

## ACOUSTIC STUDIES IN TERNARY LIQUID SYSTEMS OF SUBSTITUTED BENZENES WITH 1-CHLOROBUTANE AT DIFFERENT TEMPERATURES

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### ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for the ternary mixtures of substituted benzenes such as chlorobenzene, bromobenzene and nitrobenzene with 1-chlorobutane in cyclohexane at 303, 308 and 313K. The experimental data have been used to calculate the acoustical parameters namely adiabatic compressibility ( $\beta$ ), free length ( $L_f$ ), free volume ( $V_f$ ) internal pressure ( $\pi_i$ ), relaxation time ( $\tau$ ), Gibb's free energy ( $\Delta G^*$ ), acoustic impedance ( $Z$ ) and molar volume ( $V_m$ ). Some of the above excess parameters have also been evaluated and fitted to Redlich-Kister polynomials. Weak dipole-dipole interaction is observed in the present systems of liquid mixtures. It is also interesting to note that chlorobenzene is acting as an effective diluent in the mixtures comparing other two substituted benzenes.

**Keywords:** Adiabatic compressibility; Free length; Free volume; Acoustic impedance; Dipole-dipole interactions.

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### INTRODUCTION

Ultrasonic investigation of liquid mixtures consisting of polar and non-polar components is of considerable importance in understanding intermolecular interaction between the component molecules and they find applications in several industrial and technological processes<sup>1-2</sup>. Further, such studies as a function of concentration are useful in gaining insight into the structure and bonding of associated molecular complexes and other molecular processes. A survey of literature reveals that the studies for the binary mixture of substituted benzenes such as chlorobenzene, bromobenzene and nitrobenzene with non-polar components like cyclohexane have been done, but no attempt has been done to study the various ultrasonic and thermodynamic properties for the above binary mixture with a dipolar liquid such as 1-chlorobutane which is an important liquid used currently in the various chemical applications to analyze its compounds and also in various chemical engineering related applications. Moreover, the behaviour of a non-polar molecule in a different polar environment can also be discussed with the ternary system. These liquid mixtures are of interest to organic chemists who want to know about the types of bonds, type of molecular interactions, etc. Further, the values of ultrasonic velocity, density, viscosity and adiabatic compressibility as a function of concentration will be of much help in providing such information. Hence, the authors have carried out the ultrasonic study in the ternary systems of substituted benzenes with 1-chlorobutane in cyclohexane at different temperatures. Accurate knowledge of thermodynamic mixing properties such as adiabatic compressibility, intermolecular free length, free volume, internal pressure and molar volume and their excess values for mixtures of protic, non-protic and associated liquids has a great importance in theoretical and applied areas of research.

The present study deals with such a substituted benzenes with 1-chlorobutane is of interesting one. Nitrobenzene have higher dipole moment and dielectric constant values than those of chlorobenzene and bromobenzene. Nitrobenzene is supposed to be a relatively complex molecule and its non-ideality in all probability may be due to the polarity arisen out of nitro-group is concerned, it rotates freely along the C-N axis where it likely to give more flexibility to the interactions arising due to the two highly polar N $\rightarrow$ O

bonds<sup>3</sup>. Chlorine atom in chlorobenzene is an electron-withdrawing atom, tends to attract to  $\pi$ -electrons of the benzene ring, thereby, decreases the electron density of ring. As a result, the benzene ring in chlorobenzene becomes relatively poor electron-donor towards the electron - seeking proton of any groups<sup>4</sup>. Chlorobenzene has low dielectric constant  $\epsilon' = 5.649$  and dipole moment  $\mu = 1.69\text{D}$ . Its boiling point and melting points are  $132^\circ\text{C}$  and  $-45^\circ\text{C}$ , respectively. Chlorobenzene is neither acidic nor basic colourless, liquid with a pleasant smell. Chlorobenzene is insoluble in water and soluble in alcohol, benzene and ether. Chlorobenzene is more reactive because the chlorine atom is bonded with  $\text{SP}^3$  hybridized carbon atom and consequently can be removed easily. So, the rate of reaction with chlorobenzene is faster<sup>5</sup>. Bromobenzene is less reactive because of its double bond character between carbon and bromine atom. The slow reactions in case of bromobenzene may also be attributed to its being heavier. Thus, the molecular interactions are likely to be more affected resulting in a greater degree of variation with respect to the ultrasonic related parameters<sup>5</sup>. The above characteristics physical nature of substituted benzenes had motivated the authors to study the molecular interactions of ternary liquids mixtures of substituted benzenes with 1-chlorobutane in cyclohexane at different temperatures.

### EXPERIMENTAL

The liquid mixtures of various concentrations in mole fraction were prepared by taking AR grade Chemicals, which were purified by standard methods<sup>6</sup>. In all systems, the mole fraction of the second component, cyclohexane ( $X_2 = 0.4$ ) was kept fixed while the mole fractions of the remaining two were varied from 0.0 to 0.6 so as to have the mixtures of different compositions. There is nothing significant on fixing the second component at the  $X_2 = 0.4$ . The ultrasonic velocity in liquid mixtures have been measured using an ultrasonic interferometer (MITTAL ENTERPRISES, NEW DELHI, Model: F81) working at frequency 3MHz with an overall accuracy of  $\pm 2 \text{ ms}^{-1}$ . The density and viscosity are measured using a Pyckno meter and an Ostwald's Viscometer an accuracy of  $\pm 0.01\text{kg m}^{-3}$  and  $\pm 0.001 \text{ Nsm}^{-2}$  respectively. All the precautions were taken to minimise the possible experimental error. The set-up is checked for known liquids. The values obtained are compared with literature and found that they makes very well with each other. The chemicals used in the present work were analytical reagent (AR) and spectroscopic reagent (SR) grade with minimum assay of 99.9% were obtained from Sd fine chemicals India and E-Merck, Germany.

