane solutions are calculated for the four system at 303 K. These values are plotted against concentration (Fig. 4). It may be inferred from the plots that the molecular attraction between cyclic ketones and chloroform increases with increase in concentration and the interaction is maximum at characteristic concentration. This is suggested by the minimum internal pressure at a particular concentration in these plots. The variation in internal pressure with concentration at the experimental temperature confirms the formation of charge transfer complexes between carbonyl compounds and chloroform.

The strength of the intermolecular attraction in the liquid mixtures can be determined from molecular interaction parameters. These interaction parameters are computed as a function of ultrasonic velocity (X_u), density (X_ρ) and viscosity (X_η). These values at different concentrations and at 303 K are given in Table IV for the four systems. The data in Table IV indicate that the X_u values are either positive or negative for the four systems investigated. Thus, chloroform forms donor–acceptor complexes with four cyclic ketones. This is further supported by negative values of X_ρ and X_η for all the four systems. The cohesive energy values are analysed as a function of molecular interaction parameters. Figure 5 contains the plots of cohesive energy against X_u. These plots indicate that the cohesive energy is minimum at a particular concentration at which the molecular interaction parameter (X_u) is negative. At this concentration there are strong

TABLE III Free energy of activation, free volume and cohesive energy values of cyclic ketones with chloroform in *n*-hexane solutions at 303 K

Conc.,*/ M × 10^{-5}	*Free energy of activation* (ΔG*) kJ				*Free volume* × 10^{-7} (V_f) cm^3				*Cohesive energy* (*CE*) kJ			
	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$
1.0	3.49	3.42	3.35	3.28	0.642	0.986	1.02	1.05	29.05	28.84	28.42	28.05
2.5	3.42	3.36	3.36	3.28	0.642	1.04	1.03	1.07	28.63	28.38	28.34	27.62
5.0	3.37	3.37	3.28	3.22	0.664	1.04	1.08	1.11	28.37	28.48	27.08	27.55
7.5	3.30	3.30	3.22	3.22	0.665	1.08	1.12	1.11	27.97	28.13	27.70	27.34
10	3.31	3.24	3.15	3.16	0.688	1.11	1.16	1.15	28.10	27.75	27.34	26.95
25	3.23	3.26	3.09	3.10	0.692	1.10	1.20	1.19	27.74	27.86	26.94	26.95
50	3.37	3.19	3.22	3.02	0.734	1.14	1.13	1.24	28.37	27.47	27.59	26.56
75	3.30	3.36	3.22	3.22	0.774	1.04	1.13	1.13	28.12	28.40	27.56	27.14
100	3.24	3.29	3.16	3.16	0.721	1.08	1.17	1.16	27.67	27.98	27.31	26.91
500	3.18	3.24	3.10	3.09	0.905	1.12	1.21	1.20	27.39	27.74	27.09	26.87

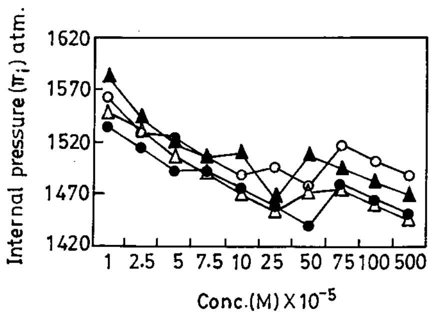

FIGURE 4 Plot of internal pressure *versus* concentration of cyclic ketones with chloroform in *n*-hexane solutions at 303 K.

molecular interactions between the donor and acceptor molecules. Cohesive energy values are plotted against X_ρ (Fig. 6) and X_η values (Fig. 7). These plots are similar to the plots of cohesive energy *versus* X_u suggesting that cohesive energy is minimum at the concentration at which complexation is maximum. These observations indicate that chloroform molecules are strongly attracted by the molecule of cyclic ketones probably through inter molecular hydrogen bond resulting in the formation of charge transfer complexes.

The thermodynamic stability of the donor and acceptor complexes formed between the cyclic ketones and chloroform can be compared by determining the formation constants of these complexes at different temperatures. In order to determine the stability constants of these complexes, ultrasonic velocity, density and viscosity values of pure components are required. These values at 293, 298, 303, 308 and 313 K are listed in Table V. Table VI contains the formation constants of charge transfer complexes formed between four cyclic ketones and chloroform at 303 K. For each system, the stability constant values are almost constant and independent of concentration. The formation constant values indicate that the stability of charge transfer complexes formed between cyclic ketones and chloroform are in the order cyclooctanone > cyclohexanone $\geq$ cycloheptanone > cyclopentanone.

