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Ultrasonic study of molecular dynamics in some binary mixtures

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ABSTRACT

The study of propagation of ultrasonic waves in liquids and liquid mixtures in very much useful for examining the nature of intermolecular interactions in chemical systems. Ultrasonic velocity is an important physical parameter which mainly depends on the structure of molecules. In the present investigation, ultrasonic velocities have been measured in binary mixtures of (i) Methanol - Chlorobenzene, (ii) Ethanol - Chlorobenzene and (iii) 1-Propanol - Chlorobenzene to understand the molecular interactions. Various models have been employed to calculate the acoustical parameters in order to substantiate these interactions. The various acoustic parameters such as adiabatic compressibility, free length, acoustic impedance, relaxation time, free volume, available volume and internal pressure were also measured to substantiate these interactions. Many interesting features were observed and they are carefully discussed.

Key Words: Ultrasonic study, Molecular dynamics, Binary mixture, Acoustic parameter, Acoustic impedance.

INTRODUCTION

Ultrasonic is a branch of acoustics dealing with sound above the audible range, and in many respects analogues to microwave physics in the field of electromagnetism. Both are characterized by special instrumentation and measuring techniques. Ultrasonic's frequencies are higher than 20,000 Hz and their wavelengths are small. The sound waves of frequency lower than the audible limit are called infrasonic. Supersonics refers to the velocities higher than the velocity of sound. Ultrasonic velocity is an important physical parameter having structural dependence [1-5]. The study of propagation of ultrasonic waves in liquids and liquid mixtures is very much

useful for examining the nature of intermolecular and intramolecular interactions in these systems. Phsyico-chemical properties can be understand among the interacting components from ultrasonic velocity measurements and it can be coupled with other experimental data such as density and viscosity to calculate various acoustical parameters such as adiabatic compressibility, free length, acoustic impedance, relaxation time, free volume, available volume and internal pressure, which are useful in understanding the molecular interactions in binary mixtures [6-8]. In the present investigation, ultrasonic velocities have been measured in binary mixtures to understand the molecular interactions. Various models have been employed to calculate the acoustical parameters in order to substantiate these interactions. Ultrasonic studies were carried out in the following binary mixtures containing chlorobenzene as one of the components. (i). Methanol - Chlorobenzene, (ii). Ethanol - Chlorobenzene and (iii).1-Propanol – Chlorobenzene. The acoustical parameters have been calculated for these three binary mixtures at different concentrations of Chlorobenzene at 303K.

EXPERIMENTAL SECTION

Reagents

All the chemicals used in this study are of AR grade. Methanol, Ethanol and 1-Propanol were refluxed and distilled before use. The spectral grade Chlorobenzene of BDH make was used after simple distillations.

Preparation of binary mixtures

Jobs continuous variation method was used to prepare the binary mixtures of required proportions [9-13]. The binary liquid mixtures were preserved in well stoppered conical flasks. After mixing the liquids thoroughly, the flasks were left undisturbed to attain thermal equilibrium.

Measurement of Ultrasonic Velocity

The different methods that can be employed for the detection of the ultrasonic velocity are, (i) Optical method, (ii) Pulse technique and (iii) Interferometric method. In this investigation the interferometric method has been employed for the determination of ultrasonic velocity. In the interferometer a standing wave is set up between the generating quartz crystal and a reflector. The wavelength is measured by moving the reflector or by using the standing wave as a grating for diffraction of light. In this way velocity could be measured with an accuracy better 1 part in 10^5. The principle used is the measurement of wavelength in the medium. Density was determined by the specific gravity method. Viscosity was measured by Ostwald's viscometer method. Measurement of Ultrasonic velocity (U), Viscosity (η) and Density (ρ) of liquids are useful to determine the thermodynamic and acoustic parameters of the binary mixtures. These acoustical and the thermodynamic properties help us understand the characteristics of the liquid. The nature of the molecular interaction in the liquid can be proved by making use of the parameters such as Adiabatic compressibility (β), free length (L_f), Acoustic impedance (Z) and Relaxation time (τ), free volume (V_f), available volume (V_a) and internal pressure (π_i). These parameters were measured by the standard procedures available in the literatures.

