

Thermodynamic Parameters and Their Excess Values for Binary Mixtures of Cyclohexane Plus Benzene and Substituted Benzenes at Different Ultrasonic Frequencies

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Abstract: Different thermodynamic parameters like acoustic impedance, Gibb's free energy, adiabatic compressibility, free length, free volume, internal pressure and their excess values are studied at various ultrasonic frequencies keeping temperature constant at 318K.

Keywords: Gibb's free energy, acoustic impedance, free length and free volume.

I. INTRODUCTION

Ultrasonic investigations of liquid mixtures, consisting of polar and non-polar components are of considerable importance in understanding the intermolecular interactions between the component molecules, which finds applications in several industrial and technological processes [1-10]

In the present paper we have studied the various thermodynamic parameters along with their excess values from the study of variation in ultrasonic velocity at different frequencies for the following binary mixtures.

Mixture - I: Cyclohexane + Benzene

Mixture - II: Cyclohexane + Chlorobenzene

Mixture - III: Cyclohexane + Nitrobenzene

Mixture - IV: Cyclohexane + Pyridine

The temperature has been maintain at a constant value (318K).

Cyclohexane belongs to the group of alicyclic hydrocarbons. It is non-polar, unassociated, inert hydrocarbon and has a globular structure. It is highly inert towards an electrophille or nucleophile at ordinary temperature. Due to the above properties dispersive types of interactions are possible between cyclohexane and other components.

Benzene is a non-polar solvent. It is a cyclic hydrocarbon with a continuous pi bond. Chlorobenzene is a poor electron donor towards the electron seeking proton of any group. It has low dielectric constant and dipole moment. The chlorine atom being an electron withdrawing atom attracts the π -

electron of benzene ring and thus a decrease of electron density of the

ring takes place. This makes the benzene ring a relatively poor electron donor towards the Cyclohexane molecules.

Nitrobenzene is a polar solvent with high dielectric constant and dipole moment. Hence intermolecular interaction in this case is large.

Pyridine is a basic heterocyclic organic compound with a lower dielectric constant and dipole moment. Pyridine molecules are spherical in shape and tightly packed.

II. EXPERIMENTAL TECHNIQUE:

The liquid mixtures of fixed concentration (6:4) in mole fraction were prepared by taking analytical reagent grade and spectroscopic reagent grade chemicals with minimum assay of 99.9% and obtained from E.Merck Ltd (India).

The density, viscosity, and ultrasonic velocity of all liquid mixtures were measured at temperature 318K and for different frequencies 2 MHz, 4 MHz, 6 MHz, 8 MHz.

Ultrasonic velocity measurements were made using an ultrasonic interferometer (Model M-84, supplied by M/S Mittal Enterprises, New Delhi), at different temperatures and different frequencies with the accuracy of $\pm 0.1 \text{ m}\cdot\text{s}^{-1}$. The measuring cell of interferometer is a specially designed double-walled vessel with provision for temperature constancy. An electronically operated digital constant temperature bath (Model SSI-03 Spl, supplied by M/S Mittal Enterprises, New Delhi), operating in the temperature range of -10°C to 85°C with an accuracy of $\pm 0.1^\circ\text{C}$ has been used to circulate water through the outer jacket of the double-walled measuring cell containing the experimental liquid.

The densities of the mixture were measured using a 10-ml specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01 \text{ kg}\cdot\text{m}^{-3}$. The specific gravity bottle

with the experimental mixture was immersed in the temperature-controlled water bath. The weight of the sample was measured using an electronic digital balance with an accuracy of ± 0.1 mg (Model: SHIMADZU AX-200, Kyoto, Japan).

An Oswald viscometer (10 ml) with an accuracy of ± 0.001 $\text{Ns}\cdot\text{m}^{-2}$ was used for the viscosity measurement. The flow time was determined using a digital racer stopwatch with an accuracy of ± 0.1 s.

