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Studies of Mixing Properties of Binary Mixtures of 1-Propanolwithtoluene, Isomeric Chlorotoluenes and Toluidineat T = (298.15, 303.15, 308.15, and 313.15) K

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Abstract:
The density (ρ), speed of sound (u) of binary mixtures of 1-propanol with toluene, isomeric chlorotoluenes and toluidine at T = (298.15,303.15, 308.15 and 313.15) K were measured. The experimental data have been used to calculate excess volume (V^E) and excess isentropic compressibility (K_s^E) over the wide range of composition. These excess thermodynamic data were tabulated and presented graphically. The excess properties have been fitted by Redlich-Kister and Hwang polynomial equations and the results were used to obtain fitting parameters and root mean square deviations. Further the theoretical models namely crystal field theory (CFT) and free length theory (FLT) were used to analyze the experimental speed of sound data. More over the experimental results have been used to understand the nature of interactions between unlike molecules in terms of hydrogen bonding, dipole-dipole interaction, and dispersive forces.

Keywords: *Density, speed of sound, excess volume, excess isentropic compressibility*

1. Introduction

The investigation of excess thermodynamic properties of binary organic liquid mixtures using thermodynamic properties such as densities, speeds of sound and viscosities are very much necessary to understand the intermolecular interactions, structural effects and the extent of deviations from non-ideality of organic liquid mixtures at different temperatures[i-iii].The immense knowledge of thermodynamic properties of binary liquid mixtures is important in many industrial processes which include design calculation, heat transfer, mass transfer, fluid flow, etc.[iv].Moreover, the understanding of thermodynamic properties of binary mixtures of alkanols, aromatic hydrocarbons and aromatic halo compounds is essential due to their wide utility in different fields such as plastics, detergents, rubber, aerosol propellants, pesticides, industrial solvents, pharmaceuticals and dye industries [iii-vi].1-Alkanols are said to be resourceful compounds and play a vital role in many industrial, chemical and technological applications [vii]. Toluene and isomeric chlorotoluenes compounds are used as solvents and intermediates in chemical processes in many industries respectively [vi].

Review of literature shows that 1-alkanols are polar self-associated molecules through hydrogen bonding and its self-associationvary when they are mixed with non-polar and polar compounds due to difference in specific intermolecular interactions between them [viii-xi]. A survey of literature has shown that, few studies on densities and derived properties of binary mixtures containing 1-propanol with toluene [xii-xxi], o-chlorotoluene [iii], p-chlorotoluene [xxii] were reported. Moreover, densities of binary mixtures of 1-propanol with toluene at different temperatures were measured but not the speed of sound data at different temperatures. In thereported thermodynamic data of 1-propanol with o-chlorotoluene and p-chlorotoluene at 298.15K to 308.15K,no correlation of excess properties with Hwang polynomial equation and speed of sound with collision factor (CFT) and free length (FLT) theories was found.

To the best of our knowledge no experimental data of densities and speedof sound binary mixture of 1-propanol with m-chlorotoluene and toluidine were found at different temperatures. In the present study, we measured densities, speeds of sound of binary mixtures of 1-propanol with toluene, isomeric chlorotoluenes and toluidine at different temperatures(298.15K-313.15K) and calculated excess

volumes and excess isentropic compressibility. An effort was made to investigate the nature of molecular interactions and effect of degree of self-association of 1-propanol at different temperatures withthe introduction of chloro group and amino groups and also change of position(o-,m-,p-) of chloro group in toluene molecule. The variation in the sign and magnitude of excess properties at different temperatures under study were also analysed using graphical data. The obtained excess properties data was correlated using Redlich-kister and Hwang polynomial equations and also the speed of sound data was correlated using collision factor (CFT) and free length (FLT) theories.

2. Experimental

2.1. Chemicals

In the present study, all the chemicals were procured from S.D fine Chemicals, Ltd., India and their purities, CAS number, purity analysis method and water content in mass fraction were reported in Table 1.Earlier to the experimental measurements the chemicals under study are subjected to double distillation and were partially degasified using vacuum pump in an inert atmosphere. The purity of the chemicals was also assessed by comparing the measured density and speed of sound values at 298.15K which were in good agreement with the literature values [iii,viii,xxiii-xxxiii] and were reported in Table 2. In the present study all the binary mixtures were prepared in glass bottles with air tight stoppers and sufficient precautions were taken to minimize evaporation losses. Mass measurements of solutions were done using Acculab ALC-210.4 digital electronic balance with a precision of ± 0.1mg.

Compound	**Supplier**	**CAS number**	**Purity in mass fraction (as received from supplier)**	**Water content (%)**
1-propanol	S.D.fine chemicals	71-23-8	0.995	0.036
Toluene	S.D.fine chemicals	108-88-3	0.995	0.038
(o)Cl-Toluene	S.D.fine chemicals	95-49-8	0.995	0.040
(m)Cl-Toluene	S.D.fine chemicals	108-41-8	0.998	0.050
(p)Cl-Toluene	S.D.fine chemicals	106-43-4	0.995	0.048
Toluidine	S.D.fine chemicals	95-53-4	0.995	0.045

Table 1: Name of the chemical, supplier, CAS number, purity in mass fraction and water content (in %) of the chemicals used in this work

Compound	**ρ (g. cm^{-3})**		**u (m.s^{-1})**		**α (10^{-3}K^{-1})**	**C_p (JK^{-1}mol^{-1})**
	Exp.	**Lit.**	**Exp.**	**Lit.**		
1-propanol	0.79982	0.80050[23] 0.80009[24] 0.79965[3] 0.79960[25]	1204	1206.54[3] 1205.93[27]	1.0002	144.47[27]
Toluene	0.86223	0.86223[3] 0.86221[29	1302	1303.92[3] 1304.00[29]	1.0723	157.06[3,28]
(o)Cl-Toluene	1.07763	1.07738[3] 1.07741[8]	1300	1299.82[3] 1301.00[8]	0.8781	177.79[3,27]
(m)Cl-Toluene	1.06725	1.06721[3] 1.06729[8]	1296	1296.97[3] 1298.00[8]	0.8387	171.13[3,27]
(p)Cl-Toluene	1.06512	1.06510[3] 1.06511[8]	1290	1288[3] 1289[8]	1.0645	171.38[3,27]
Toluidine	0.99458	0.99435[30] 0.99430[31]	1603.62	1602.57[30] 1603[32]	0.8290	217.4[30,33]

Table 2: Density (ρ), speed of sound (u), α and C_p values of the pure components at T=298.15 K and atmospheric pressure respectively

2.2. Apparatus and Procedure

The density measurements were carried using a Rudolph Research Analytical digital densitimeter (DDM-2911 Model), furnished with a built- in solid-state thermostat and a resident program. After preparing the sample, with the help of a medical syringe the bubble-free homogeneous sample was transferred into the U-tube of the densitimeter. The speeds of sound of binary mixtures were measured using a multi frequency ultrasonic interferometer (F-05 Model, Mittal Enterprise, New Delhi, India) operated at 2 MHz, by circulating water from a thermostatically controlled bath. The values of the sound speed are accurate to ± 0.5 %.

