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ULTRASONIC STUDIES IN TERNARY MIXTURES OF SUBSTITUTED BENZENES IN TOLUENE WITH PYRIDINE 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 pyridine in toluene at 303, 308 and 313K. The experimental data have been used to calculate the acoustical parameters namely adiabatic compressibility (β), free length (L_f), free volume (V_f) internal pressure (π_i), acoustic impedance (Z) and molar volume (V_m). Some of the above excess parameters have been fitted to Redlich-Kister Polynomials. It is observed that dipole-dipole interaction existing between the substituted benzenes with pyridine. It is also seen that chlorobenzene is a more effective diluents in the mixtures, than other substituted benzenes.The elevation of temperature facilitates an agitation in thermal energy resulting in an increase in the molecular separation in the liquid mixtures

Keywords: adiabatic compressibility, dipole-dipole interaction, hydrogen bonding.

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[1,2]. 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 aromatic hydrocarbon like toluene 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 pyridine, which is an important liquid used currently in the extraction process for coal to analyze its compounds and in the manufacture of vitamin-B6 and other drugs. 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 helpful in providing such information. Hence, the authors have carried out the ultrasonic study in the ternary systems of substituted benzenes with pyridine in toluene at different temperatures. Accurate knowledge of thermodyanamic 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.

Nitrobenzenes 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→O bonds[3]. Chlorine atom in chlorobenzene is an electron-withdrawing atom, tends to attract to π-electrons of the benzene ring, thereby, and 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. Chorobenzene has low dielectric constant ε' = 5.649 and dipole moment μ = 1.69D. Its boiling point and melting points are 132ºC and -45ºC 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 SP^3 hybridized carbon atom and consequently can be removed easily. So, the rate of reaction with chlorobenzene is faster[4]. 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 is likely to be more affected resulting in a greater degree of variation with respect to the ultrasonic related parameters[4]. Pyridine is recognized as the non-aqueous aprotic solvent having dielectric constant of ε' = 12.40 at 25ºC, dipole moment μ = 2.222 D at 25ºC and bp is 115ºC. Pyridine is negligibly basic and it has property to form complexes with many salts. It is used wide variety of reactions including electrophilic substitution, nucleophilic substitution, oxidation and reduction[5].

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 pyridine in toluene at different temperatures.

EXPERIMENTAL

The liquid mixtures of various concentrations in mole fraction were prepared by taking AR grade Chemicals as such without further purification. In all systems, the mole fraction of the second component, toluene ($X_2 = 0.4$) 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 $\pm 2\ \mathrm{ms}^{-1}$. The density and viscosity are measured using a Pyckno meter and an Ostwald's Viscometer an accuracy of ± 0.1mg and $\pm 0.001\ \mathrm{Nsm}^{-2}$ respectively. All the precautions were taken to minimise the possible experimental error.

Theory and Calculation

Using the measured data, the following acoustical parameters have been calculated

$$\beta = \frac{1}{U^2 \rho} \tag{1}$$

Intermolecular free length (L_f) has been calculated from relation,

$$L_f = K_T \sqrt{B} \tag{2}$$

where K_T is a temperature dependent constant.

Free volume (V_f) has been calculated from relation,

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

where M_{eff} is the effective molecular weight ($M_{eff} = \Sigma m_i x_i$, 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 4.28×10^9 for all liquids.

Internal pressure (π_i) has been calculated from relation,

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

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

The acoustic impedance can be related as

$$Z = U\rho \tag{5}$$

where U is a ultrasonic velocity in medium and ρ is density.

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

$$A^E = A_{\exp} - A_{id} \tag{6}$$

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

The excess parameters β^E, L_f^E, V_f^E were fitted to Redlich-Kister[6] polynomial equation

$$Y^E = x_1 x_3 \sum_{i=1}^{K} A_i (x_1 - x_3)^i \tag{7}$$

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 (σ). The calculated values of A_i along with the tabulated standard deviation (σ) are listed in the Table-5. The standard deviation (σ) was calculated using the equation

$$\sigma^2 = \frac{1}{n-m}\left[\overset{E}{Y}_{\exp} - \overset{E}{Y}_{cal}\right]^2 \tag{8}$$

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	+ toluene	+ pyridine
System-II	bromobenzene	+ toluene	+ pyridine
System-III	nitrobenzene	+ toluene	+ pyridine

The experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (U) of the ternary systems I-III at 303, 308, and 313K are presented in Table-1. The values of adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i) of three systems at different temperatures are given in Table-2, The values of acoustic impedance (Z) and molar volume (V_m) are furnished in Table 3.The some of the above excess values of these parameters have been evaluated and presented in Table-4.