III. THEORY

1. *Adiabatic compressibility*: The ultrasonic velocity in a liquid medium, in terms of Bulk modulus (B) and density of the medium is given by the Newton-Laplace equation [11].

$$U = \sqrt{\frac{B}{\rho}} = \sqrt{\frac{1}{\rho \cdot \beta}}$$

$$\text{Or, } \beta = \frac{1}{\rho \cdot U^2} \dots \dots (\text{N}^{-1} \cdot \text{m}^2) \dots \dots (1)$$

2. *Intermolecular free length*: Intermolecular free length (L_f), is calculated using the standard expression [12]

$$L_f = K_T \cdot \beta^{1/2} \dots (\text{m}) \dots (2)$$

Where, ' K_T ' $\{=(93.875 + 0.375 \cdot T) \times 10^{-8}\}$ is Jacobson's temperature dependent constant and ' β ' is the adiabatic compressibility.

3. *Free Volume*: Suryanarayana et al [13,14] obtained a relation for free volume in terms of ultrasonic velocity (U) and the viscosity of the liquid (η) as,

$$V_f = \left(\frac{M_{\text{eff}} \cdot U}{K \cdot \eta} \right)^{3/2} \dots \dots (\text{m}^3 \cdot \text{mol}^{-1}) \dots \dots (3)$$

Where ' M_{eff} ' is the effective mass of the mixture, ' K ' is a dimensionless constant independent of temperature and liquid. Its value is 4.281×10^9 .

4. *Internal Pressure*: Internal pressure can be calculated by using the relation [15,16]

$$\pi_i = bRT \left(\frac{K\eta}{U} \right)^{1/2} \left(\frac{\rho^3}{M^6} \right) \dots \dots (\text{N} \cdot \text{m}^{-2}) \dots \dots (4)$$

Where, ' b ' stands for the cubic packing factor, which is assumed to be '2' for all liquids and solutions. ' K ' is a dimensionless constant independent of temperature and nature of liquids. Its value is 4.281×10^9 , R is the gas constant, T is the absolute temperature, η is the viscosity, U is the ultrasonic velocity, ρ is the density and M is the effective molecular weight.

5. *Gibb's free energy*: The variation of ' τ ' with temperature can be expressed in the form of Eyring salt process theory [17].

$$\frac{1}{\tau} = \frac{KT}{h} \exp\left(\frac{-\Delta G}{KT}\right) \dots \dots (5)$$

The above equation can be rearranged as

$$\Delta G = 2.30 \cdot KT \log\left(\frac{KT\tau}{h}\right) \dots (\text{kJ} \cdot \text{mol}^{-1}) \dots (6)$$

Where, ' τ ' is the viscous relaxation time, ' T ' is the absolute temperature, ' K ' is the Boltzmann's constant and ' h ' is the Planck's constant.

6. *Acoustic impedance (Z)*: The specific acoustic impedance is given by [18]

$$Z = \rho \cdot U \dots (\text{Kg} \cdot \text{m}^2 \cdot \text{s}^{-1}) \dots \dots (6)$$

7. Excess Parameters (A^E)

In order to study the non-ideality of the liquid mixtures, the difference between the values of the real mixture (A_{exp}) and those corresponding to an ideal mixture (A_{id}), namely the excess parameters (A^E) of some of the acoustic parameters, were computed using the equation

$$A^E = A_{\text{exp}} - A_{\text{id}} \dots \dots (7)$$

Where $A_{\text{id}} = \sum A_i X_i$, ' A_i ' is any parameters and ' X_i ' the mole fraction of the liquid components of 'i'.

IV. RESULT AND DISCUSSION:

The experimental values of density, viscosity and velocity are presented in table-1. Calculated values of acoustic and thermodynamic parameters are presented in table-2 and 3. Excess values of the parameters are shown in table-4 and 5. Variations of these parameters and their excess values with frequency are shown in fig.1 to fig.12.

Ultrasonic velocity increases in the following order. It is maximum for mixture-I and increases from mixture-II to mixture-III and finally to mixture-IV. Since benzene and cyclohexane both are non-polar, their intermolecular interaction is weak; hence ultrasonic velocities in such mixtures are minimum.

