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Compressibility Studies in Cyclic Ketone with a Non-Polar Solvent through Ultrasonic Techniques

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Abstract*: The acoustical parameter -Compressibility elucidates the compatibility and intermolecular interaction prevailing in binary liquid mixtures. Intermolecular interaction possesses an important role in various industrial, biological and chemical processes like engineering material design, drug design, material science and nanotechnology. In the present investigation, ultrasonic velocities, densities and viscosities of the binary liquid mixtures of Cyclic ketones and a non polar solvent have been measured over the entire mole fraction range at 308 K. From these data, thermo acoustical parameters are calculated. The magnitude of these parameters shows specific interaction existing between the unlike molecules.
Keywords: Ultrasonic speeds; acoustical parameters; Ketone; unlike molecules.

I. INTRODUCTION

Ultrasonic Interferometer is a proficient and highly incisiveness device to interpret the molecular interaction existing in solids and liquids. Several researchers executed the ultrasonic study on liquids like non – electrolytes, nanofluids, liquid Iron, phase transitions, leaf extract, thermal conductivity, super conductors, glass, cement, resin, polymer, semiconductors, etc [1-4]. The present study is focussed on aliphatic cyclic ketones like cyclopentanone, cyclohexanone with a non polar solvent like benzene.

Cyclopentanone is an antecedent to Jasmine fragrance. Cyclopentanone is also used to synthesise pesticides like pencycuron, pentethylcyclanone. It also exists in foods like butter, meat, roasted peanut and used as a flavouring agent in industries. Cyclohexanone is a precursor to nylon varieties [5]. Benzene is obtained from the fractional distillation of crude oil. It acts as an intermediate in the synthesis of alkylbenzene, cyclic ketones, polymers, detergents, drugs, pesticides, explosives, additives in gasoline, etc.,. These chemicals act as the key ingredient in industries especially polymer industries. An attempt has been made to predict the molecular interactions existing between cyclopentanone and cyclohexanone with benzene using compressibility factors. Compressibility factors mainly applied to transport properties and fluid dynamics of liquid mixtures in Industries.

II. EXPERIMENTAL METHODS

The chemicals cyclopentanone(Spectrochem-99%) cyclohexanone (Merck- 99% purity), and benzene (Reachem- 99.5% purity) used in the present investigation were decontaminated using standard methods [6].Ultrasonic waves possess high frequency waves greater than 20,000 Hz. Ultrasonic velocity of liquid measurements can be carried out using acoustical grating, pulse echo system techniques, quartz crystal ultrasonic interferometer. In the present investigation, Ultrasonic velocity measurements are performed using quartz crystal ultrasonic interferometer (Mittal enterprises) of frequency 2 Mhz at different temperatures using thermostated water bath maintained at 308 K temperature accuracy (0.1%). Due to the vibration of quartz crystal, frequencies (f) of waves are produced. The wave length (λ) of the standing wave is measured. From the measured values of the wavelength and frequency ultrasonic velocity of liquids and liquid mixtures are computed.The viscosities (η) measurements were carried out using 20 ml Ostwald Viscometer by monitoring the flow time of liquids. Densities of liquids are determined using 10ml specific gravity bottle. The velocity, viscosity and density values are standardized first with double distilled water and then the liquid values are identified.

III. FORMULAE

A. Thermo Acoustical Parameters

1) *Theoretical Formulations:* Using the ultrasonic velocities, densities and viscosities data of the binary liquids cyclopentanone with benzene and cyclohexanone with benzene, the acoustical parameters like adiabatic compressibility [7], isentropic compressibility[8], free length [9], Molecular interaction parameters [10], Gruneisen Parameter[11], Wada Constant [12] are computed.

a) Adiabatic Compressibility (□S): □S□□□1/u²ρ□□□

b) Isothermal Compressibility (□T): □T □□□17.1 *10^-4) / u²T^4/9 ρ□□□

c) Intermolecular Free Path Length (Lf): $L_f = K_{ad}$ □□□

d) Molecular Interaction Parameter (χ): $\chi = (u_{exp}^2/u_{ideal}l^2)-1$

e) Gruneisen Parameter (Γmix□): Γ_{mix}□□□ $\frac{b}{3}\left[\frac{K\eta_{mix}}{u}\right]^{1/2}\left[\frac{V_{mix}^{1/2}}{M_{mix}^{1/2}}\right]$

f) Wada Constant (W): $W = (M.\beta^{-1/7}) / \rho$

where β= adiabatic compressibility, u = ultrasonic velocity, ρ =density, T = Temperature, K = temperature dependent Jacobson's Constant, b = packing factor, η = viscosity, V=Molar volume, M = Effective molecular weight.

