



Densities, Speeds of Sound and Viscosities of Binary Mixtures of Nonan-1-ol with *o*-Chlorotoluene, *m*-Chlorotoluene and *p*-Chlorotoluene at $T = (298.15, 303.15 \text{ and } 308.15) \text{ K}$

Surbhi Soni and Pankaj Sharma*

*Department of Chemistry, Maharishi Markandeshwar University, Sadopur- Ambala, **INDIA**

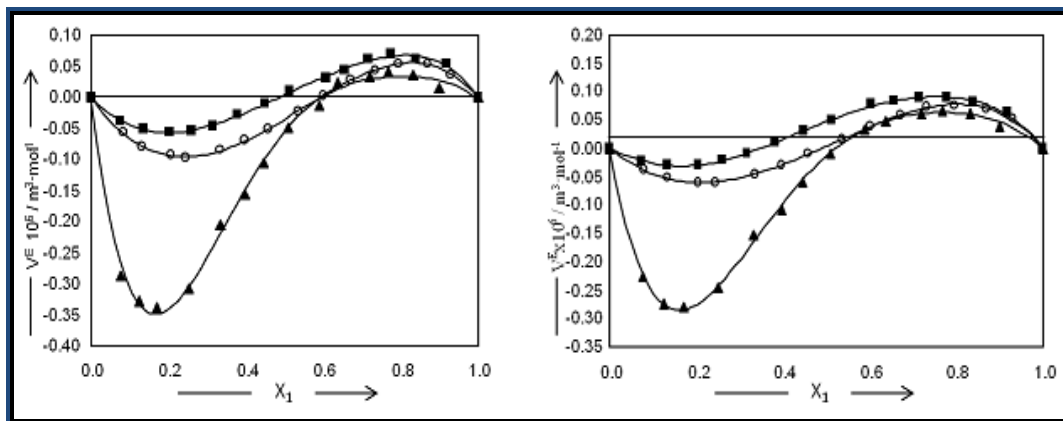
Email: pankz.chem@gmail.com

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ABSTRACT

Densities, speeds of sound, and viscosities of binary mixtures of nonan-1-ol with *o*-chlorotoluene, *m*-chlorotoluene and *p*-chlorotoluene were measured over the entire range of composition from $T = (298.15, 303.15 \text{ and } 308.15) \text{ K}$ and at a pressure of 0.1 MPa. The experimental values of densities were used to calculate the excess molar volumes of the binary liquid mixtures. Excess molar volumes have been fitted to the Redlich-Kister polynomial equation to derive the binary coefficients, and the standard errors between the experimental and the calculated quantities. For the binary mixtures of nonan-1-ol with *o*-chlorotoluene, *m*-chlorotoluene and *p*-chlorotoluene, the curves show sigmoid trend, and the excess molar volumes are negative in the low mole fraction region and positive in the high mole fraction region.

Graphical Abstract:



Keywords: Nonan-1-ol, Excess molar Volume, Densities, Speeds of sound.

INTRODUCTION

Systematic studies of thermodynamic properties of binary liquid mixtures of higher alcohols and isomeric chlorotoluenes are important to understand the nature of molecular interactions and the physicochemical behavior of the binary liquid mixtures [1-5], but the review of the literature on the thermodynamic, acoustic and transport properties of binary mixtures containing higher alcohols with isomeric chlorotoluenes reveals that the data bases are limited. It is, therefore, quite interesting in this area of research to carry out systematic investigations involving the physical properties of the binary liquid mixtures containing higher alcohols with isomeric chlorotoluenes. In an attempt to explore the nature of interactions occurring between the nonan-1-ol with isomeric chlorotoluenes, the densities, speeds of sound, and viscosities of binary mixtures of nonan-1-ol with o-chlorotoluene, m-chlorotoluene and p-chlorotoluene have been measured over the entire range of composition at $T = (298.15, 303.15 \text{ and } 308.15)$ K and at a pressure of 0.1 MPa. From the experimental data, excess molar volumes were calculated. The calculated excess functions have been fitted to the Redlich-Kister polynomial equation to derive the binary coefficients, and the standard errors between the experimental and the calculated quantities.

