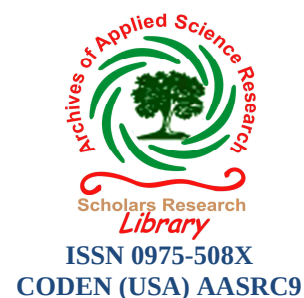




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Ultrasonic and thermodynamic studies in ternary liquid system of toluene+1-dodecanol+cyclohexane at 298, 308 and 318K

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ABSTRACT

Sound speed is determined for the ternary system of toluene + 1-dodecanol + cyclohexane as a function of composition and temperature. The observed data have been utilized to evaluate derived parameters like molar volume, molar free volume, isentropic compressibility, intermolecular free length, acoustic impedance and internal pressure. Further, these derived parameters are utilized to compute excess parameters. Various theories given by different researchers are also applied to the experimental sound speed and their percentage deviations have been calculated. By fitting excess parameters into Redlich-Kister polynomial equation smoothing coefficients and their standard deviations have been evaluated.

Key words: Ternary liquid mixture, molecular interactions, acoustic parameters, density, viscosity, sound speed

INTRODUCTION

Theoretical prediction of excess acoustic, volumetric, viscometric and thermodynamic properties of non-binary liquid mixtures have been satisfactory in explaining the sign and magnitude in terms of extent of interactions between mixing components. The significance of volumetric, acoustic and thermodynamic studies in mixtures have been used for understanding the intermolecular interactions by many researchers for interpreting different type of interactions viz. dipole-dipole [1-4] and dipole-induced dipole[5-8] in polar-polar[9-11] and non-polar systems[12-15]. An exhaustive literature survey reveals that less work has been done to investigate the thermo-acoustic properties of 1-dodecanol and multicomponent systems comprising it as a component[16]. For ternary mixtures, the predictive approach is more complex and thus empirical methods based on experimental binary data have to be used. However, if significant interactions occur in the liquids, considerable errors may get introduced if we attempt to express the excess properties in terms of binary contributions. A search of literature of ternary liquid mixtures suggested that the system under investigation has not been studied so far. Components taken for study find various applications in different chemical and industrial processes.

MATERIALS AND METHODS

All chemicals used were of analytical grade. Toluene (Merck, India), 1-dodecanol (SISCO, India) and cyclohexane (S.D. Fine, India) with purity > 99% were used drying by standard procedures[17-19]. Ternary liquid mixtures taken for investigation in the mole fraction range 0.0000 to 1.0000 were prepared by mixing known masses of pure liquids in air tight narrow mouthed ground stoppered bottles, taking due precautions to minimize the evaporation losses. The measurements of mass for different liquids were performed on an electronic balance (Denver Instruments, Germany) accurate upto ± 0.1 mg. The densities of pure liquids and their mixtures were measured using a precalibrated bicapillary pycnometer, the accuracy of data being within ± 0.057 %, sound speed was measured by single crystal ultrasonic interferometer at 2 MHz frequency and data were accurate upto ± 0.03 %. Viscosity was measured using Ostwald's viscometer and the accuracy fell within ± 0.09 %. All measurements were made in a thermostatically controlled water bath with temperature accuracy of $\pm 0.1^\circ\text{C}$. The purity of the components was

ascertained by comparing the boiling point, density and viscosity of pure components with those reported in literature. The observed and literature values of boiling point for toluene are 109.8°C and 110.0°C; for 1-dodecanol are 258.8°C and 259.0°C respectively. Density and viscosity for toluene at 298 K are 862.3 kgm⁻³ and 862.5 kgm⁻³; 0.5598 × 10⁻³ Nm⁻²s and 0.5600 × 10⁻³ Nm⁻²s respectively. The observed and literature values of density at 297 K for 1-dodecanol are 831.1 kgm⁻³ and 830.9 kgm⁻³ respectively; observed viscosity at 298 K is 19.7457 × 10⁻³ Nm⁻²s. The literature value of viscosity is not found at any temperature. The observed and literature values of boiling point, density and viscosity for cyclohexane are 80°C and 79°C; 773.7²⁵ kgm⁻³ & 773.9²⁵ kgm⁻³; 0.8938²⁵ × 10⁻³ Nm⁻²s & 0.8940²⁵ × 10⁻³ Nm⁻²s respectively.

RESULTS AND DISCUSSION

The experimentally measured density (ρ), sound speed (u) and viscosity (η) are used to evaluate derived properties like intermolecular free length (L_f), isentropic compressibility (κ_s), acoustic impedance (Z), molar volume (V), free volume (V_f), internal pressure (π_i) and their excess parameters by using well established relations[20-23].

The intermolecular free length is the average distance travelled by sound waves between surfaces of the two molecules. It is an important parameter, which correlates the strength of interactions with sound speed and density. Jacobson suggested the following relation for the intermolecular free length[24].

$$L_f = \frac{K}{u\rho^{\frac{1}{2}}}$$

Where K is Jacobson constant which is temperature dependent as tabulated by him between 273.15 – 310.15 K by the formula but it is independent of nature of liquid.

$$K = (93.875 + 0.375 T) \times 10^{-8}$$

Isentropic compressibility is a characteristic property and is of central importance in the ultrasonic study of liquids and liquid mixtures as it is the measure of intermolecular arrangement and orientation of constituent molecules. For pure liquid and liquid mixtures it can be calculated from the measured values of sound speed and density by using the following relation[25]:

$$\kappa_s = \frac{1}{u^2 \rho}$$

Acoustic impedance of a sound medium on a given surface lying in a wavefront is also defined as the complex quotient of sound pressure on that surface divided by the flux (linear velocity divided by the area) through the surface. Elpiner has defined specific acoustic impedance by the relation[26]:

$$Z = u\rho$$

where u and ρ are sound speed and density of the medium respectively. Its unit is kgm⁻²s⁻¹ or Rayl.

