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Research Article

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Study of structural and temperature dependence on stability constants of certain charge transfer complexes in solution by ultrasonic method

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ABSTRACT

The ultrasonic velocity (U), density (ρ) and coefficient of viscosity (η) of solutions containing equimolar concentration of two ketones (cyclohexanone and Ethyl methyl ketone) and Pyridine in n-hexane solvent have been measured at 293K, 298K and 303K. Acoustical parameters such as adiabatic compressibility (β), Intermolecular free length (L_f), internal pressure (π_i) and cohesive energy (CE) values are calculated from the experimental values of U, ρ and η. These investigations indicate the formation of weak charge transfer complexes between various ketones and pyridine in n-hexane solvent. Stability constant (K) values of the charge transfer complexes in solution have been evaluated using Marwein and Bhatt equation. The free energy of activation ($\Delta G\#$) for the formation of these complexes is also computed from K values. The free energy of formation (ΔG^0_F) and viscous relaxation time (τ) are found to be almost constant for these complexes indicating the formation of similar charge transfer complexes in these systems.

Keywords: Charge Transfer Complexes, Stability Constant, Adiabatic Compressibility and Intermolecular free length.

INTRODUCTION

The donor-acceptor complex formation is biologically important. Oxygen transfer in blood involves reversible complexation between haeme and oxygen. Electron-deficient carbons of carbonyl group can act as electrophiles. Basic groups like amino groups can interact with this group to form a complex and influence the properties of such compound [1].The study of molecular interactions and the variations in these interactions due to structural changes has been carried out by various experimental techniques such as Infrared [2],Nuclear magnetic resonance [3,4], Raman spectra [5], and dielectric property measurement [6].The complete understanding of the nature of intermolecular and intramolecular interaction may not be possible by any single method. A number of workers have been reported the study through ultrasonic method [7-11].Ultrasonic velocity measurement has been used for detection and interpretation of weak and strong molecular interactions present in binary [12-13] and ternary [14-15] liquid mixtures. These studies can also be used to determine the stability constants of donor-acceptor complexes [16,17, 18]. In this background, an attempt has been made to determine the stability constant values of charge transfer complexes formed in solution of two ketones (Acceptor) and Pyridine (Donor) in n-hexane at 293K, 298K and 303K by ultrasonic method. These studies are made mainly to investigate structural and temperature dependence on the stability of this type of complexes and the factors, which plays important role in the complexation.

EXPERIMENTAL SECTION

High purity spectroscopic and HPLC grade samples of (purities of 99.5% or better) Cyclohexanone, Ethyl methyl ketone, Pyridine and n- Hexane were purchased from Merck Co. Their purities were 99.5% or better and no further purification has been done. The chemicals were stored over molecular sieves. Densities, Viscosities and Ultrasonic Velocities were measured at 293K, 298 K and 303K over a wide range of concentrations (0.02-0.2M). The densities of pure compounds and their solutions were measured accurately using Rudolph digital densitometer (accuracy ± 0.1). Viscosities of pure compounds and their mixtures were determined using Ostwald's Viscometer calibrated with double distilled water.

The ultrasonic velocity was measured by using variable path single crystal interferometer (Model F-81S, Mittal Enterprise, India) at fixed frequency 2 MHz with accuracy of ± 0.1 ms^{-1}. The temperature was maintained with an accuracy of 0.1^0C. Electronically digital operated constant temperature bath (Plasto Craft Industries) for low temperature bath model 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 (accuracy ±0.01). Acoustical parameters such as adiabatic compressibility (β), free length (L_f),internal pressure (π_i), The cohesive energy (CE),relaxation time (τ), stability constant (K) and the free energy of formation (ΔG^0_F) were calculated using standard equations [19-22].

$$\beta = 1/U^2\rho \ kg^{-1} \ ms^{-2} \qquad \text{……….} (1)$$

$$Lf = k/ \sqrt{U\rho} A^0 \qquad \text{……….} (2)$$

where, k is Jacobson's constant. This constant is a temperature dependent parameter whose value at any temperature (T) is given by $(93.875+0.345T) \times 10^{-8}$.

$$\pi_i=bRT(K\eta/U)^{1/2} (\rho^{2/3}/M_{eff}{}^{7/6}) \ atm \qquad \text{……….} (3)$$

Where b is the cubic packing factor which is assumed to be 2 for all solutions, K is the temperature dependent constant whose value is 4.28×10^9, R is the universal gas constant, T is the absolute temperature, M_{eff} is the effective molecular weight which is expressed as:

$$M_{eff} = (X_1M_1 + X_2M_2 + X_3M_3) \qquad \text{………} (4)$$

Where X and M are the mole fraction and molar weight of the individual constituent in the mixture respectively.