The thermodynamic parameters, such as free energy change, enthalpy change and entropy change for the formations of the

TABLE IV Molecular interaction parameter values with respect to velocity, density and viscosity for cyclic ketones and chloroform in *n*-hexane solutions at 303 K

Conc.,*/ M × 10^{-5}	*Interaction parameter with respect to velocity* (X_U)				*Interaction parameter with respect to density* (X_ρ)				*Interaction parameter with respect to viscosity* (X_η)			
	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$
1.0	– 0.0068	– 0.0056	– 0.0039	– 0.0039	– 0.029	– 0.027	– 0.023	– 0.019	– 0.1089	– 0.1507	– 0.1857	– 0.3078
2.5	– 0.0072	– 0.0062	– 0.0041	– 0.0045	– 0.032	– 0.027	– 0.024	– 0.023	– 0.1546	– 0.1895	– 0.1837	– 0.3476
5.0	– 0.0081	– 0.0071	– 0.0047	– 0.0054	– 0.041	– 0.035	– 0.033	– 0.031	– 0.1969	– 0.1912	– 0.2307	– 0.3485
7.5	– 0.0088	– 0.0080	– 0.0052	– 0.0063	– 0.046	– 0.044	– 0.040	– 0.037	– 0.2367	– 0.2367	– 0.2695	– 0.3837
10	– 0.0095	– 0.0089	– 0.0056	– 0.0072	– 0.051	– 0.051	– 0.048	– 0.044	– 0.2370	– 0.2751	– 0.3122	– 0.4177
25	– 0.0014	– 0.0113	– 0.0037	– 0.0050	– 0.127	– 0.100	– 0.100	– 0.097	– 0.3239	– 0.3035	– 0.3736	– 0.4446
50	0.0027	– 0.0098	0.0062	– 0.0008	– 0.197	– 0.177	– 0.195	– 0.174	– 0.3029	– 0.3847	– 0.3660	– 0.5084
75	0.0066	0.0118	0.0109	0.0122	– 0.258	– 0.253	– 0.258	– 0.253	– 0.3755	– 0.3387	– 0.4069	– 0.4963
100	0.0101	0.0142	0.0152	0.0166	– 0.308	– 0.305	– 0.309	– 0.305	– 0.4375	– 0.4079	– 0.4664	– 0.5486
500	0.0770	0.0818	0.0818	0.0838	– 0.653	– 0.653	– 0.655	– 0.653	– 0.6979	– 0.6816	– 0.7138	– 0.7464

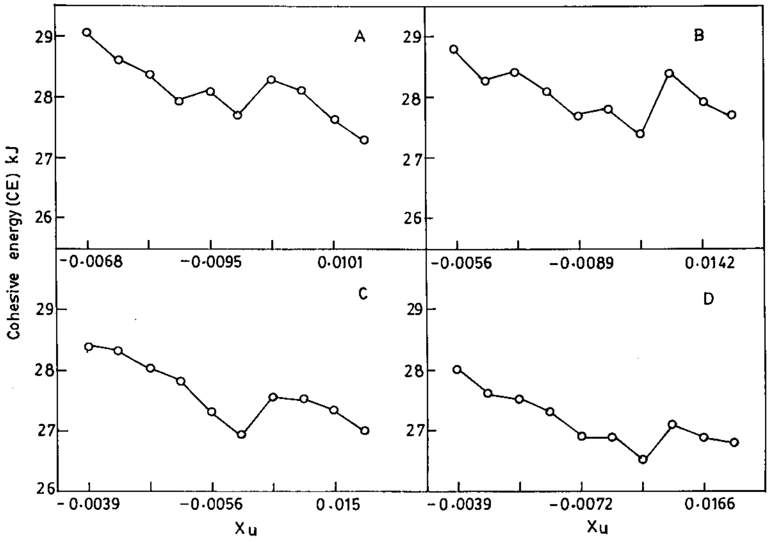

FIGURE 5 Plot of cohesive energy *versus* molecular interaction parameter X_u of cyclic ketones with chloroform in *n*-hexane solutions at 303 K.