Generally, the molar volume of ternary liquid mixtures is calculated by using the following equation[27]:

$$V_m = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{\rho_{mix}}$$

According to thermodynamic equation of state the formula of free volume of liquid systems as derived by dimensional analysis is given by[28,29]:

$$V_f = \left[\frac{M_{eff} u}{k \eta} \right]^{\frac{1}{2}}$$

where k has been found to be independent on the nature of liquids having a value of 4.28×10^{-9} . M_{eff} is the effective molecular weight = $\sum M_i x_i$ where M_i and x_i are the molecular weight and mole fraction of the i^{th} component respectively.

Internal pressure is inversely related to molar free volume and is given by the following equation[30]:

$$\pi_i (V_f)^x = K$$

where x is a constant. It is evaluated by finding the slope of the family of straight lines obtained from the slope of $\log (1/V_f)$ against $\log \pi_i$. The value of this relationship presented by the equation $\pi_i V_i^x = K$ is checked and verified[31].

The internal pressure of pure liquids and their binary liquid mixtures are calculated using the following relation[32]:

$$\pi_i = bRT \left[\frac{k\eta}{u} \right]^{\frac{1}{2}} \frac{\rho^{\frac{2}{3}}}{M^{\frac{7}{6}}}$$

where b stands for cubic packing which is assumed to be 2 for liquids, k is dimensionless constant which is independent of temperature and nature of liquids and its value is 4.28×10^9 , η is viscosity in Nm^{-2}s , R is gas constant, T is absolute temperature and M_{eff} is effective molecular weight.

Excess parameters have been calculated from following equation:

$$Y^E = Y_{\text{mix}} - (x_1 Y_1 + x_2 Y_2 + x_3 Y_3)$$

All the excess parameters are fitted to Redlich-Kister polynomial equation to estimate the adjustable parameters[33].

$$Y^E = x_1 x_2 x_3 \sum_{i=0}^m A_i (1 - 2x_1)^{i-1}$$

$$Y^E = x_1 x_2 x_3 [A_0 + (1 - 2x_1)A_1 + (1 - 2x_1)^2 A_2 + (1 - 2x_1)^3 A_3]$$

where x is the mole fraction and subscripts 1, 2 and 3 represent the three components of the system respectively. A_i is the smoothening coefficient and Y^E represent the theoretical excess functions. The standard deviation was evaluated by using the following equation:

$$\sigma(Y^E) = \left[\frac{\sum (Y_{\text{obs}}^E - Y_{\text{cal}}^E)^2}{n - p} \right]^{\frac{1}{2}}$$

where n is the total number of experimental points and p is the degree of fitting ($p = 3$ in present case).

Excess enthalpy of ternary liquid mixtures as calculated by other researchers is obtained using the following expression[34]:

$$H^E = [x_{(1)} \pi_{i(1)} V_{m(1)} + x_{(2)} \pi_{i(2)} V_{m(2)} + x_{(3)} \pi_{i(3)} V_{m(3)}] - \pi_{i(\text{mix})} V_{m(\text{mix})}$$

Gibb's free energy of activation of viscous flow as reported by other researchers has been calculated using the following relation based on transition state theory to analyze the relative viscosities[35]:

$$G^{*E} = RT [\ln \eta_{\text{mix}} V_{m(\text{mix})} - (x_{(1)} \ln \eta_{(1)} V_{m(1)} + x_{(2)} \ln \eta_{(2)} V_{m(2)} + x_{(3)} \ln \eta_{(3)} V_{m(3)})]$$

The theoretical values of sound speeds are evaluated using the following relationships:

Sound speed by Jacobson's Free Length Theory is calculated using the following formula[36,37]:

$$u^{FLT} = \frac{K}{L_{f(mix)} \rho_{Exp}^{\frac{1}{2}}}$$

where K is Jacobson's constant depends only on temperature and $L_{f mix}$ is intermolecular free length of mixture.

The empirical formula for sound speed in ternary liquid mixtures given by Nomoto can be written as[38,39]:

$$u^{NOM} = \left[\frac{x_1 R_1 + x_2 R_2 + x_3 R_3}{x_1 V_1 + x_2 V_2 + x_3 V_3} \right]^3$$

where x , R and V represent mole fraction, molar sound speed and molar volume. Subscripts 1, 2 and 3 represent system components 1, 2 and 3 respectively.

Table 1:- Sound speed (u), density (ρ), viscosity (η), acoustic impedance (Z), isentropic compressibility (κ_s), intermolecular free length (L_f) and internal pressure (π_i) for toluene (x_1) + 1-dodecanol (x_2) + cyclohexane (x_3) system at 298, 308 and 318K