3. Results and Discussion

3.1. Excess Molar Volumes (V^E)

The experimental density values of 1-propanol with toluene, isomeric chlorotoluene and toluidine binary mixtures were measured over the whole composition range at temperatures T=298.15K to313. 15K.These values were used to calculate excess volume (V^E) using the following equation

$$V^E / cm^3 mol^{-1} = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (1)$$

where $x_1$andx_2 are the mole fractions, ρ_1,ρ_2,and ρare densities of the pure components and binary mixture and M_1, M_2 are molecular weights of 1-propanol and toluene, isomeric chlorotoluenes and toluidine respectively.

The calculated excess volume (V^E) values for the binary mixtures of 1-propanol with toluene, isomeric chlorotoluenes and toluidine molecules were corresponded with Redlich-Kister [xxxiv] and Hwang [xxxv] polynomial equations respectively and are reported in Table 3.

Redlich–Kister: $V^E / cm^3 mol^{-1} = x_1 x_2 \left[a_0 + a_1 (x_1 - x_2) + a_2 (x_1 - x_2)^2 \right]$ (2)

Hwang: $V^E / cm^3 mol^{-1} = x_1 x_2 \left[b_0 + b_1 x_1^{\ 3} + b_2 x_2^{\ 3} \right]$ (3)

where$x_1$and$x_2$are the mole fractions of 1-propanol and toluene, isomeric chlorotoluenes and toluidine ; a_0, a_1 and a_2 and b_0, b_1 and b_2 are adjustable parameters. The 'b' co-efficients in the above equation was depicted previously [xxxvi, xxxvii].

The standard deviations in excess volumes for the binary mixtures of 1-propanol with toluene, isomeric chlorotoluenes and toluidine were obtained by the using the following relation,

$$\sigma\left(V^E / cm^3 mol^{-1}\right) = \left[\frac{\sum (V^E_{\exp} - V^E_{cal})^2}{n - p} \right]^{\frac{1}{2}} \quad (4)$$

where 'n' is the number of results and 'p' is the number of parameters used in Eq. (2&3). The values of adjusted parameters along with standard deviations σ (V^E) were reported in the Table 4.

x_1	Density (ρ) (g cm^{-3})	V^E /(cm^3 mol^{-1})		
		Exp.	**Redlich–Kister**	**Hwang**
1-propanol(1) + Toluene(2) T=298.15K				
0.1365	0.85550	0.059	0.056	0.059
0.2623	0.84916	0.068	0.070	0.068
0.3787	0.84302	0.054	0.058	0.055
0.4867	0.83698	0.031	0.034	0.034
0.5871	0.83099	0.004	0.007	0.010
0.6808	0.82492	-0.014	-0.015	-0.013
0.7684	0.81881	-0.027	-0.030	-0.029
0.8505	0.81261	-0.030	-0.033	-0.035
0.8896	0.80946	-0.027	-0.030	-0.033
0.9275	0.80630	-0.023	-0.024	-0.027
0.9643	0.80310	-0.015	-0.014	-0.016
0.9787	0.80179	-0.009	-0.009	-0.010
T=303.15K				
0.1365	0.85088	0.066	0.066	0.068
0.2623	0.84460	0.078	0.079	0.077
0.3787	0.83852	0.067	0.066	0.063
0.4867	0.83255	0.044	0.042	0.041
0.5871	0.82663	0.016	0.016	0.019
0.6808	0.82067	-0.005	-0.004	-0.001
0.7684	0.81462	-0.017	-0.017	-0.016
0.8505	0.80852	-0.022	-0.021	-0.023
0.8896	0.80541	-0.02	-0.019	-0.022
0.9275	0.80229	-0.015	-0.015	-0.019
0.9643	0.79915	-0.010	-0.009	-0.011
0.9787	0.79787	-0.005	-0.006	-0.007
T=308.15K				
0.1365	0.84621	0.068	0.068	0.070
0.2623	0.83999	0.083	0.084	0.082

0.3787	0.83398	0.072	0.074	0.071
0.4867	0.82805	0.053	0.051	0.051
0.5871	0.82220	0.027	0.027	0.029
0.6808	0.81630	0.007	0.006	0.008
0.7684	0.81038	-0.010	-0.009	-0.008
0.8505	0.80435	-0.015	-0.015	-0.016
0.8896	0.80129	-0.014	-0.014	-0.017
0.9275	0.79823	-0.012	-0.012	-0.015
0.9643	0.79513	-0.007	-0.007	-0.009
0.9787	0.79390	-0.005	-0.004	-0.006
T=313.15K				
0.1365	0.84170	0.072	0.073	0.075
0.2623	0.83556	0.087	0.089	0.088
0.3787	0.82959	0.080	0.078	0.075
0.4867	0.82374	0.060	0.055	0.054
0.5871	0.81794	0.035	0.031	0.033
0.6808	0.81213	0.013	0.011	0.014
0.7684	0.80629	-0.006	-0.002	-0.001
0.8505	0.80033	-0.011	-0.008	-0.010
0.8896	0.79731	-0.010	-0.008	-0.011
0.9275	0.79430	-0.009	-0.007	-0.010
0.9643	0.79124	-0.004	-0.004	-0.006
0.9787	0.79000	-0.001	-0.003	-0.004
1-propanol(1) + (o)chlorotoluene(2) T=298.15K				
0.1480	1.04953	0.034	0.033	0.035
0.2809	1.02194	0.013	0.013	0.009
0.4012	0.99456	-0.027	-0.027	-0.031
0.5103	0.96725	-0.073	-0.068	-0.068
0.6099	0.93975	-0.100	-0.099	-0.095
0.7010	0.91214	-0.115	-0.114	-0.111
0.7848	0.88433	-0.112	-0.112	-0.111
0.8621	0.85634	-0.091	-0.092	-0.095
0.8986	0.84224	-0.070	-0.075	-0.079
0.9336	0.82814	-0.051	-0.054	-0.058
0.9674	0.81403	-0.030	-0.029	-0.032
0.9806	0.80835	-0.019	-0.018	-0.020
T=303.15K				
0.1480	1.04477	0.048	0.052	0.054
0.2809	1.01720	0.032	0.032	0.029
0.4012	0.98982	-0.001	-0.012	-0.015
0.5103	0.96259	-0.048	-0.055	-0.055
0.6099	0.93529	-0.086	-0.087	-0.083
0.7010	0.90779	-0.104	-0.102	-0.098
0.7848	0.88009	-0.102	-0.099	-0.098
0.8621	0.85223	-0.085	-0.080	-0.083
0.8986	0.83821	-0.068	-0.065	-0.069
0.9336	0.82418	-0.050	-0.046	-0.051
0.9674	0.81009	-0.026	-0.024	-0.028
0.9806	0.80440	-0.012	-0.015	-0.017
T=308.15K				
0.1480	1.04007	0.054	0.058	0.060
0.2809	1.01249	0.047	0.044	0.040
0.4012	0.98520	0.011	0.004	0.001
0.5103	0.95799	-0.032	-0.037	-0.037
0.6099	0.93070	-0.065	-0.068	-0.064
0.7010	0.90329	-0.084	-0.083	-0.080