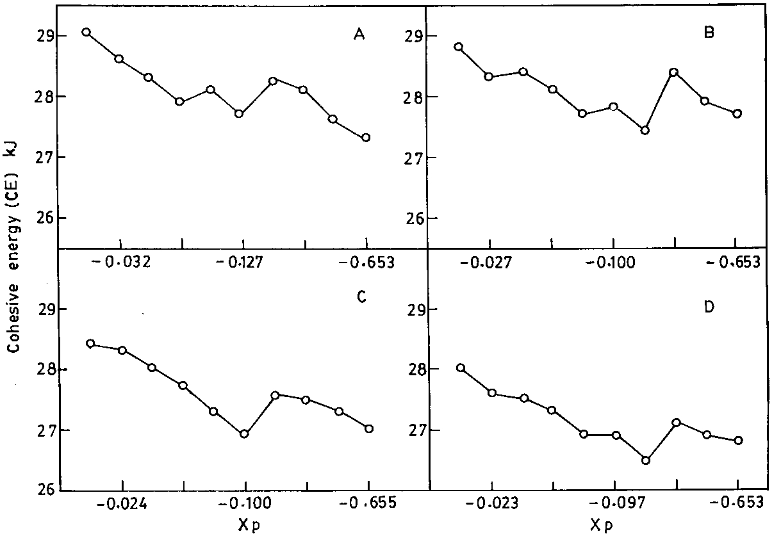

FIGURE 6 Plot of cohesive energy *versus* molecular interaction parameter X_p of cyclic ketones with chloroform in *n*-hexane solutions at 303 K.

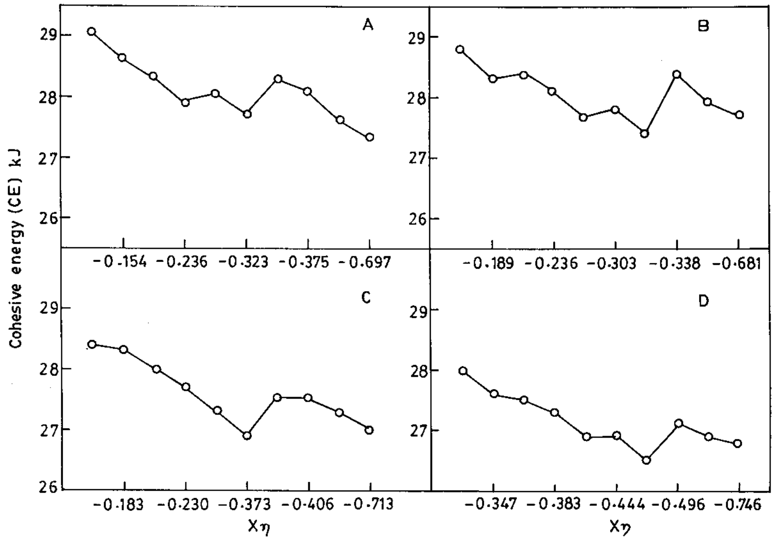

FIGURE 7 Plot of cohesive energy *versus* molecular interaction parameter X_η of cyclic ketones with chloroform in *n*-hexane solutions at 303 K.

charge transfer complexes are determined. The enthalpy change (ΔH) values are obtained from the plots of $\ln K$ *versus* $1/T$ (Fig. 8). All the plots have negative slopes indicating that the enthalpy change values are negative for all the four donor–acceptor complexes. It can therefore be inferred that the formation of the change transfer complexes between cyclic ketones and chloroform in *n*-hexane solution is exothermic. The thermodynamic parameters for the complexation are given in Table VII. The trend in the free energy of formation is similar to the trend in the stability constants of the four complexes. The entropy change (ΔS) for the formation of donor–acceptor complexes between four cyclic ketones and chloroform are large negative. This may probably be due to the complexation between donor and acceptor molecules, besides the solvation of the complexes. The acoustical and thermodynamic parameters determined for *n*-hexane solutions containing cyclic ketones and chloroform prove that the chloroform molecules are strongly attracted by the molecules of the carbonyl compounds in non-polar medium like *n*-hexane. In order to determine the relation between the extent of complexation and the structure of carbonyl

TABLE V Ultrasonic velocity, density, viscosity and internal pressure of a pure cyclic ketones, *n*-hexane and chloroform at different temperatures