It is observed that in all the three liquid systems, the ultrasonic velocity (U) decreases with increasing molar concentration of substituted benzenes such as chlorobenzene, bromobenzene and nitrobenzene. Such a decrease in ultrasonic velocity (U) with increasing concentration of substituted benzenes is an indication of existence of molecular association between the components of the liquid mixtures[7-8]. As toluene is weakly polar molecule, interactions are possible between pyridine and substituted benzenes, whereas the interactions of toluene with any one of the other two is not so favoured. This is further supported by the decreasing velocity trend with increasing mole fraction of substituted benzenes.

As the concentration of substituted benzenes increases, the number of dipolar pyridine molecules are restricted without change in non-polar toluene molecules, which leads to possible interactions. Further, the associative nature of substituted benzenes disturbs the perfect symmetry with toluene molecule and leads to breaking of some bonds in toluene molecules, i.e. the toluene structure is ruptured and the medium is more rarefied. Similar observations were observed by earlier workers[9] supports the present investigation.

In the entire mole fraction range, the concentration is toluene is almost unaltered. The pyridine concentration is decreased, whereas that of substituted benzenes is increased. As substituted benzenes are more polar than pyridine[10] contains more carbon atoms enhancing it can freely interact with its neighbours, whereas pyridine is not that extent.

Normally, pyridine is recognized as the non-aqueous aprotic solvent having dielectric constant of $\varepsilon' = 12.40$ at 25ºC, dipole moment $\mu = 2.222$ D at 25ºC and bp is 115ºC. Pyridine is negligibly basic and it has property to form complexes with many salts. It is used wide variety of reactions including electrophilic substitution, nucleophilic substitution, oxidation and reduction[5].

The Table-2 furnishing the values of adiabatic compressibility (β) showing an increasing trend in all the three liquid systems with increasing concentration of substituted benzenes. Such an increasing trend observed in the β values suggesting that the medium is more and more rarefied. This is further confirmed by the increasing trend of free length (L_f) values in all the three liquid systems, which are furnished in the Table. Also, it is observed that an increase in temperature makes the free length to increase due to the thermal expansion of liquids. Further among the three components, toluene and pyridine both are spherical shapes and are monomers[11] and as the concentration of substituted benzenes is increased, due to lack of perfect symmetry, the available space between the components molecules will be increased. Hence, the substituted benzenes can freely interact with toluene than pyridine, the increased interaction between the components make them to interact more resulting an increase in free volume (V_f) is observed, which are tabulated in Table-2. The internal pressure (π_i) which generally reflects the cohesive/adhesive forces available in the medium. The decreasing trend of internal pressure in all the three liquid systems clearly confirm this, which are furnished in the Table-2.

Further, in all three liquid systems, the value 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 rise in 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[12]. The excess values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E) and internal pressure (π_i^E) for all the three liquid systems are furnished in Table-4.

In the present investigation, the values excess adiabatic compressibility (β^E) is negative for the system-I concerned and it becomes positive for the systems II & III over the entire range of composition for all the three liquid systems. The chlorine atom in chlorobenzene is an electron-withdrawing atom, tends to attract to π-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[13]. Also in the polar liquids, the chlorobenzene is more reactive because the chlorine atom is bonded with SP^3 hybridised carbon atom and consequently can be removed easily. So, the rate of reaction with chlorobenzene is faster[4], which results in negative excess compressibility. Such a negative excess compressibility suggests that the medium is highly packed[14-16]. This indicates the molecular interaction is more prominent in the system-I concerned comparing the other two systems. The positive values of excess adiabatic compressibility (β^E) may be attributed to the loss of mutual dipole association[17] and different in size, shape and mass of unlike component molecules in the mixtures. The same is reflected in the case of excess free length for all the three liquid systems which are furnished in Table 4.