0.7848	0.87569	-0.085	-0.083	-0.082
0.8621	0.84797	-0.073	-0.068	-0.071
0.8986	0.83404	-0.061	-0.055	-0.060
0.9336	0.82007	-0.043	-0.039	-0.044
0.9674	0.80604	-0.022	-0.021	-0.024
0.9806	0.80040	-0.010	-0.013	-0.015
T=313.15K				
0.1480	1.03543	0.059	0.064	0.066
0.2809	1.00790	0.054	0.051	0.048
0.4012	0.98065	0.021	0.013	0.010
0.5103	0.95350	-0.020	-0.027	-0.027
0.6099	0.92628	-0.052	-0.057	-0.053
0.7010	0.89895	-0.071	-0.072	-0.068
0.7848	0.87149	-0.077	-0.072	-0.071
0.8621	0.84386	-0.065	-0.059	-0.062
0.8986	0.82999	-0.054	-0.048	-0.052
0.9336	0.81607	-0.038	-0.034	-0.038
0.9674	0.80213	-0.019	-0.018	-0.021
0.9806	0.79651	-0.007	-0.011	-0.013
1-propanol(1) + (m)chlorotoluene(2) T=298.15K				
0.1492	1.04002	0.053	0.051	0.054
0.2829	1.01330	0.049	0.049	0.046
0.4035	0.98685	0.017	0.020	0.017
0.5127	0.96050	-0.023	-0.016	-0.015
0.6122	0.93404	-0.049	-0.048	-0.045
0.7031	0.90751	-0.069	-0.070	-0.066
0.7865	0.88082	-0.074	-0.077	-0.076
0.8633	0.85398	-0.064	-0.068	-0.071
0.8994	0.84051	-0.054	-0.057	-0.061
0.9342	0.82699	-0.040	-0.042	-0.047
0.9677	0.81347	-0.026	-0.023	-0.026
0.9808	0.80800	-0.015	-0.014	-0.016
T=303.15K				
0.1492	1.03558	0.059	0.060	0.062
0.2829	1.00885	0.060	0.059	0.056
0.4035	0.98240	0.034	0.032	0.029
0.5127	0.95607	-0.003	-0.004	-0.004
0.6122	0.92972	-0.037	-0.036	-0.033
0.7031	0.90327	-0.059	-0.057	-0.054
0.7865	0.87668	-0.067	-0.065	-0.065
0.8633	0.84991	-0.057	-0.058	-0.061
0.8994	0.83649	-0.049	-0.049	-0.053
0.9342	0.82302	-0.036	-0.036	-0.041
0.9677	0.80953	-0.021	-0.020	-0.023
0.9808	0.80409	-0.012	-0.012	-0.014
T=308.15K				
0.1492	1.03114	0.062	0.063	0.065
0.2829	1.00442	0.067	0.066	0.064
0.4035	0.97799	0.042	0.042	0.039
0.5127	0.95165	0.009	0.009	0.010
0.6122	0.92529	-0.018	-0.021	-0.018
0.7031	0.89890	-0.043	-0.042	-0.039
0.7865	0.87240	-0.054	-0.052	-0.051
0.8633	0.84574	-0.049	-0.048	-0.050
0.8994	0.83234	-0.039	-0.041	-0.045
0.9342	0.81893	-0.029	-0.030	-0.034

0.9677	0.80552	-0.019	-0.017	-0.019
0.9808	0.80009	-0.009	-0.010	-0.012
T=313.15K				
0.1492	1.02672	0.068	0.070	0.072
0.2829	1.00005	0.071	0.071	0.069
0.4035	0.97361	0.053	0.046	0.043
0.5127	0.94731	0.021	0.015	0.016
0.6122	0.92100	-0.007	-0.011	-0.008
0.7031	0.89464	-0.028	-0.028	-0.025
0.7865	0.86819	-0.039	-0.035	-0.034
0.8633	0.84163	-0.038	-0.031	-0.034
0.8994	0.82828	-0.029	-0.026	-0.030
0.9342	0.81490	-0.019	-0.019	-0.023
0.9677	0.80155	-0.010	-0.011	-0.013
0.9808	0.79619	-0.005	-0.006	-0.008
1-propanol(1) + (p) chlorotoluene (2) T=298.15K				
0.1495	1.03878	-0.020	-0.022	-0.020
0.2834	1.01265	-0.062	-0.062	-0.065
0.4040	0.98660	-0.110	-0.106	-0.108
0.5132	0.96046	-0.146	-0.143	-0.142
0.6126	0.93417	-0.168	-0.167	-0.163
0.7035	0.90771	-0.172	-0.173	-0.170
0.7868	0.88106	-0.158	-0.160	-0.159
0.8635	0.85418	-0.124	-0.126	-0.129
0.8996	0.84065	-0.098	-0.102	-0.106
0.9344	0.82712	-0.073	-0.073	-0.076
0.9678	0.81353	-0.042	-0.039	-0.041
0.9808	0.80802	-0.023	-0.024	-0.026
T=303.15K				
0.1495	1.03332	-0.015	-0.017	-0.015
0.2834	1.00733	-0.053	-0.052	-0.054
0.4040	0.98139	-0.094	-0.091	-0.093
0.5132	0.95539	-0.128	-0.125	-0.124
0.6126	0.92924	-0.146	-0.147	-0.144
0.7035	0.90298	-0.153	-0.154	-0.151
0.7868	0.87650	-0.139	-0.143	-0.142
0.8635	0.84987	-0.112	-0.113	-0.116
0.8996	0.83647	-0.091	-0.091	-0.095
0.9344	0.82300	-0.064	-0.065	-0.069
0.9678	0.80956	-0.039	-0.035	-0.037
0.9808	0.80409	-0.020	-0.021	-0.023
T=308.15K				
0.1495	1.02781	-0.010	-0.011	-0.009
0.2834	1.00193	-0.041	-0.041	-0.043
0.4040	0.97612	-0.079	-0.076	-0.078
0.5132	0.95024	-0.107	-0.106	-0.106
0.6126	0.92425	-0.125	-0.126	-0.123
0.7035	0.89812	-0.129	-0.131	-0.129
0.7868	0.87184	-0.119	-0.121	-0.121
0.8635	0.84542	-0.096	-0.096	-0.098
0.8996	0.83212	-0.077	-0.077	-0.080
0.9344	0.81881	-0.057	-0.055	-0.058
0.9678	0.80547	-0.033	-0.029	-0.032
0.9808	0.80005	-0.016	-0.018	-0.02
T=313.15K				
0.1495	1.02246	-0.008	-0.004	-0.003

