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Research Article

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Acoustical studies on ternary mixture of toluene in cyclohexane & nitrobenzene at 308k using ultrasonic technique.

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ABSTRACT

The experimental density (ρ), viscosity (η) and velocity (U) have been measured for ternary mixtures of toluene+ cyclohexane + nitrobenzene at temperature 308K. These data were used to determine the adiabatic compressibility, free length, free volume, relaxation time, acoustic impedance and Gibb's free energy. From the properties of these parameters, the nature and the strength of interactions in the ternary mixture are discussed.

Keywords: Ultrasonic velocity, adiabatic compressibility, free length, free volume, molecular interaction, ternary system.

INTRODUCTION

The ultrasonic study of liquids plays an important role in understanding the nature and strength of molecular interactions [1, 2]. A large number of studies have been made on the molecular interaction in liquid systems by various physical methods like, Raman effect [3], Nuclear Magnetic Resonance, ultra violet and ultrasonic method[4,5]. In recent years ultrasonic technique has become a powerful tool in providing information regarding the molecular behavior of liquids and solids owing to its ability of characterizing physiochemical behavior of the medium. The ultrasonic velocity data for ternary liquid mixtures have been used for by many researchers [6, 7]. However, no effort appears to have been made to collect the ultrasonic velocity data of ternary mixtures of toluene, cyclohexane with nitrobenzene at308K.

The thermodynamics and transport properties of liquid mixtures have been extensively use [8, 9] to study the departure of a real liquid mixture behavior from ideality. Further, these properties have been widely used to study the intermolecular interaction between the various species in the mixture [10-12].

In present study, the molecular interactions in the system (toluene+ cyclohexane + nitrobenzene) at 308K have been characterized. The addition of nitrobenzene, which is non-associative and highly polar when added to non-polar toluene molecules, induces dipole moment and further addition of cyclohexane (non-polar) leads to new kind of dipole- induced dipole interaction for formation of complex between cyclohexane and toluene molecules.

EXPERIMENTAL SECTION

The liquid mixtures of various concentrations in mole fraction were prepared by taking AR grade chemicals. In the ternary mixture system, the mole fraction of second component, cyclohexane(X_2) is kept fixed arbitrarily at X_2 = (0.4). Mole fraction of toluene (X_1) is increased from 0.0 to 0.6 while mole fraction of nitrobenzene (X_3) is decreased from 0.6 to 0.0.

The ultrasonic velocity in the liquid mixtures have been measured using an ultrasonic interferometer (Mittal type: Model: M-83) working at frequency 3MHz with an overall accuracy of ± 0.1 ms^{-1}, an electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of a steel containing the experimental solution at the desired temperature. The density of pure liquids and liquid mixtures was determined using a 25ml specific gravity bottle with an accuracy of ± 0.1 Kgm^{-3}. An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with an accuracy of ±0.0001NSm^{-2}. The viscometer was calibrated before used. The time of flow of water (t_w) and time flow of solution (t_s) was measured with digital stop watch having an accuracy ±3x10^{-6} NSm^{-2}. All the precautions were taken to minimize the possible experimental error.

THEORY

Adiabatic compressibility (β_a) has been calculated from the ultrasonic velocity (U) and the density (ρ) of the medium using the equation as:

$$\beta_a = 1 / U^2 \rho \quad \text{…… (1)}$$

Intermolecular free length has been determined as:

$$L_f = K_T (\beta_a)^{1/2} \quad \text{…….. (2)}$$

Where K_T – is a Jacobson's constant.

Free volume in terms of ultrasonic velocity (U) and viscosity of the liquid (η) as:

$$V_f = [M_{eff.} U / K \eta]^{3/2} \quad \text{…….. (3)}$$

Where, $M_{eff.}$ is the effective molecular weight ($M_{eff.} = \sum m_i X_i$, in which m_i and X_i are the molecular weights and the mole fraction of the individual constituents respectively). K is a temperature independent constant which is equal to 4.28 x 10^9 for all liquids.

Relaxation time in terms of adiabatic compressibility (β_a) and viscosity of the liquid (η) as:

$$\tau = 4/3 \beta_a \eta \quad \text{……. (5)}$$

The specific acoustic impedance in terms of ultrasonic velocity (U) and the density (ρ) as:

$$Z = U \rho \quad \text{…….. (6)}$$

Gibb's free energy can be calculated from the following relation:

$$\Delta G = KT \ln (KT\tau /h) \quad \text{…… (7)}$$

Where, τ is the relaxation time, K the Boltzmann constant, T the absolute temperature and h is the Planks constant

RESULTS AND DISCUSSION

The experimental values of density (ρ), viscosity (η) and velocity (U), for pure liquids at 308K are listed in **Table-1.**The values of density(ρ), viscosity(η) and velocity(U) for the ternary liquid mixtures (toluene + cyclohexane + nitrobenzene) at 308K presented in**Table-2.**

Table 1:- The values of density (ρ), viscosity (η) and velocity (U) for pure liquids at 308 K.