Mole fraction of toluene (x_1)	Mole fraction of 1-dodecanol (x_2)	ρ kgm ⁻³	$\eta \times 10^{-3}$ Nm ⁻² s	u ms ⁻¹	$Z \times 10^5$ Rayl	$\kappa_s \times 10^{-10}$ Pa	L_f Å	π_i atm
298 K								
0.0000	0.4175	822.3	5.2389	1463.0	12.0303	5.6816	0.4901	1.8702
0.1067	0.3844	827.9	4.2865	1460.6	12.0918	5.6620	0.4893	1.7413
0.2105	0.3521	833.6	3.6315	1441.6	12.0176	5.7722	0.4940	1.6591
0.3184	0.3131	839.6	2.8419	1423.5	11.9517	5.8778	0.4985	1.5298
0.4195	0.2765	845.6	2.2443	1421.0	12.0159	5.8565	0.4976	1.4076
0.5145	0.2421	849.5	2.1332	1393.6	11.8388	6.0610	0.5062	1.4296
0.6037	0.2098	852.9	1.8148	1380.3	11.7727	6.1540	0.5101	1.3649
0.6790	0.1706	854.5	1.4036	1369.2	11.6990	6.2430	0.5138	1.2516
0.7490	0.1342	855.5	0.9997	1358.7	11.6239	6.3319	0.5174	1.0991
0.8142	0.1002	857.2	0.7669	1348.1	11.5559	6.4190	0.5210	1.0007
0.8751	0.0685	858.5	0.5183	1338.1	11.4874	6.5056	0.5245	0.8537
0.9216	0.0387	859.4	0.4768	1327.0	11.4044	6.6078	0.5286	0.8498
0.9646	0.0111	861.1	0.4346	1315.5	11.3271	6.7111	0.5327	0.8413
1.0000	0.0000	862.3	0.5598	1304.8	11.2513	6.8116	0.5367	0.9699
308 K								
0.0000	0.4175	810.9	4.0707	1364.8	11.0670	6.6208	0.5387	1.7478
0.1067	0.3844	816.4	3.2595	1361.2	11.1126	6.6108	0.5383	1.6106
0.2105	0.3521	821.7	2.4373	1354.9	11.1335	6.529	0.5391	1.4352
0.3184	0.3131	827.4	1.8798	1346.1	11.1382	6.6695	0.5407	1.3095
0.4195	0.2765	833.0	1.4091	1343.9	11.1949	6.6469	0.5398	1.1736
0.5145	0.2421	835.6	1.3463	1330.0	11.1130	6.7657	0.5446	1.1884
0.6037	0.2098	837.2	1.0748	1324.1	11.0845	6.8136	0.5465	1.0947
0.6790	0.1706	839.8	0.9813	1316.9	11.0587	6.8668	0.5487	1.0902
0.7490	0.1342	841.0	0.8845	1310.9	11.0254	6.9187	0.5507	1.0754
0.8142	0.1002	844.6	0.6960	1302.7	11.0024	6.9769	0.5530	0.9924
0.8751	0.0685	847.4	0.4940	1295.4	10.9776	7.0322	0.5552	0.8679
0.9216	0.0387	849.9	0.4534	1287.7	10.9442	7.0958	0.5577	0.8630
0.9646	0.0111	850.0	0.4167	1279.9	10.8792	7.1817	0.5611	0.8558
1.0000	0.0000	851.8	0.4162	1272.0	10.8349	7.2756	0.5639	0.8683
318 K								
0.0000	0.4175	796.9	2.9457	1276.8	10.1743	7.6980	0.5913	1.5687
0.1067	0.3844	801.8	2.5848	1274.7	10.2198	7.6765	0.5905	1.5119
0.2105	0.3521	806.7	2.2257	1272.4	10.2648	7.6562	0.5897	1.4433
0.3184	0.3131	811.8	1.8053	1269.7	10.3072	7.6410	0.5891	1.3470
0.4195	0.2765	816.9	1.4026	1267.7	10.3560	7.6169	0.5882	1.2285
0.5145	0.2421	821.5	1.1826	1264.0	10.3833	7.6195	0.5883	1.1663
0.6037	0.2098	826.2	0.9553	1258.8	10.4004	7.6380	0.5890	1.0833
0.6790	0.1706	829.5	0.8311	1255.4	10.4132	7.6497	0.5895	1.0522
0.7490	0.1342	832.7	0.7077	1253.8	10.4409	7.6388	0.5890	1.0088
0.8142	0.1002	835.2	0.5726	1249.6	10.4367	7.6679	0.5902	0.9420
0.8751	0.0685	836.7	0.4344	1247.4	10.4379	7.6801	0.5906	0.8491
0.9216	0.0387	838.4	0.3987	1246.4	10.4493	7.6784	0.5906	0.8416
0.9646	0.0111	839.7	0.3607	1245.3	10.4578	7.6784	0.5906	0.8266
1.0000	0.0000	840.3	0.2509	1244.0	10.4531	7.6901	0.5910	0.6976

Table 2:- Excess parameters $\Delta\kappa_s$, $\Delta\eta$, L_f^E , Z^E , V^E , V_f^E , π^E , G^{*E} and H^E for toluene (x_1) + 1-dodecanol (x_2) + cyclohexane (x_3) system at 298, 308 and 318K