IV. RESULTS AND DISCUSSION

The measured parameters of ultrasonic velocity(u), density(ρ) and viscosity (η) at 308.15 K for Cyclopentanone – Benzene and Cyclohexanone – Benzene systems are shown in Table 1 and Table 3 respectively.The calculated parameters of Adiabatic Compressibility (□S), Isothermal Compressibility (□T), Intermolecular Free Path Length (L_f), Molecular interaction parameter (χ) , Gruneisen Parameter (Γ_{mix}□) and Wada Constant (W) for Cyclopentanone – Benzene and Cyclohexanone – Benzene systems are shown in Table 2 and Table 4 respectively.

Table 1 and Table 3 indicates a decrease in velocity , viscosity and decrease in cyclopentanone + benzene compared with cyclohexanone + benzene system. Dipole moment values of cyclopentanone is 3.28 D and cyclopentanone is 2.9 D. The higher values of dipole moment attribute specific interaction between unlike molecules in cyclopentanone system[13]. The dense cloud of electrons attributed by carbonyl group of cyclopentanone create the strong electrostriction effect in benzene. The increase in ultrasonic velocity with increasing molefraction in the systems infers the existence of cohesive forces between the polar groups.

The variation of molefraction with acoustical parameters like Adiabatic Compressibility (□S), Isothermal Compressibility (□T), Intermolecular Free Path Length (L_f), Molecular interaction parameter (χ) , Gruneisen Parameter (Γ_{mix}□) and Wada Constant (W) ensues the dipole-induced dipole interaction in Cyclopentanone system. Adiabatic compressibility determines the change in molecular internal structure. The decreasing trend in adiabatic compressibility with increasing concentration of solute molecules shows the strong structural arrangement of molecules. Electronegativity of oxygen creates the inductive effect in carbonyl group carbon. The decrease in adiabatic, isothermal and free length values (Table 2,4) represents the strong interactions at lower concentration of solute molecules. The decreasing free length data attribute less compression in the system due to the strong interaction between the unlike components [14]. This is mainly due to the electrostatic field existing between the components of liquid mixture. The electrostatic effect changes the spherical shape and size of the benzene molecules. It is very strenuous to measure the isothermal compressibility for liquid mixtures experimentally, but the ultrasonic investigation helps in estimating the compressibility factors.

Table 1 - Measured Parameters for Cyclopentanone - Benzene at 308.15 K

mole fraction x_{C5H8O}	Ultrasonic velocity (u) m/s	Density (ρ) Kg/m³	Viscosity (η) Pa.s.
0.1007	1281.60	855.10	241.45
0.2012	1287.60	860.50	248.73
0.3016	1293.60	865.90	256.08
0.4018	1305.60	872.50	265.16
0.5019	1317.60	879.10	274.35
0.6018	1332.40	886.90	287.33
0.7016	1347.20	894.70	300.49
0.8012	1352.40	901.35	312.10
0.9007	1357.60	908.00	323.85
1.0000	1369.60	911.90	344.22