In the cyclohexane chlorobenzene mixture, the intermolecular interaction is also weak as mentioned before; hence velocity is less than that in the mixtures III and IV.

Nitrobenzene has a larger dipole moment compared to pyridine but the intermolecular interaction is weaker in mixture-III compared to mixture-IV because of steric hindrance in nitrobenzene (Nitrobenzene being a complex and big molecule).

When frequency increases, velocity in each case decreases indicating weakening of intermolecular interaction. Intermolecular free length (L_f) is maximum for mixture-I. This is obvious as the molecular interaction in this case is weakest. For the mixture-III, L_f is the next as the interaction in this case is next as expected due to steric hindrance. L_f for mixture-IV comes the next. L_f is minimum for mixture-II. Although intermolecular interaction in this case (mixture-II) is small, the molecules in the mixture fit in to each other yielding minimum intermolecular space.

Excess free length (L_f^E) is positive for system-I, III and IV and decreases in the same order. Positive L_f^E indicates weak interaction. This may be due to the non-polar nature of molecules or steric hindrance or expansion in volume from additivity. However because of comparatively stronger interaction in mixture-IV, L_f^E is positive but small. In mixture-II, ' L_f^E ' is negative. This may be due to the fact that the molecules fit well into each other and L_f decreases in the mixture. L_f^E does not vary with frequency in all the cases.

Adiabatic compressibility (β) decreases in the following order of the mixture-I, III, IV and II. It changes in the same way as free length changes. At low frequencies L_f and β are small for

V. TABULATION

TABLE – 1: Values of Density (ρ), Viscosity (η) and velocity (U) in binary mixtures for different frequencies.

Binary mixture	Density (ρ) Kg.m ⁻³	Viscosity $\eta \times 10^{-3}$ (N.s.m ⁻²)	Velocity (U) m.s ⁻²			
			2 MHz	4 MHz	6 MHz	8 MHz
M-I: Ben+C.H	818.226	0.455	1168.6	1167.2	1165.1	1164.4
M-I: C.Ben+C.H	975.25	0.549	1172	1169	1166	1165.9
M-I: N.Ben+C.H	856.69	0.646	1170	1169	1166	1164.5
M-I: Pyr.+C.H	869.56	0.571	1247	1238	1225	1209.7

TABLE – 2: Calculated values of β , L_f , and V_f in binary mixtures for different frequencies.

Binary mixture	Adiabatic compressibility (β) ($10^{-10} \text{N}^{-1} \cdot \text{m}^2$)				Free length (L_f) (10^{-10}m)				Free volume (V_f) ($10^{-7} \text{m}^3 \cdot \text{mol}^{-1}$)			
	2 MHz	4 MHz	6 MHz	8 MHz	2 MHz	4 MHz	6 MHz	8 MHz	2 MHz	4 MHz	6 MHz	8 MHz
M-I: Ben+C.H	8.949	8.971	9.003	9.014	0.608	0.608	0.609	0.610	3.364	3.358	3.349	3.346
M-I: C.Ben+C.H	7.462	7.501	7.537	7.543	0.555	0.556	0.558	0.558	3.590	3.576	3.563	3.561
M-I: N.Ben+C.H	8.524	8.549	8.584	8.608	0.593	0.594	0.595	0.596	3.069	3.062	3.053	3.046
M-I: Pyr.+C.H	7.393	7.499	7.669	7.859	0.552	0.556	0.562	0.569	2.663	2.635	2.591	2.544

TABLE – 3: Calculated values of ΔG , Z and Π_i in binary mixtures for different frequencies.