The Table 4 further shows the excess free volume (V_f^E) values with increasing concentration of substituted benzenes. These values exhibit negative magnitude at lower mole fraction range and at higher mole fraction range it shows the positive values with the same increasing concentration of the substituted benzenes. In the lower mole fraction range, pyridine is available in more number than substituted benzenes, whereas toluene is almost unaltered. As mentioned earlier, toluene and pyridine molecules are almost spherical in shape, existence of pyridine molecules supports, close packing and free volume becomes negative. However, the picture got reversed at higher mole fraction range of substituted benzenes, the packing environment is less and the benzene group highly disturbs the existing symmetry and hence the excess free volume shifts to negative to positive magnitude. The negative values of excess internal pressure (π_i^E) in all the three systems clearly confirm this prediction.

CONCLUSION

It is concluded that there exists a dipole-dipole interaction between the substituted benzenes and pyridine. The molecular interactions is of the order : System III < System II < System I. The molecular interaction is more prominent in chlorobenzene system (System-I) comparing the other two systems. This shows that the chlorobenzene is probably more effective diluents in the mixtures, than other two substituted benzenes. The elevation of temperature facilitates an agitation in thermal energy resulting in an increase in the molecular separation in the liquid mixtures

.Table-1:The values of density (ρ), viscosity (η) and velocity (U) at 303, 308 and 313K for Systems I, II and III

X_1	X_3	DENSITY $\rho/(kg/m^3)$			VISCOSITY $\eta/(\times10^{-3}\,NSm^{-2})$			VELOCITY U/(m/s)		
		303K	308K	313K	303K	308K	313K	303K	308K	313K
System I: chlorobenzene + toluene + pyridine										
0.0000	0.6000	902.2	891.8	884.0	0.7150	0.6496	0.6175	1358.0	1352.2	1347.0
0.1002	0.5002	935.2	925.5	916.6	0.7039	0.6449	0.6018	1331.9	1325.4	1319.5
0.2000	0.3995	941.2	932.4	924.8	0.7021	0.6402	0.5956	1323.8	1317.3	1311.4
0.2999	0.3000	947.7	938.2	930.6	0.6942	0.6381	0.5914	1315.0	1310.5	1306.0

0.4000	0.1999	955.7	945.6	937.1	0.6641	0.6265	0.5826	1306.0	1301.0	1298.0
0.4999	0.1000	960.4	953.9	946.9	0.6593	0.6170	0.5773	1300.0	1294.0	1288.0
0.6000	0.0000	964.5	956.8	950.6	0.6485	0.6131	0.5722	1295.0	1291.0	1286.0
System II: bromobenzene + toluene + pyridine										
0.0000	0.6000	902.2	891.8	884.0	0.7150	0.6496	0.6076	1358.1	1352.2	1347.0
0.1000	0.5000	941.5	930.0	922.0	0.7284	0.6716	0.6175	1320.0	1314.0	1307.0
0.2002	0.3999	946.6	936.6	932.4	0.7372	0.6950	0.6535	1316.0	1311.0	1304.0
0.2999	0.3000	950.7	942.4	936.9	0.7699	0.7168	0.6743	1312.0	1306.4	1300.0
0.3999	0.2000	954.5	947.0	942.8	0.8015	0.7460	0.6951	1309.0	1303.0	1295.0
0.4999	0.1000	958.9	951.9	947.1	0.8264	0.7552	0.7045	1303.0	1297.0	1290.0
0.5999	0.0000	963.1	955.9	949.6	0.8361	0.7749	0.7273	1298.2	1293.3	1288.0
System III: nitrobenzene + toluene + pyridine										
0.0000	0.6000	902.2	891.8	884.0	0.7150	0.6496	0.6176	1358.1	1352.2	1347.0
0.0999	0.4999	951.8	945.2	940.3	0.7271	0.6886	0.6303	1335.1	1325.2	1316.0
0.2000	0.3999	957.5	950.5	945.4	0.7786	0.7256	0.6819	1327.0	1315.5	1311.8
0.2999	0.3000	961.2	957.8	951.7	0.8456	0.7776	0.7212	1323.8	1308.0	1304.0
0.3999	0.2000	966.9	962.2	958.0	0.8734	0.8023	0.7331	1319.0	1302.2	1296.4
0.4999	0.1000	973.5	970.3	968.4	0.9353	0.8814	0.8121	1311.8	1292.0	1287.0
0.5999	0.0000	980.1	977.7	975.0	0.9974	0.9279	0.8638	1305.4	1286.5	1283.4