#### Theory and Calculations

Using the measured data, the acoustical parameters have been calculated

$$\text{Adiabatic Compressibility } \beta = \frac{1}{U^2 \rho} \quad (1)$$

Intermolecular frelength ( $L_f$ ) has been calculated from relation,

$$L_f = K_T \sqrt{B} \quad (2)$$

where  $K_T$  is a temperature dependent constant.

Free volume ( $V_f$ ) has been calculated from relation,

$$V_f = \left( \frac{M_{eff} U}{K \eta} \right)^{3/2} \quad (3)$$

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 weight and the mole fraction of the individual constituents respectively).  $K$  is a temperature independent constant which is equal to  $4.28 \times 10^9$  for all liquids.

The internal pressure ( $\pi_i$ ) can be found out as

$$\pi_i = bRT \left( \frac{K \eta}{U} \right)^{1/2} \left( \frac{\rho^{2/3}}{M_{eff}^{7/6}} \right) \quad (4)$$

K is a constant, T the absolute temperature,  $\eta$  the viscosity in  $\text{Nsm}^{-2}$ , U the ultrasonic velocity in  $\text{ms}^{-1}$ ,  $\rho$  the density in  $\text{Kgm}^{-3}$ ,  $M_{\text{eff}}$  the effective molecular weight.

The relaxation time is estimated from the following relation,

$$\tau = \frac{4}{3} \eta \beta \quad (5)$$

knowing the viscosity of the liquid ( $\eta$ ) and adiabatic compressibility ( $\beta$ ), then  $\tau$  can be calculated.

The Gibb's free energy can be related as

$$\Delta G^* = -2.303KT \log \frac{h}{KT\tau} \quad (6)$$

where K is Boltzmann's constant and h, the Planck's constant.

The acoustic impedance can be related as

$$Z = U\rho \quad (7)$$

where U is a velocity of ultrasound in medium and  $\rho$  is density.

Excess value ( $A^E$ ) has been calculated by using the relation

$$A^E = A_{\text{exp}} - A_{\text{id}} \quad (8)$$

where  $A_{\text{id}} = \sum_{i=1}^n A_i X_i$ ,  $A_i$  is any acoustical parameters and  $X_i$  the mole fraction of the liquid component i.

The excess properties  $\beta^E, L_f^E, V_f^E, V_m^E$  and  $Z^E$  were fitted to Redlich-Kister<sup>7</sup> polynomial equation

$$Y^E = x_1 x_3 \sum_{i=1}^K A_i (x_1 - x_3) \quad (9)$$

Where  $Y^E$  refers to excess properties,  $x_1$  and  $x_3$  are the mole fraction of the components of the ternary mixtures. The coefficients ( $A_i$ ) were obtained by fitting equation to experimental values using a least to square regression method. In each case, the optimal number of coefficients were ascertained from an approximation of the variation in the standard deviation ( $\sigma$ ). The calculated values of  $A_i$  along with the tabulated standard deviation ( $\sigma$ ) are listed in the Table-6. The standard deviation ( $\sigma$ ) was calculated using the equation

$$\sigma^2 = \frac{1}{n-m} \left[ \sum_{\text{exp}} \frac{Y^E}{\text{exp}} - \sum_{\text{cal}} \frac{Y^E}{\text{cal}} \right]^2 \quad (10)$$

where 'n' is the number of data points and 'm' is the number of coefficients.

## RESULTS AND DISCUSSION

The present systems taken up for study at 303, 308 and 313 K are-

System-I	chlorobenzene	+ cyclohexane	+ 1-chlorobutane
System-II	bromobenzene	+ cyclohexane	+ 1-chlorobutane
System-III	nitrobenzene	+ cyclohexane	+ 1-chlorobutane

It is observed that in all the three ternary liquid systems, the density ( $\rho$ ), the ultrasonic velocity (U) and the viscosity ( $\eta$ ) increases with increasing concentrations of substituted benzenes, such as chlorobenzene, bromobenzene and nitrobenzene. These are tabulated in Table-1. The acoustical parameters such as adiabatic compressibility ( $\beta$ ), intermolecular free length ( $L_f$ ), free volume ( $V_f$ ), internal pressure ( $\pi_i$ ) are furnished for the systems I, II and system III are represented in Table 2. Similarly, viscous relaxation

time ( $\tau$ ), Gibb's free energy ( $\Delta G^*$ ), molar volume ( $V_m$ ) and acoustic impedance ( $Z$ ) for system I, II and III are given in Table-3.

