

Densities, Viscosities, Speeds of Sound, and Refractive Indices of Binary Mixtures of 1-Decanol with Isomeric Chlorotoluenes

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Received: 8 August 2010 / Accepted: 19 April 2011 / Published online: 11 May 2011
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Abstract Densities, ρ , viscosities, η , speeds of sound, u , and refractive indices, n_D , of binary liquid mixtures of 1-decanol with *o*-chlorotoluene, *m*-chlorotoluene, and *p*-chlorotoluene have been measured over the entire range of composition at 298.15 K, 303.15 K, and 308.15 K and at atmospheric pressure. From the experimental data of density, speed of sound, viscosity and refractive index, the values of the excess molar volume, V^E , deviations in isentropic compressibility, $\Delta\kappa_S$, and deviations in molar refraction, ΔR , have been calculated. The calculated excess and deviation functions have been analyzed in terms of molecular interactions and structural effects.

Keywords 1-Decanol · Excess molar volume · Isomeric chlorotoluene · Molar refraction

1 Introduction

The variations in the volumetric, acoustic and refractive properties of binary mixtures of alkanols, with aliphatic hydrocarbons with the molecular size, shape, chain length, and degree of molecular association of normal alkanols have been reported earlier [1–4]. Alkanols are polar and self-associated liquids, and the dipolar association of alkanols decreases when they are mixed with polar compounds containing halogen atoms, due to some sort of specific intermolecular interactions. In an attempt to explore the nature of interactions occurring between the mixing components, the densities, ρ , speeds of sound, u , viscosities, η , and refractive indices, n_D , of binary mixtures of 1-decanol with *o*-chlorotoluene, *m*-chlorotoluene, and *p*-chlorotoluene have been

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measured over the entire range of composition at 298.15 K, 303.15 K, and 308.15 K and at atmospheric pressure. From the experimental values of density, speed of sound, viscosity, and refractive index, the values of the excess molar volume, V^E , deviations in isentropic compressibility, $\Delta\kappa_S$, and deviations in molar refraction, ΔR , have been calculated. The calculated excess and deviation functions have been analyzed in terms of molecular interactions and structural effects.

2 Experimental

2.1 Chemicals

The mass fraction purity of all the liquids from SD Fine Chemicals, Ltd., India was as follows: 1-decanol (99.5 %), *o*-chlorotoluene (99.5 %), *m*-chlorotoluene (99.5 %), and *p*-chlorotoluene (99.6 %). Prior to experimental measurements, all liquids were used after double distillation and partially degassed with a vacuum pump under an inert atmosphere. The purity of these solvents was ascertained by comparing the measured density, speed of sound, viscosity, and refractive index of the pure components with the available literature [5–12] as shown in Table 1.

Table 1 Densities, ρ , speeds of sound, u , viscosities, η , and refractive indexes, n_D of the pure liquid components at different temperatures

$T(K)$	$\rho \times 10^{-3}(\text{kg} \cdot \text{m}^{-3})$		$u (\text{m} \cdot \text{s}^{-1})$		$\eta (\text{mPa} \cdot \text{s})$		n_D	
	This study	Literature	This study	Literature	This study	Literature	This study	Literature
1-Decanol								
298.15	0.82641	0.82637 [5]	1380	1380 [10]	11.817	11.825 [10]	1.4346	1.4345 [12]
303.15	0.82292	0.82295 [5]	1365	1365 [10]	9.766	9.754 [10]	1.4326	1.4323 [12]
308.15	0.81942	0.81957 [5]	1346	1346 [10]	8.130	8.135 [10]	1.4305	1.4303 [12]
<i>o</i>-Chlorotoluene								
298.15	1.07741	1.0764 [6]	1301	–	0.943	–	1.5219	–
303.15	1.07283	1.0728 [7]	1284	1284 [7]	0.885	0.884 [7]	1.5189	–
308.15	1.06824	–	1266	–	0.805	–	1.5169	–
<i>m</i>-Chlorotoluene								
298.15	1.06729	1.07219 ^a [8]	1298	–	0.798	–	1.5207	–
303.15	1.06281	1.06524 [7]	1280	1280 [7]	0.746	–	1.5189	–
308.15	1.05833	–	1262	–	0.705	–	1.5169	–
<i>p</i>-Chlorotoluene								
298.15	1.06511	1.06514 [9]	1289	–	0.828	0.838 [11]	1.5188	1.5188 [11]
303.15	1.05951	1.06052 [7]	1271	1271 [7]	0.784	0.785 [11]	1.5166	1.5160 [11]
308.15	1.05390	–	1253	–	0.730	–	1.5138	–