RESULTS AND DISCUSSION

The acoustic parameters were calculated for various compositions of Methanol, Ethanol, 1-Propanol with Chlorobenzene binary mixtures from ultrasonic velocities and the results are given in Tables 1-6. These data are discussed in the light of molecular interaction between the components.

.Ultrasonic velocity (U)

The ultrasonic velocity increases with increase in the mole fraction of Chlorobenzene in all the three systems investigated (Table 1-3). This suggests that there are molecular interactions between the components of binary mixtures. The ultrasonic velocity for a given composition of 1-Propanol – Chlorobenzene mixture is greater than that of similar composition of Ethanol – Chlorobenzene and Methanol-Chlorobenzene mixtures. Ultrasonic velocity increases with increase in chain length of alcohol (Table 1-3). The plot of ultrasonic velocity against mole fraction of Chlorobenzene for the three systems is given in fig.1.

TABLE 1: Ultrasonic Velocity (U), Density (ρ) and Viscosity (η) values for the binary mixture of Methanol - Chlorobenzene at 303K

Mole fraction of Chlorobenzene	Ultrasonic velocity(U),ms^{-1}	Density ((ρ),Kgm-3	Viscosity (η)×10^{-3},$Nm^{-2}s$
0.0000	1089.8	780.2	0.5984
0.0424	1105.0	811.2	0.6907
0.0906	1119.2	847.4	0.7105
0.1459	1124.0	870.9	0.7189
0.2098	1140.0	907.9	0.7377
0.2849	1150.0	932.8	0.7458
0.3741	1161.2	967.6	0.7673
0.4818	1182.4	1001.6	0.7878
0.6144	1198.4	1030.6	0.8039
0.7819	1212.0	1068.9	0.7782
1.0000	1241.5	1093.2	0.8882

TABLE 2: Ultrasonic Velocity (U), Density (ρ) and Viscosity (η) values for the binary mixture of Ethanol - Chlorobenzene at 303K

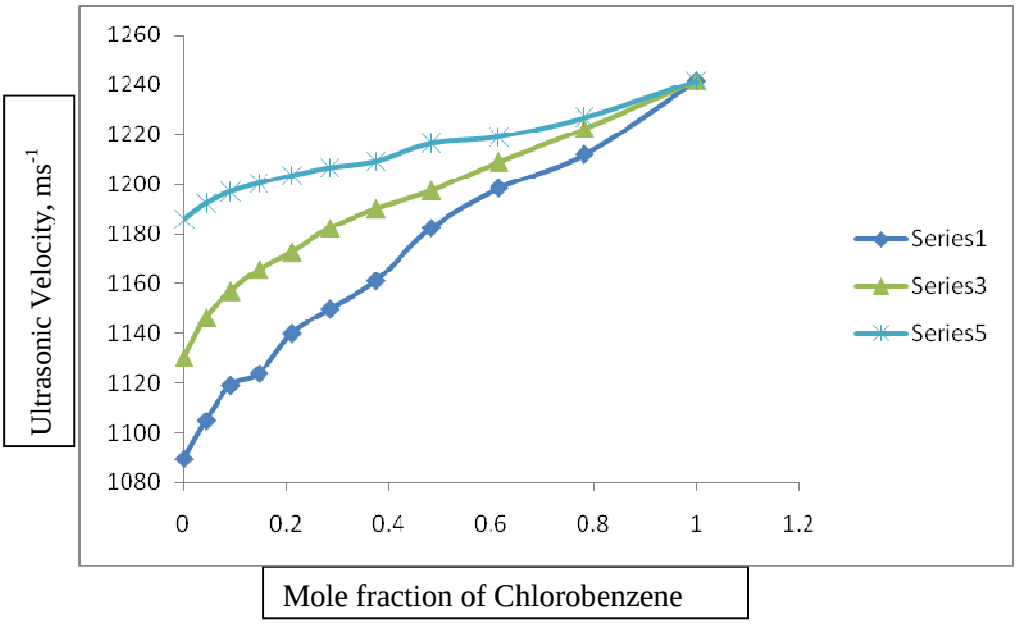
Mole fraction of Chlorobenzene	Ultrasonic velocity(U),ms^{-1}	Density ((ρ),Kgm-3	Viscosity (η)×10^{-3},$Nm^{-2}s$
0.0000	1130.3	782.9	1.0178
0.0598	1146.4	822.1	1.2184
0.1250	1157.0	846.3	1.1662
0.1968	1165.7	876.4	1.0368
0.2759	1172.8	907.9	1.0386
0.3637	1182.4	936.4	0.9860
0.4611	1190.2	969.5	0.9327
0.5715	1197.4	997.4	0.9206
0.6957	1209.0	1028.9	0.8962
0.8372	1222.4	1057.2	0.8796
1.0000	1241.5	1093.2	0.8882