Compounds		20°C	25°C	30°C	35°C	40°C
C_5H_8O	U (m s^{-1})	1414	1396.1	1376.8	1360	1338.4
	ρ (kg m^{-3})	950.99	949.75	948.6	947.4	942.4
	η (N s m^{-2})	0.001144	0.001022	0.000957	0.000857	0.00079
	π_i (atm)	4933	4688	4565	4343	4199
$C_6H_{10}O$	U (m s^{-1})	1430.2	1409.6	1390.1	1371	1349.8
	ρ (kg m^{-3})	945.49	943.98	942.08	941.63	940.24
	η (N s m^{-2})	0.00225	0.002009	0.001872	0.001872	0.001487
	π_i (atm)	5723	5442	5283	5001	4772
$C_7H_{12}O$	U (m s^{-1})	1468.2	1448.6	1430.4	1410.7	1392.1
	ρ (kg m^{-3})	950.97	949.57	948.17	946.11	943.58
	η (N s m^{-2})	0.003405	0.002483	0.002278	0.001997	0.001761
	π_i (atm)	5970	5127	4937	4648	4386
$C_8H_{14}O$	U (m s^{-1})	1509.9	1489.4	1469.6	1452.1	1432.5
	ρ (kg m^{-3})	957.71	956.4	955.26	953.84	951.6
	η (N s m^{-2})	0.010184	0.008192	0.007214	0.005915	0.005551
	π_i (atm)	8914	8042	7592	6909	6728
$CHCl_3$	U (m s^{-1})	987.5	975.9	957.8	942.8	925
	ρ (kg m^{-3})	1525.8	1523.12	1520.68	1509.12	1496.68
	η (N s m^{-2})	0.00067	0.000633	0.000633	0.000592	0.000559
	π_i (atm)	4114	4019	4053	3930	3835
C_6H_{14}	U (m s^{-1})	1092.1	1069.2	1048.1	1028.1	1007.4
	ρ (kg m^{-3})	653	652.1	651.5	647	643.8
	η (N s m^{-2})	0.000341	0.000317	0.000312	0.000286	0.000272
	π_i (atm)	2319	2905	2260	2175	2136

TABLE VI Formation constants of charge transfer complexes between cyclic ketones with chloroform in *n*-hexane solutions at 303 K

C_5H_8O *Conc.* (M)			$C_6H_{10}O$ *Conc.* (M)			$C_7H_{12}O$ *Conc.* (M)			$C_8H_{14}O$ *Conc.* (M)		
$a \times 10^{-5}$	$b \times 10^{-5}$	$K \times 10^3$	$a \times 10^{-5}$	$b \times 10^{-5}$	$K \times 10^3$	$a \times 10^{-5}$	$b \times 10^{-5}$	$K \times 10^3$	$a \times 10^{-5}$	$b \times 10^{-5}$	$K \times 10^3$
7.5	10	2.37	2.5	5.0	4.06	2.5	5.0	3.54	2.5	5.0	6.36
1.0	5.0	2.73	1.0	5.0	3.94	7.5	10	3.27	2.5	75	6.24
5.0	10	2.30	2.5	7.5	3.97	1.0	50	2.67	5.0	10	6.30
1.0	7.5	2.58	1.0	7.5	3.91	2.5	7.5	3.33	1.0	7.5	6.08
2.5	10	2.73	2.5	10	4.00	2.5	10	3.31	2.5	10	6.33
1.0	10	2.54	1.0	10	3.95	1.0	10	2.87	1.0	10	6.17