The variation of ultrasonic velocity in a mixture depends upon the increase (or) decrease of intermolecular free length after mixing the components. On the basis of a model, for sound propagation proposed by Eyring and Kincaid<sup>8</sup>, ultrasonic velocity should decrease, if the intermolecular free length increase and vice-versa. This is in fact observed in the present investigation for all the three liquid systems. However, a reverse trend is observed in the case of adiabatic compressibility ( $\beta$ ) and intermolecular free length ( $L_f$ ), which are tabulated in Table2. i.e both the parameters are found to be decreased with increasing molar concentration of substituted benzenes. in all the three liquid systems. The increase in ultrasonic velocity ( $U$ ) and corresponding decrease in adiabatic compressibility ( $\beta$ ) with concentration indicate that the molecules are forming a more tightly bound system<sup>9</sup>. Since 1-chlorobutane is highly polar and it has high percentage of ionic character. Hence, one could expect a strong interactions with substituted benzenes. In the case of substituted benzenes, the bromine, chlorine and nitrogen has a tendency to act as an electron acceptor. However, the decrease of adiabatic compressibility ( $\beta$ ) and free length ( $L_f$ ) is observed in the experimental results, which indicate the prevailing of weaker interactions in all the ternary mixtures. Such a decrease in  $\beta$  and  $L_f$  may also be attributed to the internal interaction between the  $\pi$ -electrons of C=O bond and  $\pi$ -electrons of the benzene ring<sup>10</sup>. Further, Cyclohexane belongs to alicyclic hydrocarbon (closed chain). The packing of carbon atoms in this even numbered alkane group allows the maximum intermolecular attractions<sup>11</sup> and therefore these molecules are highly inert towards an electrophile or nucleophile at ordinary temperature. In the present study, among the three components, Cyclohexane is not expected to involve in any interactions either with 1-chlorobutane or with substituted benzenes due to its non-polar nature.

In the present study, it is observed that the adiabatic compressibility ( $\beta$ ) and intermolecular free length ( $L_f$ ) values comparatively larger in bromobenzene system (system-II). Similarly, these values are comparatively smaller in chlorobenzene system (system-I). The polar liquids, such as chlorobenzene is more reactive, because the chlorine atom is bounded with  $SP^3$  hybridized<sup>5</sup> carbon atom and consequently can be removed easily. So, the rate of reaction with chlorobenzene is faster. This leads to a small value of  $\beta$  and  $L_f$  in the case of chlorobenzene system. On the other hand, bromobenzene is less reactive because of its double bond character between carbon and bromine atom. The slow reaction in the case of bromobenzene may also be attributed to its being heavier. Thus, the molecular interaction<sup>5</sup> is likely to be more affected resulting in a greater degree of variation in the ultrasonic related parameters. This leads to a possession of higher values of  $\beta$  and  $L_f$  in the system. Hence, it is obvious that molecular association is more pronounced in Chlorobenzene system than in bromobenzene system. However, the increase in temperature makes the free length to increase as expected due to the thermal expansion of the liquids. The values of free volume ( $V_f$ ) and internal pressure ( $\pi_i$ ) are furnished in the Table-2. The values of free volume ( $V_f$ ) decrease and the values of internal pressure ( $\pi_i$ ) increase in all the three liquid systems with increasing molar concentration of substituted benzenes. Such, a decrease in free volume ( $V_f$ ) and an increase in internal pressure ( $\pi_i$ ) in all the systems clearly indicates the increasing magnitude of interactions.<sup>12</sup>

From Table-3, it is observed that the relaxation time ( $\tau$ ) increases continuously with increase in mole fraction of substituted benzenes and same decrease with rise in temperature. The relaxation time, which is of the order of  $10^{-12}$  seconds, is due to structural relaxation process<sup>13</sup> and such situation suggests that the molecules get rearranged due to co-operation process<sup>14</sup>. The Gibb's free energy ( $\Delta G^*$ ) (Table-3) increases with increase in composition of substituted benzenes in all the systems. The increasing positive values of Gibb's function suggest that the closer approach of unlike molecules is due to hydrogen bonding<sup>15,16</sup>. The decrease in  $\Delta G^*$  with temperature in all the mixtures indicates the need for shorter time for the co-operative process or the rearrangement of the molecules in the mixtures<sup>17</sup>.

Further, in all three liquid systems, the values of acoustic impedance ( $Z$ ) is found to be increased, which are listed in Table-3. When an acoustic wave travels in a medium, there is a variation of pressure from particle to particle. The ratio of the instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that particle is known as 'specific acoustic impedance' of the medium. This factor is governed by the inertial and elastic properties of the medium. It is important to examine specific acoustic impedance in relation to concentration and temperature. When a plane ultrasonic wave is set up in a liquid, the pressure and hence density and refractive index show specific variations with distance from the source along the direction of propagation. In the present investigation, it is observed that these acoustic impedance ( $Z$ ) values increase with increasing concentration of substituted benzenes. Such an increasing values of acoustic impedance ( $Z$ ) further supports the possibility of molecular interactions between the unlike molecules.

It is seen from the Table-3, the values of molar volume ( $V_m$ ) increases with increasing concentration of substituted benzenes in all the three liquid systems. Moreover, molar volume ( $V_m$ ) is also increases with elevation of temperature in the present study, which may probably would be caused from the fact that thermal energy facilitates an increase in the molecular separation in the liquid mixtures which leads to an increase in molar volume ( $V_m$ ) with elevation of temperature.