TABLE 3: Ultrasonic Velocity (U), Density (ρ) and Viscosity (η) values for the binary mixture of 1-Propanol - Chlorobenzene at 303K

Mole fraction of Chlorobenzene	Ultrasonic velocity(U),ms^{-1}	Density ((ρ), Kgm-3	Viscosity (η)×10^{-3},$Nm^{-2}s$
0.0000	1185.9	794.7	1.9423
0.0753	1192.4	826.5	1.8158
0.1551	1197.1	852.8	1.5743
0.2394	1200.4	889.3	1.3295

0.3249	1203.5	912.1	1.2450
0.4234	1206.7	943.3	1.1281
0.5242	1209.2	971.6	1.0736
0.6315	1216.4	1005.7	0.9413
0.7461	1219.1	1024.1	0.9186
0.8686	1226.8	1055.9	0.9060
1.00000	1241.5	1093.2	0.8882

Fig.1 Variation of ultrasonic velocity



[Series-1=1-Propanol; series-3=Ethanol; series-5=Methanol]

Density (ρ)

In all the three systems, the density increases with increase in concentration of Chlorobenzene due to increase in the presence of ions or particles. As the number of particles increases, the electrostriction and density increases. Table (1-3) shows the increase in density with the increase in concentration. It is also observed that density for 1-Propanol-Chlorobenzene is greater than that for other two systems. Density increases with increase in chain length of alcohol (Table 1-3).

TABLE 4: Acoustical parameters for Methanol -Chlorobenzene Binary Mixture at 303K

Mole fraction of Chlorobenzene	Adiabatic compressibility, $\beta\times10^{-10}$, $Kg^{-1}ms^2$	Free length, L_f, Å	Acoustic impedance,$Z\times10^6Kgm^{-2}s^{-1}$	Relaxation time, $\tau\times10^{-9}$,s	Free volume,$V_f\times10^{-7}$,mL	Available volume, $Va\times10^{-2}$,m^3	Internal pressure II_1, Atm
0.0000	10.7919	0.6570	0.8503	0.8610	0.50	2.8	86772
0.0424	10.0959	0.6355	0.8964	0.9297	0.48	3.0	84416
0.0906	9.4210	0.6139	0.9484	0.8925	0.55	3.2	80526
0.1459	9.0886	0.6029	0.9789	0.8712	0.64	3.5	69960
0.2098	8.4752	0.5822	1.0350	0.8336	0.74	3.8	63544
0.2849	8.1062	0.5694	1.0727	0.8061	0.88	4.2	56530
0.3741	7.6646	0.5537	1.1236	0.7841	1.10	4.9	48075
0.4818	7.1413	0.5345	1.1843	0.7501	1.24	5.2	44694
0.6144	6.7563	0.5199	1.2351	0.7242	1.51	5.9	38797
0.7819	6.3688	0.5047	1.2955	0.6608	2.07	6.8	32079
0.0000	5.9348	0.4872	1.3572	0.7028	2.23	8.0	33343

TABLE 5: Acoustical parameters for Ethanol - Chlorobenzene Binary Mixture at 303K

Mole fraction of Chlorobenzene	Adiabatic compressibility, $\beta\times10^{-10}$, $Kg^{-1}ms^2$	Free length ,L_f, Å	Acoustic impedance,$Z\times10^6Kgm^{-2}s^{-1}$	Relaxation time, $\tau\times10^{-9}$,s	Free volume,$V_f\times10^{-7}$,mL	Available volume, $Va\times10^{-2}$,m^3	Internal pressure II_1, Atm
0.0000	9.9978	0.6324	0.8849	0.8610	0.41	4.2	72803
0.0598	9.2556	0.6085	0.9245	0.9297	0.36	4.4	74183
0.1250	8.8269	0.5942	0.9792	0.8925	0.45	4.6	66861
0.1968	8.3970	0.5796	1.0216	0.8712	0.61	4.9	58275
0.2759	8.0078	0.5660	1.0648	0.8336	0.70	5.2	53894
0.3637	7.6385	0.5528	1.1072	0.8061	0.87	5.5	48003
0.4611	7.2814	0.5397	1.1539	0.7841	1.09	5.9	43194
0.5715	6.9928	0.5289	1.1943	0.7501	1.29	6.3	39192
0.6957	6.6493	0.5157	1.2439	0.7242	1.57	6.8	35221
0.8372	6.3302	0.5032	1.2923	0.6608	1.90	7.3	31547
1.0000	5.9348	0.4872	0.7028	0.7028	2.23	8.0	33343