MATERIALS AND METHODS

Nonan-1-ol (CAS Registry No.: 143-08-8 with mass fraction purity of 0.980), o-chlorotoluene (CAS Registry No.: 95-49-8 with mass fraction purity of 0.980), m-chlorotoluene (CAS Registry No.: 108-41-8 with mass fraction purity of 0.960) and p-chlorotoluene (CAS Registry No.: 106-43-4 with mass fraction purity of 0.990) were obtained from S.D. Fine Chemical Ltd, India and were used after double- distillation and partially degassed with a vacuum pump under nitrogen atmosphere. The purity of these solvents was ascertained by comparing the measured densities, speeds of sound and viscosities of the components at $T = 303.15$ K with the available literature [6-13] shown in the table 1. All the liquids mixtures were prepared by weighing appropriate amounts of pure liquids on an electronic balance (Afcoset-ER-120A, India) with a precision of ± 0.1 mg by syringing each component into airtight stoppered bottles to minimize the evaporation losses. The accuracy of the mole fraction was $\pm 1 \cdot 10^{-4}$.

Table 1: Comparison of Experimental Densities Speeds of Sound u , and Viscosities, η , of Pure Components with Available Literature Values at $T = 303.15$ K

Component	$\rho \cdot 10^{-3} / \text{kg} \cdot \text{m}^{-3}$		$u / \text{m} \cdot \text{s}^{-1}$		$\eta / \text{mPa} \cdot \text{s}$	
	exp.	lit.	exp.	lit.	Exp.	lit.
nonan-1-ol	0.8209	0.8214[13]	1347	1348[13]	7.457	7.806[11]
o-chlorotoluene	1.0723	1.0727[6]	1280	1284[6]	0.894	0.884[6]
m-chlorotoluene	1.0615	1.0652[6]	1276	1280[6]	0.764	0.782[6]
p-chlorotoluene	1.0594	1.0605[6,7]	1270	1271[6,7]	0.770	0.902[6]

Densities, ρ , and speeds of sound, u , of the pure liquids and their mixtures were measured with density and sound speed analyzer apparatus (Anton Paar DSA 5000, Austria-Europe) with precision in densities and speeds of sound better than $\pm 2 \cdot 10^{-6} \text{ g} \cdot \text{cm}^{-3}$ and $\pm 0.01 \text{ m} \cdot \text{s}^{-1}$, respectively and the temperature was kept constant within ± 0.001 K using the Peltier method. The uncertainty in experimental measurements has been found to be lower than $\pm 10^{-4} \text{ g} \cdot \text{cm}^{-3}$ for the density and $\pm 1 \text{ m} \cdot \text{s}^{-1}$ for the speed of sound. The viscosities of the pure liquids and their binary mixtures at 298.15, 303.15 and 308.15 K over the entire range of mixture mole fraction were measured with a modified Ubbelohde suspended level viscometer suspended in a thermostated water bath maintained at ± 0.01 K.

RESULTS AND DISCUSSION

The experimental data of density, ρ , speed of sound, u , viscosity, η , and excess molar volume, V^E , for the studied binary liquid mixtures at $T = (298.15 \text{ to } 308.15) \text{ K}$ and $p = 0.1 \text{ MPa}$ are reported in Table 2.

Table 2: Densities ρ , Excess Molar Volume V^E , Speeds of Sound u and Viscosities of binary liquid mixtures at $T = 298.15 \text{ to } 308.15 \text{ K}$