In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in term of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behaviour with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The extent of deviation depends upon the nature of the constituents and composition of the mixtures. It is learnt that the dispersion forces are responsible for possessing positive excess values, while dipole-dipole, dipole-induced dipole, charge transfer interaction and hydrogen bonding between unlike molecules are responsible for possessing negative excess values<sup>18</sup>. The excess values of adiabatic compressibility ( $\beta^E$ ), free length ( $L_f^E$ ) and free volume ( $V_f^E$ ) for all the three liquid systems are furnished in Table-4. In the present study, the excess value of adiabatic compressibility ( $\beta^E$ ) and free length ( $L_f^E$ ) exhibit positive values over the entire composition range for all the three liquid systems. Such a positive deviation exhibited by the excess value of  $\beta^E$  and  $L_f^E$  may be attributed to the loss of mutual dipole association<sup>19</sup> and different in size, shape and mass of the unlike component molecules in the mixtures. From Table-4, these positive values decrease with increasing concentration in the systems I & II and whereas, it increases with same concentration in the system III, which clearly show very weak dipole-dipole interactive forces existing in the nitrobenzene system than the other two systems. Further, the positive values reflected by these parameters also exhibit an increasing trend as the temperature increases, justifying the existence of weak dispersive forces present in the mixtures.

Moreover, the values of excess molar volume ( $V_m^E$ ) which are given in Table-4. They exhibit positive values over the entire range of composition in all the three liquid systems clearly suggest that the existence of weak interactive forces present in the mixtures. Also, the positive values increases with increasing concentration again support the systems studied are tending towards the weak molecular association between the unlike molecules.

The perusal of Table-5 shows that the values of excess viscosity ( $\eta^E$ ) which are found to possess negative values in all the three liquid systems over the entire range of composition. According to Fort & Moore<sup>15</sup> the excess viscosity tend to become more positive as the strength of the interaction increases. The excess viscosity variation gives a qualitative estimation of the strength of the intermolecular interactions. The excess viscosities<sup>20-23</sup> may be generally explained by considering the following factors:

- (1) The difference in size and shape of the component molecules and the loss of dipolar associations in pure component may contribute to a decrease in viscosity, and
- (2) Specific interactions between the unlike molecules such as charge-transfer complexes and hydrogen bond formations may cause for increase in viscosity in mixtures than in pure components.

The former effect produces negative excess viscosity and latter effect produces positive deviations in excess viscosity. Hence, such a negative deviation of excess viscosity ( $\eta^E$ ) lends further additional support for the existence of weak magnitude of dispersive forces present in the components of the mixtures.

### CONCLUSION

It is concluded that there exists a generally weak molecular interaction present in the liquid mixtures. From the evaluated acoustical parameters and its related some of the excess values, it is very obvious that a weak dipole-dipole interactions prevail between the unlike molecules present in the mixtures. Such a weak dipole-dipole interaction prevails comparatively in 1-chlorobutane-nitrobenzene system (system-III) than the other two systems. The molecular association comparatively stronger in 1-chlorobutane - chlorobenzene system(system-I), which suggests that the chlorobenzene is probably a more effective diluent in the mixtures, than other two substituted benzenes.

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**Table-1:** The values of density ( $\rho$ ), viscosity ( $\eta$ ) and velocity (U) at 303, 308 and 313K for Systems I, II and III

$X_1$	$X_3$	DENSITY $\rho/(\text{kg/m}^3)$			VISCOSITY $\eta/(\times 10^{-3} \text{Nsm}^{-2})$			VELOCITY U/(m/s)		
		303K	308K	313K	303K	308K	313K	303K	308K	313K
<b>System I: chlorobenzene + cyclohexane + 1-chlorobutane</b>										
0.0000	0.6000	893.04	888.09	880.28	0.5707	0.5379	0.5074	1226.7	1221.9	1219.5
0.0998	0.5001	900.84	895.63	881.72	0.5841	0.5343	0.5074	1230.9	1226.7	1220.7
0.2000	0.4001	903.51	897.55	891.46	0.6175	0.5672	0.5294	1232.7	1227.9	1225.5
0.0702	0.0707	906.18	898.99	893.50	0.7037	0.6658	0.5463	1234.5	1231.5	1229.0
0.3950	0.1991	908.99	903.99	899.94	0.8082	0.7482	0.6935	1236.9	1232.7	1230.0
0.4942	0.0994	914.00	909.99	901.99	0.8278	0.7715	0.764	1239.3	1234.5	1231.5
0.5954	0.0000	917.00	912.99	908.00	1.0178	0.8878	0.8353	1244.1	1236.9	1232.1
<b>System II: bromobenzene + cyclohexane + 1-chlorobutane</b>										
0.0000	0.6000	799.99	793.09	788.10	0.5260	0.4880	0.4440	1225.5	1219.5	1215.9
0.0998	0.5001	803.09	798.09	793.09	0.5449	0.5139	0.4862	1227.9	1221.9	1216.5
0.1998	0.4000	808.99	802.09	797.00	0.5562	0.5251	0.4955	1232.1	1226.1	1220.1
0.2996	0.3008	814.98	810.00	808.99	0.5682	0.5364	0.5068	1238.1	1230.9	1225.5
0.4006	0.1998	821.00	816.00	809.99	0.5813	0.5493	0.5180	1242.9	1237.5	1230.9
0.5001	0.0999	826.99	821.99	816.98	0.5939	0.5578	0.5286	1243.5	1239.3	1234.5
0.6001	0.0000	832.99	826.99	818.99	0.6154	0.5822	0.5410	1249.5	1242.9	1237.5
<b>System III: nitrobenzene + cyclohexane + 1-chlorobutane</b>										
0.0000	0.6000	884.09	879.09	874.20	0.5996	0.5670	0.5191	1231.5	1225.5	1219.5
0.0999	0.5000	889.99	884.09	879.09	0.6119	0.5700	0.5299	1236.9	1231.5	1226.1
0.2000	0.4000	894.19	889.10	884.09	0.6258	0.5898	0.5574	1240.5	1234.5	1228.5
0.2999	0.2999	899.08	894.20	889.10	0.6384	0.6016	0.5696	1244.1	1238.1	1231.5
0.4000	0.2000	904.49	899.29	894.19	0.6500	0.6141	0.5815	1249.5	1243.5	1239.3
0.5000	0.1000	910.00	903.20	898.10	0.6649	0.6257	0.5917	1254.9	1248.9	1242.9
0.6000	0.0000	915.19	910.30	904.19	0.6850	0.6482	0.6124	1258.5	1252.5	1246.5