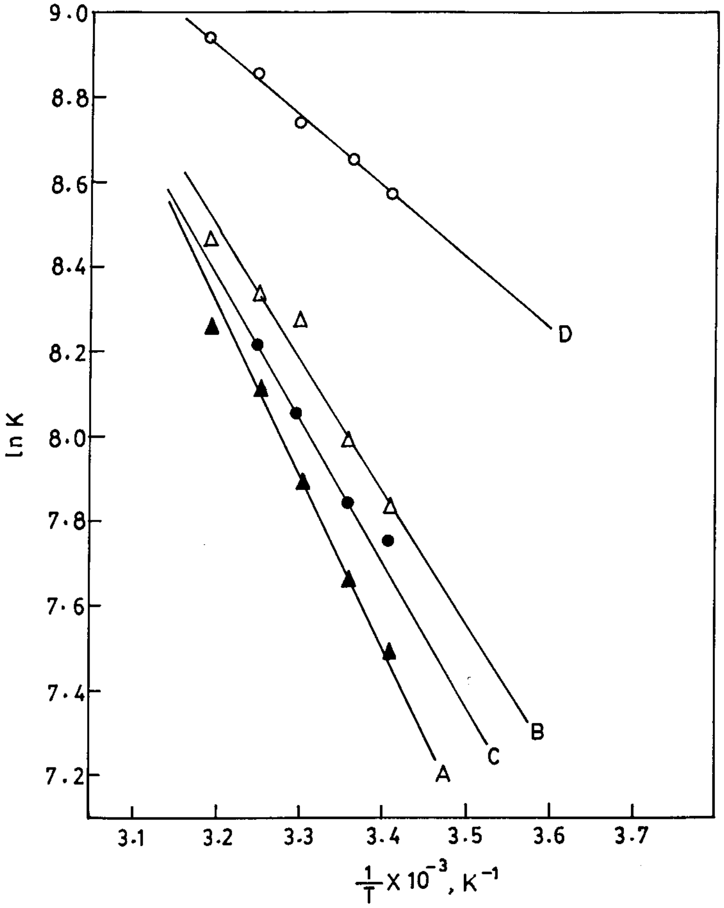

FIGURE 8 Plot of $\ln K$ *versus* $1/T$ of cyclic ketones.

compounds two molecular parameters, polarisability and first ionisation potential are computed for the four cyclic ketones by semi empirical molecular orbital calculations at the PM3 level (Table VIII). Figure 9a contains the plot of $\log K$ *versus* polarisability. It indicates that the formation constant is directly related to the polarisability of the carbonyl compounds. The plot of $\log K$ *versus* ionisation potential is given in Fig. 9b. It is also linear but has negative slope. These observations suggest that the charge transfer complexes are formed between

TABLE VII Free energy, enthalpy change and entropy changes for the formation of charge transfer complexes between cyclic ketones and chloroform in *n*-hexane solutions

Cyclic ketones	ΔG *at* 303 K (kJ mol^{-1})	ΔS *at* 303 K (JK^{1} mol^{-1})	ΔH (kJ mol^{-1})
C_5H_8O	− 19.76	− 167	− 30.88
$C_6H_{10}O$	− 20.89	− 156	− 26.60
$C_7H_{12}O$	− 20.31	− 164	− 29.56
$C_8H_{14}O$	− 22.03	− 118	− 14.03

TABLE VIII Polarisability and ionisation potential values of cyclic ketones

Cyclic ketones	$\alpha \times 10^{-24}$ (cm^3)	*Ionisation potential* (eV)
C_5H_8O	8.35	10.60
$C_6H_{10}O$	10.1	10.48
$C_7H_{12}O$	11.7	10.51
$C_8H_{14}O$	13.2	10.43

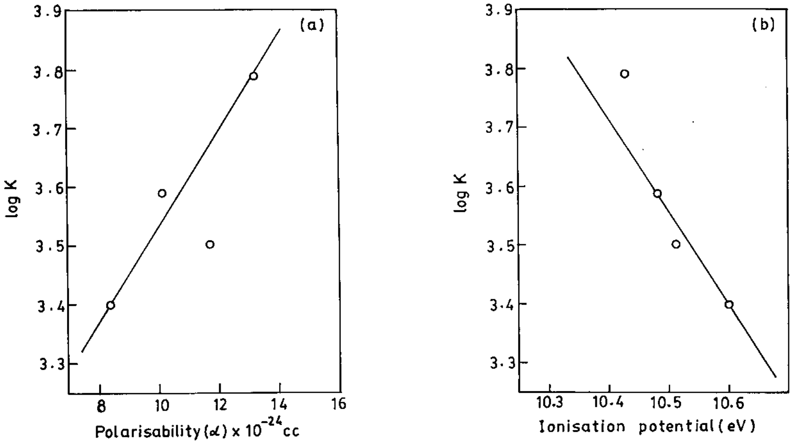

FIGURE 9 Plot of log *K versus* (a) polarisability and (b) ionisation potential of cyclic ketones.

the four cyclic ketones and chloroform due to strong dipolar interactions and consequently the ketone molecules are polarized. The formation constant, therefore, increases with increase in polarisability of the cyclic ketones, but decreases with increase in ionisation potential.

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