0.2834	0.99669	-0.032	-0.035	-0.037
0.4040	0.97100	-0.065	-0.069	-0.071
0.5132	0.94523	-0.089	-0.096	-0.095
0.6126	0.91941	-0.107	-0.110	-0.108
0.7035	0.89344	-0.111	-0.112	-0.110
0.7868	0.86735	-0.103	-0.100	-0.100
0.8635	0.84110	-0.081	-0.076	-0.078
0.8996	0.82792	-0.065	-0.061	-0.063
0.9344	0.81470	-0.046	-0.042	-0.045
0.9678	0.80146	-0.025	-0.022	-0.024
0.9808	0.79609	-0.010	-0.014	-0.015
1-propanol (1) + Toluidine (2) T=298.15K				
0.1374	0.97575	-0.069	-0.073	-0.071
0.2639	0.95682	-0.123	-0.124	-0.125
0.3806	0.93783	-0.171	-0.161	-0.163
0.4887	0.91866	-0.199	-0.187	-0.187
0.5891	0.89932	-0.209	-0.200	-0.199
0.6826	0.87977	-0.199	-0.198	-0.197
0.7699	0.86006	-0.174	-0.179	-0.179
0.8515	0.84018	-0.134	-0.141	-0.142
0.8904	0.83012	-0.103	-0.114	-0.116
0.9281	0.82011	-0.077	-0.081	-0.084
0.9646	0.81001	-0.043	-0.044	-0.045
0.9789	0.80599	-0.031	-0.027	-0.028
T=303.15K				
0.1374	0.97134	-0.047	-0.050	-0.048
0.2639	0.95239	-0.098	-0.098	-0.099
0.3806	0.93343	-0.145	-0.139	-0.141
0.4887	0.91431	-0.175	-0.168	-0.169
0.5891	0.89503	-0.188	-0.183	-0.182
0.6826	0.87555	-0.182	-0.182	-0.180
0.7699	0.85593	-0.162	-0.163	-0.163
0.8515	0.83612	-0.124	-0.127	-0.128
0.8904	0.82609	-0.094	-0.102	-0.104
0.9281	0.81612	-0.069	-0.072	-0.075
0.9646	0.80607	-0.037	-0.038	-0.040
0.9789	0.80208	-0.027	-0.023	-0.025
T=308.15K				
0.1374	0.96710	-0.037	-0.040	-0.038
0.2639	0.94807	-0.080	-0.080	-0.081
0.3806	0.92904	-0.120	-0.116	-0.118
0.4887	0.90992	-0.149	-0.144	-0.144
0.5891	0.89069	-0.166	-0.161	-0.159
0.6826	0.87128	-0.164	-0.163	-0.161
0.7699	0.85173	-0.148	-0.149	-0.148
0.8515	0.83198	-0.113	-0.118	-0.119
0.8904	0.82206	-0.091	-0.095	-0.098
0.9281	0.81208	-0.064	-0.068	-0.071
0.9646	0.80208	-0.035	-0.036	-0.038
0.9789	0.79810	-0.025	-0.022	-0.024
T=313.15K				
0.1374	0.96284	-0.023	-0.022	-0.020
0.2639	0.94379	-0.061	-0.061	-0.063
0.3806	0.92477	-0.100	-0.101	-0.103
0.4887	0.90569	-0.132	-0.132	-0.132
0.5891	0.88648	-0.148	-0.149	-0.147

0.6826	0.86713	-0.149	-0.151	-0.148
0.7699	0.84765	-0.137	-0.136	-0.135
0.8515	0.82797	-0.105	-0.105	-0.107
0.8904	0.81807	-0.084	-0.084	-0.087
0.9281	0.80815	-0.060	-0.059	-0.062
0.9646	0.79821	-0.034	-0.031	-0.033
0.9789	0.79416	-0.017	-0.019	-0.021

Table 3: Mole fraction of 1-propanol (x_1), densities (ρ),experimental excess volumes (V^E) and predicted excess volumes(V^E) Redlich–Kister(eq.2) and Hwang(eq.3) at T = 298.15–313.15 K for the binary mixtures of 1-propanol with Toluene, (o)chlorotoluene, (m)chlorotoluene, (p)chlorotoluene and Toluidine

Temperature	**Redlich-Kister**				**Hwang**			
	a_0	a_1	a_2	$\sigma(V^E)$ $cm^3.mol^{-1}$	b_0	b_1	b_2	$\sigma(V^E)$ $cm^3.mol^{-1}$
1-propanol (1) + Toluene (2)								
298.15K	0.1224	-0.5203	-0.0412	0.0029	0.1361	-0.6744	0.5645	0.0037
303.15K	0.1536	-0.5051	0.0695	0.0012	0.1304	-0.5086	0.6940	0.0027
308.15K	0.1920	-0.4818	0.0597	0.0011	0.1721	-0.4940	0.6532	0.0023
313.15K	0.2066	-0.4755	0.1302	0.0031	0.1632	-0.3925	0.7397	0.0037
1-propanol (1) + (o)chlorotoluene (2)								
298.15K	-0.2574	-0.7217	0.0192	0.0027	-0.2638	-0.8336	0.8847	0.0054
303.15K	-0.2052	-0.7599	0.1588	0.0053	-0.2581	-0.6929	1.1163	0.0065
308.15K	-0.1340	-0.7245	0.1665	0.0045	-0.1895	-0.6405	1.0845	0.0055
313.15K	-0.0940	-0.7040	0.2100	0.0057	-0.1640	-0.5581	1.1181	0.0061
1-propanol (1) + (m)chlorotoluene (2)								
298.15K	-0.0450	-0.6840	-0.0640	0.0035	-0.0240	-0.8996	0.7290	0.0053
303.15K	0.0010	-0.6750	-0.0100	0.0015	0.0043	-0.8169	0.7902	0.0044
308.15K	0.0530	-0.6310	0.0001	0.0018	0.0529	-0.7511	0.7513	0.0035
313.15K	0.0750	-0.5740	0.1430	0.0042	0.0273	-0.4927	0.8740	0.0049
1-propanol (1) + (p)chlorotoluene (2)								
298.15K	-0.5550	-0.6260	-0.1120	0.0029	-0.1518	-0.8946	0.5959	0.0042
303.15K	-0.4840	-0.5750	-0.1090	0.0026	-0.4477	-0.8299	0.5392	0.0034
308.15K	-0.4110	-0.5100	-0.0610	0.0021	-0.3907	-0.6885	0.5258	0.0024
313.15K	-0.3720	-0.4310	0.0720	0.0046	-0.3960	-0.4171	0.6091	0.0046
1-propanol (1) + Toluidine (2)								
298.15K	-0.7570	-0.3560	-0.2160	0.0078	-0.6850	-0.7118	0.1358	0.0083
303.15K	-0.6830	-0.4100	-0.0630	0.0048	-0.6620	-0.5721	0.4041	0.0055
308.15K	-0.5860	-0.4200	-0.1010	0.0038	-0.5523	-0.6347	0.3653	0.0049
313.15K	-0.5370	-0.4500	0.0440	0.0014	-0.5517	-0.4770	0.5944	0.0023

Table 4: Standard deviation $\sigma(V^E)$ and values of constants (a_0, a_1, a_2; b_0, b_1, b_2) for Redlich-Kister, Eq. (2) and Hwang, Eq. (3) for the binary mixtures of 1-propanol with Toluene, (o)chlorotoluene, (m)chlorotoluene, (p)chlorotoluene and Toluidine.

With the aid of excess volumes data, we could understand the physical, chemical and structural effects existing among the mixtures. The physical effects include dispersion forces and weak nonspecific interactions while the chemical effects were due to breaking up of associate molecules present in the pure components, leading to positive (V^E) deviations. The structural effect includes specific interactions like H-bonding, donor-acceptor complexes and strong dipole-dipole interactions prevailing among the component molecules in the mixture, leading to negative (V^E) deviations [xxxviii-xl]. The V^E plots for the binary mixtures of 1-propanol with toluene, isomeric chlorotoluenes and toluidine molecules were represented at temperatures T=298.15K to 313.15K respectively in figures 1 to 6.