x_1	x_2	$\Delta\kappa_s \times 10^{-10}$ Pa	$\Delta\eta \times 10^{-3}$ Nm ⁻² s	$Z^E \times 10^5$ Rayl	L_f^E A°	V^E m ³ mol ⁻¹	$V_f^E \times 10^{-3}$ m ³ mol ⁻¹	π_i^E atm	$G^{*E} \times 10^3$ Jmol ⁻¹	H^E Jmol ⁻¹
298 K										
0.0000	0.4175	-3.0572	-3.5256	1.3949	-0.0610	-3.0572	-1.9665	0.1387	-2.1332	0.0133
0.1067	0.3844	-3.1011	-3.8178	1.3635	-0.0591	-3.1011	-2.5944	0.0791	-2.4974	0.0236
0.2105	0.3521	-3.1533	-3.8307	1.1989	-0.0518	-3.1533	-3.2135	0.0643	-2.7642	0.0263
0.3184	0.3131	-3.1738	-3.8477	1.0522	-0.0451	-3.1738	-3.6710	0.0110	-3.1725	0.0334
0.4195	0.2765	-3.1945	-3.7214	1.0408	-0.0440	-3.1945	-3.9043	-0.0400	-3.5409	0.0391
0.5145	0.2421	-2.8921	-3.1531	0.7927	-0.0335	-2.8921	-4.6657	0.0488	-3.4235	0.0248
0.6037	0.2098	-2.5372	-2.8324	0.6598	-0.0278	-2.5372	-4.9220	0.0470	-3.5543	0.0225
0.6790	0.1706	-2.0553	-2.4798	0.5582	-0.0238	-2.0553	-4.5366	-0.0010	-3.7948	0.0246
0.7490	0.1342	-1.5437	-2.1735	0.4572	-0.0199	-1.5437	-2.9883	-0.0927	-4.1667	0.0313
0.8142	0.1002	-1.1477	-1.7444	0.3650	-0.0161	-1.1477	-1.1222	-0.1344	-4.2523	0.0314
0.8751	0.0685	-0.7323	-1.3746	0.2740	-0.0123	-0.7323	4.2984	-0.2284	-4.4850	0.0371
0.9216	0.0387	-0.4148	-0.8385	0.1872	-0.0086	-0.4148	4.9215	-0.1861	-3.6472	0.0271
0.9646	0.0111	-0.2153	-0.3462	0.1065	-0.0049	-0.2153	5.9095	-0.1518	-2.0955	0.0184
1.0000	0.0000	—	—	—	—	—	—	—	—	—
308 K										
0.0000	0.4175	-2.5152	-1.9552	0.9587	-0.0483	-2.5152	-2.1508	0.1643	-1.8565	-0.0006
0.1067	0.3844	-2.5891	-2.3110	0.9014	-0.0450	-2.5891	-3.2155	0.0948	-2.2879	0.0121
0.2105	0.3521	-2.6146	-2.6904	0.8221	-0.0407	-2.6146	-3.9321	-0.0146	-2.8820	0.0295
0.3184	0.3131	-2.6432	-2.7175	0.7351	0.0360	-2.6432	-4.5773	-0.0675	-3.3410	0.0371
0.4195	0.2765	-2.6541	-2.6914	0.7057	0.0340	-2.6541	-4.5947	-0.1353	-3.8547	0.0455
0.5145	0.2421	-2.1712	-2.2879	0.5430	0.0264	-2.1712	-5.8030	-0.0566	-3.7164	0.0326
0.6037	0.2098	-1.5741	-2.1208	0.4386	0.0219	-1.5741	-5.5518	-0.0900	-4.0096	0.0345
0.6790	0.1706	-1.3104	-1.6946	0.3754	0.0189	-1.3104	-6.1436	-0.0350	-3.8397	0.0240
0.7490	0.1342	-0.8670	-1.3084	0.3073	0.0160	-0.8670	-6.4659	0.0056	-3.6263	0.0154
0.8142	0.1002	-0.7804	-1.0467	0.2519	0.0128	-0.7804	-4.9446	-0.0257	-3.6623	0.0158
0.8751	0.0685	-0.6087	-0.8281	0.1968	0.0099	-0.6087	-0.3353	-0.1019	-3.7936	0.0209
0.9216	0.0387	-0.5178	-0.4772	0.1529	-0.0074	-0.5178	0.1734	-0.0659	-2.9638	0.0129
0.9646	0.0111	-0.1352	-0.1519	0.0783	-0.0041	-0.1352	0.8318	-0.0352	-1.4122	0.0055
1.0000	0.0000	—	—	—	—	—	—	—	—	—
318 K										
0.0000	0.4175	-1.3720	-1.6181	0.5152	-0.0298	-1.3720	1.1604	0.0811	-1.9912	0.0058
0.1067	0.3844	-1.4106	-1.6244	0.4526	-0.0262	-1.4106	-2.2736	0.1019	-2.1900	0.0052
0.2105	0.3521	-1.4330	-1.6388	0.3925	-0.0227	-1.4330	-5.5035	0.1087	-2.4259	0.0062
0.3184	0.3131	-1.4423	-1.6491	0.3369	-0.0194	-1.4423	-8.5883	0.0942	-2.7609	0.0095
0.4195	0.2765	-1.4626	-1.6676	0.2940	-0.0167	-1.4626	-10.9880	0.0523	-3.1908	0.0158
0.5145	0.2421	-1.3932	-1.5270	0.2350	-0.0132	-1.3932	-13.3532	0.0620	-3.3798	0.0139
0.6037	0.2098	-1.3499	-1.4151	0.1711	-0.0093	-1.3499	-14.9148	0.0466	-3.6543	0.0150
0.6790	0.1706	-1.2488	-1.1429	0.1400	-0.0074	-1.2488	-16.4430	0.0795	-3.6017	0.0084
0.7490	0.1342	-1.1480	-0.8977	0.1270	-0.0065	-1.1480	-17.2880	0.0957	-3.5273	0.0038
0.8142	0.1002	-0.9472	-0.6892	0.0847	-0.0041	-0.9472	-16.7870	0.0843	-3.4714	0.0023
0.8751	0.0685	-0.6259	-0.5065	0.0504	-0.0024	-0.6259	-13.6626	0.0433	-3.4001	0.0038
0.9216	0.0387	-0.4675	-0.2454	0.0463	-0.0022	-0.4675	-13.7536	0.0787	-2.4909	-0.0037
0.9646	0.0111	-0.2877	-0.0088	0.0404	-0.0019	-0.2877	-13.0999	0.1033	-0.7821	-0.0097
1.0000	0.0000	—	—	—	—	—	—	—	—	—

Vandael Vangael ideal mixing relation is computed from the following formula[40,41]:

$$\left[\frac{1}{x_1 M_1 + x_2 M_2 + x_3 M_3} \right] \left[\frac{1}{u^{(VAN)^2}} \right] = \frac{x_1}{M_1 u_1^2} + \frac{x_2}{M_2 u_2^2} + \frac{x_3}{M_3 u_3^2}$$

Where x_1 , x_2 and x_3 are mole fractions and u_1 , u_2 and u_3 are sound speeds of components of the system.

The sound speed in the mixture as given by Impedance Dependence Relation as[42]:

$$u^{IDR} = \sum \frac{x_i Z_i}{x_i \rho_i}$$

Experimental values of density (ρ), sound speed (u) and viscosity (η) alongwith derived parameters are presented in table 1. The variation of excess parameters with composition for the system under investigation is listed in table 2 at 298, 308 and 318 K. Table 3 carries the values of smoothening coefficients for different excess parameters by Redlich-Kister polynomial equation with their standard deviations. The percentage deviations of various theoretical

approaches applied to the experimental sound speed are depicted in table 4. It is evident from table 1 that u , η , Z and π_i show a decrease whereas κ_s , ρ and L_f show a continuous increase at all the three investigating temperatures with increasing mole fraction of toluene. Acoustic impedance shows a linear variation with increase and then decrease with the mole fraction of benzene at 308 and 318 K.