Liquids	Density (ρ) (Kgm^{-3})		Viscosity (η) ($10^{-3}NSm^{-2}$)		Velocity (U)(ms^{-1})	
	Expt.	Literature	Expt.	Literature	Expt.	Literature
Toluene	865.05	867.0 (25^0C)	0.5086	0.590 (25^0C)	1234.00	1304 (25^0C)
Cyclohexane	767.90	773.8 (25^0C)	0.7254	1.000 (25^0C)	1182.00	1232 (25^0C)
Nitrobenzene	1207.87	-	1.4300	1.863 (25^0C)	1375.80	-

Table 2 :- The values of density (ρ), viscosity (η) and velocity (U) for the ternary system :- Toluene + Cyclohexane + Nitrobenzene at 308 K.

Mole fraction X_1	X_3	Density (ρ) (Kgm^{-3})	Viscosity (η) (10^{-3} NSm^{-2})	Velocity (U) (ms^{-1})
	0.600			
0.0000	0	1020.04	0.984	1278.00
	0.500			
0.1000	0	992.55	0.891	1270.80
	0.400			
0.1999	1	940.71	0.797	1264.80
	0.300			
0.2999	1	932.43	0.724	1249.20
	0.200			
0.4000	0	894.22	0.641	1228.80
	0.099			
0.5001	9	854.80	0.559	1216.80
	0.000			
0.6000	0	852.57	0.498	1213.20

Table 3 :- The values of adiabatic compressibility (β_a), free length (L_f) and free volume(V_f)) for the ternary system :- Toluene + Cyclohexane + Nitrobenzene at 308 K.

Mole fraction X_1	X_3	Compressibility (β_a) (10^{-10} m^2N^{-1})	Free length (L_f) (10^{-10} m)	Free volume (V_f) (10^{-7} m^3 mol^{-1})
	0.600			
0.0000	0	6.002	0.4924	1.863
	0.500			
0.1000	0	6.238	0.5020	2.050
	0.400			
0.1999	1	6.645	0.5181	2.300
	0.300			
0.2999	1	6.872	0.5269	2.490
	0.200			
0.4000	0	7.406	0.5470	2.776
	0.099			
0.5001	9	7.901	0.5649	3.198
	0.000			
0.6000	0	7.968	0.5674	3.599

Table 4:- The values of Relaxation time(τ), Acoustic impedance(Z) and Gibb's free energy(ΔG) for the ternary system: - Toluene + Cyclohexane + Nitrobenzene at 308K.

Mole fraction X_1	X_3	Relaxation time(τ) (10^{-12} Sec)	Acoustic impedance(Z) (10^6 Kgm^2S^{-1})	Gibb's free energy(ΔG) (10^{-20} KJ mol^{-1})
0.0000	0.6000	0.7877	1.3036	0.5699
0.1000	0.5000	0.7416	1.2613	0.5470
0.1999	0.4001	0.7066	1.1898	0.5287
0.2999	0.3001	0.6638	1.1648	0.5050
0.4000	0.2000	0.6337	1.0988	0.4874
0.5001	0.0999	0.5894	1.0401	0.4600
0.6000	0.0000	0.5293	1.0343	0.4193

The values of adiabatic compressibility (β_a) free length (L_f) and free volume (V_f) for ternary mixtures at 308K are given in **Table-3** and the values of relaxation time(τ), acoustic impedance(Z) and Gibb's free energy(ΔG) for ternary mixtures at 308K are presented in **Table-4. Fig.1** - represent the variation of adiabatic compressibility (β_a), free length (L_f), free volume (V_f), relaxation time (τ), acoustic impedance (Z) and Gibb's free energy (ΔG) with mole fraction of ternary liquid mixtures at 308K. In the ternary liquid mixtures, the ultrasonic velocity decreases with increasing concentration of toluene.

The variation of ultrasonic velocity in a solution depends upon the increase or decrease of intermolecular free length after mixing the components. As ultrasonic velocity for ternary mixtures (toluene + cyclohexane + nitrobenzene) decreases with increasing mole fraction of toluene , the adiabatic compressibility (β_a) free length (L_f) and free volume (V_f) show reverse trends i.e these parameters found to be increase.

The increase in adiabatic compressibility, free length and free volume with increasing mole fraction of toluene indicates significant interactions between nitrobenzene and toluene through dipole- induced dipole interaction.