TABLE 6: Acoustical parameters for 1-Propanol - Chlorobenzene Binary Mixture at 303K

Mole fraction of Chlorobenzene	Adiabatic compressibility, $\beta\times10^{-10}$, $Kg^{-1}ms^2$	Free length, L_f, Å	Acoustic impedance,$Z\times10^6$ $Kgm^{-2}s^{-1}$	Relaxation time, $\tau\times10^{-9}$,s	Free volume,$V_f\times10^{-7}$,mL	Available volume, $Va\times10^{-2}$,m^3	Internal pressure II_1, Atm
0.0000	8.9468	0.5982	0.9425	2.3170	0.25	5.6	72725
0.0753	8.5097	0.5834	0.9855	2.0602	0.31	5.8	66830
0.1551	8.1832	0.5721	1.0209	1.7177	0.42	6.0	58901
0.2394	7.8035	0.5587	1.0675	1.3833	0.60	6.1	51657
0.3249	7.5699	0.5503	1.0977	1.2566	0.73	6.4	47345
0.4234	7.2806	0.5397	1.1382	1.0951	0.93	6.6	42676
0.5242	7.0391	0.5306	1.1749	1.0076	1.12	6.8	39393
0.6315	6.7201	0.5185	1.2233	0.8434	1.49	7.0	35044
0.7461	6.5706	0.5127	1.2484	0.8048	1.71	7.4	32536
0.8686	6.2926	0.5017	1.2954	0.7601	1.93	7.7	30558
0.0000	5.9348	0.4872	1.3572	0.7028	2.23	8.0	33343

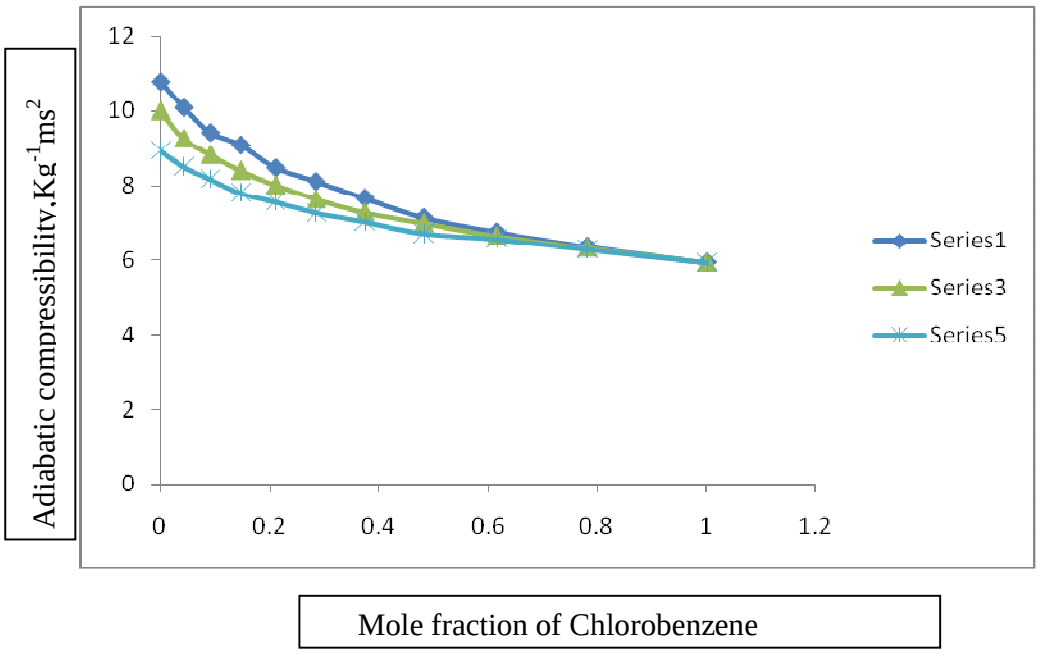
Adiabatic compressibility (β)