X	$\rho \cdot 10^{-3}$	$V^E \cdot 10^6$	u	η
	kg·m ⁻³	m ³ ·mol ⁻¹	m·s ⁻¹	mPa·s
T/K=298.15				
<i>x</i> o-chlorotoluene + (1- <i>x</i>) nonan-1-ol				
0.0000	0.8243	0.000	1364	8.859
0.0806	0.8387	-0.056	1358	7.557
0.1328	0.8483	-0.079	1354	6.774
0.2042	0.8620	-0.092	1349	5.786
0.2440	0.8699	-0.096	1345	5.285
0.3346	0.8886	-0.085	1338	4.263
0.3970	0.9022	-0.070	1332	3.661
0.4581	0.9162	-0.050	1327	3.154
0.5361	0.9349	-0.021	1321	2.598
0.6006	0.9513	0.002	1316	2.212
0.6722	0.9706	0.027	1310	1.859
0.7326	0.9878	0.043	1306	1.617
0.7957	1.0068	0.054	1303	1.401
0.8688	1.0303	0.052	1299	1.196
0.9290	1.0510	0.036	1298	1.057
1.0000	1.0771	0.000	1298	0.920
<i>x</i> m-chlorotoluene + (1- <i>x</i>) nonan-1-ol				
0.0000	0.8243	0.000	1364	8.859
0.0731	0.8368	-0.038	1359	7.536
0.1332	0.8474	-0.050	1354	6.496
0.2034	0.8603	-0.055	1348	5.432
0.2589	0.8710	-0.054	1344	4.687
0.3159	0.8823	-0.045	1339	4.039
0.3800	0.8956	-0.028	1333	3.400
0.4477	0.9103	-0.010	1327	2.849
0.5122	0.9250	0.009	1322	2.415
0.6050	0.9475	0.031	1314	1.908
0.6550	0.9603	0.044	1310	1.680
0.7146	0.9762	0.062	1306	1.447
0.7761	0.9937	0.069	1302	1.251
0.8396	1.0127	0.062	1299	1.078
0.9171	1.0375	0.053	1296	0.914
1.0000	1.0664	0.000	1294	0.801
<i>x</i> p-chlorotoluene + (1- <i>x</i>) nonan-1-ol				
0.0000	0.8243	0.000	1364	8.859
0.0751	0.8382	-0.280	1358	7.475
0.1242	0.8471	-0.329	1354	6.665
0.1697	0.8553	-0.339	1351	5.955
0.2503	0.8703	-0.286	1344	4.829
0.3336	0.8864	-0.205	1337	3.860

0.3955	0.8991	-0.155	1332	3.273
0.4439	0.9094	-0.112	1328	2.859
0.5083	0.9237	-0.053	1323	2.412
0.5871	0.9423	-0.001	1316	1.963
0.6374	0.9548	0.022	1312	1.723
0.7195	0.9766	0.036	1306	1.407
0.7669	0.9899	0.040	1302	1.260
0.8308	1.0087	0.035	1298	1.095
0.9002	1.0305	0.020	1295	0.950
1.0000	1.0644	0.000	1294	0.799

T/K=303.15

x o-chlorotoluene + (1- *x*) nonan-1-ol

0.0000	0.8209	0.000	1347	7.457
0.0806	0.8351	-0.047	1342	6.507
0.1328	0.8447	-0.065	1338	5.870
0.2042	0.8582	-0.077	1332	5.019
0.2440	0.8661	-0.080	1329	4.557
0.3346	0.8847	-0.066	1321	3.631
0.3970	0.8983	-0.050	1315	3.068
0.4581	0.9121	-0.031	1310	2.618
0.5361	0.9307	-0.001	1304	2.121
0.6006	0.9470	0.021	1298	1.807
0.6722	0.9662	0.046	1293	1.519
0.7326	0.9833	0.062	1289	1.333
0.7957	1.0022	0.071	1285	1.171
0.8688	1.0256	0.066	1282	1.043
0.9290	1.0461	0.050	1280	0.955
1.0000	1.0723	0.000	1280	0.894