The cohesive energy (CE), relaxation time (τ) and free energy of formation (ΔG^0_F) were calculated using equation (5-7).

$$CE= \pi_i \times V_m \quad kJmol^{-1} \qquad \text{……..}(5)$$

Where π_i is the internal pressure and V_m is the molar volume given by $V_m = M_{eff} / \rho$

$$\tau = 4\eta/3\rho U^2 \ s \qquad \text{……..} (6)$$

$$\Delta G^0_F = - RT \ln K \quad kJmol^{-1} \qquad \text{……….} (7)$$

Where R is the universal gas constant, T is the absolute temperature and K is the stability constant.

The stability constant is calculated using the relation

$$K = Y/ (b-y)^2 \ dm^3 \ mol^{-1}$$

$$\text{Where, } Y = (a-k^{1/2} b) / (k-k^{1/2}) \qquad \text{………} (8)$$

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 fractions of the components using additive principle.
This equation can be used to calculate stability constant value for different combinations of concentrations 'a' and 'b'.

RESULTS AND DISCUSSION

The measured ultrasonic velocities, densities, viscosities and calculated values for various acoustical parameters such as β, L_f, π_i and CE at various equimolar concentrations of cyclohexanone and ethyl methyl ketone with pyridine in n-hexane are given in Table 1, 2 and 3.

Table 1.Values of ultrasonic velocity, density, viscosity, adiabatic compressibility, free length, internal pressure and cohesive energy of donor-acceptor complexes at 293K

Conc. (M)	Ultrasonic velocity (ms^{-1})	Density Kg m^{-3}	Viscosity (η) ×10-4 Nsm^{-2}	Adiabatic Compressibility (β) ×10^{-9}kg-^{1}ms^{2}	Free length (A^{0})	Internal Pressure (π_i)×10^{13} Pascal	Cohesive Energy (CE) kJ mol-1
Cyclohexanone + Pyridine + Hexane							
0.02	1001.0	670.3	14.93	1.653	0.025	4.904	62.25
0.04	1002.5	671.5	14.95	1.481	0.023	4.904	62.22
0.06	1003.1	672.9	14.98	1.476	0.023	4.914	62.22
0.08	1004.7	673.7	15.00	1.470	0.023	4.914	62.17
0.10	1005.1	675.1	15.03	1.466	0.023	4.924	62.18
0.12	1006.2	676.8	15.07	1.459	0.023	4.934	62.17
0.14	1007.9	679.4	15.13	1.448	0.023	4.954	62.15
0.16	1010.5	682.5	15.20	1.434	0.023	4.964	62.11
0.18	1011.2	684.0	15.23	1.429	0.023	4.975	62.11
0.20	1012.4	686.2	15.28	1.400	0.024	4.995	62.25
Ethyl methyl ketone + Pyridine + Hexane							
0.02	1005.0	666.4	14.42	1.485	0.023	4.812	61.23
0.04	1004.1	668.9	14.47	1.482	0.023	4.863	61.33
0.06	1003.7	670.0	14.50	1.481	0.023	4.894	61.39
0.08	1001.2	674.0	14.58	1.480	0.023	4.954	61.56
0.10	999.2	676.1	14.63	1.481	0.023	4.995	61.69
0.12	998.1	677.8	14.67	1.480	0.023	5.025	61.78
0.14	997.0	680.2	14.72	1.479	0.023	5.076	61.88
0.16	996.1	683.4	14.79	1.474	0.023	5.127	61.99
0.18	995.0	685.9	14.84	1.472	0.023	5.167	62.09
0.20	994.1	687.4	14.87	1.470	0.023	5.197	61.23