The adiabatic compressibility values for various compositions of the three binary mixtures have been calculated from the measured ultrasonic velocities (Table 4 - 6). The plots of adiabatic compressibility against mole fraction of Chlorobenzene for the three systems are given in fig.2. It may be noted that in all the three cases adiabatic compressibility decreases with increase in concentration of Chlorobenzene indicating relatively stronger Hydrogen bonding over wide range of concentration. According to Fort and Moore, Hydrogen bonding between unlike components makes a negative contribution to compressibility [14]. The compressibility data also shows that dipole induced dipole attraction are stronger in Methanol-Chlorobenzene binary mixture than in Ethanol-Chlorobenzene and in 1-Propanol – Chlorobenzene binary mixtures. Adiabatic compressibility decreases with increase in chain length of Alcohol (Table 4 - 6).

Linear free length (L_f)

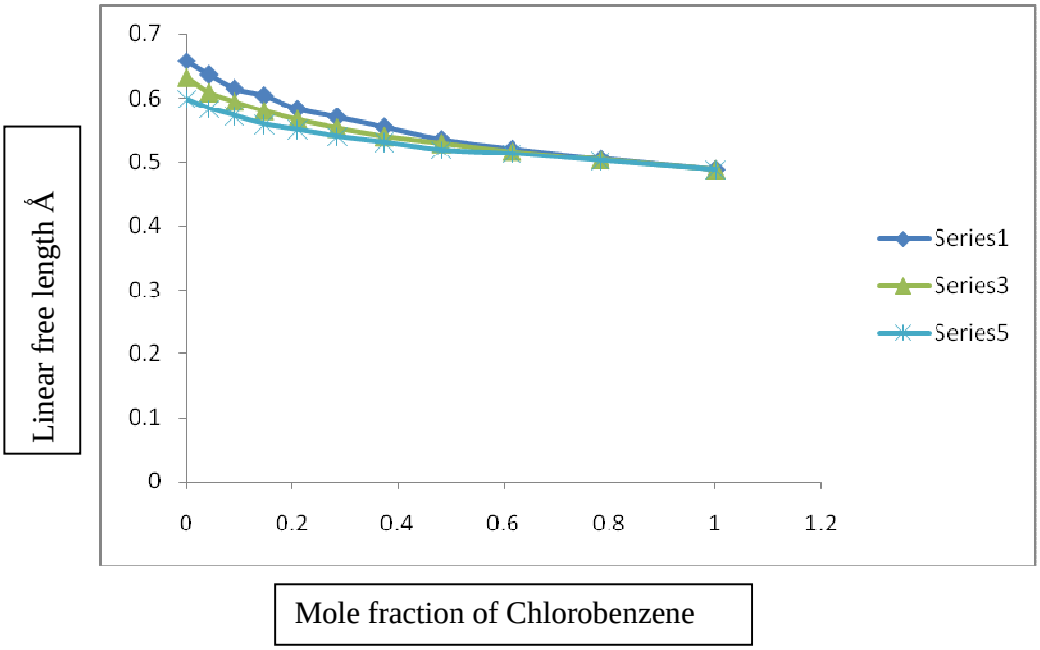
Intermolecular free length is related to ultrasonic velocity. As the ultrasonic velocity increases due to the increase in concentration, the intermolecular free length has to decrease and vice versa [15]. Increase in concentration leads to decrease in gap between two species and which is referred by intermolecular free length. It may be noted that in all the three cases linear free length decreases with increase with increase in concentration of Chlorobenzene (Table 4 - 6). This shows that dipole induced dipole attraction increases with the concentration of Chlorobenzene. The linear free length for a given composition for Methanol – Chlorobenzene binary mixture is greater than that for similar compositions in other two systems. Linear free length decreases with increase in chain length of alcohol (Table 4-6). The plots of linear free length against mole fraction of Chlorobenzene for the three systems are given in fig.3.