Table-2:The values of adiabatic compressibility (β), free length (L_f) free volume(V_f) and internal pressure (π_i) at 303, 308 and 313K

X_1	X_3	Adiabatic compressibility $\beta/(\times10^{-10}\,m^2\,N^{-1})$			Free length $L_f/(\times10^{-10}\,m)$			Free volume $V_f/(\times10^{-7}m^3\,mol^{-1})$			Internal pressure $\pi_i/(\times10^6\,Nm^{-2})$		
		303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
System I: chlorobenzene + toluene + pyridine													
0.0000	0.6000	6.0100	6.1328	6.2345	0.4892	0.5002	0.5069	2.29	2.62	2.82	400	385	377
0.1002	0.5002	6.0275	6.1509	6.2660	0.4908	0.5013	0.5082	2.41	2.73	3.00	392	380	371
0.2000	0.3995	6.0630	6.1805	6.2875	0.4913	0.5025	0.5090	2.54	2.89	3.20	377	364	356
0.2999	0.3000	6.1020	6.2055	6.2998	0.4929	0.5035	0.5100	2.69	3.04	3.39	363	353	344
0.4000	0.1999	6.1344	6.2482	6.3341	0.4942	0.5047	0.5109	3.00	3.26	3.62	344	338	330
0.4999	0.1000	6.1608	6.2602	6.3658	0.4953	0.5057	0.5122	3.17	3.48	3.82	335	326	319
0.6000	0.0000	6.1821	6.2706	6.3766	0.4961	0.5068	0.5130	3.39	3.68	4.05	322	314	307
System II: bromobenzene + toluene + pyridine													
0.0000	0.6000	6.0092	6.1328	6.2345	0.4891	0.5002	0.5069	2.28	2.56	2.82	400	385	377
0.1000	0.5000	6.0956	6.2073	6.2586	0.4926	0.5011	0.5079	2.43	2.73	3.07	380	369	359
0.2002	0.399	6.1001	6.2118	6.2881	0.4941	0.5013	0.5090	2.68	2.92	3.18	350	344	338
0.2999	0.3000	6.1105	6.2209	6.3150	0.4962	0.5016	0.5102	2.80	3.1	3.37	329	322	317
0.3999	0.2000	6.1139	6.2294	6.3249	0.4976	0.5027	0.5124	2.92	3.23	3.56	311	304	298
0.4999	0.1000	6.1419	6.2443	6.3451	0.4992	0.5036	0.5041	3.06	3.47	3.82	294	285	280

0.5999	0.0000	6.1627	6.2568	6.3479	0.5005	0.5045	0.5115	3.27	3.65	3.99	277	270	265
System III: nitrobenzene + toluene + pyridine													
0.0000	0.6000	6.0101	6.1328	6.2345	0.4892	0.4981	0.5069	2.28	2.56	2.82	400	385	377
0.0999	0.4999	6.2948	6.2359	6.2640	0.5006	0.5022	0.5081	2.34	2.58	2.84	395	384	379
0.2000	0.3999	6.3339	6.3427	6.3562	0.5024	0.5041	0.5110	2.50	2.67	2.87	391	384	377
0.2999	0.3000	6.3437	6.3625	6.3794	0.5045	0.5049	0.5137	2.63	2.77	2.94	388	379	370
0.3999	0.2000	6.3751	6.3899	6.3945	0.5057	0.5081	0.5139	2.75	2.84	3.03	376	368	357
0.4999	0.1000	6.4069	6.4241	6.4354	0.5086	0.5097	0.5150	2.85	2.92	3.18	373	366	351
0.5999	0.0000	6.4690	6.4849	6.5307	0.5102	0.5122	0.5160	2.97	3.04	3.38	372	365	350

Table-3:The values of Molar volume (V_m) and Acoustic impedance (Z) at 303, 308 and 313K for Systems I, II and III