^aAt 293.15 K

2.2 Measurements

All liquid mixtures were prepared by weighing the appropriate amounts of pure liquids on an electronic balance (Afcoset, ER-120A, India) with a precision of $\pm 0.1\text{ mg}$ by syringing each component into airtight stopper bottles to minimize evaporation losses. The uncertainty of the mole fraction was $\pm 1 \times 10^{-4}$.

Densities and speeds of sound of the pure liquids and their mixtures were measured with density and sound speed analyzer apparatus (Anton Paar DSA 5000, Austria–Europe) with a precision in densities and speeds of sound better than $\pm 0.002\text{ kg} \cdot \text{m}^{-3}$ and $\pm 0.01\text{ m} \cdot \text{s}^{-1}$, respectively, and the temperature was kept constant within $\pm 0.001\text{ K}$ using the Peltier method. Before each series of measurements, calibration of the apparatus was carried out with benzene, toluene, and double-distilled water at the desired temperatures. The uncertainty in the experimental measurements has been estimated to be less than $10^{-2}\text{ kg} \cdot \text{m}^{-3}$ for the density and $0.5\text{ m} \cdot \text{s}^{-1}$ for the speed of sound.

Kinematic viscosities, at 298.15 K, 303.15 K, and 308.15 K were measured with a modified Ubbelohde suspended-level viscometer. The viscometer was suspended in a thermostated water bath maintained to $\pm 0.01\text{ K}$. An electronic digital stop watch with an uncertainty of 0.01 s was used for flow-time measurements. At least four flow-time measurements were performed for each composition and temperature, and the results were averaged. Calibration of the viscometer was carried out with high purity benzene (99.7%) and toluene (99.7%). The equation for viscosity, according to Poiseuille's law is

$$\eta = \rho v = \rho(kt - c/t) \quad (1)$$

where k and c are the viscometer constants and t , η , and v are the efflux time, dynamic viscosity, and kinematic viscosity, respectively. The uncertainty in the viscosity measurements was of the order of 0.003 mPa · s.

Refractive indices were measured with a thermostatic Abbe refractometer (Erma, A-302A, India) using the sodium–D line with an error less than ± 0.0001 units at 298.15 K, 303.15 K, and 308.15 K. The temperature in the refractometer was regulated by using a circulation pump connected with a constant temperature water bath with $\pm 0.01\text{ }^{\circ}\text{C}$ stability. Calibration of the instrument was done by measuring the refractive indices of benzene, toluene, and double-distilled water at known temperatures. The uncertainty in the refractive index measurements was of the order of 0.0002.

3 Results and Discussion

The experimental values of densities, ρ , speeds of sound, u , excess molar volumes, V^E , and deviations in isentropic compressibilities, $\Delta\kappa_S$ for the binary liquid mixtures studied at 298.15 K, 303.15 K, and 308.15 K are reported in Table 2.

The excess molar volumes, V^E , of the binary liquid mixtures were calculated from the densities of the pure liquids and their mixtures using the following equation:

$$V^E = (x_1 M_1 + x_2 M_2)/\rho - (x_1 M_1/\rho_1 + x_2 M_2/\rho_2) \quad (2)$$

Table 2 Experimental values of density, ρ , speed of sound, u , excess molar volume, V^E , and deviation in isentropic compressibility, $\Delta\kappa_S$, for the binary liquid mixtures at 298.15 K, 303.15 K, and 308.15 K