Fig.2 Variation of Adiabatic compressibility



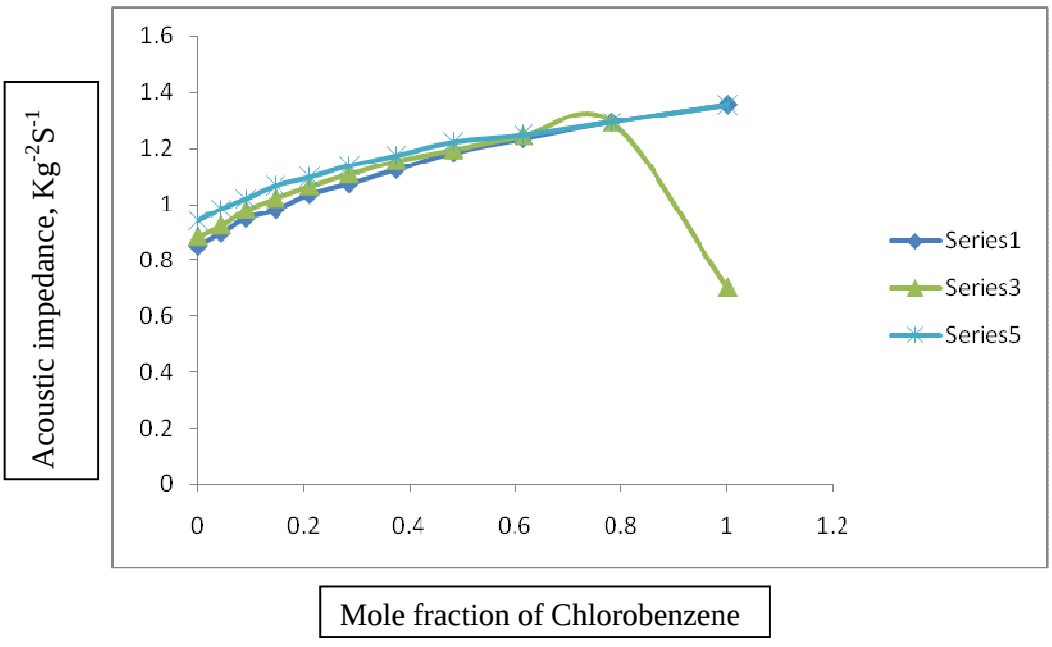
[Series-1=1-Propanol; series-3=Ethanol; series-5=Methanol]

Fig.3 Variation of linear free length



[Series-1=1-Propanol; series-3=Ethanol; series-5=Methanol]

Fig.4 Variation of Acoustic impedance



[Series-1=1-Propanol; series-3=Ethanol; series-5=Methanol]

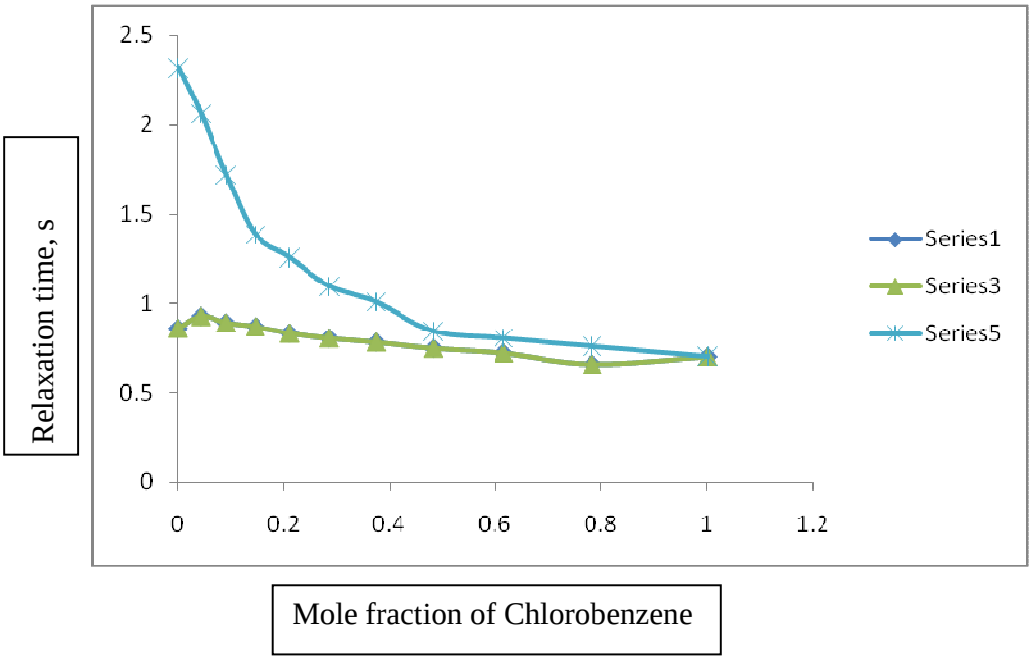
Acoustic impedance (Z)