Binary mixture	Gibb's free energy (ΔG) ($\times 10^{-20} \text{kJ} \cdot \text{mol}^{-1}$)				Acoustic impedance (Z) ($\times 10^6 \text{Kg} \cdot \text{m}^2 \cdot \text{s}^{-1}$)				Internal pressure (Π_i) ($\times 10^6 \text{N} \cdot \text{m}^{-2}$)			
	2 MHz	4 MHz	6 MHz	8 MHz	2 MHz	4 MHz	6 MHz	8 MHz	2 MHz	4 MHz	6 MHz	8 MHz
M-I: Ben+C.H	0.562	0.563	0.564	0.565	0.956	0.955	0.953	0.953	356.7	356.9	357.2	357.3
M-I: C.Ben+C.H	0.564	0.567	0.569	0.569	1.143	1.140	1.138	1.137	336.9	337.4	337.8	337.9
M-I: N.Ben+C.H	0.695	0.696	0.698	0.699	1.002	1.001	0.999	0.998	312.8	313.0	313.3	313.5
M-I: Pyr.+C.H	0.578	0.584	0.594	0.605	1.085	1.077	1.065	1.052	399.6	401.0	403.2	405.7

TABLE –4: Excess values β^E , L_f^E , V_f^E in binary mixtures for different frequencies.

Binary mixture	Excess Adiabatic comp. (β^E) ($10^{-10} \text{N}^{-1} \cdot \text{m}^2$)				Excess Free length (L_f^E) (10^{-10}m)				Excess Free volume (V_f^E) ($10^{-7} \text{m}^3 \cdot \text{mol}^{-1}$)			
	2 MHz	4 MHz	6 MHz	8 MHz	2 MHz	4 MHz	6 MHz	8 MHz	2 MHz	4 MHz	6 MHz	8 MHz
M-I: Ben+C.H	0.3138	0.3119	0.3238	0.3127	0.012	0.011	0.012	0.011	0.9438	0.9427	0.9379	0.9395
M-I: C.Ben+C.H	-0.31	-0.291	-0.274	-0.287	-0.008	-0.008	-0.007	-0.008	0.266	0.260	0.253	0.257
M-I: N.Ben+C.H	1.965	1.975	1.999	2.009	0.083	0.083	0.084	0.084	0.391	0.388	0.382	0.379
M-I: Pyr.+C.H	0.03	0.115	0.265	0.422	0.006	0.009	0.014	0.020	-0.451	-0.471	-0.508	-0.544

TABLE – 5: Excess values Π_i^E , Z^E AND ΔG^E in binary mixtures for different frequencies.

Binary mixture	Excess internal pressure(Π_i^E) ($\times 10^6$ N.m $^{-2}$)				Excess acoustic impedance (Z^E) ($\times 10^6$ Kg.m 2 .s $^{-1}$)				Excess Gibb's free energy (ΔG^E) ($\times 10^{-20}$ k.J.mol $^{-1}$)			
	2 MHz	4 MHz	6 MHz	8 MHz	2 MHz	4 MHz	6 MHz	8 MHz	2 MHz	4 MHz	6 MHz	8 MHz
M-I: Ben+C.H	-47.829	-47.892	-47.808	-47.951	-0.024	-0.024	-0.025	-0.024	-0.092	-0.092	-0.091	-0.092
M-I: C.Ben+C.H	-2.998	-2.833	-2.638	-2.771	0.012	0.011	0.010	0.011	-0.031	-0.031	-0.030	-0.030
M-I: N.Ben+C.H	-52.69	-52.64	-52.44	-52.38	-0.330	-0.330	-0.331	-0.332	0.072	0.073	0.074	0.074
M-I: Pyr.+C.H	16.523	17.594	19.571	21.555	-0.045	-0.050	-0.061	-0.071	0.056	0.061	0.069	0.078

mixture-IV compared to mixture-II but is just the opposite when frequency increases.

Excess adiabatic compressibility (β^E) is positive for mixture-I, III and IV and decreases in the same order. β^E is negative for mixture-II. β^E changes in the same way as L_f^E .

Free volume (V_f) at any frequency is maximum for mixture-II and decreases successively from mixture-I o III to IV. Since L_f decreases in the order mixture-I. III. IV and II, V_f should change accordingly but for system-II it is maximum. When chlorobenzene and cyclohexane are mixed, L_f is minimum. The molecules in this case are close to each other and the vibrations are transmitted through the molecules to a large distance increasing the apparent free volume. Free volume decreases very slowly with increase in frequency.

Excess free volume (V_f^E) is positive for mixture-I, III and IV and decreases in that order. In case of mixture-I, positive V_f^E is due to expansion in volume because of additivity.