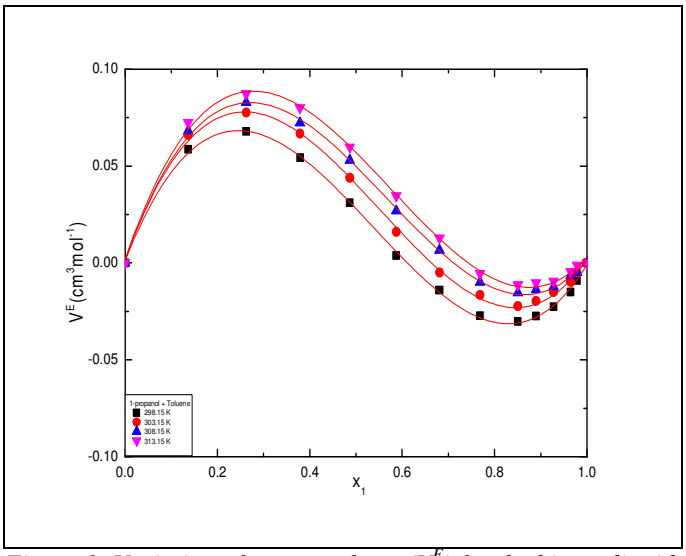

Figure 1: Variation of excess volume (V^E) for the binary liquid mixture of 1-propanol (1) with Toluene (2) at 298.15 K (■), 303.15 K (●), 308.15 K (▲) and 313.15 K (▼).

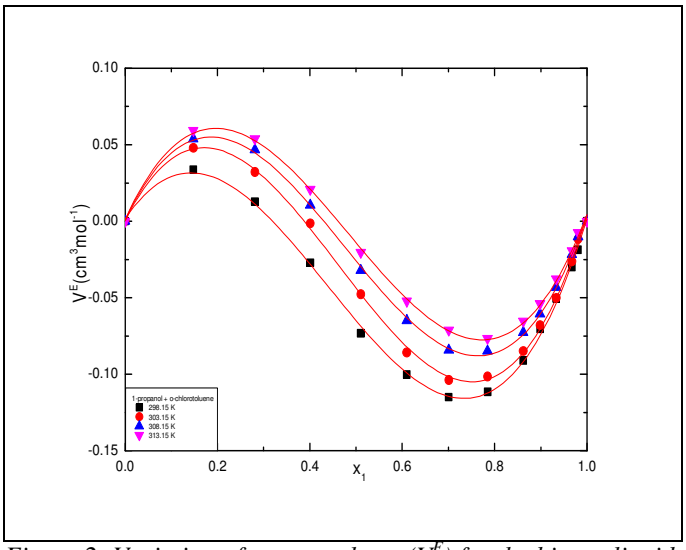

Figure 2: Variation of excess volume (V^E) for the binary liquid mixture of 1-propanol (1) with (o)chlorotoluene (2) at 298.15 K (■), 303.15 K (●), 308.15 K (▲) and 313.15 K (▼).

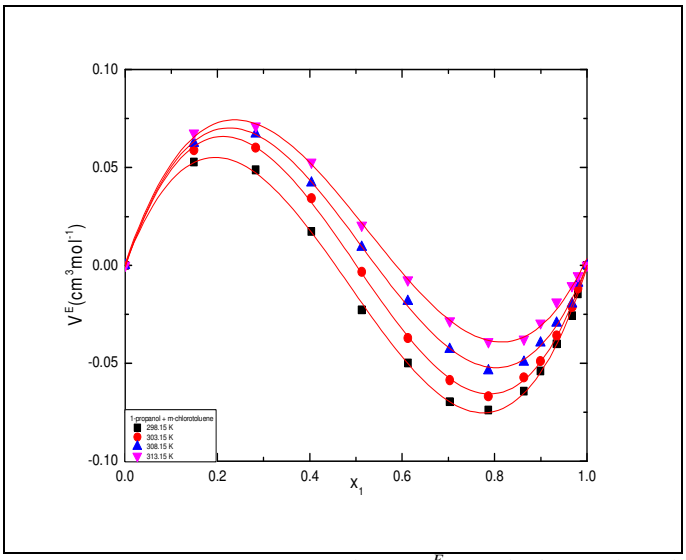

Figure 3: Variation of excess volume (V^E) for the binary liquid mixture of 1-propanol (1) with (m)chlorotoluene (2) at 298.15 K (■), 303.15 K (●), 308.15 K (▲) and 313.15 K (▼).

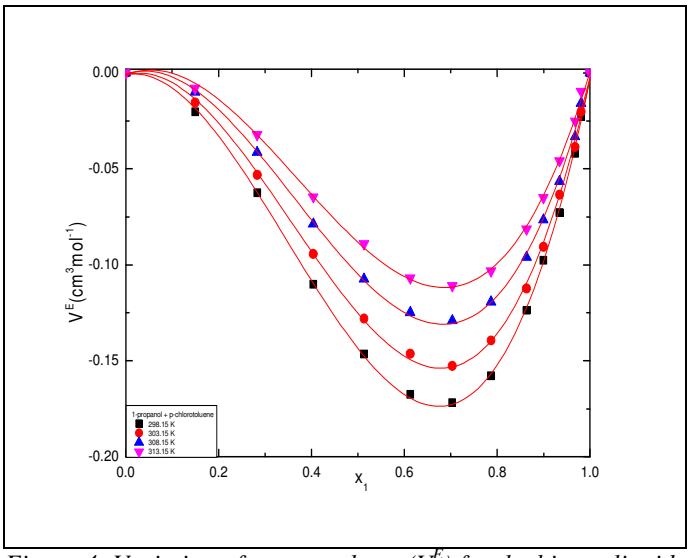

Figure 4: Variation of excess volume (V^E) for the binary liquid mixture of 1-propanol (1) with(p)chlorotoluene (2) at 298.15 K (■), 303.15 K (●), 308.15 K (▲) and 313.15 K (▼).

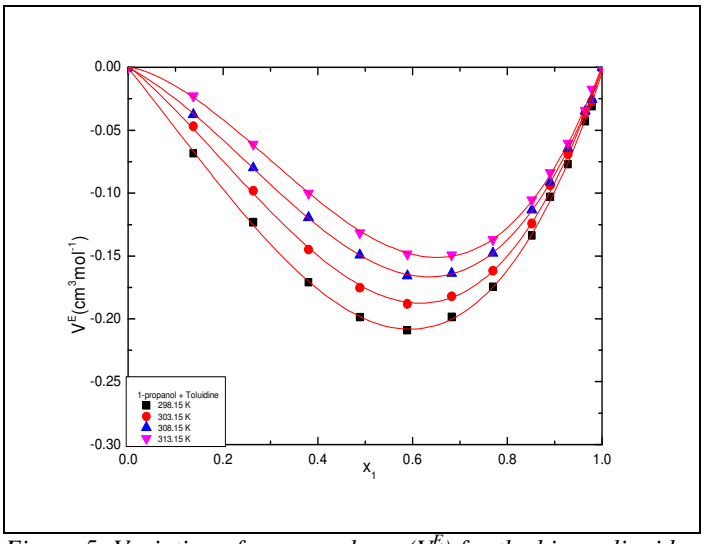

Figure 5: Variation of excess volume (V^E) for the binary liquid mixture of 1-propanol (1) with Toluidine (2) at 298.15 K (■), 303.15 K (●), 308.15 K (▲) and 313.15 K (▼).