x_1	$\rho \times 10^{-3} (\text{kg} \cdot \text{m}^{-3})$	$u (\text{m} \cdot \text{s}^{-1})$			$V^E \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1})$			$\Delta\kappa_S (\text{TPa}^{-1})$		
		298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
$x_1 o\text{-Chlorotoluene} + x_2 1\text{-Decanol}$										
0.0000	0.82641	0.82292	0.81942	1.380.1	1364.9	1346.0	0.0000	0.0000	0.00	0.00
0.0734	0.83840	0.83473	0.83110	1.373.9	1358.4	1339.3	-0.0790	-0.0491	-0.0335	0.58
0.1537	0.85215	0.84830	0.84455	1.366.5	1350.5	1330.9	-0.1233	-0.0693	-0.0422	2.03
0.2064	0.86161	0.85765	0.85384	1.361.3	1344.9	1324.9	-0.1351	-0.0687	-0.0365	2.11
0.2747	0.87440	0.87031	0.86640	1.354.2	1337.3	1316.8	-0.1317	-0.0523	-0.0133	3.60
0.3450	0.88832	0.88408	0.88008	1.346.6	1329.3	1308.2	-0.1145	-0.0238	0.0213	5.32
0.4107	0.90206	0.89772	0.89362	1.339.4	1321.7	1300.0	-0.0859	0.0095	0.0601	7.04
0.4890	0.91952	0.91505	0.91082	1.330.9	1312.7	1290.6	-0.0468	0.0530	0.1081	8.99
0.5555	0.93539	0.93083	0.92651	1.323.8	1305.2	1283.1	-0.0108	0.0871	0.1456	10.51
0.6158	0.95072	0.94609	0.94168	1.317.6	1298.8	1276.7	0.0171	0.1122	0.1705	11.63
0.6813	0.96852	0.96384	0.95932	1.311.5	1292.5	1270.8	0.0437	0.1297	0.1893	12.35
0.7475	0.98782	0.98310	0.97830	1.306.0	1286.9	1266.1	0.0629	0.1378	0.1935	12.43
0.8205	1.01087	1.00613	1.00149	1.301.2	1282.3	1262.5	0.0718	0.1313	0.1774	11.49
0.8840	1.03261	1.02790	1.02323	1.298.7	1280.0	1261.6	0.0683	0.1088	0.1443	9.31
0.9469	1.05604	1.05138	1.04671	1.298.5	1280.6	1262.2	0.0406	0.0610	0.0823	5.44
1.0000	1.07741	1.07283	1.066824	1.301.2	1284.1	1266.1	0.0000	0.0000	0.00	0.00
$x_1 m\text{-Chlorotoluene} + x_2 1\text{-Decanol}$										
0.0000	0.82641	0.82292	0.81942	1.380.1	1364.9	1346.0	0.0000	0.0000	0.00	0.00
0.0745	0.83798	0.83443	0.83088	1.371.6	1355.2	1335.0	-0.0307	-0.0275	-0.0272	2.41
0.1337	0.84761	0.84401	0.84040	1.364.4	1347.0	1325.8	-0.0409	-0.0344	-0.0305	4.62
										6.72
										9.50