**Table-2:** The values of adiabatic compressibility ( $\beta$ ), free length ( $L_f$ ) free volume ( $V_f$ ) and internal pressure ( $\pi_i$ ) at 303, 308 and 313K for systems I, II and III

$X_1$	$X_3$	Adiabatic compressibility $\beta/(\times 10^{-10} \text{ m}^2 \text{ N}^{-1})$			Free length $L_f/(\times 10^{-10} \text{ m})$			Free volume $V_f/(\times 10^{-7} \text{ m}^3 \text{ mol}^{-1})$			Internal pressure $\pi_i/(\times 10^6 \text{ Nm}^{-2})$		
		303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
<b>System I: chlorobenzene + cyclohexane + 1-chlorobutane</b>													
0.000	0.6000	7.4413	7.5417	7.6386	0.5442	0.5523	0.5611	0.7369	0.8006	0.8713	349	344	338
0.0998	0.5001	7.3266	7.4198	7.6111	0.5046	0.5478	0.5600	0.7152	0.8133	0.8724	355	344	338
0.2000	0.4001	7.2837	7.3895	7.4691	0.5384	0.5467	0.5548	0.6594	0.7448	0.8234	365	355	347
0.0702	0.0707	7.5871	7.3345	7.4097	0.5495	0.5446	0.5526	0.5433	0.5881	0.7889	390	384	353
0.3950	0.1991	7.1906	7.2798	7.3447	0.5350	0.5426	0.5502	0.4426	0.4944	0.5523	419	409	399
0.4942	0.0994	7.1236	7.2107	7.3107	0.5325	0.5400	0.5489	0.4283	0.4733	0.5057	425	416	412
0.5954	0.0000	7.0456	7.1592	7.2547	0.5296	0.5381	0.5468	0.3160	0.3845	0.4188	471	447	440
<b>System II: bromobenzene + cyclohexane + 1-chlorobutane</b>													
0.0000	0.6000	8.3231	8.4783	8.5827	0.5756	0.5886	0.5947	0.8314	0.9238	1.0597	311	304	294
0.0998	0.5001	8.0586	8.3922	8.5202	0.5734	0.5826	0.5925	0.7910	0.8572	0.9253	318	313	309
0.1998	0.4000	8.1426	8.2932	8.4285	0.5693	0.5791	0.5893	0.7710	0.8342	0.9035	322	317	312
0.2996	0.3008	8.0046	8.1483	8.2305	0.5645	0.5741	0.5824	0.7521	0.8129	0.8792	326	322	318
0.4006	0.1998	7.8847	8.0024	8.1484	0.5602	0.5689	0.5795	0.7310	0.7905	0.8565	331	326	321
0.5001	0.0999	7.8200	7.9210	8.0316	0.5579	0.5660	0.5753	0.7084	0.7742	0.8344	336	330	326
0.6001	0.0000	7.6893	7.8275	7.9731	0.5532	0.5626	0.5732	0.6765	0.7294	0.8089	343	338	330
<b>System III: nitrobenzene + cyclohexane + 1-chlorobutane</b>													
0.0000	0.6000	7.4582	7.5742	7.6917	0.5449	0.5535	0.5630	0.6883	0.7429	0.8418	355	350	340
0.0999	0.5000	7.3442	7.4582	7.5668	0.5407	0.5492	0.5584	0.6720	0.7426	0.8229	359	351	344
0.2000	0.4000	7.2673	7.3802	7.4947	0.5378	0.5463	0.5557	0.6525	0.7080	0.7649	364	358	354
0.2999	0.2999	7.1860	7.2954	7.4162	0.5348	0.5432	0.5528	0.6361	0.6904	0.7434	365	363	358
0.4000	0.2000	7.0814	7.1913	7.2814	0.5309	0.5393	0.5478	0.6231	0.6737	0.7274	372	367	362
0.5000	0.1000	6.9781	7.0984	7.2078	0.5270	0.5358	0.5450	0.6063	0.6594	0.7117	377	371	366
0.6000	0.0000	6.8989	7.0026	7.1179	0.5240	0.5322	0.5416	0.5823	0.6281	0.6790	384	379	374



**Table-3:** The values of viscous relaxation time ( $V_\tau$ ), Gibb's free energy ( $\Delta G^*$ ), molar volume ( $V_m$ ) and acoustic impedance ( $Z$ ) at 303, 308 and 313K for Systems I, II and III