Table 3:- Values of adjustable parameters and their standard deviations for toluene +1-dodecanol + cyclohexane systems at 298, 308 and 318K

	A_0	A_1	A_2	σ
298 K				
$V^E \text{ m}^3 \text{ mol}^{-1}$	-11.508	-7.711	-3.258	0.0971
$V_f^E \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$	-41.817	5.307	172.762	0.4777
$L_f^E \text{ A}^0$	-0.141	-0.145	-0.153	0.0013
$Z^E \times 10^5 \text{ Rayl}$	3.302	3.512	3.467	0.0379
$\Delta\eta \times 10^{-3} \text{ Nm}^{-2}\text{s}$	-13.438	-8.842	-8.706	0.0597
$\Delta\kappa_s \times 10^{-10} \text{ Pa}$	-12.023	-7.356	-0.550	0.0281
$G^E \times 10^3 \text{ J mol}^{-1}$	-8.819	3.864	-55.153	0.086
$H^E \text{ J mol}^{-1}$	0.064	0.063	0.564	0.0032
$\pi_i^E \text{ atm}$	0.6187	0.030	-4.879	0.0247
308 K				
$V^E \text{ m}^3 \text{ mol}^{-1}$	-7.671	-9.316	-10.104	0.0625
$V_f^E \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$	-36.181	11.576	77.531	0.5538
$L_f^E \text{ A}^0$	-0.116	-0.113	-0.130	0.0024
$Z^E \times 10^5 \text{ Rayl}$	0.281	2.614	1.961	0.0893
$\Delta\eta \times 10^{-3} \text{ Nm}^{-2}\text{s}$	-9.614	-6.858	-4.358	0.0553
$\Delta\kappa_s \times 10^{-10} \text{ Pa}$	-7.667	-3.341	-10.197	0.0615
$G^E \times 10^3 \text{ J mol}^{-1}$	-11.115	2.578	-39.738	0.1227
$H^E \text{ J mol}^{-1}$	0.107	0.103	0.258	0.0031
$\pi_i^E \text{ atm}$	0.023	-0.351	-1.922	0.0233
318 K				
$V^E \text{ m}^3 \text{ mol}^{-1}$	-3.059	-2.863	-3.131	0.0612
$V_f^E \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$	-40.537	50.318	-139.372	0.4118
$L_f^E \text{ A}^0$	-0.056	-0.077	0.051	0.0004
$Z^E \times 10^5 \text{ Rayl}$	0.922	1.299	1.682	0.0162
$\Delta\eta \times 10^{-3} \text{ Nm}^{-2}\text{s}$	-6.426	-3.242	-0.144	0.0232
$\Delta\kappa_s \times 10^{-10} \text{ Pa}$	-6.057	-1.224	-1.669	0.0212
$G^E \times 10^3 \text{ J mol}^{-1}$	-10.868	5.294	-27.481	0.073
$H^E \text{ J mol}^{-1}$	0.055	0.008	-0.098	0.0015
$\pi_i^E \text{ atm}$	0.273	0.081	0.923	0.0108

Figure 1 shows the variation of deviation in isentropic compressibility ($\Delta\kappa_s$) as a representative figure over the complete range of temperature taken for investigation. The sign of V^E , V_f^E , $\Delta\kappa_s$, L_f^E , $\Delta\eta$ and Z^E play a vital role in assigning the compactness due to molecular arrangement after mixing the pure components to prepare a mixture of varying composition. The weak magnitudes of negative values of V^E , V_f^E , $\Delta\kappa_s$, L_f^E , $\Delta\eta$ and positive values of Z^E are attributed to weak intermolecular interactions present between the components of the system. The increase in negative sign may be interpreted as increase in the dipole-induced-dipole type of interactions upto ~ 0.4 mole fraction between the system components. The large difference in the molar volumes of the components could facilitate interstitial accommodation of the smaller components (toluene and cyclohexane) into the voids created by bigger 1-dodecanol molecules. After $x \sim 0.4$ mole fraction system tends to behave as ideal ones due to decrease in the concentration of 1-dodecanol molecules in the system unable the interstitial accommodation leading to much free polar and non-polar molecules in the mixture. Generally, in ternary systems fewer interactions are reported because the addition of third component decrease the energy of interaction and the system behave as ideal ones[43-45]. Our results are also supported by the results reported by Ali *et al*[46] in the ternary mixture of DMSO + CCl_4 + benzene, DMSO + CCl_4 + toluene but in contrast with the results obtained for DMSO + CCl_4 + chlorobenzene. Negative excess volumes are found in ternary liquid mixtures of water with butylacetate and ethyl propionate in methanol by Fonseca *et al*[47] in ternary liquid mixtures of squalane with (hexane + benzene), (cyclohexane + benzene) and (hexane + cyclohexane) by Bhatia *et al*[48]. Negative variation of deviation in viscosity ($\Delta\eta$) is found in ternary liquid mixture of ethan-1,2-diol with polar (acetone and ethyl methyl ketone) and non-polar (benzene, toluene, carbon tetra chl:oride) by Singh *et al*[49] and in Ti-n-butyl phosphate- C_6H_6 - CCl_4 at four different temperatures by Chakravorty *et al*[50]. Positive variation in $\Delta\kappa_s$ and L_f^E are reported by Sumathi *et al*[51] in ternary liquid mixtures of methyl acetate + toluene + pentanol/hexanol/heptanol due to presence of dispersive forces.