Table 2 continued

x_1	$\rho \times 10^{-3}$ (kg · m $^{-3}$)	u (m · s $^{-1}$)			$V^E \times 10^6$ (m 3 · mol $^{-1}$)			$\Delta\kappa_S$ (TPa $^{-1}$)
T (K)	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15
0.2017	0.85918	0.85550	0.85182	1356.0	1337.4	1315.4	-0.0391	-0.0266
0.2741	0.87219	0.88842	0.86464	1347.0	1327.4	1305.0	-0.0250	-0.0059
0.3471	0.88608	0.88221	0.87833	1338.0	1318.0	1295.4	-0.0002	0.0246
0.4139	0.89955	0.89558	0.89160	1329.9	1309.9	1287.6	0.0260	0.0585
0.4616	0.90968	0.90565	0.90159	1324.3	1304.4	1282.4	0.0450	0.0814
0.5532	0.93044	0.92626	0.92206	1314.9	1295.5	1273.9	0.0828	0.1270
0.6282	0.94888	0.94459	0.94026	1308.1	1289.3	1268.3	0.1070	0.1540
0.6772	0.96172	0.95736	0.95294	1304.1	1285.8	1265.4	0.1168	0.1644
0.7447	0.98055	0.97611	0.97161	1300.0	1281.9	1261.9	0.1247	0.1696
0.8245	1.00478	1.00026	0.99570	1296.6	1278.3	1258.4	0.1169	0.1555
0.8876	1.02562	1.02106	1.01644	1296.2	1276.7	1257.5	0.0940	0.1255
0.9433	1.04543	1.04084	1.03625	1297.1	1276.5	1257.8	0.0638	0.0879
1.0000	1.06729	1.00281	1.05833	1298.3	1280.1	1262.1	0.0000	0.0000
$x_1 p$ -Chlorotoluene + x_2 1-Decanol								
0.0000	0.82641	0.82292	0.81942	1380.1	1364.9	1346.0	0.0000	0.0000
0.0718	0.83782	0.83411	0.83035	1373.1	1357.3	1338.2	-0.1064	-0.0767
0.1353	0.84832	0.84443	0.84048	1366.4	1350.1	1330.8	-0.1666	-0.1166
0.1976	0.85901	0.85495	0.85084	1359.4	1342.7	1323.1	-0.1985	-0.1340
0.2703	0.87209	0.86783	0.86356	1350.9	1333.7	1313.8	-0.2085	-0.1287
0.3410	0.88546	0.88103	0.87662	1342.3	1324.7	1304.8	-0.1947	-0.1055
0.4103	0.89931	0.89471	0.89019	1333.9	1315.9	1295.9	-0.1654	-0.0708
0.4820	0.91452	0.90975	0.90512	1325.0	1307.0	1286.9	-0.1243	-0.0276

Table 2 continued

x_1	$\rho \times 10^{-3} (\text{kg} \cdot \text{m}^{-3})$			$u (\text{m} \cdot \text{s}^{-1})$			$V^E \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1})$			$\Delta\kappa_S (\text{TPa}^{-1})$		
	$T(\text{K})$	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15
0.5531	0.93057	0.92566	0.92091	1316.5	1298.4	1278.3	-0.0765	0.0151	0.0813	4.81	6.89	9.46
0.6234	0.94755	0.94250	0.93762	1308.6	1290.5	1270.5	-0.0291	0.0570	0.1167	5.70	7.61	10.17
0.7045	0.96872	0.96353	0.95846	1300.2	1282.3	1262.5	0.0188	0.0918	0.1471	6.51	7.90	10.43
0.7497	0.98135	0.97609	0.97092	1296.1	1278.3	1258.5	0.0365	0.1009	0.1533	6.60	7.82	10.31
0.8196	1.00221	0.99685	0.99150	1291.0	1273.0	1253.9	0.0526	0.1015	0.1472	6.17	7.20	9.07
0.8907	1.02523	1.01978	1.01428	1288.0	1269.5	1250.7	0.0587	0.0885	0.1238	4.69	5.78	7.19
0.9556	1.04823	1.04269	1.03710	1287.5	1269.1	1251.0	0.0310	0.0434	0.0614	2.34	3.03	3.42
1.0000	1.06511	1.05951	1.05390	1289.1	1271.0	1253.1	0.0000	0.0000	0.0000	0.00	0.00	0.00

Table 3 Literature and calculated values of the molar heat capacity, C_p , and isobaric expansion coefficients, α , for the pure liquid components at 298.15 K, 303.15 K, and 308.15 K

Liquids	C_p (J · mol ⁻¹ · K ⁻¹)			α (kK ⁻¹)		
T (K)	298.15	303.15	308.15	298.15	303.15	308.15
1-Decanol	373.10 [10]	380.40 [10]	385.40 [10]	0.8429	0.8465	0.8555
<i>o</i> -Chlorotoluene	177.79 [14]	179.59 [14]	181.29 [14]	0.8495	0.8531	0.8594
<i>m</i> -Chlorotoluene	171.73 [14]	173.07 [14]	174.56 [14]	0.8395	0.8431	0.8461
<i>p</i> -Chlorotoluene	171.38 [14]	172.74 [14]	173.98 [14]	1.0525	1.0580	1.0637

where ρ is the density of the mixture and x_1 , M_1 , ρ_1 , and x_2 , M_2 and ρ_2 are the mole fraction, molecular mass, and the density of pure components 1 and 2, respectively.