x m-chlorotoluene + (1- *x*) nonan-1-ol

0.0000	0.8209	0.000	1347	7.457
0.0731	0.8332	-0.028	1341	6.352
0.1332	0.8438	-0.039	1336	5.547
0.2034	0.8566	-0.039	1330	4.704
0.2589	0.8672	-0.032	1325	4.109
0.3159	0.8784	-0.020	1320	3.563
0.3800	0.8916	-0.003	1315	3.034
0.4477	0.9062	0.017	1309	2.534
0.5122	0.9208	0.037	1303	2.154
0.6050	0.9431	0.061	1296	1.706
0.6550	0.9559	0.069	1292	1.508
0.7146	0.9718	0.074	1288	1.315
0.7761	0.9892	0.070	1284	1.150
0.8396	1.0082	0.059	1281	1.016
0.9171	1.0329	0.036	1278	0.882
1.0000	1.0615	0.000	1276	0.764

x p-chlorotoluene + (1- *x*) nonan-1-ol

0.0000	0.8209	0.000	1347	7.377
0.0751	0.8345	-0.240	1341	6.312
0.1242	0.8433	-0.292	1337	5.660

0.1697	0.8516	-0.307	1333	5.086
0.2503	0.8664	-0.262	1325	4.183
0.3336	0.8825	-0.187	1317	3.373
0.3955	0.8951	-0.131	1311	2.868
0.4439	0.9053	-0.085	1306	2.526
0.5083	0.9195	-0.030	1300	2.139
0.5871	0.9381	0.012	1292	1.748
0.6374	0.9505	0.035	1288	1.542
0.7195	0.9721	0.057	1281	1.276
0.7669	0.9853	0.061	1277	1.149
0.8308	1.0040	0.053	1274	1.012
0.9002	1.0257	0.031	1271	0.894
1.0000	1.0594	0.000	1270	0.770

T/K=308.15

x o-chlorotoluene + (1- *x*) nonan-1-ol

0.0000	0.8174	0.000	1331	6.044
0.0806	0.8315	-0.037	1325	5.283
0.1328	0.8410	-0.052	1321	4.765
0.2042	0.8545	-0.060	1315	4.077
0.2440	0.8623	-0.059	1311	3.729
0.3346	0.8808	-0.043	1304	3.051
0.3970	0.8942	-0.028	1298	2.626
0.4581	0.9080	-0.010	1293	2.289
0.5361	0.9266	0.016	1286	1.908
0.6006	0.9428	0.038	1281	1.634
0.6722	0.9618	0.059	1275	1.395
0.7326	0.9789	0.071	1271	1.216
0.7957	0.9977	0.077	1268	1.064
0.8688	1.0209	0.069	1264	0.927
0.9290	1.0414	0.052	1263	0.854
1.0000	1.0674	0.000	1262	0.793

x m-chlorotoluene + (1- *x*) nonan-1-ol

0.0000	0.8174	0.000	1331	6.044
0.0731	0.8297	-0.021	1325	5.199
0.1332	0.8402	-0.029	1319	4.567
0.2034	0.8529	-0.027	1313	3.920
0.2589	0.8634	-0.020	1308	3.479
0.3159	0.8745	-0.007	1303	3.046
0.3800	0.8876	0.009	1298	2.634
0.4477	0.9021	0.030	1292	2.238
0.5122	0.9166	0.050	1286	1.918
0.6050	0.9388	0.077	1279	1.525
0.6550	0.9515	0.085	1275	1.349
0.7146	0.9674	0.090	1271	1.171
0.7761	0.9846	0.091	1267	1.020
0.8396	1.0034	0.081	1263	0.891
0.9171	1.0281	0.048	1260	0.774

1.0000	1.0566	0.000	1258	0.705
<i>x</i> p-chlorotoluene + (1- <i>x</i>) nonan-1-ol				
0.0000	0.8174	0.000	1331	6.044
0.0751	0.8308	-0.199	1324	5.239
0.1242	0.8396	-0.260	1320	4.732
0.1697	0.8478	-0.284	1316	4.277
0.2503	0.8626	-0.244	1308	3.539
0.3336	0.8785	-0.162	1300	2.878
0.3955	0.8910	-0.094	1294	2.460
0.4439	0.9011	-0.041	1289	2.175
0.5083	0.9152	0.018	1283	1.860
0.5871	0.9336	0.065	1276	1.523
0.6374	0.9460	0.077	1271	1.348
0.7195	0.9676	0.074	1264	1.120
0.7669	0.9808	0.067	1261	1.016
0.8308	0.9994	0.056	1257	0.896
0.9002	1.0209	0.040	1254	0.795
1.0000	1.0545	0.000	1252	0.704

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

$$V^E = \sum_{i=1}^2 x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (1)$$

where ρ_i is the density of the pure component i , ρ is the density of the mixture, and x_i and M_i are the mole fraction, and the molecular weight (1-nonanol=144.26, o-chlorotoluene = 126.6, m-chlorotoluene=126.6, p-chlorotoluene=126.6) of the component i of the system, respectively.