Table 2.Values of ultrasonic velocity,density,viscosity,adiabatic compressibility,free length,internal pressure and cohesive energy of donor-acceptor complexes at 298K

Conc. (M)	Ultrasonic velocity (ms^{-1})	Density Kg m^{-3}	Viscosity (η) ×10-4 Nsm^{-2}	Adiabatic Compressibility (β) ×10^{-9}kg-^{1}ms^{2}	Free length (A^{0})	Internal Pressure (π_i)×10^{13} Pascal	Cohesive Energy (CE) kJ mol-1
Cyclohexanone + Pyridine + Hexane							
0.02	1008.0	666.3	13.29	1.477	0.024	4.671	59.67
0.04	1009.5	667.7	13.32	1.469	0.023	4.681	59.64
0.06	1010.2	670.0	13.37	1.462	0.023	4.691	59.65
0.08	1012.7	671.9	13.40	1.451	0.023	4.701	59.60
0.10	1013.8	673.6	13.44	1.444	0.023	4.711	59.58
0.12	1015.2	675.8	13.48	1.435	0.023	4.721	59.57
0.14	1016.3	678.4	13.53	1.427	0.023	4.742	59.57
0.16	1017.2	680.5	13.58	1.420	0.023	4.752	59.57
0.18	1018.3	682.0	13.61	1.413	0.023	4.762	59.56
0.20	1019.0	685.2	13.67	1.405	0.023	4.782	59.67
Ethyl methyl ketone + Pyridine + Hexane							
0.02	1011.0	662.8	12.83	1.476	0.024	4.590	58.67
0.04	1010.2	664.0	12.85	1.475	0.024	4.620	58.74
0.06	1009.7	666.1	12.89	1.473	0.023	4.660	58.82
0.08	1008.2	667.9	12.93	1.471	0.023	4.691	58.92
0.10	1007.5	669.2	12.95	1.470	0.023	4.721	59.00
0.12	1005.7	672.5	13.02	1.469	0.023	4.772	59.13
0.14	1004.1	674.6	13.06	1.468	0.023	4.812	59.24
0.16	1003.0	676.2	13.09	1.466	0.023	4.853	59.32
0.18	1002.1	681.8	13.20	1.465	0.023	4.914	59.46
0.20	1000.0	683.0	13.22	1.464	0.023	4.954	58.67

Table 3.Values of ultrasonic velocity,density,viscosity,adiabatic compressibility,free length,internal pressure and cohesive energy of donor-acceptor complexes at 303K

Conc. (M)	Ultrasonic velocity (ms^{-1})	Density Kg m^{-3}	Viscosity (η) ×10-4 Nsm^{-2}	Adiabatic Compressibility (β) ×10^{-9}kg-^{1}ms^{2}	Free length (A^{0})	Internal Pressure (π_i)×10^{13} Pascal	Cohesive Energy (CE) kJ mol-1
Cyclohexanone + Pyridine + Hexane							
0.02	1010.0	664.1	11.38	1.476	0.024	4.387	56.15
0.04	1011.1	667.0	11.43	1.466	0.024	4.397	56.16
0.06	1012.8	669.4	11.47	1.456	0.024	4.417	56.14
0.08	1013.2	672.9	11.53	1.447	0.024	4.438	56.17
0.10	1014.7	674.1	11.56	1.440	0.023	4.442	56.14
0.12	1016.3	675.8	11.58	1.432	0.023	4.449	56.12
0.14	1017.0	677.6	11.62	1.426	0.023	4.458	56.12
0.16	1018.5	680.2	11.66	1.417	0.023	4.478	56.11
0.18	1019.1	683.2	11.71	1.409	0.023	4.498	56.13
0.20	1020.9	686.5	11.77	1.397	0.023	4.508	56.15
Ethyl methyl ketone + Pyridine + Hexane							
0.02	1014.2	662.8	11.00	1.466	0.024	4.316	55.15
0.04	1013.5	663.1	11.00	1.468	0.024	4.336	55.20
0.06	1012.2	665.9	11.05	1.465	0.024	4.377	55.31
0.08	1011.7	667.9	11.08	1.462	0.024	4.407	55.38
0.10	1010.2	670.0	11.12	1.462	0.024	4.448	55.47
0.12	1009.1	672.1	11.15	1.461	0.024	4.478	55.56
0.14	1008.5	674.9	11.20	1.456	0.024	4.519	55.64
0.16	1007.2	678.3	11.26	1.453	0.024	4.559	55.75
0.18	1005.2	681.3	11.31	1.452	0.024	4.610	55.87
0.20	1003.7	685.2	11.37	1.448	0.024	4.660	55.15