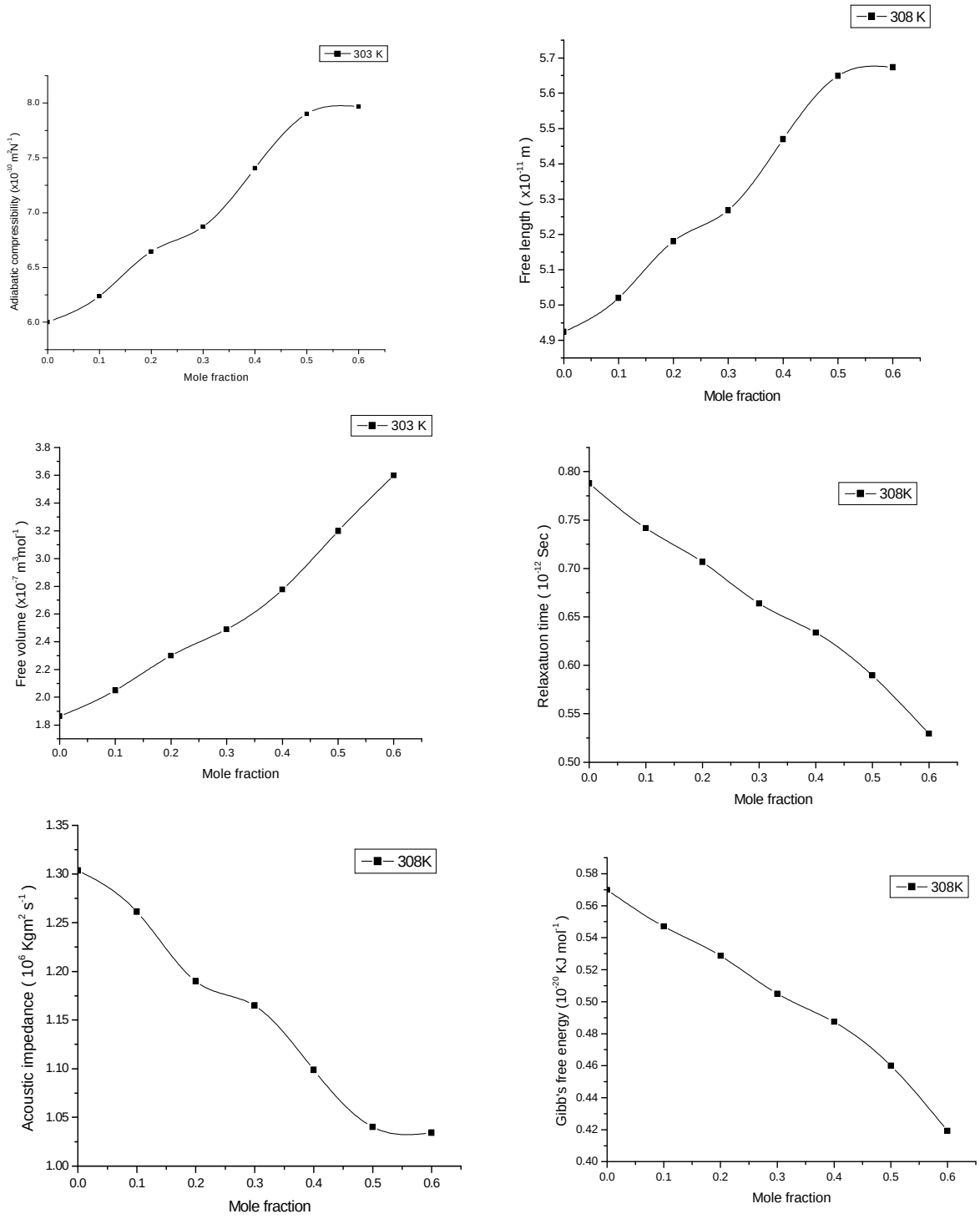

Fig 1:- The variation of adiabatic compressibility (β_a), free length (L_f), free volume(V_f), relaxation time(τ), acoustic impedance(Z) and Gibb's free energy(ΔG) with mole fraction of ternary liquid mixtures at 308 K

Further, Table-4 shows that the relaxation time decreases with increasing mole fraction of toluene which is in the order of 10^{-12} sec., indicates that the molecules get rearranged due to co-operative process [13], acoustic impedance decreases with increasing mole fraction of toluene and the Gibb's free energy decreases with increasing mole fraction of toluene may be due to the intermediate compound formation between the ternary liquid mixtures.

As toluene is a liquid which is associated through Wander Waal's force, mixed with nitrobenzene, the $–NO_2$ group which acts as an electron acceptor towards the π- electrons of toluene ring. This is due to the fact that $–CH_3$ group of toluene is an electron donar group through induction, enhances the π- electron density of the toluene ring. Thus this makes the donation of π- electron for $–NO_2$ group easier forming donar – acceptor complex between toluene and nitrobenzene molecules.

As cyclohexane is non- polar molecule doesn't possess dipole moment, when it interacts with nitrobenzene which is polar molecule posse's dipole moment then cyclohexane posses induced dipole moment. This is the induced dipole – dipole interaction between cyclohexane and nitrobenzene molecule.

Hence the formation of donar – acceptor complex between toluene – nitrobenzene molecules and dipole – induced dipole interaction between nitrobenzene- cyclohexane molecules clearly enhance the increase in adiabatic compressibility (β_a), free length (L_f) and free volume (V_f).

CONCLUSION

From ultrasonic velocity, related acoustic parameters for ternary mixtures of toluene with nitrobenzene in cyclohexane for various concentration at 308 K, it has been found that there exists a dipole- induced dipole interaction between nitrobenzene and cyclohexane and the donar- acceptor complex is observed between toluene and nitrobenzene molecules.

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