Table 2-Computed values of acoustical Parameters for Cyclopentanone - Benzene at 308.15 K

mole fraction x_{C5H8O}	β_S 10^{-10} Pa^{-1}	β_T 10^{-15} Pa^{-1}	L_f Å	χ	Γ_{mix} 10^3	W $m^3mole^{-1}Pa^{1/7}$
0.1007	7.1200	10.0466	0.5337	0.0314	1.1049	1.9468
0.2012	7.0095	9.8700	0.5295	0.0215	1.0751	1.9295
0.3016	6.9013	9.6974	0.5254	0.0119	1.0561	1.9123
0.4018	6.7238	9.4241	0.5186	0.0118	1.0365	1.8955
0.5019	6.5523	9.1607	0.5119	0.0117	1.0174	1.8789
0.6018	6.3512	8.8534	0.5040	0.0159	0.9976	1.8613
0.7016	6.1583	8.5594	0.4963	0.0201	0.9832	1.8439
0.8012	6.0659	8.4103	0.4926	0.0098	0.9691	1.8249
0.9007	5.9754	8.2646	0.4889	-0.0002	0.9558	1.8062
1.0000	5.8461	8.0741	0.4836	0.0000	0.9434	1.7949

Table 3 - Measured Parameters for Cyclohexanone - Benzene at 308.15 K

mole fraction x_{C6H10O}	Ultrasonic velocity (u) m/s	Density (ρ) Kg/m^3	Viscosity (η) Pa.s.
0.0869	1289.20	851.30	251.38
0.1764	1297.40	858.60	265.08
0.2685	1305.60	865.90	278.98
0.3635	1315.60	872.05	296.52
0.4614	1325.60	878.20	314.27
0.5623	1329.40	884.75	347.84
0.6665	1333.20	891.30	381.87
0.7741	1345.40	897.75	428.40
0.8852	1357.60	904.20	475.55
1.0000	1376.20	909.10	549.87

Table 4 -Computed values of acoustical Parameters for Cyclohexanone - Benzene at 308.15 K

mole fraction x_{C6H10O}	β_S 10^{-10} Pa^{-1}	β_T 10^{-15} Pa^{-1}	L_f Å	χ	Γ_{mix} 10^3	W $m^3mole^{-1}Pa^{1/7}$
0.0869	7.0677	9.9876	0.5317	0.0455	1.3544	2.3389
0.1764	6.9193	9.7501	0.5261	0.0401	1.2696	2.4664
0.2685	6.7750	9.5200	0.5206	0.0343	1.2118	2.5906
0.3635	6.6254	9.2877	0.5148	0.0308	1.1510	2.7158
0.4614	6.4801	9.0628	0.5091	0.0268	1.1018	2.8381
0.5623	6.3954	8.9222	0.5058	0.0129	1.0502	2.9527
0.6665	6.3123	8.7846	0.5025	-0.0013	1.0253	3.0642
0.7741	6.1538	8.5435	0.4961	-0.0034	0.9997	3.1789
0.8852	6.0006	8.3109	0.4899	-0.0060	0.9788	3.2911
1.0000	5.8080	8.0297	0.4820	0.0000	0.9580	3.4103

The non-linear variation in molecular interaction parameter (fig. 3) infers the interaction between the like and unlike molecules [15]. Gruneisen parameter helps in analysing the lattice spacing and clustering phenomenon of the liquids. The increasing size of the alkyl group in cyclohexanone infers the increase in Gruneisen parameter. Cyclohexanone molecules undergo agglomeration, due to the contraction of crystalline lattice spacing in the liquid system. From table 2 and 4, it is noted that the increasing mole fraction of cyclopentanone to cyclohexanone molecules shows the cluster formation in the components.

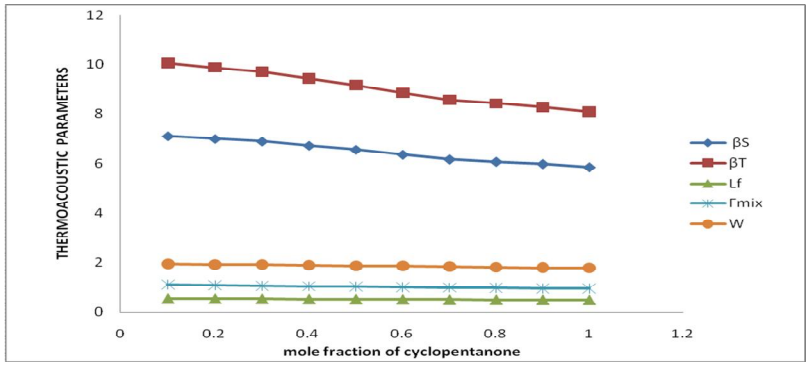

Fig.1.Variation of Thermoacoustic parameters with mole fraction of cyclopentanone for cyclopentanone + benzene system