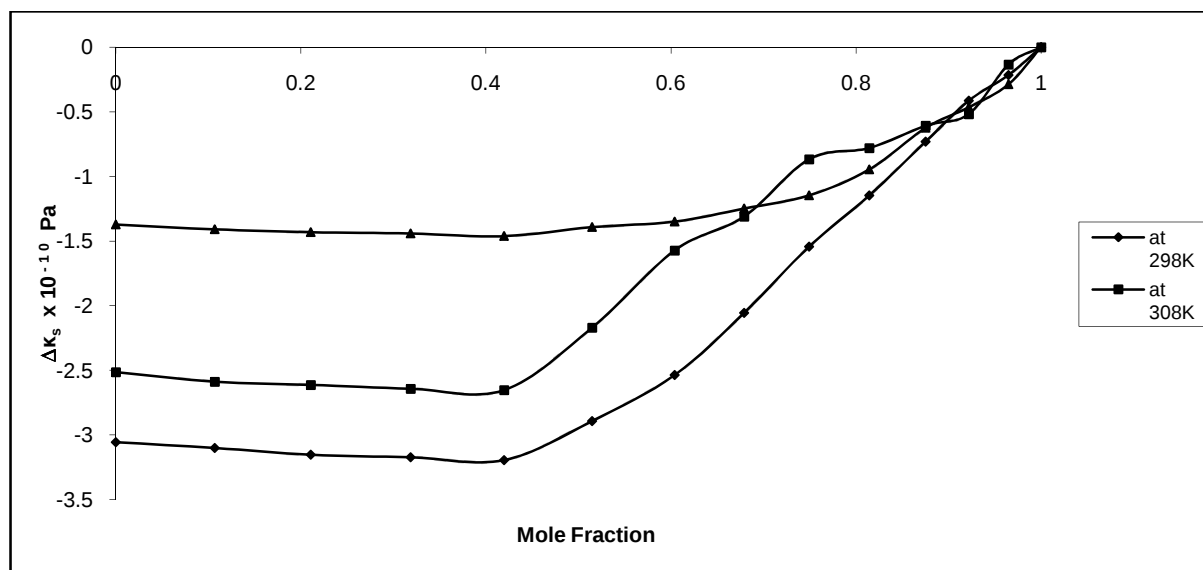


Fig. 1: Variation of $\Delta\kappa_s$ with mole fraction of toluene in toluene + 1-dodecanol + cyclohexane system at 298 (♦), 308 (■) and 318 (▲) K

The variation in excess enthalpy (H^E) and excess Gibbs's free energy of activation of viscous flow (G^{*E}) is depicted in Figs. 2 and 3. The relative low positive values of H^E and negative values of G^{*E} shows the exothermic behaviour and can be inferred in terms of breaking of dipolar associations of 1-dodecanol associates by the addition of third component i.e. cyclohexane leading to smaller excess enthalpies. The positive excess enthalpy was also reported by Tong *et al*[52] for the ternary liquid mixtures of $x_1\text{CH}_3(\text{CH}_2)\text{CH}_3 + x_2(\text{CH}_3)_3\text{COCH}_3 + x_3[\text{CH}_3(\text{CH}_2)_3]_2\text{O}$ and for $x_1\text{CH}_3(\text{CH}_2)_8\text{CH}_3 + x_2(\text{CH}_3)_3\text{COCH}_3 + x_3[\text{CH}_3(\text{CH}_2)_3]_2\text{O}$.

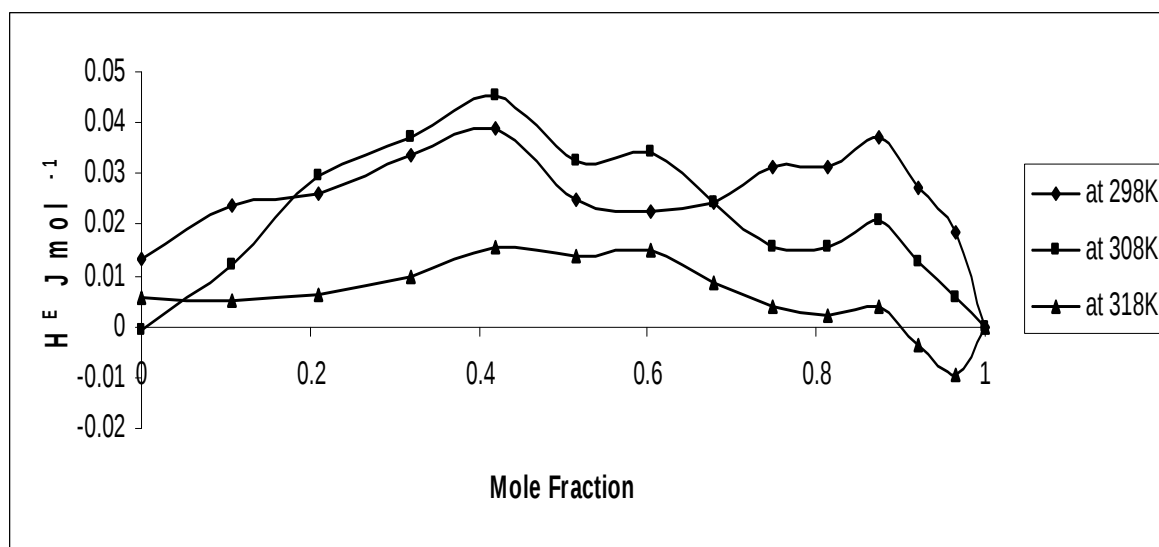


Fig. 2: Variation of H^E with mole fraction of toluene in toluene + 1-dodecanol + cyclohexane system at 298 (♦), 308 (■) and 318 (▲) K

The negative deviations of G^{*E} over the whole composition range at 298, 308 and 318 K implies that the van der Waals attraction decreases considerably in between the pure components when these components are mixed to form a system. There is a certain degree of association in the pure 1-dodecanol due to hydrogen bond formation, though these associations are broken down on formation of mixture. In summary, three types of interactions namely the attractions due to van der Waals forces, the dipole-induced-dipole attractions and hydrogen bonded interaction, with an additional interaction of interstitial accommodation undergo an overall decrease in G^{*E} , making the process markedly endothermic as a whole.