X_1	X_3	Molar volume $V_m/(\times10^{-3}\ m^3\ mol^{-1})$			Acoustic impedance $Z/(\times10^4\ Kg\ m^2\ s^{-1})$		
		303K	308K	313K	303K	308K	313K
System I: chlorobenzene + toluene + pyridine							
0.0000	0.6000	0.9342	0.9449	0.9534	122.52	120.58	119.07
0.1002	0.5002	0.9373	0.9472	0.9564	124.47	122.66	120.94
0.2000	0.3995	0.9673	0.9765	0.9849	124.59	122.82	121.24
0.2999	0.3000	0.9951	1.0058	1.0133	124.62	122.96	121.54
0.4000	0.1999	1.0494	1.0328	1.0427	124.78	123.01	121.62
0.4999	0.1000	1.0517	1.0588	1.0666	124.85	123.44	121.96
0.6000	0.0000	1.0824	1.0911	1.0985	124.91	123.52	122.56
System II: bromobenzene + toluene + pyridine							
0.0000	0.6000	0.9344	0.9451	0.9536	122.53	120.58	119.07
0.1000	0.5000	0.9783	0.9904	1.0036	124.28	122.20	120.52
0.2002	0.3999	1.0554	1.0661	1.0714	124.56	122.85	121.76
0.2999	0.3000	1.1321	1.1424	1.1488	124.73	123.08	121.80
0.3999	0.2000	1.2095	1.2192	1.2248	124.87	123.39	122.08
0.4999	0.1000	1.2854	1.2948	1.3016	124.95	123.47	122.17
0.5999	0.0000	1.3608	1.3708	1.3801	125.01	123.61	122.38
System III: nitrobenzene + toluene + pyridine							
0.0000	0.6000	0.9344	0.9451	0.9536	122.53	120.58	119.07
0.0999	0.4999	0.9359	0.9662	0.9733	127.07	125.23	123.74
0.2000	0.3999	0.9724	0.9883	0.9948	127.16	125.25	124.02
0.2999	0.3000	1.0143	1.0179	1.0239	127.24	125.27	124.10
0.3999	0.2000	1.0539	1.0593	1.0638	127.53	125.28	124.16
0.4999	0.1000	1.0915	1.0960	1.0984	127.70	125.36	124.60
0.5999	0.0000	1.1297	1.1324	1.1355	127.91	125.72	125.09

Table-4:The excess values of adiabatic compressibility (β), free length (L_f) free volume (V_f) and internal pressure (π_i) at 303, 308 and 313K