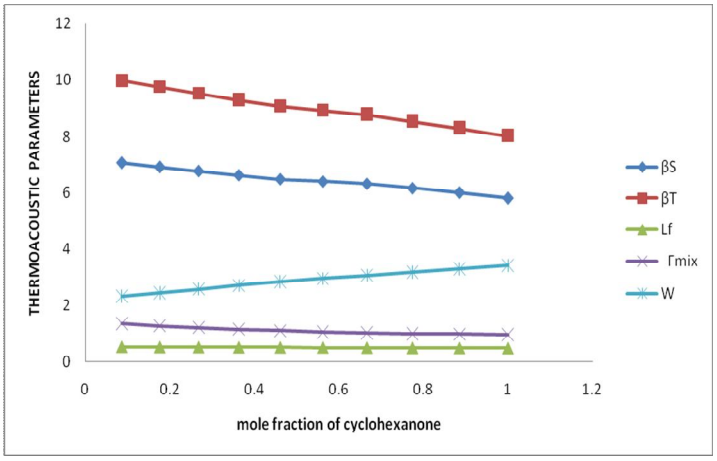

Fig.2.Variation of Thermoacoustic parameters with mole fraction of cyclohexanone for cyclohexanone + benzene system

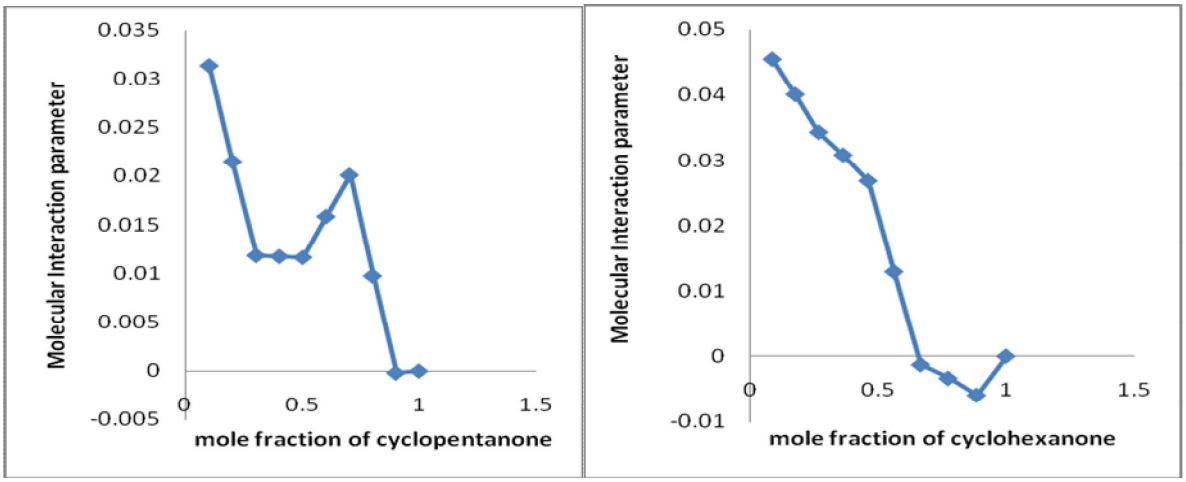

Fig.3 .Plot of Molecular Interaction parameter with mole fraction for cyclopentanone + benzene and cyclohexanone + benzene system.

The variation in Wada's constant with mole fraction in Fig. 1. quirks the solute - solvent interaction in both the systems[16].

V. CONCLUSION

The computed Adiabatic Compressibility, Isothermal Compressibility, Intermolecular Free Path Length, Molecular interaction parameter, Gruneisen Parameter and Wada Constant parameters exhibit the strong dipole-induced dipole interaction in both the systems. Resonance effect is contributed in addition to the higher polarizability nature of the cyclopentanone. Thus the present attempt throws the limelight on the strong intermolecular interaction extant between the cyclopentanone systems compared to cyclohexanone systems.Benzene can be used as an effective solvent in the extraction process in both the systems.