The experimental results of V^E , were fitted to the Redlich-Kister equation of the type [10]

$$Y(x) = x(1-x) \sum_{k=1}^n A_k (1-2x)^{k-1} \quad (2)$$

where k is the number of estimated parameters and A_k , the polynomial coefficients, were obtained by fitting the equation to the experimental results by least-squares regression method. The standard deviations, σ for V^E were calculated using the relation

$$\sigma(Y) = \left[\sum_i^n \{Y(x)_{\text{exp}} - Y(x)_{\text{cal}}\}^2 / (N - n) \right]^{1/2} \quad (3)$$

where $Y(x)_{\text{exp}}$, $Y(x)_{\text{cal}}$, N and n are values of the experimental and calculated property, the number of data points and the number of parameter of the fitting equation, respectively. The polynomial coefficients and the standard deviation between the experimental and the calculated values of V^E are given in Table 3.

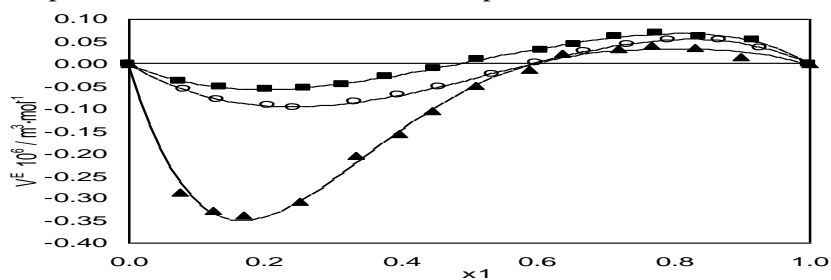
Table 3: Coefficients A_i , of Redlich-Kister equation and standard Deviations σ , for Excess Molar Volume V^E , for binary liquid mixtures at $T = 298.15$ to 308.15 K.

T/K	A_1	A_2	A_3	Σ
<i>x</i> o-chlorotoluene + (1- <i>x</i>) nonan-1-ol				
298.15	-0.142	0.736	0.076	0.0006
303.15	-0.062	0.750	0.080	0.0012
308.15	0.019	0.689	0.063	0.0012
<i>x</i> m-chlorotoluene + (1- <i>x</i>) nonan-1-ol				
298.15	0.018	0.587	0.004	0.0037
303.15	0.136	0.604	-0.118	0.0004
308.15	0.189	0.610	0.015	0.0012
<i>x</i> p-chlorotoluene + (1- <i>x</i>) nonan-1-ol				
298.15	-0.246	1.575	-1.293	0.004
303.15	-0.163	1.468	-1.299	0.003
308.15	0.048	1.612	-2.256	0.003

The plots of V^E with mole fraction, x for the binary mixtures of 1-nonanol with o-chlorotoluene, m-chlorotoluene and p-chlorotoluene at 298.15 K and 308.15 K are depicted in figures 1 and 2 respectively. For these binary liquid mixtures of 1-nonanol with o-chlorotoluene, m-chlorotoluene and p-chlorotoluene the curve is s-shaped and V^E is negative below $x \approx 0.53$ in (o-chlorotoluene + 1-nonanol), $x \approx 0.44$ in (m-chlorotoluene + 1-nonanol) and $x \approx 0.58$ in (p-chlorotoluene + 1-nonanol) binary mixtures, and it becomes positive above the mole fraction range indicated for the binary mixtures. Similar trend is observed for these systems studied at different temperatures and the maxima in V^E curves occur at $x \approx 0.79$ in (o-chlorotoluene + 1-nonanol), at $x \approx 0.77$ in (m-chlorotoluene + 1-nonanol) and at $x \approx 0.76$ in (p-chlorotoluene + 1-nonanol) systems. The nature of V^E versus x_1 curves for all the binary mixtures in the investigated temperature interval is almost identical, but the V^E , values increase with the increase of temperature. The excess molar volumes, V^E , at the minimum of the curves vary in the order:

$$V_{p-cl-tolu}^E > V_{o-cl-tolu}^E > V_{m-cl-tolu}^E$$

Since the molar volumes of 1-nonanol (174.99×10^{-6}) $\text{m}^3 \text{mol}^{-1}$, o-chlorotoluene (117.52×10^{-6}) $\text{m}^3 \text{mol}^{-1}$, m-chlorotoluene (118.71×10^{-6}) $\text{m}^3 \text{mol}^{-1}$, p-chlorotoluene (118.94×10^{-6}) $\text{m}^3 \text{mol}^{-1}$ differ considerably, it seems that the isomeric chlorotoluenes molecules intercalate between the polymeric entities of 1-nonanol and may involve in the formation of specific H-bond interactions of the type Cl...H-O, and π - bond interaction of the type π ...H-O, between the isomeric chlorotoluenes and the 1- nonanal molecules resulting in the negative value of V^E in the low mole fraction range indicated for these binary mixtures. However, in the higher concentration regions, due to the disruption of H-bonding in 1-nonanol and the dipolar interactions in the isomeric chlorotoluenes, there is an increase in the total volume of the solutions indicating weaker dispersive interactions between the component molecules.

**Figure 1:** Excess molar volume, $V^E \times 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$, plotted against mole fraction, x , for [*x* isomeric chlorotoluene and] systems at $T = 298.15$ K: (○), o-chlorotoluene; (■), m-chlorotoluene; (▲), p-chlorotoluene.

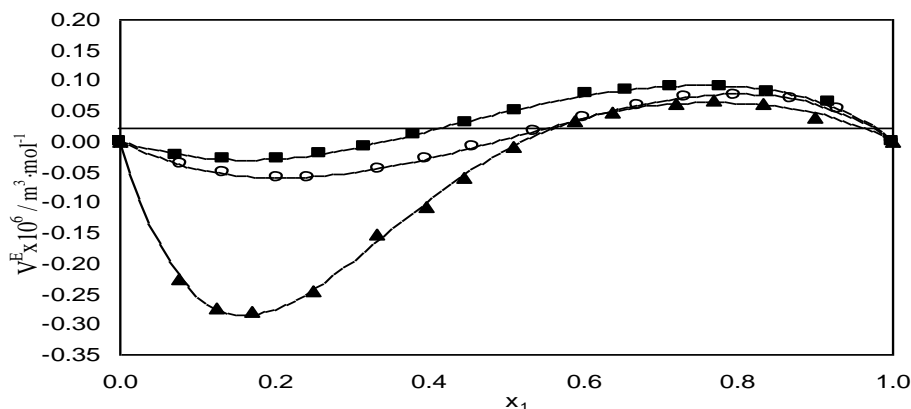


Figure 2: Excess molar volume, $V^E \times 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$, plotted against mole fraction, x , for [x isomeric chlorotoluene and] systems at $T = 308.15 \text{ K}$: (\circ), o-chlorotoluene; (\blacksquare), m-chlorotoluene; (\blacktriangle), p-chlorotoluene.

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AUTHORS' ADDRESSES

1. **Surbhi Soni**

Assistant Professor, Department of Chemistry,
Maharishi Markandeshwar University, Sadopur- Ambala (India) 134007.
Phone: 07988417501, E-mail: uniquesurbhi@gmail.com

2. **Pankaj Sharma**

Assistant Professor, Department of Chemistry,
Maharishi Markandeshwar University, Sadopur- Ambala (India) 134007.
Phone: 08059933198, E-mail: pankz.chem@gmail.com