X_1	X_3	Excess adiabatic compressibility $\beta^E/(\times10^{-10}\,m^2\,N^{-1})$			Excess free length $L_f^E/(\times10^{-10}\,m)$			Excess free volume $V_f^E/(\times10^{-7}m^3\,mol^{-1})$			Excess internal pressure $\pi_i^E/(\times10^6\,Nm^{-2})$		
		303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
System I: chlorobenzene + toluene + pyridine													
0.0000	0.6000	-0.0452	-0.0937	-0.2111	-0.0004	-0.0003	-0.0078	-0.09	-0.01	-0.08	-16	-24	-19
0.1002	0.5002	-0.0767	-0.1162	-0.2269	-0.0001	-0.0009	-0.0077	-0.10	-0.02	-0.02	-11	-16	-15
0.2000	0.3995	-0.0888	-0.1258	-0.2315	-0.0025	-0.0013	-0.0079	0.01	0.01	0.04	-12	-18	-18
0.2999	0.3000	-0.1019	-0.1440	-0.2531	-0.0030	-0.0022	-0.0084	0.04	0.02	0.10	-12	-16	-18
0.4000	0.1999	-0.1194	-0.1434	-0.2487	-0.0038	-0.0028	-0.0088	0.12	0.10	0.18	-18	-18	-19
0.4999	0.1000	-0.1426	-0.1726	-0.2461	-0.0049	-0.0035	-0.0087	0.17	0.19	0.24	-13	-16	-18
0.6000	0.0000	-0.1704	-0.2028	-0.2648	-0.0061	-0.0041	-0.0092	0.27	0.25	0.33	-12	-15	-17
System II: bromobenzene + toluene + pyridine													
0.0000	0.6000	2.8229	0.0070	0.0109	0.0001	0.0002	0.0023	-0.10	-0.06	-0.06	-16	-24	-22
0.1000	0.5000	2.4430	0.0010	0.0234	0.0004	0.0015	0.0044	-0.03	-0.01	-0.01	-24	-29	-28
0.2002	0.3999	1.9815	0.2580	0.0446	0.0006	0.0026	0.0068	0.13	0.11	0.11	-42	-40	-38
0.2999	0.3000	1.5271	0.0553	0.0387	0.0008	0.0037	0.0002	0.17	0.19	0.19	-50	-49	-47
0.3999	0.2000	1.0656	0.0847	0.0286	0.0103	0.0058	0.0027	0.20	0.40	0.29	-55	-55	-54
0.4999	0.1000	0.0627	0.1190	0.0172	0.0124	0.0075	0.0057	0.26	0.36	0.45	-59	-61	-61
0.5999	0.0000	0.1824	0.1517	0.0592	0.0137	0.0092	0.0044	0.39	0.44	0.52	-63	-63	-64
System III: nitrobenzene + toluene + pyridine													
0.0000	0.6000	0.0054	0.0072	0.0709	-0.0003	-0.0023	-0.0077	-0.01	-0.06	-0.06	-16	-24	-22
0.0999	0.4999	0.3659	0.1456	0.0532	0.0169	0.0081	0.0005	0.002	0.003	0.0034	-19	-22	-17
0.2000	0.3999	0.5308	0.3904	0.1973	0.0244	0.0163	0.0103	0.20	0.13	0.08	-20	-20	-21
0.2999	0.3000	0.6647	0.5470	0.3787	0.0323	0.0233	0.0202	0.37	0.28	0.19	-21	-22	-31
0.3999	0.2000	0.7623	0.7119	0.5411	0.0393	0.0328	0.0240	0.54	0.38	0.33	-31	-30	-31
0.4999	0.1000	0.9785	0.8822	0.7338	0.0480	0.0408	0.0354	0.68	0.50	0.52	-31	-29	-34
0.5999	0.0000	1.1661	1.0798	0.9813	0.0575	0.0495	0.0434	0.84	0.66	0.77	-30	-27	-33

Table-5:Redlich-Kister Coefficients and standard deviation (σ) values

Parameters	System	Temperature (K)	a_0	a_1	a_2	σ
$\beta^E/(\times10^{-10}\,m^2\,N^{-1})$	I	303	-3.0505	-15.4584	-286.9820	0.0885
		308	-4.4739	-31.9462	-398.8140	0.1125
		313	-8.3129	-56.3856	-564.6350	0.1720
	II	303	74.6934	904.0590	3155.8800	1.4976

		308	4.6680	77.6060	580.7550	0.1110
		313	1.2881	7.1840	38.6038	0.0302
	III	303	17.3481	44.6548	1682.5700	0.5836
		308	11.2069	-77.7675	914.1150	0.5416
		313	5.8225	-98.4291	683.6280	0.4933
L_f^E /(×10^{-10} m)	I	303	-0.0584	0.5127	-4.5688	0.0031
		308	-0.0448	0.2642	-3.9342	0.0021
		313	-0.2807	-1.8693	-19.8297	0.0061
	II	303	0.0007	-2.2578	13.8590	0.0070
		308	0.0803	-0.4589	10.0397	0.0046
		313	0.1729	4.7204	37.6551	0.0029
	III	303	0.8011	0.0335	70.7146	0.0288
		308	0.4923	-3.1473	47.1849	0.0248
		313	0.2868	-4.6081	32.1478	0.0223
V_f^E /(×$10^{-7}$$m^3$ mol^{-1})	I	303	-1.1112	-71.9006	-67.2099	0.1477
		308	-0.1042	-14.4163	328.9630	0.1255
		313	0.7944	-54.5479	124.5210	0.1705
	II	303	2.6737	-45.2198	131.3510	0.2068
		308	2.2394	-137.0000	-199.7130	0.2241
		313	2.6244	-48.7545	533.2430	0.2642
	III	303	5.0816	-131.8560	375.4130	0.4228
		308	3.5732	-95.5423	283.3970	0.3335
		313	2.2261	-58.8525	643.6550	0.3869

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