The acoustic impedance increases with increase in concentration of Chlorobenzene in all the three systems studied. The increase in acoustic impedance with the concentration can be explained on the basis of lyophobic interaction between solute and solvent molecules [16, 17] which increases the intermolecular distance, making relatively wider gap between the molecules. It is also observed that acoustic impedance for 1-Propanol-Chlorobenzene binary mixture is greater than that for the other two systems. The plots of acoustic impedance verses mole fraction of Chlorobenzene for the three systems are given in fig.4. Acoustic impedance increases with increase in chain length of alcohol (Table 4-6).

Relaxation time (τ)

The relaxation time increases at lower concentration and decreases at higher concentration of Chlorobenzene for all the three systems (Table 4 – 6). This shows that molecular interaction is strong at lower concentration of Chlorobenzene and relatively weak at higher concentration. It is also observed that relaxation time for 1-Propanol – Chlorobenzene binary mixture is greater than that for other two systems. The plots of relaxation time versus mole fraction of Chlorobenzene for the three systems are given in fig.5. Relaxation time increases with increase in chain length of alcohol (Table 4 - 6).

Fig.5 Variation of Relaxation time

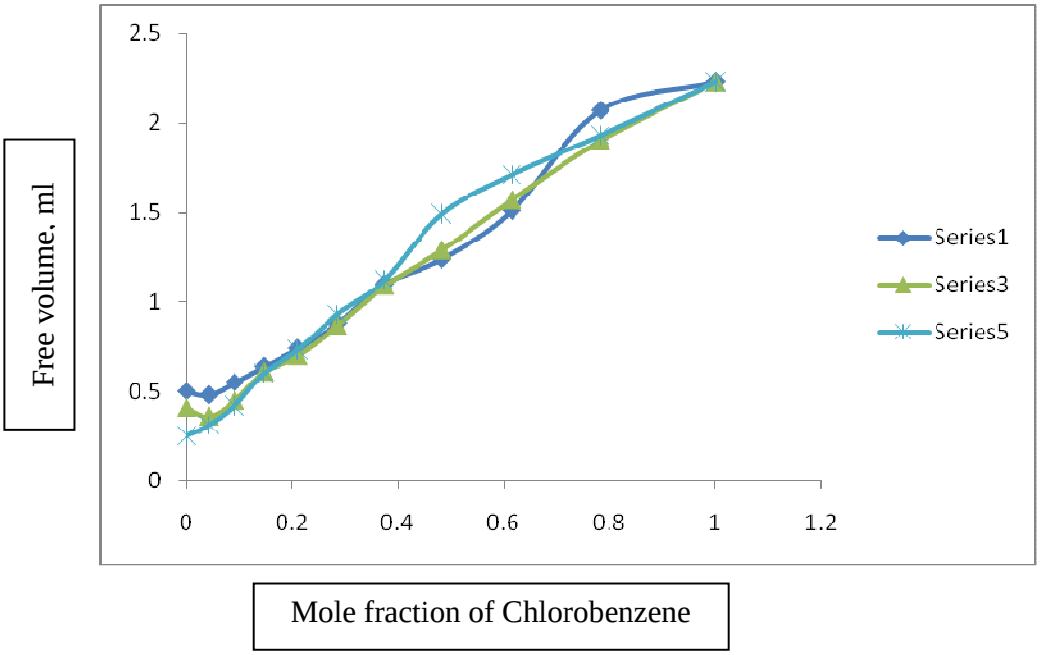


[Series-1=1-Propanol; series-3=Ethanol; series-5=Methanol]

Available volume (V_a)