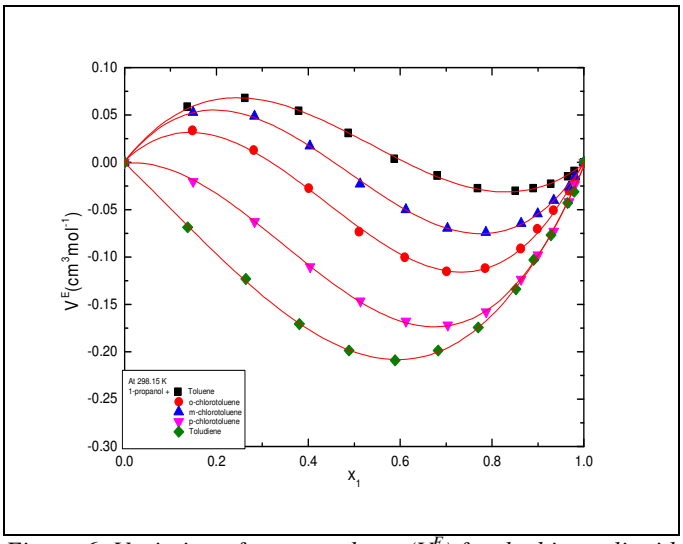

Figure 6: Variation of excess volume (V^E) for the binary liquid mixture of 1-propanol (1) withToluene (■), (o)chloro toluene (●),(m)chloro toluene (▲), (p)chloro toluene (▼) and Toluidine (♦) at 298.15 K.

A perusal of these plots show that with an increase in 1-propanol composition at studied temperatures there is deviation from positive to negative in magnitude and sign of V^E values for binary mixtures of 1-propanol with toluene, o-chlorotoluene, m-chlorotoluene molecules whereas for the binary mixture of 1-propanol with p-chlorotoluene and toluidine the magnitude and sign of V^E values was observed to be completely negative over the entire composition range at studied temperatures. In our present study,the V^E plots suggests that physical and chemical effects prevail initially in the binary mixture of 1-propanol with toluene and later on these effects decrease with increase in 1-propanol composition in the mixture. In the case of binary mixtures of 1-propanol with o-chlorotoluene,m-chlorotoluene both chemical and structural effects prevail. The more negative deviation in these mixtures when compared to 1-propanol with toluene mixture may be due to dipole- dipole interactions with the introduction of chloro group in the toluene molecule while in 1-propanol with p-chlorotoluene binary mixture structural effects dominates leading to inversion in sign which could be attributed to the presence of electron repelling -CH_3 group in para position in chlorotoluene molecule increasing the π electron density on the ring and making the chloro group more negative and contributing for more dipole-dipole interactions between electron seeking hydrogen atom of –OH group of 1-propanol and chloro group of p-chlorotoluene when compared to toluene,o-chlorotoluene,m-chlorotoluene molecules. While in case of binary mixture of 1-propanol with toluidine, the complete inversion in sign may be attributed due to the hydrogen bond formation between -OH group of 1-propanol and –NH_2 group of toluidine.Moreover, for all the binary mixtures in the present study it isobserved thatthe excessV^E data tends to shift towards lesser negative side with increase of temperature (298.15 K-313.15 K). This may be due to decrease in molecular interactions with increase of temperature. The algebraic V^E values of 1-propanol with toluene, isomeric chlorotoluenes andtoluidine will adapt the following order:
Toluidine<p-chlorotoluene < o-chlorotoluene < m-chlorotoluene < Toluene.

3.2. Excess Isentropic Compressibilities (κ_s^E)

The speed of sound(u) values for the binary mixtures of 1-propanol with toluene, isomeric chlorotoulenes and toluidine molecules were measured over whole composition range at temperatures T=298.15 K to 313.15K respectively. The experimental densities (ρ) sound speed (u) values were used to calculate isentropic compressibility (κ_s) using the following equation

$$\kappa_s = u^{-2}\rho^{-1} \quad (5)$$

Moreover, the excess isentropic compressibility (κ_s^E) values were calculated using the equations proposed by Benson and Kiyohara[xli] and Douheret etal. [xlii]

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \quad (6)$$

$$\kappa_s^{id} = \sum_{i=1}^{2}\phi_i\left[\kappa_{s,i} + TV_i\left(\alpha_i^2\right)/C_{p,i}\right] - \left\{T\left(\sum_{i=1}^{2}\chi_i V_i\right)\left(\sum_{i=1}^{2}\phi_i\alpha_i\right)^2 / \sum_{i=1}^{2}x_i C_{pi}\right\} \quad (7)$$

The ϕ_i ,κ_{si}, V_i, C_{pi} and $\alpha_i$are the volume fraction, isentropic compressibility, molar volume, molar heat capacity and the thermal expansion coefficient respectively of the pure component i, T represents absolute temperature and $x_1$represents the mole fraction of component i in the binary mixture. The values of C_p for the investigated liquids have been obtained from the literature [iii,xxvii,xxviii,xxx,xxxiii] and α were derived from the experimental density data using the expression,

$$\alpha_i = -(1/\rho)(\partial\rho/\partial T) \quad (8)$$

The calculated excess isentropic compressibility(κ_s^E) values for the binary mixtures of 1-propanol with toluene, isomeric chlorotoluenes and toluidine molecules are corresponded with Redlich-Kister and Hwang polynomial equations respectively,

Redlich-Kister: $\kappa_s^E = x_1 x_2 \left[a_0 + a_1 (x_1 - x_2) + a_2 (x_1 - x_2)^2 \right]$ (ix)

Hwang: $\kappa_s^E = x_1 x_2 \left[b_0 + b_1 x_1^3 + b_2 x_2^3 \right]$ (x)

The sound speed (u),isentropic compressibility (κ_s), excess isentropic compressibility (κ_s^E)along with corresponded excess isentropic compressibility (κ_s^E)values obtained from Redlich-Kister and Hwang polynomial equations(eq.9 & eq.10) were reported in Table 5. The excess isentropic compressibilities (κ_s^E)data for all the binary mixtures of 1-propanol in the present work were also plotted at temperatures T=298.15K to 313.15 and represented in figures 7 to 12.The standard deviations in excess isentropic compressibility (κ_s^E)for these binary mixtures were obtained by using the following relation:

$$\sigma\left(\kappa_s^E\right) = \left[\frac{\sum (\kappa_{\exp}^E - \kappa_{cal}^E)^2}{n - p} \right]^{\frac{1}{2}} \quad \text{(xi)}$$

where 'n' is the number of results and 'p' is the number of parameters used in Eq. (9&10). The values of adjusted parameters along with standard deviations $\sigma(\kappa_s^E)$ are reported in the Table 6.