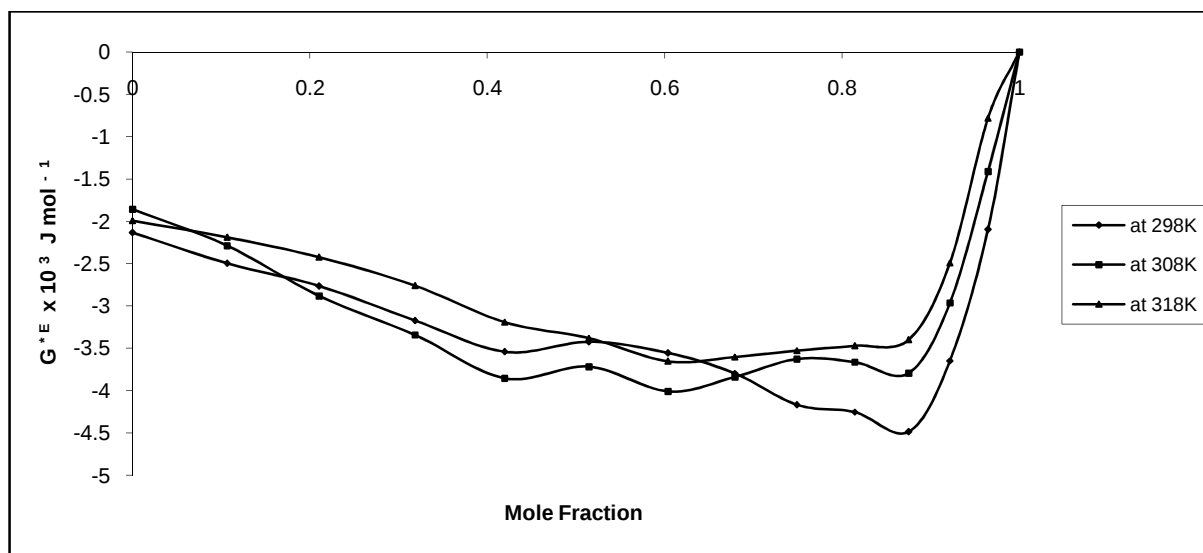


Fig. 3: Variation of G^E with mole fraction of toluene in toluene + 1-dodecanol + cyclohexane system at 298 (♦), 308 (■) and 318 (▲) K

The variation of excess internal pressure (π_i^E) is presented in Table 2 and variation of $\log \pi_i$ with $\log 1/V_f$ at 298 K is presented in Fig. 4 for the system under investigation. The non-linear variation with both positive and negative deviations of π_i^E with composition is indicative of weak specific interactions between the components of the system. This view is supported by the negative deviations of free volume without any specific maxima. The tetrahedral molecules of toluene and planar molecules of cyclohexane can be easily interstitially accommodated into voids formed by the dissociation of the self-association of 1-dodecanol. This results in reduction in internal pressure of the system. The importance of π_i^E and $1/V_f$ in fixing the liquid state properties thermodynamically is significant by virtue of the straight lines obtained from the Fig. 4.

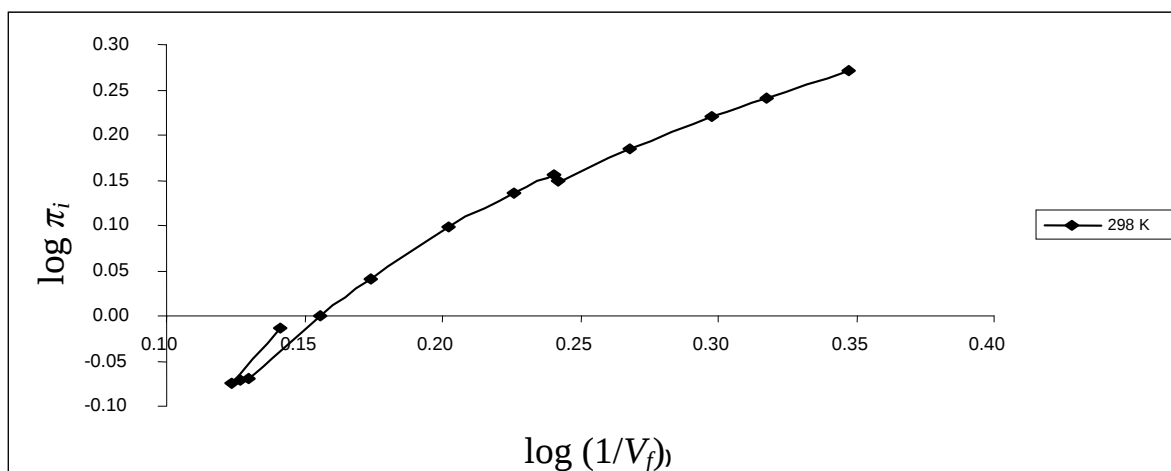


Fig. 4: Variation of $\log \pi_i$ with $\log (1/V_f)$ in toluene + 1-dodecanol + cyclohexane system at 298 (♦), 308 (■) and 318 (▲) K

The deviations of Jacobson's Free Length Theory (u^{FLT}), Nomoto Relation (u^{NOM}), Impedance Dependence Relation (u^{IDR}) and Vandeal Vangael Ideal Mixing Relation (u^{VAN}) from the experimental values of sound speed (u^{EXP}) is presented in Table 4. From the Table 4 it is evident that u^{FLT} is best suited to this system without any deviation from the experimental sound speed over the range of temperature from 298 to 318 K by the interval of 10 K. A perusal of Table 4 reveals that maximum deviations are found in Vandeal Vangael Mixing Relation while some deviations are observed in Nomoto Relation (u^{NOM}), Impedance Dependence Relation (u^{IDR}), suggesting the least applicability of u^{VAN} for the system under investigation from 298 to 318 K. The increasing order of deviations from experimental values is as follows.

$$u^{Exp} = u^{FLT} < u^{NOM} < u^{IDR} < u^{VAN}$$

Table 4:-Comparison of Free Length Theory (FLT), Impedance Dependence Relation (IDR), Nomoto's Relation (NOM) and Vandeel Vangeel Ideal mixing relation (VAN) with experimental values (EXP) of sound speed for binary system of toluene (x_1) + 1-dodecanol (x_2) + cyclohexane (x_3) system at 298, 308 and 318 K