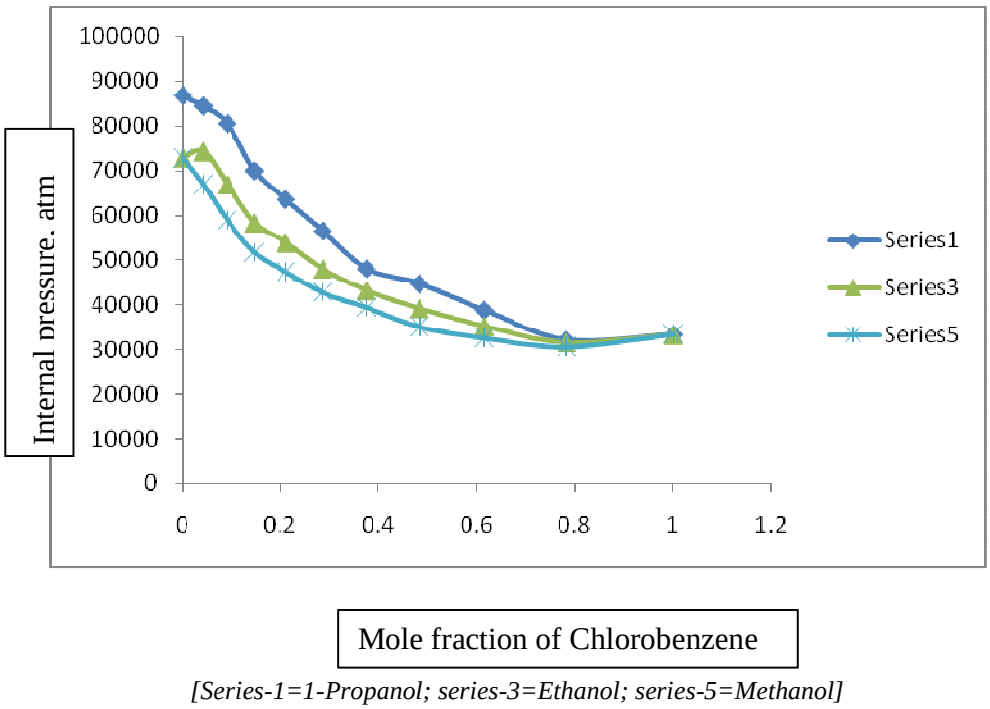
For all the three systems, available volume increases with increase in concentration of Chlorobenzene (Table 4-6). It is also observed that available volume for 1-Propanol – Chlorobenzene binary mixture is greater than that for other two systems. Available volume increases with increase in chain length of alcohol (Table 4-6) (fig. 6).

Fig.6 Variation of free volume



[Series-1=1-Propanol; series-3=Ethanol; series-5=Methanol]

Fig.7 Variation of Internal pressure



[Series-1=1-Propanol; series-3=Ethanol; series-5=Methanol]

Internal pressure (π_i)

The internal pressure in a binary liquid mixture is a measure of cohesive forces between the components. The internal pressure values for the three binary mixtures at different compositions are given in (Table 4-6). These values indicate that the internal pressure changes with composition of the alcohols and hence cohesive forces changes with the concentration of Chlorobenzene. The internal pressure is maximum when the concentration of Chlorobenzene is the lowest. It is also interesting to observe that the free volume of the binary liquid mixtures increases as internal pressure decreases. The variations of internal pressure with respect to the mole fraction of the chlorobenzene for the three systems are given in fig.7. It is also observed that internal pressure for methanol- chlorobenzene binary mixture is greater than that for the other two systems. Internal pressure decreases with increase in chain length of alcohol (Table 4-6).

CONCLUSION

The various acoustic parameters such as adiabatic compressibility, free length, acoustic impedance, relaxation time free volume, available volume and internal pressure have been evaluated from ultrasonic velocity, density and viscosity for the binary liquid mixture of Methanol – Chlorobenzene, Ethanol – Chlorobenzene and 1- Propanol - Chlorobenzene systems at 303K. In the present investigation, it could be inferred that there are inter molecular interactions among the components of the binary mixtures, leading to the possible hydrogen bond formation of the type Cl…H-O between unlike molecules. Molecular interaction increases with increase in the concentration of Chlorobenzene in all the three systems. It is also observed that molecular interaction increases with increase in chain length of alcohol in the order 1-Propanol > Ethanol >Methanol.

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