x_1	u (exp) (m s^{-1})	κ_s (TPa^{-1})	κ_s^E(TPa^{-1})		
			Exp.	Redlich–Kister	Hwang
1-propanol(1) + Toluene(2) T=298.15K					
0.1365	1283.75	709.28	5.09	5.00	5.32
0.2623	1271.98	727.86	4.25	4.39	4.12
0.3787	1263.04	743.58	1.09	1.12	0.73
0.4867	1255.51	757.96	-2.90	-2.92	-2.98
0.5871	1248.58	771.92	-6.85	-6.50	-6.19
0.6808	1240.85	787.32	-8.93	-8.86	-8.46
0.7684	1232.60	803.84	-9.49	-9.55	-9.40
0.8505	1223.66	821.86	-8.19	-8.35	-8.61
0.8896	1218.92	831.48	-6.80	-7.01	-7.43
0.9275	1214.16	841.31	-5.12	-5.16	-5.64
0.9643	1209.07	851.79	-2.71	-2.82	-3.19
0.9787	1207.20	855.82	-1.88	-1.75	-2.00
T=303.15K					
0.1365	1268.10	730.85	5.55	5.79	6.10
0.2623	1255.49	751.14	5.32	5.16	4.89
0.3787	1246.22	767.88	2.25	1.75	1.37
0.4867	1238.70	782.82	-1.97	-2.27	-2.32
0.5871	1231.21	798.03	-5.32	-5.65	-5.35
0.6808	1223.88	813.49	-7.87	-7.73	-7.34
0.7684	1215.89	830.34	-8.52	-8.21	-8.06
0.8505	1207.58	848.16	-7.73	-7.03	-7.28
0.8896	1202.76	858.27	-5.96	-5.83	-6.24
0.9275	1198.07	868.37	-4.11	-4.25	-4.71
0.9643	1193.56	878.37	-2.25	-2.30	-2.65
0.9787	1191.74	882.48	-1.37	-1.42	-1.66
T=308.15K					
0.1365	1244.70	762.77	6.06	6.58	6.88
0.2623	1232.61	783.57	6.11	5.82	5.56
0.3787	1223.87	800.53	3.14	2.19	1.83
0.4867	1216.72	815.76	-0.81	-1.84	-1.89
0.5871	1210.19	830.46	-4.62	-5.00	-4.70
0.6808	1203.23	846.16	-6.80	-6.73	-6.36
0.7684	1195.98	862.70	-7.56	-6.94	-6.79
0.8505	1188.24	880.53	-6.52	-5.72	-5.96
0.8896	1184.23	889.90	-5.36	-4.65	-5.04

0.9275	1179.95	899.80	-3.55	-3.31	-3.76
0.9643	1175.84	909.64	-1.69	-1.75	-2.08
0.9787	1174.15	913.68	-0.81	-1.07	-1.30
T=313.15K					
0.1365	1220.56	797.49	6.16	6.29	6.55
0.2623	1210.48	816.79	6.74	6.80	6.58
0.3787	1203.08	832.81	4.89	4.59	4.29
0.4867	1197.23	846.95	1.93	1.52	1.48
0.5871	1191.96	860.50	-0.90	-1.32	-1.07
0.6808	1187.05	873.85	-3.30	-3.34	-3.03
0.7684	1181.91	887.86	-4.46	-4.26	-4.14
0.8505	1176.59	902.57	-4.39	-3.99	-4.20
0.8896	1173.78	910.33	-3.76	-3.41	-3.74
0.9275	1170.87	918.34	-2.76	-2.54	-2.91
0.9643	1167.82	926.70	-1.31	-1.40	-1.68
0.9787	1166.68	929.98	-0.76	-0.87	-1.06
1-propanol(1) + (o)chlorotoluene(2) **T=298.15K**					
0.1480	1278.98	582.47	1.86	1.22	1.59
0.2809	1266.81	609.75	-2.33	-1.84	-2.29
0.4012	1257.97	635.37	-8.14	-7.09	-7.56
0.5103	1250.36	661.30	-13.60	-12.73	-12.70
0.6099	1243.53	688.14	-18.11	-17.33	-17.00
0.7010	1235.95	717.69	-19.87	-19.88	-19.40
0.7848	1228.15	749.69	-19.14	-19.72	-19.61
0.8621	1220.06	784.50	-15.59	-16.45	-16.80
0.8986	1215.78	803.26	-12.43	-13.59	-14.20
0.9336	1212.11	821.89	-9.41	-9.89	-10.50
0.9674	1208.43	841.24	-5.66	-5.36	-5.82
0.9806	1206.70	849.57	-3.57	-3.32	-3.63
T=303.15K					
0.1480	1261.52	601.44	2.62	2.51	2.86
0.2809	1248.83	630.36	-0.98	-0.80	-1.24
0.4012	1239.67	657.40	-6.36	-6.35	-6.79
0.5103	1232.35	684.06	-12.04	-11.88	-11.82
0.6099	1225.13	712.35	-16.01	-16.03	-15.55
0.7010	1218.17	742.34	-18.21	-18.03	-17.54
0.7848	1210.60	775.31	-17.36	-17.49	-17.39
0.8621	1203.02	810.77	-13.96	-14.28	-14.69
0.8986	1199.49	829.19	-11.55	-11.67	-12.26
0.9336	1196.00	848.23	-8.49	-8.41	-9.03
0.9674	1192.49	868.08	-4.62	-4.51	-4.95
0.9806	1191.05	876.34	-2.75	-2.78	-3.08
T=308.15K					
0.1480	1242.72	622.57	3.03	3.52	3.82
0.2809	1229.20	653.67	0.59	0.26	-0.11
0.4012	1219.40	682.63	-3.92	-5.04	-5.42
0.5103	1212.03	710.58	-9.38	-9.95	-9.91
0.6099	1204.79	740.23	-13.07	-13.28	-12.87
0.7010	1197.70	771.75	-14.83	-14.56	-14.14
0.7848	1190.38	805.90	-13.91	-13.71	-13.63
0.8621	1183.99	841.26	-11.73	-10.85	-11.20
0.8986	1180.17	860.84	-8.72	-8.73	-9.23
0.9336	1177.49	879.50	-6.62	-6.20	-6.72
0.9674	1174.81	898.89	-3.77	-3.28	-3.65
0.9806	1173.16	907.77	-1.50	-2.01	-2.26
T=313.15K					