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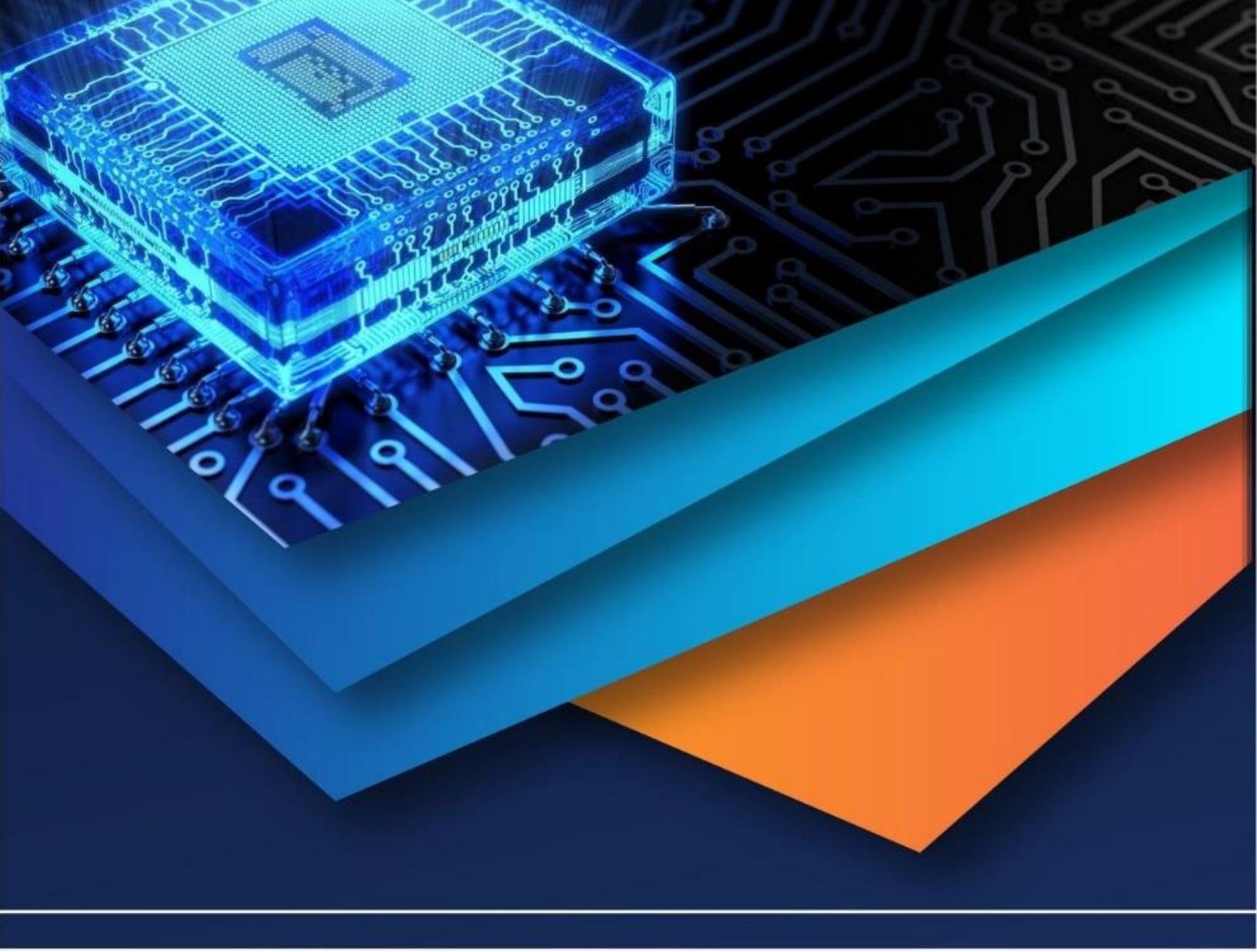

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