V_f^E decreases with increase in frequency. In mixture-III, V_f^E is less than that in mixture-I. The interaction in system-III being stronger, the expansion is less. However V_f^E is less in mixture-IV than system-III as the interaction in mixture-III is less compared to mixture-IV because of steric hindrance in nitrobenzene solution. In mixture-II, V_f^E is negative and becomes more and more negative as frequency increases.

When molecules are subjected to larger frequencies they vibrate rapidly, increasing the interaction between the molecules, which is of dispersive type. This reduces the free volume and hence the above observation.

Internal pressure is maximum for mixture-IV and then decreases in the order mixture-I, II and III at any frequency. Pyridine molecules are spherical in shape, closely packed and have a finite dipole moment. Hence the intra-molecular as well as intermolecular interaction is maximum in case of mixture-IV. In case of system-III, it is the minimum. Nitrobenzene has a high dipole moment, but the complex structure of nitrobenzene molecules leads to less intermolecular forces and for the same reason also gives a less force of cohesion. Mixture-I and II show more internal pressure compared to mixture-III because of the molecular arrangement even though benzene is non-polar and dipole moment of chlorobenzene is low. Internal pressure increases very slowly with increase in frequency for mixture-I, II and III, but comparatively more in mixture-IV. This is because, when frequency increases molecular motion increases and the molecular interaction increases.

Excess internal pressure (π_i^E) is negative for mixture-I, II and III at all frequencies. It is maximum negative for mixture-III and then for mixture-I and II. For mixture-II the negative value is much less than that of mixture-III and I. This is obvious as internal pressure is minimum in mixture-III and increases for mixture-II and I. However π_i^E is very small for mixture-II. The variation in π_i^E with change in frequency is negligible. π_i is positive for system-IV. This is because π_i is larger for system-IV. In this case, π_i^E increases considerably, when frequency increases.