From the results of speeds of sound, u , and densities, ρ , the isentropic compressibility, κ_S , was calculated as

$$\kappa_S = 1/(u^2 \rho) = -V^{-1}(\partial V/\partial P)_S = V^2/(Mu^2) \quad (3)$$

where V is the molar volume and M is the molar mass of the mixtures.

The corresponding deviations in isentropic compressibilities, $\Delta\kappa_S$, were obtained from the relation [13],

$$\Delta\kappa_S = \kappa_S - \kappa_S^{\text{id}} \quad (4)$$

where κ_S^{id} is the ideal value of the isentropic compressibility and was calculated from the Benson and Kiyohara relation [13],

$$\kappa_S^{\text{id}} = \sum_{i=1}^2 \phi_i \left[\kappa_{S,i} + \frac{TV_i(\alpha_i^2)}{C_{pi}} \right] - \left\{ \frac{T \left(\sum_{i=1}^2 x_i V_i \right) \left(\sum_{i=1}^2 \phi_i \alpha_i \right)^2}{\sum_{i=1}^2 x_i C_{pi}} \right\} \quad (5)$$

Here, C_{pi} and α_i are the molar heat capacity and the thermal expansion coefficient of the i th component, respectively. The values of C_{pi} were obtained from the literature [10, 14, 15], and the values of α_i has been calculated from the equation $\alpha = (\partial V/\partial T)_p/V = -1/\rho(\partial\rho^{-1}/\partial T)_p$. These values are shown in Table 3. The volume fraction, ϕ_i was calculated as $\phi_i = x_i V_i / \sum x_i V_i$.

Deviations of molar refraction, ΔR , have been computed using the relation [16–18],

$$\Delta R = \frac{\sum M_i x_i}{\rho} \frac{n_D^2 - 1}{n_D^2 + 2} - \sum x_i \frac{M_i}{\rho_i} \frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \quad (7)$$

The experimental values of viscosities, η , refractive index, n_D , and deviations in molar refraction, ΔR , for the binary liquid mixtures studied at 298.15 K, 303.15 K, and 308.15 K are reported in Table 4.

Table 4 Experimental values of the viscosity, η , refractive index, n_D , and deviation in molar refraction, ΔR , for the binary liquid mixtures at 298.15 K, 303.15 K, and 308.15 K