$X_1$	$X_3$	Viscous relaxation time $V_\tau/(\times 10^{-12} \text{ S})$			Gibb's free energy $\Delta G^*/(\times 10^{-20} \text{ KJ mol}^{-1})$			Molar volume $V_m/(\times 10^{-3} \text{ m}^3 \text{ mol}^{-1})$			Acoustic impedance $Z/(\times 10^6 \text{ Kg m}^2 \text{ s}^{-1})$		
		303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
<b>System I: chlorobenzene + cyclohexane + 1-chlorobutane</b>													
0.0000	0.6000	0.5648	0.5395	0.5154	0.5316	0.5209	0.5236	0.0998	0.1004	0.1013	1.0954	1.0851	1.0734
0.0998	0.5001	0.5691	0.5496	0.5243	0.5357	0.5348	0.5310	0.1012	0.1018	0.1034	1.1088	1.0986	1.0763
0.2000	0.4001	0.5982	0.5574	0.5259	0.5556	0.5417	0.5324	0.1031	0.1038	0.1045	1.1137	1.1020	1.0924
0.0702	0.0707	0.7100	0.6494	0.5383	0.6273	0.6067	0.5424	0.1056	0.1064	0.1071	1.1138	1.1071	1.0981
0.3950	0.1991	0.7729	0.7244	0.6774	0.6628	0.6531	0.6417	0.1067	0.1073	0.1078	1.1243	1.1143	1.1069
0.4942	0.0994	0.7842	0.7398	0.7159	0.6689	0.6621	0.6620	0.1083	0.1088	0.1097	1.1327	1.1233	1.1108
0.5954	0.0000	0.9537	0.8453	0.8060	0.7507	0.7188	0.7168	0.1100	0.1106	0.1113	1.1408	1.1292	1.1187
<b>System II: bromobenzene + cyclohexane + 1-chlorobutane</b>													
0.0000	0.6000	0.5823	0.5502	0.5068	0.5444	0.5362	0.5164	0.1114	0.1124	0.1131	0.0980	0.0967	0.0958
0.0998	0.5001	0.5985	0.5731	0.5510	0.5558	0.5535	0.5525	0.1190	0.1160	0.1167	0.0986	0.0975	0.0964
0.1998	0.4000	0.6023	0.5792	0.5554	0.5585	0.5580	0.5559	0.1261	0.1272	0.1280	0.0996	0.0983	0.0972
0.2996	0.3008	0.6049	0.5813	0.5563	0.5603	0.5596	0.5566	0.1331	0.1339	0.1341	1.0090	0.0997	0.0991
0.4006	0.1998	0.6096	0.5847	0.5613	0.5635	0.5621	0.5605	0.1402	0.1410	0.1421	1.0204	1.0097	0.0997
0.5001	0.0999	0.6176	0.5877	0.5647	0.5690	0.5642	0.5631	0.1468	0.1477	0.1486	1.0283	1.0186	1.0085
0.6001	0.0000	0.6293	0.6052	0.5737	0.5768	0.5767	0.5699	0.1535	0.1546	0.1561	1.0408	1.0278	1.0134
<b>System III: nitrobenzene + cyclohexane + 1-chlorobutane</b>													
0.0000	0.6000	0.5947	0.5712	0.5311	0.5532	0.5521	0.5366	0.1008	0.1011	0.1020	1.0887	1.0773	1.0660
0.0999	0.5000	0.5977	0.5757	0.5333	0.5553	0.5478	0.5384	0.1036	0.1043	0.1049	1.1008	1.0887	1.0778
0.2000	0.4000	0.6048	0.5789	0.5556	0.5602	0.5578	0.5561	0.1070	0.1078	0.1084	1.1092	1.0975	1.0860
0.2999	0.2999	0.6101	0.5837	0.5618	0.5639	0.5613	0.5609	0.1080	0.1086	0.1092	1.1185	1.1071	1.0949
0.4000	0.2000	0.6122	0.5874	0.5631	0.5653	0.5640	0.5619	0.1121	0.1127	0.1134	1.1301	1.1182	1.1081
0.5000	0.1000	0.6170	0.5907	0.5673	0.5686	0.5664	0.5651	0.1148	0.1156	0.1163	1.1419	1.1280	1.1162
0.6000	0.0000	0.6285	0.6036	0.5797	0.5763	0.5756	0.5744	0.1174	0.1181	0.1189	1.1517	1.1401	1.1270

**Table-4:** The excess values of adiabatic compressibility ( $\beta^E$ ), free length ( $L_f^E$ ) free volume ( $V_f^E$ ), molar volume ( $V_m^E$ ) and acoustic impedance ( $Z^E$ ) at 303, 308 and 313K for systems I, II and III.