VI. FIGURES:

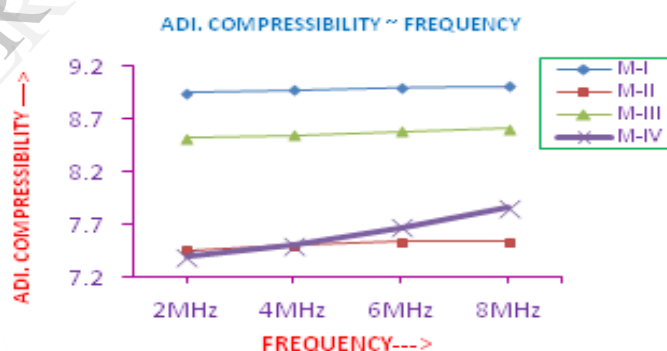


Fig.1: Variation of β with frequency

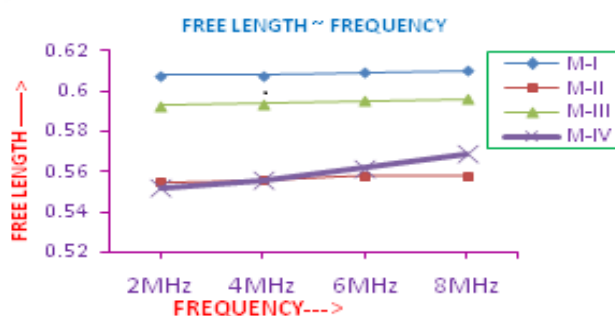


Fig.2: Variation of L_f with frequency

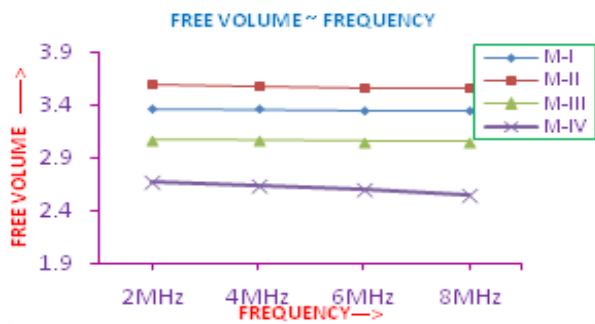


Fig.3: Variation of V_f with frequency

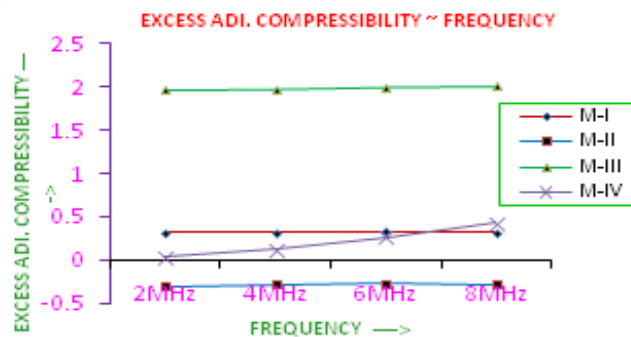


Fig.7: Variation of β^E with frequency

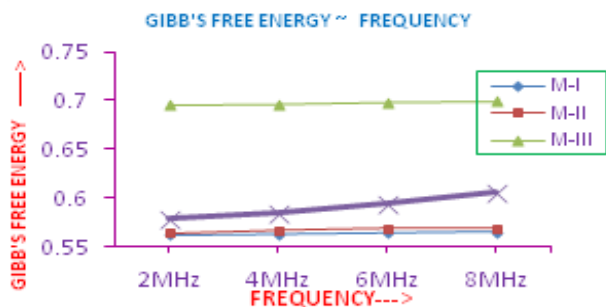


Fig.4: Variation of ΔG with frequency

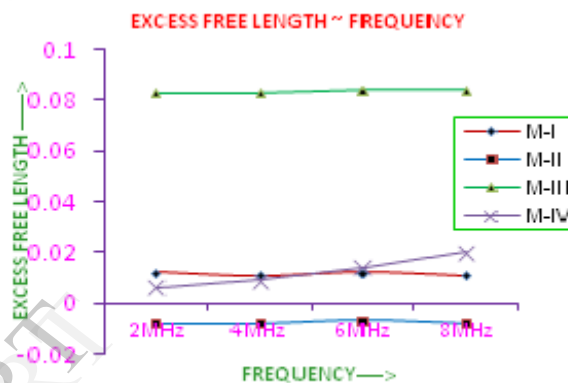


Fig.8: Variation of L_f^E with frequency

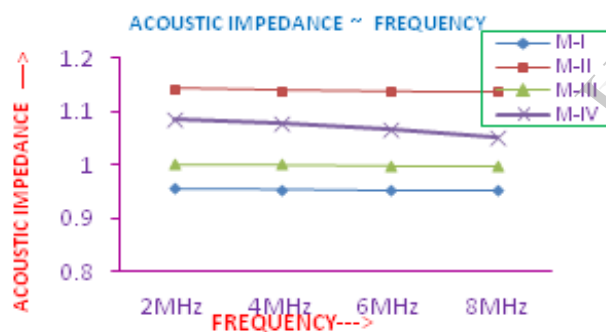


Fig.5: Variation of Z with frequency

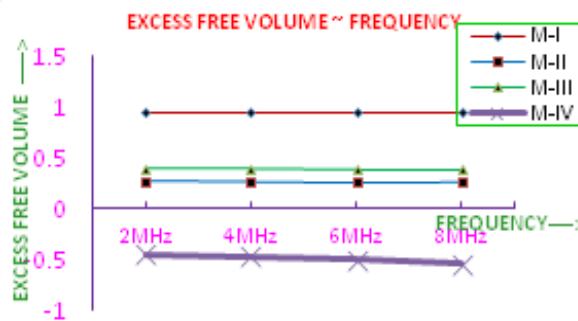


Fig.9: Variation of V_f^E with frequency

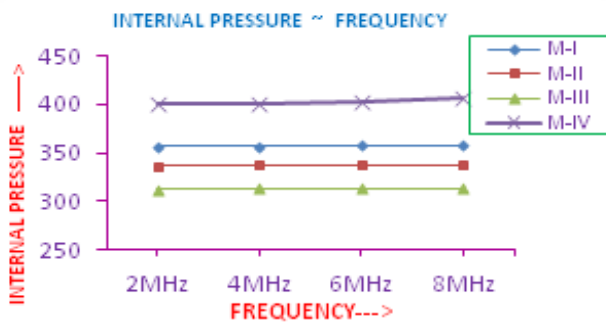


Fig.6: Variation of π_i with frequency

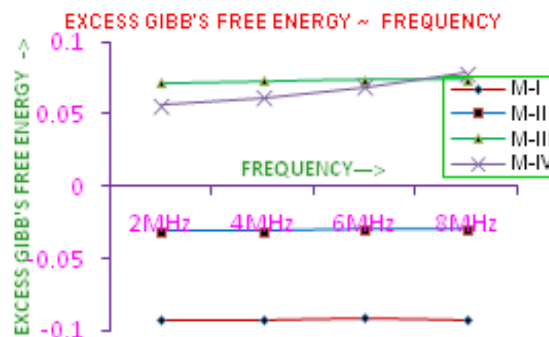


Fig.10: Variation of ΔG^E with frequency

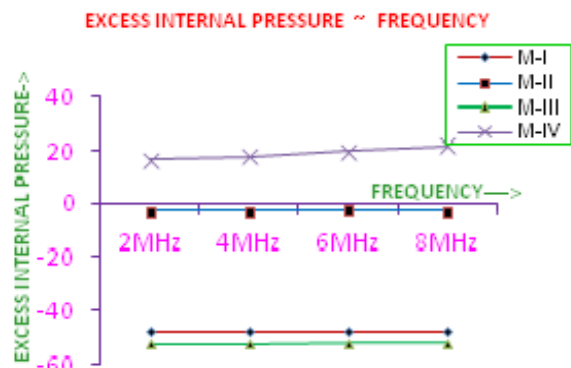


Fig.11: Variation of π_i^E with frequency

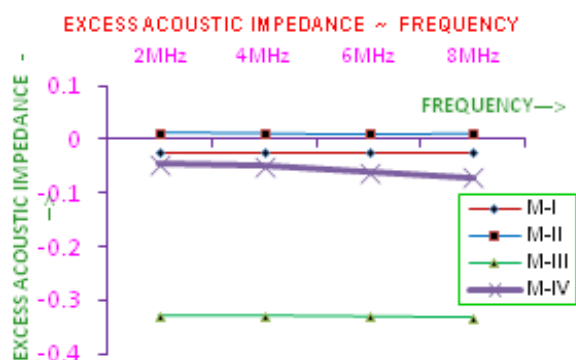


Fig.12: Variation of Z^E with frequency

Gibb's free energy (ΔG) is maximum for mixture-III and then for mixture-IV, II & I in that order. In all the cases, ΔG increases slowly with increase in frequency. Increase in ΔG suggests shorter time for rearrangement of molecules in the mixture. This may be due to the fact that, when frequency increases, the energy imparted to the molecules expedites the rearrangement procedure.

Excess Gibb's free energy (ΔG^E) is negative for mixture-I & II and is positive for mixture-III & IV. In mixture-I & II ΔG decreases in the mixture indicating longer time for rearrangement of molecules, as the intermolecular interaction in both of them are comparatively small. In mixture-III and IV, ΔG was large and hence ΔG^E is positive. In the above two mixtures, interaction being stronger, shorter time is required for rearrangement of molecules in the mixture. ΔG^E changes rapidly with frequency for mixture-IV.

VII. CONCLUSION:

Variation of ultrasonic velocity with frequency in the binary mixture of cyclohexane and benzene group of liquids enabled us to study the thermodynamic parameters and their excess values. These indicated the nature of the interaction between the components of the mixture. Although cyclohexane is non-polar the intermolecular interaction is evident through the excess values of the thermodynamic parameters.

It has been observed that, the change in velocity with change in frequency is conspicuous in mixture-IV. This leads to large variation in the parameters and their excess values with change in frequency compared to the other mixtures.

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