x_1	η (mPa · s)			n_D			ΔR (cm ³ · mol ⁻¹)		
T (K)	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
$x_1 o\text{-Chlorotoluene} + x_2 1\text{-Decanol}$									
0.0000	11.817	9.766	8.130	1.4346	1.4326	1.4305	0.000	0.000	0.000
0.0734	10.002	8.289	6.889	1.4377	1.4359	1.4339	-0.479	-0.449	-0.439
0.1537	8.277	6.862	5.734	1.4413	1.4394	1.4378	-0.952	-0.922	-0.871
0.2064	7.283	6.042	5.078	1.4440	1.4423	1.4406	-1.210	-1.159	-1.117
0.2747	6.130	5.103	4.313	1.4479	1.4462	1.4445	-1.486	-1.430	-1.388
0.3450	5.101	4.266	3.637	1.4524	1.4505	1.4489	-1.706	-1.659	-1.608
0.4107	4.289	3.603	3.080	1.4569	1.4549	1.4534	-1.859	-1.814	-1.756
0.4890	3.477	2.952	2.528	1.4628	1.4608	1.4592	-1.961	-1.912	-1.865
0.5555	2.906	2.486	2.134	1.4685	1.4664	1.4648	-1.966	-1.926	-1.876
0.6158	2.468	2.133	1.837	1.4741	1.4719	1.4702	-1.916	-1.878	-1.837
0.6813	2.075	1.806	1.566	1.4806	1.4784	1.4767	-1.799	-1.759	-1.717
0.7475	1.742	1.538	1.338	1.4878	1.4855	1.4839	-1.598	-1.564	-1.522
0.8205	1.446	1.294	1.135	1.4966	1.4941	1.4924	-1.278	-1.254	-1.219
0.8840	1.235	1.124	0.995	1.5050	1.5023	1.5005	-0.902	-0.891	-0.869
0.9469	1.062	0.984	0.879	1.5140	1.5111	1.5092	-0.446	-0.443	-0.432
1.0000	0.943	0.885	0.805	1.5219	1.5189	1.5169	0.000	0.000	0.000
$x_1 m\text{-Chlorotoluene} + x_2 1\text{-Decanol}$									
0.0000	11.817	9.766	8.130	1.4346	1.4326	1.4305	0.000	0.000	0.000
0.0745	10.083	8.289	6.908	1.4371	1.4353	1.4334	-0.521	-0.499	-0.480
0.1337	8.723	7.171	6.001	1.4394	1.4378	1.4360	-0.887	-0.846	-0.814
0.2017	7.280	6.013	5.022	1.4424	1.4408	1.4391	-1.250	-1.209	-1.167
0.2741	5.927	4.905	4.123	1.4460	1.4445	1.4430	-1.574	-1.524	-1.462
0.3471	4.762	3.977	3.348	1.4501	1.4488	1.4473	-1.831	-1.764	-1.702
0.4139	3.862	3.261	2.771	1.4545	1.4533	1.4518	-1.984	-1.910	-1.849
0.4616	3.322	2.821	2.423	1.4579	1.4567	1.4553	-2.055	-1.985	-1.916
0.5532	2.496	2.161	1.862	1.4653	1.4641	1.4628	-2.092	-2.024	-1.948
0.6282	1.985	1.744	1.521	1.4723	1.4711	1.4697	-2.010	-1.944	-1.881
0.6772	1.724	1.523	1.343	1.4772	1.4761	1.4747	-1.911	-1.841	-1.778
0.7447	1.429	1.282	1.142	1.4847	1.4835	1.4820	-1.693	-1.635	-1.583
0.8245	1.170	1.063	0.960	1.4947	1.4932	1.4917	-1.312	-1.279	-1.233
0.8876	1.016	0.934	0.851	1.5034	1.5017	1.5000	-0.918	-0.902	-0.874
0.9433	0.906	0.844	0.777	1.5117	1.5099	1.5082	-0.496	-0.491	-0.467
1.0000	0.798	0.746	0.705	1.5207	1.5189	1.5169	0.000	0.000	0.000
$x_1 p\text{-Chlorotoluene} + x_2 1\text{-Decanol}$									
0.0000	11.817	9.766	8.130	1.4346	1.4326	1.4305	0.000	0.000	0.000
0.0718	9.725	8.053	6.713	1.4376	1.4357	1.4337	-0.455	-0.438	-0.419
0.1353	8.154	6.766	5.652	1.4405	1.4387	1.4367	-0.814	-0.781	-0.754
0.1976	6.842	5.705	4.769	1.4437	1.4418	1.4398	-1.113	-1.081	-1.048

Table 4 Continued

x_1	η (mPa · s)			n_D			ΔR (cm ³ · mol ⁻¹)		
T (K)	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
0.2703	5.561	4.658	3.909	1.4477	1.4458	1.4439	-1.407	-1.371	-1.323
0.3410	4.546	3.825	3.230	1.4519	1.4501	1.4481	-1.637	-1.588	-1.543
0.4103	3.733	3.162	2.678	1.4566	1.4547	1.4527	-1.784	-1.742	-1.700
0.4820	3.045	2.608	2.224	1.4618	1.4600	1.4580	-1.876	-1.827	-1.785
0.5531	2.495	2.157	1.851	1.4676	1.4657	1.4637	-1.892	-1.847	-1.800
0.6234	2.058	1.798	1.558	1.4738	1.4719	1.4698	-1.832	-1.791	-1.751
0.7045	1.654	1.472	1.289	1.4818	1.4798	1.4776	-1.660	-1.629	-1.594
0.7497	1.472	1.325	1.166	1.4866	1.4846	1.4824	-1.516	-1.492	-1.454
0.8196	1.239	1.134	1.008	1.4947	1.4926	1.4902	-1.218	-1.202	-1.176
0.8907	1.047	0.972	0.875	1.5035	1.5015	1.4990	-0.823	-0.803	-0.784
0.9556	0.907	0.850	0.781	1.5124	1.5104	1.5078	-0.364	-0.349	-0.337
1.0000	0.828	0.784	0.730	1.5188	1.5166	1.5138	0.000	0.000	0.000