The trend in the ultrasonic velocity with concentration in the case of systems containing ketones suggests that there are feeble interactions between molecules of ketones and pyridine. The increasing trend in ultrasonic velocity suggests that the complexation increases with increase in concentration. The ultrasonic velocity decreases with increase in concentration in the case of ethyl methyl ketone - acetone. This shows that the complexation is significant even at lower concentration in these two systems. A similar observation was made by Kannappan in the study of donor–acceptor complexes between iodine monochloride and ethers [23]. Thus the donor-acceptor complex formation is significant in this concentration range for this system. There is an increase in density in this concentration range and this suggests that the complexation is concentration dependent. The viscosities are determined for these systems at various concentrations of the donor-acceptor mixtures. The increase in viscosity with concentration in all these systems suggests that the extent of complexation increases with the increase in concentration.

Adiabatic compressibility (β) is a measure of intermolecular association or dissociation or repulsion. It also determines the orientation of the solvent molecules around the liquid molecule. The structural arrangement of the molecule affects the adiabatic compressibility. There is a weak bond between the donor and acceptor molecules. Hence, the compressibility of charge transfer is slightly greater than that of pure component. Further, adiabatic compressibility of all the systems at different temperature are almost constant at the concentration investigated .This suggests that similar type of complexes are formed in these systems. A similar observation was made by Singh and Kalsh stated that adiabatic compressibility should be independent of temperature and pressure for unassociated and weakly associated molecules [24].Intermolecular free length (L_f) is the distance between the surfaces of the neighbouring molecules. The decrease in free length indicates strengthening of intermolecular interaction. The lower free length values indicate the formation of weak complex between ketone-amine at different temperatures. The internal pressure is a measure of cohesive forces between the component molecules. The internal pressure values are gradually increases with increase in concentration. This suggests the existence of similar type of complexes in these systems. The cohesive energy (CE) in liquid mixtures is an indicative of the force of attraction between the component molecules. The cohesive energy values are found to be almost constant for a given system at particular temperature indicating similar type of cohesive forces in that system.

The stability constants are calculated from measured ultrasonic velocities using modified Marwein and Bhatt equation. These values for all the donor-acceptor complexes at different temperature are given in Table 4.

Table 4. Stability constant (dm3mol-1), free energy of formation (kJmol-1),Mean free energy of activation (kJmol-1) and mean viscous relaxation time (10-8 s) values of certain charge transfer complexes at different temperatures

Acceptor	Donor- Pyridine			
	K (dm^3mol^{-1})	Δ G ($kJmol^{-1}$)	ΔG# (kJmol-^{1})	τ (10^{-8})s
		T=293K		
Cyclohexanone	2.166×10^{-5}	25.56	29.47	2.93
Ethyl methyl ketone	3.321×10^{-5}	25.98	27.52	1.31
		T=298K		
Cyclohexanone	3.08×10^{-5}	26.17	29.71	2.58
Ethyl methyl ketone	2.84×10^{-5}	26.37	29.67	2.54
		T=303K		
Cyclohexanone	3.41×10^{-5}	25.91	29.86	2.21
Ethyl methyl ketone	3.93×10^{-5}	25.55	29.81	2.17

From the stability constants obtained for the above systems, the free energy of formation (ΔG^0_F) and free energy of activation ($\Delta G^\#$) are calculated at 293K, 298K & 303K. For all the systems, ΔG^0_F values are positive indicating that the charge transfer complexes are thermodynamically unstable. The free energy of activation ($\Delta G^\#$) and relaxation time (τ) are inherent properties of a charge transfer complexes. The two properties are almost constant in all these systems at different temperature.

CONCLUSION

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. The complexation between ketones and amine can be detected by ultrasonic method. The stabilities of these complexes depend on the structure of donor-acceptor molecule and concentration of both donor-acceptors. It is also temperature dependent.

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