$X_1$	$X_3$	Excess adiabatic compressibility $\beta^E/(\times 10^{-10} \text{ m}^2 \text{ N}^{-1})$			Excess free length $L_f^E/(\times 10^{-10} \text{ m})$			Excess free volume $V_f^E/(\times 10^{-7} \text{ m}^3 \text{ mol}^{-1})$			Excess molar volume $V_m^E/(\times 10^{-5} \text{ m}^3 \text{ mol}^{-1})$		
		303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
<b>System I: chlorobenzene + cyclohexane + 1-chlorobutane</b>													
0.0000	0.6000	0.8078	0.8545	0.8839	0.0305	0.0310	0.0322	-0.1692	-0.2398	-0.2960	0.8732	0.8972	0.9058
0.0998	0.5001	0.6512	0.6952	0.8183	0.0294	0.0302	0.0315	-0.3560	-0.3990	-0.4783	0.9058	0.9113	0.9270
0.2000	0.4001	0.5792	0.6283	0.6390	0.0285	0.0295	0.0304	-0.5778	-0.6402	-0.7117	0.9250	0.9314	0.9381
0.2702	0.2707	0.4011	0.6020	0.7026	0.0276	0.0286	0.0295	-0.6532	-0.6697	-0.7328	0.9476	0.9548	0.9615
0.3950	0.1991	0.3992	0.4287	0.4638	0.0262	0.0274	0.0286	-0.7392	-0.7840	-0.8192	0.9612	0.9666	0.9713
0.4942	0.0994	0.2954	0.3212	0.3498	0.0251	0.0265	0.0278	-0.7940	-0.8064	-0.8439	0.9774	0.9818	0.9904
0.5954	0.000	0.1865	0.2373	0.2613	0.0238	0.0241	0.0250	-0.8539	-0.8382	-0.8752	0.9945	0.9999	1.0065
<b>System II: bromobenzene + cyclohexane + 1-chlorobutane</b>													
0.0000	0.6000	1.6896	1.7912	1.8280	0.0609	0.0643	0.0650	-0.3817	-0.4679	-0.5757	1.0077	1.0172	1.0238
0.0998	0.5001	1.6527	1.7418	1.8091	0.0612	0.0658	0.0662	-0.5244	-0.6206	-0.7565	1.0435	1.0530	1.0597
0.1998	0.4000	1.5652	1.6804	1.7619	0.0628	0.0668	0.0670	-0.6708	-0.7760	-0.9377	1.1544	1.1649	1.1725
0.2996	0.3008	1.4569	1.5742	1.6095	0.0638	0.0669	0.0682	-0.8155	-0.9218	-1.1141	1.2242	1.2317	1.2334
0.4006	0.1998	1.3552	1.4556	1.5616	0.0642	0.0672	0.0695	-0.9710	-1.0978	-1.2960	1.2949	1.3024	1.3131
0.5001	0.0999	1.3272	1.4201	1.4975	0.0647	0.0678	0.0705	-0.9832	-1.1835	-1.3392	1.3608	1.3693	1.3781
0.6001	0.0000	1.2239	1.3631	1.4824	0.0649	0.0682	0.0731	-1.1765	-1.1954	-1.3565	1.4277	1.4381	1.4529
<b>System III: nitrobenzene + cyclohexane + 1-chlorobutane</b>													
0.0000	0.6000	0.8247	0.8871	0.9370	0.0312	0.0322	0.0342	-0.2178	-0.2923	-0.3252	0.9015	0.9072	0.9128
0.0999	0.5000	0.8522	0.9133	0.9576	0.0352	0.0358	0.0361	-0.2290	-0.2975	-0.3434	0.9298	0.9363	0.9419
0.2000	0.4000	0.9133	0.9775	1.0310	0.0370	0.0378	0.0379	-0.2437	-0.3216	-0.4005	0.9638	0.9714	0.9770
0.2999	0.2999	0.9785	1.0363	1.0993	0.0492	0.0502	0.0528	-0.2548	-0.3335	-0.4207	0.9739	0.9794	0.9851
0.4000	0.2000	1.0149	1.0739	1.1094	0.0546	0.0556	0.0572	-0.2631	-0.3450	-0.4360	1.0149	1.0204	1.0271
0.5000	0.1000	1.0536	1.1236	1.1817	0.0600	0.0615	0.0640	-0.2749	-0.3539	-0.4507	1.0421	1.0494	1.0562
0.6000	0.0000	1.1172	1.1713	1.2386	0.0664	0.0673	0.0703	-0.2939	-0.3797	-0.4240	1.0682	1.0746	1.0823

**Table-5:** The excess values of acoustic impedance ( $Z^E$ ) and viscosity ( $\eta^E$ ) at 303, 308 and 313K for systems I, II and III.