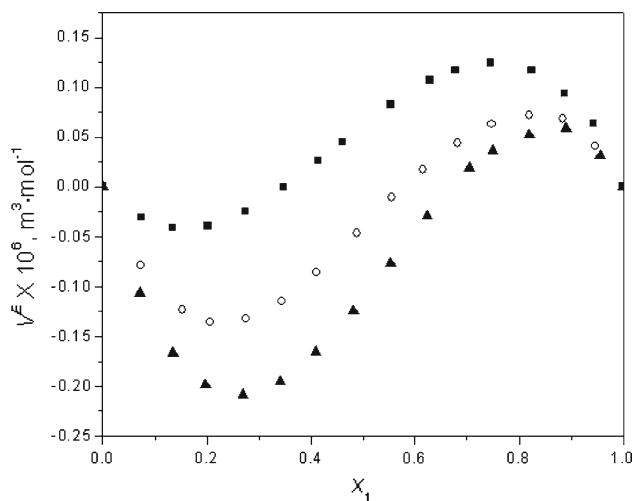


Fig. 1 Plots of excess molar volumes, $V^E \times 10^6$ (m³ · mol⁻¹), against mole fraction (x_1) of 1-decanol with *o*-chlorotoluene (open circle), *m*-chlorotoluene (filled square), and *p*-chlorotoluene (filled triangle) at 298.15 K

Figure 1 shows the variation of the excess molar volumes, V^E , with mole fraction, x_1 , of 1-decanol with isomeric chlorotoluene over the entire composition range at 298.15 K. The excess molar volumes at the maximum of the curves for 1-decanol decrease in the following sequence: *m*-chlorotoluene > *o*-chlorotoluene > *p*-chlorotoluene. Addition of isomeric chlorotoluenes in 1-decanol causes the disruption of hydrogen bonds in 1-decanol and loosening of dipolar associations in isomeric chlorotoluenes and possibly through new H-bonds of the type O-H···CI, and π -bonds of the type $\pi\cdots\text{H}-\text{O}$ involving π -electron of the benzene rings of the aromatic nucleus

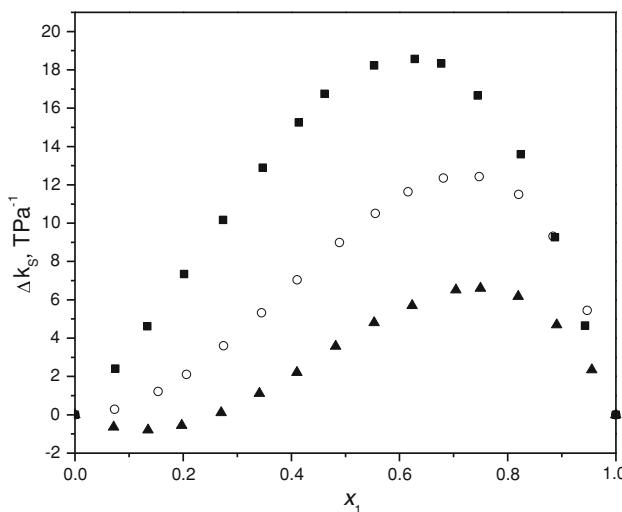


Fig. 2 Plots of deviation in isentropic compressibilities, $\Delta\kappa_S$ (TPa^{-1}) against mole fraction (x_1) of 1-decanol with *o*-chlorotoluene (open circle), *m*-chlorotoluene (filled square), and *p*-chlorotoluene (filled triangle) at 298.15 K