(x ₁)	(x ₂)	u ^{EXP} ms ⁻¹	u ^{FLT} ms ⁻¹	u ^{IDR} ms ⁻¹	u ^{NOM} ms ⁻¹	u ^{VAN} ms ⁻¹	% Deviation			
							u ^{FLT}	u ^{IDR}	u ^{NOM}	u ^{VAN}
298 K										
0.0000	0.4175	1463.0	1463.0	1335.3	1366.3	1195.0	0.0	8.7324	6.6413	18.3177
0.1067	0.3844	1460.6	1460.6	1334.1	1364.0	1203.6	0.0	8.6600	6.6136	17.5974
0.2105	0.3521	1441.6	1441.6	1333.0	1361.7	1212.2	0.0	7.5302	5.5402	15.9107
0.3184	0.3131	1423.5	1423.5	1330.8	1358.0	1221.4	0.0	6.5113	4.6046	14.1968
0.4195	0.2765	1221.0	1221.0	1328.8	1354.2	1230.5	0.0	6.4938	4.7040	13.4065
0.5145	0.2421	1393.6	1393.6	1326.9	1350.4	1239.6	0.0	4.7917	3.0996	11.0555
0.6037	0.2098	1380.3	1380.3	1325.1	1346.7	1248.5	0.0	3.9976	2.4326	9.5462
0.6790	0.1706	1369.2	1369.2	1321.3	1340.1	1257.0	0.0	3.4971	2.1202	8.1905
0.7490	0.1342	1358.7	1358.7	1317.8	1333.6	1265.7	0.0	3.0098	1.8447	6.8399
0.8142	0.1002	1348.1	1348.1	1314.5	1327.1	1274.6	0.0	2.4903	1.5577	5.4531
0.8751	0.0685	1338.1	1338.1	1311.5	1320.7	1283.6	0.0	1.9845	1.3039	4.0763
0.9216	0.0387	1327.0	1327.0	1308.2	1313.6	1291.8	0.0	1.4183	1.0128	2.6557
0.9646	0.0111	1315.5	1315.5	1305.1	1306.6	1300.0	0.0	0.7908	0.6748	1.1791
1.0000	0.0000	1304.8	1304.8	1304.8	1304.8	1304.0	—	—	—	—
308 K										
0.0000	0.4175	1364.8	1364.8	1282.7	1311.2	1149.8	0.0	6.0118	3.9268	15.7525
0.1067	0.3844	1361.2	1361.2	1283.7	1310.5	1159.8	0.0	5.6972	3.7297	14.7962
0.2105	0.3521	1354.9	1354.9	1284.6	1309.7	1169.9	0.0	5.1895	3.3343	13.6542
0.3184	0.3131	1346.1	1346.1	1284.5	1307.7	1180.6	0.0	4.5816	2.8523	12.3000
0.4195	0.2765	1343.9	1343.9	1284.3	1305.8	1191.0	0.0	4.4303	2.8367	11.3729
0.5145	0.2421	1330.0	1330.0	1284.3	1303.8	1201.4	0.0	3.4404	1.9701	9.6724
0.6037	0.2098	1324.1	1324.1	1284.2	1301.9	1211.5	0.0	3.0131	1.6770	8.50007
0.6790	0.1706	1316.9	1316.9	1281.9	1297.2	1220.9	0.0	2.6536	1.4921	7.2858
0.7490	0.1342	1310.9	1310.9	1279.9	1292.6	1230.4	0.0	2.3712	1.3991	6.1413
0.8142	0.1002	1302.7	1302.7	1278.0	1288.0	1240.0	0.0	1.9013	1.1295	4.8145
0.8751	0.0685	1295.4	1295.4	1276.2	1283.4	1249.6	0.0	1.4825	0.9233	3.5361
0.9216	0.0387	1287.7	1287.7	1273.8	1278.1	1258.2	0.0	1.0757	0.7465	2.2920
0.9646	0.0111	1279.9	1279.9	1271.7	1272.8	1266.7	0.0	0.6414	0.5514	1.0281
1.0000	0.0000	1272.0	1272.0	1272.0	1272.0	1272.0	—	—	—	—
318 K										
0.0000	0.4175	1276.8	1276.8	1239.8	1263.7	1116.1	0.0	2.8962	1.0249	12.5846
0.1067	0.3844	1274.7	1274.7	1242.1	1264.1	1126.7	0.0	2.5517	0.8276	11.6084
0.2105	0.3521	1272.4	1272.4	1244.4	1264.5	1137.3	0.0	2.2060	0.6205	10.6189
0.3184	0.3131	1269.7	1269.7	1245.8	1264.0	1148.6	0.0	1.8868	0.4472	9.5367
0.4195	0.2765	1267.7	1267.7	1247.0	1263.5	1159.7	0.0	1.6319	0.3310	8.5208
0.5145	0.2421	1264.0	1264.0	1248.2	1263.0	1170.6	0.0	1.2451	0.0738	7.3891
0.6037	0.2098	1258.8	1258.8	1249.3	1262.5	1181.2	0.0	0.7549	-0.2942	6.1658
0.6790	0.1706	1255.4	1255.4	1248.4	1259.7	1191.1	0.0	0.5554	-0.3443	5.1172
0.7490	0.1342	1253.8	1253.8	1247.5	1256.9	1201.1	0.0	0.5006	-0.2429	4.2061
0.8142	0.1002	1249.6	1249.6	1246.8	1254.0	1211.0	0.0	0.2256	-0.3582	3.0840
0.8751	0.0685	1247.4	1247.4	1246.0	1251.2	1221.0	0.0	0.1143	-0.3043	2.1233
0.9216	0.0387	1246.4	1246.4	1244.6	1247.6	1229.8	0.0	0.1409	-0.1013	1.3278
0.9646	0.0111	1245.3	1245.3	1243.3	1244.1	1238.6	0.0	0.1644	0.1025	0.5432
1.0000	0.0000	1244.0	1244.0	1244.0	1244.0	1244.0	—	—	—	—

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