$X_1$	$X_3$	Excess acoustic impedance $Z^E / (\times 10^6 \text{ kg m}^2 \text{ s}^{-1})$			Excess viscosity $\eta^E / (\times 10^{-3} \text{ Nsm}^{-1})$		
		303K	308K	313K	303K	308K	313K
<b>System I: chlorobenzene + cyclohexane + 1-chlorobutane</b>							
0.0000	0.6000	-0.0468	-0.0474	-0.0514	-0.0537	-0.0296	-0.0070
0.0998	0.5001	-0.0469	-0.0475	-0.0546	-0.0655	-0.0579	-0.0160
0.2000	0.4001	-0.0475	-0.0479	-0.0549	-0.0663	-0.0597	-0.0172
0.2702	0.2707	-0.0482	-0.0481	-0.0552	-0.0773	-0.0770	-0.0410
0.3950	0.1991	-0.0489	-0.0483	-0.0555	-0.0819	-0.0809	-0.0800
0.4942	0.0994	-0.0491	-0.0487	-0.0562	-0.1136	-0.0895	-0.0892
0.5954	0.0000	-0.0497	-0.0492	-0.0572	-0.2415	-0.1714	-0.1659
<b>System II: bromobenzene + cyclohexane + 1-chlorobutane</b>							
0.0000	0.6000	-1.0443	-1.0358	-1.0290	-0.0984	-0.0795	-0.0562
0.0998	0.5001	-1.0817	-1.0742	-1.0684	-0.1368	-0.0872	-0.0614
0.1998	0.4000	-1.1187	-1.1125	-1.1076	-0.1829	-0.1456	-0.0995
0.2996	0.3008	-1.2476	-1.1506	-1.1459	-0.2280	-0.1857	-0.1355
0.4006	0.1998	-1.2759	-1.2613	-1.1870	-0.2739	-0.2259	-0.1730
0.5001	0.0999	-1.3046	-1.2968	-1.2902	-0.3176	-0.2680	-0.2089
0.6001	0.0000	-1.3304	-1.3204	-1.3121	-0.3535	-0.2953	-0.2441
<b>System III: nitrobenzene + cyclohexane + 1-chlorobutane</b>							
0.0000	0.6000	-0.0536	-0.0552	-0.0589	-0.0548	-0.0232	0.0189
0.0999	0.5000	-0.0819	-0.0837	-0.0870	-0.1298	-0.1047	-0.0682
0.2000	0.4000	-0.1142	-0.1150	-0.1190	-0.2334	-0.1923	-0.1389
0.2999	0.2999	-0.1452	-0.1558	-0.1498	-0.3380	-0.2876	-0.2245
0.4000	0.2000	-0.1744	-0.1746	-0.1769	-0.4440	-0.3825	-0.3109
0.5000	0.1000	-0.2031	-0.2043	-0.2088	-0.5465	-0.4782	-0.3987
0.6000	0.0000	-0.2337	-0.2340	-0.2380	-0.6437	-0.5629	-0.4759

**Table-6:** Redlich-Kister Coefficients and standard deviation ( $\sigma$ ) values

Parameters	System	Temperature (K)	$a_0$	$a_1$	$a_2$	$\sigma$
$\beta^E/(\times 10^{-10} \text{ m}^2 \text{ N}^{-1})$	I	303	21.7263	245.2760	1361.4800	0.4279
		308	24.0790	203.6240	997.5270	0.4582
		313	26.4341	212.1840	1008.7400	0.4906
	II	303	56.5890	591.8510	4507.5700	1.0723
		308	60.3881	616.9190	4713.4100	1.1536
		313	62.6852	631.4520	4905.2500	1.2068
	III	303	32.0200	211.3840	2371.6700	0.7019
		308	34.2395	235.5270	2593.5300	0.7429
		313	36.1484	256.7600	2773.1100	0.7845
$L_f^E/(\times 10^{-10} \text{ m})$	I	303	1.0514	8.2105	63.8839	0.0198
		308	1.0846	8.4148	66.8658	0.0201
		313	1.1227	8.7842	70.5977	0.0209
	II	303	2.2216	17.6715	166.8230	0.0452
		308	2.3677	19.6922	181.1860	0.0477
		313	2.3814	19.0449	182.2640	0.0497
	III	303	1.3496	3.4880	97.2944	0.0370
		308	1.3768	3.6677	100.5540	0.0376
		313	1.3987	2.9551	99.7795	0.0394
$V_f^E/(\times 10^{-7} \text{ m}^3 \text{ mol}^{-1})$	I	303	-17.8665	-26.2641	-1122.9800	0.4353
		308	-19.7074	-45.8946	-1210.2400	0.4361
		313	-22.4444	-77.0660	-1376.3500	0.4621
	II	303	-22.3764	-14.7798	-1312.1300	0.6200
		308	-26.0226	-56.2974	-1873.6700	0.6441
		313	-31.5554	-63.1532	-2026.6900	0.7399
	III	303	-8.5374	-61.4069	-653.5150	0.1850
		308	-11.1832	-78.4812	-829.7260	0.2422
		313	-13.5920	-83.6508	-970.7090	0.2692
Parameters	System	Temperature (K)	$a_0$	$a_1$	$a_2$	$\sigma$
$V_m^E/(\times 10^{-5} \text{ m}^3 \text{ mol}^{-1})$	I	303	33.4502	224.8670	2180.8300	0.6725
		308	33.6647	225.0500	2180.8900	0.6824
		313	33.9680	225.7670	2181.5600	0.6884
	II	303	39.9216	257.6550	3023.0000	0.8817
		308	40.2147	257.7400	3023.3900	0.8887
		313	40.3947	256.6240	3124.2500	0.8968
	III	303	33.8819	264.2050	2634.2200	0.7095
		308	34.0880	264.0160	2634.5700	0.7138
		313	34.2665	263.4650	2635.1600	0.7186
$Z^E/(\times 10^6 \text{ kg m}^2 \text{ s}^{-1})$	I	303	-1.7223	-11.7711	-111.0160	0.0347
		308	-1.7392	-12.3451	-113.1520	0.0348
		313	-1.9957	-14.2269	-30.9430	0.0392
	II	303	-40.0102	-249.0420	-2834.5100	0.8576
		308	-39.1225	-273.7860	-3048.1900	0.8517
		313	-39.1406	-311.6470	-3266.3200	0.8448
	III	303	-3.7547	-2.3829	-299.8030	0.1199
		308	-3.8702	-1.0164	-285.0730	0.1204
		313	-3.9357	-5.5768	-325.4650	0.1226

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RJC-384)