and the H-atom of the –OH group of 1-decanol molecules. However, the strength of O–H···Cl and $\pi\cdots\text{H–O}$ bonds formed between the isomeric chlorotoluenes and 1-decanol molecules depends upon the nature and position of the substituent groups present on the benzene ring of the aromatic compounds. The presence of electron-repelling $-\text{CH}_3$ group in the *o*- and *p*-position in the chlorotoluenes enhances the π -electron density on the ring making the availability of the π -electron for electron seeking H-atoms of –OH group of 1-decanol easier and accounting for the stronger O–H···Cl and $\pi\cdots\text{H–O}$ bonds in the case of *o*- and *p*-substituted binary mixtures of 1-decanol with *o*-chlorotoluene and *p*-chlorotoluene as compared to the binary mixture of 1-decanol with *m*-chlorotoluene [9]. Consequently, the interaction strength for such bonds in the binary mixtures of 1-decanol follows the order: *m*-chlorotoluene < *o*-chlorotoluene < *p*-chlorotoluene.

Figure 2 shows the behavior and dependence of deviations of isentropic compressibilities, $\Delta\kappa_S$, with the mole fraction, x_1 , of 1-decanol with isomeric chlorotoluene over the entire composition range at 298.15 K. While the 1-decanol + *o*-chlorotoluene/*m*-chlorotoluene binary liquid mixtures reveal positive deviations in their behavior, the 1-decanol + *p*-chlorotoluene binary liquid mixture exhibits a sigmoidal kind of behavior; the values vary from negative to positive with an increase of the *p*-chlorotoluene mole fraction. The deviations of isentropic compressibilities at the maximum of the curves for 1-decanol $\Delta\kappa_S$, vary in the following sequence: *m*-chlorotoluene > *o*-chlorotoluene > *p*-chlorotoluene.

Figure 3 shows the variation of deviations of molar refractions, ΔR , with mole fraction, x_1 , of isomeric chlorotoluene. The ΔR values show a negative trend for all the binary mixtures over the entire composition range. The absolute values of the minima for these mixtures decrease significantly with an increase in temperature. The

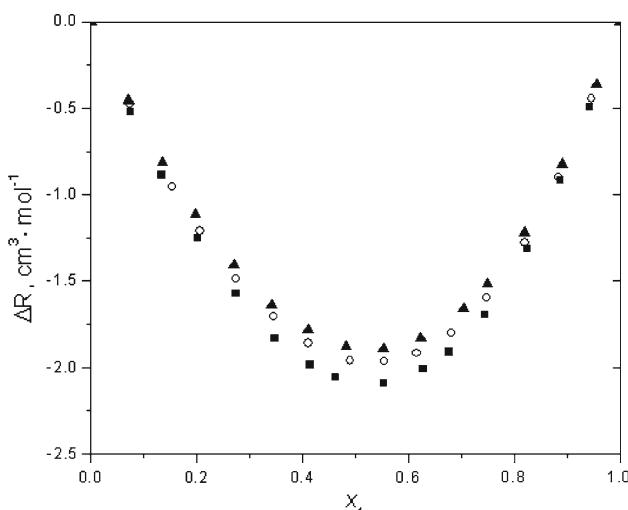


Fig. 3 Plots of molar refraction, ΔR ($\text{cm}^3 \cdot \text{mol}^{-1}$) against mole fraction (x_1) of 1-decanol with *o*-chlorotoluene (open circle), *m*-chlorotoluene (filled square), and *p*-chlorotoluene (filled triangle) at 298.15 K

minimum negative values of ΔR curves for 1-decanol are in the order: *m*-chlorotoluene > *o*-chlorotoluene > *p*-chlorotoluene.

4 Conclusions

In this article, the densities, viscosities, speeds of sound, and refractive indices of binary mixtures of 1-decanol with *o*-chlorotoluene, *m*-chlorotoluene, and *p*-chlorotoluene at three temperatures and the values of excess molar volumes, deviations of isentropic compressibilities, and deviations of molar refractions have been evaluated. The trend of V^E , $\Delta\kappa_S$, and ΔR indicates the presence of specific H-bond interactions of the type O–H \cdots Cl and $\pi\cdots$ H–O between the 1-decanol and the isomeric chlorotoluene molecules.

Acknowledgments Authors are grateful to the Kurukshetra University authorities for providing the necessary facilities to carry out the research work and for an award of a University Research Fellowship to one of the authors.

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