0.1480	1226.68	641.82	4.58	5.05	5.35
0.2809	1213.68	673.55	2.88	2.53	2.16
0.4012	1204.88	702.43	-1.57	-2.43	-2.80
0.5103	1197.55	731.30	-5.93	-7.19	-7.14
0.6099	1191.45	760.51	-9.84	-10.52	-10.12
0.7010	1185.58	791.41	-11.99	-11.95	-11.54
0.7848	1179.84	824.32	-12.04	-11.43	-11.35
0.8621	1174.53	859.02	-10.23	-9.10	-9.45
0.8986	1171.81	877.44	-8.23	-7.34	-7.82
0.9336	1169.27	896.28	-5.78	-5.21	-5.72
0.9674	1166.91	915.55	-2.89	-2.75	-3.12
0.9806	1165.81	923.76	-1.24	-1.68	-1.93
1-propanol(1) + (m)chlorotoluene(2)					
T=298.15K					
0.1492	1275.23	591.27	2.77	2.14	2.45
0.2829	1262.77	618.90	-0.20	0.07	-0.33
0.4035	1254.38	644.01	-5.62	-4.21	-4.61
0.5127	1246.54	670.02	-10.10	-9.02	-9.00
0.6122	1239.34	697.04	-13.60	-13.06	-12.61
0.7031	1232.41	725.51	-15.50	-15.44	-14.90
0.7865	1225.00	756.56	-15.00	-15.57	-15.49
0.8633	1217.80	789.59	-12.20	-13.13	-13.51
0.8994	1213.86	807.46	-10.00	-10.88	-11.41
0.9342	1210.90	824.68	-7.50	-7.95	-8.50
0.9677	1207.92	842.53	-4.80	-4.32	-4.71
0.9808	1206.27	850.55	-2.85	-2.67	-2.94
T=303.15K					
0.1492	1256.50	611.64	3.96	3.78	4.07
0.2829	1242.85	641.70	2.52	2.44	2.07
0.4035	1233.87	668.61	-2.00	-1.37	-1.74
0.5127	1225.99	695.88	-6.07	-5.79	-5.74
0.6122	1219.39	723.37	-9.85	-9.57	-9.16
0.7031	1213.09	752.31	-12.10	-11.88	-11.48
0.7865	1206.28	783.91	-11.70	-12.26	-12.19
0.8633	1200.34	816.61	-10.00	-10.45	-10.80
0.8994	1197.36	833.86	-8.32	-8.69	-9.18
0.9342	1194.65	851.35	-6.33	-6.36	-6.87
0.9677	1191.95	869.46	-3.72	-3.46	-3.83
0.9808	1190.65	877.26	-2.12	-2.14	-2.39
T=308.15K					
0.1492	1240.79	629.92	4.61	4.84	5.11
0.2829	1226.67	661.65	3.44	3.28	2.93
0.4035	1216.63	690.80	-0.25	-0.73	-1.07
0.5127	1208.81	719.13	-4.69	-4.96	-4.91
0.6122	1201.57	748.56	-7.96	-8.24	-7.87
0.7031	1195.13	778.85	-10.30	-10.01	-9.63
0.7865	1188.61	811.35	-10.40	-10.04	-9.97
0.8633	1182.29	845.90	-8.38	-8.31	-8.63
0.8994	1179.51	863.57	-6.95	-6.81	-7.27
0.9342	1176.82	881.73	-5.03	-4.91	-5.39
0.9677	1174.37	900.14	-2.84	-2.64	-2.98
0.9808	1173.21	908.05	-1.42	-1.62	-1.86
T=313.15K					
0.1492	1225.36	648.67	5.52	5.72	5.98
0.2829	1212.01	680.72	4.73	4.69	4.35
0.4035	1202.76	710.00	1.29	1.01	0.67
0.5127	1195.37	738.76	-2.53	-3.07	-3.02

0.6122	1189.13	767.85	-5.92	-6.33	-5.97
0.7031	1183.59	797.90	-8.25	-8.21	-7.85
0.7865	1178.11	829.88	-8.56	-8.49	-8.43
0.8633	1173.27	863.14	-7.51	-7.15	-7.47
0.8994	1171.02	880.43	-6.28	-5.89	-6.34
0.9342	1168.88	898.16	-4.60	-4.27	-4.74
0.9677	1166.85	916.30	-2.49	-2.30	-2.63
0.9808	1165.83	924.08	-1.12	-1.42	-1.64
1-propanol(1) + (p)chlorotoluene(2)					
T=298.15K					
0.1495	1275.16	592.03	-4.35	-4.42	-4.07
0.2834	1264.85	617.25	-10.68	-10.86	-11.31
0.4040	1257.50	640.97	-17.90	-17.74	-18.18
0.5132	1251.19	665.08	-24.20	-23.66	-23.59
0.6126	1244.42	691.26	-27.92	-27.55	-27.06
0.7035	1237.08	719.88	-28.74	-28.69	-28.20
0.7868	1228.97	751.47	-26.16	-26.64	-26.55
0.8635	1220.77	785.56	-20.71	-21.18	-21.62
0.8996	1216.60	803.70	-16.76	-17.16	-17.76
0.9344	1212.77	822.00	-12.54	-12.28	-12.91
0.9678	1208.57	841.56	-7.00	-6.55	-7.00
0.9808	1206.43	850.30	-3.84	-4.03	-4.34
T=303.15K					
0.1495	1254.89	614.55	-3.86	-3.37	-3.06
0.2834	1242.35	643.19	-7.64	-8.82	-9.21
0.4040	1234.64	668.47	-14.05	-14.75	-15.13
0.5132	1229.06	692.91	-20.63	-19.86	-20.00
0.6126	1222.34	720.26	-23.70	-23.20	-23.00
0.7035	1216.08	748.86	-24.97	-24.18	-24.00
0.7868	1208.69	780.94	-22.26	-22.44	-22.36
0.8635	1202.10	814.27	-17.83	-17.82	-18.19
0.8996	1198.26	832.62	-13.77	-14.43	-14.94
0.9344	1195.29	850.45	-10.13	-10.31	-10.85
0.9678	1192.52	868.60	-6.07	-5.50	-5.89
0.9808	1190.75	877.10	-3.18	-3.38	-3.64
T=308.15K					
0.1495	1237.89	634.93	-2.69	-1.83	-1.60
0.2834	1224.78	665.34	-5.74	-7.03	-7.35
0.4040	1216.50	692.26	-12.00	-12.62	-12.93
0.5132	1208.95	720.03	-16.03	-17.02	-16.96
0.6126	1202.72	747.97	-19.72	-19.49	-19.14
0.7035	1196.08	778.29	-20.54	-19.75	-19.40
0.7868	1189.40	810.78	-18.74	-17.78	-18.00
0.8635	1183.00	845.20	-14.59	-13.70	-14.00
0.8996	1179.25	864.17	-11.00	-10.92	-11.35
0.9344	1176.76	881.94	-8.00	-7.70	-8.14
0.9678	1174.23	900.42	-4.05	-4.05	-4.36
0.9808	1173.25	908.03	-2.34	-2.47	-2.69
T=313.15K					
0.1495	1221.40	655.60	-2.10	-1.29	-1.06
0.2834	1208.80	686.65	-4.47	-5.77	-6.08
0.4040	1201.06	713.93	-9.78	-10.79	-11.09
0.5132	1194.75	741.15	-14.42	-14.88	-14.83
0.6126	1189.04	769.31	-17.47	-17.31	-16.98
0.7035	1183.54	799.04	-18.34	-17.75	-17.42
0.7868	1178.23	830.52	-16.92	-16.14	-16.08
0.8635	1173.18	863.82	-13.17	-12.55	-12.84

0.8996	1170.56	881.51	-10.10	-10.05	-10.45
0.9344	1168.39	899.14	-6.97	-7.11	-7.53
0.9678	1166.67	916.69	-3.82	-3.75	-4.05
0.9808	1165.90	924.09	-2.15	-2.29	-2.50
1-propanol(1) + Toluidine(2)					
T=298.15K					
0.1374	1537.98	433.27	-5.48	-6.04	-5.60
0.2639	1487.77	472.17	-14.22	-13.65	-14.04
0.3806	1443.27	511.89	-22.00	-21.37	-21.90
0.4887	1403.77	552.40	-28.87	-27.93	-27.99
0.5891	1366.40	595.56	-32.93	-32.26	-31.83
0.6826	1330.67	641.94	-33.64	-33.58	-33.03
0.7699	1296.33	691.89	-30.64	-31.30	-31.10
0.8515	1263.96	745.00	-24.33	-25.06	-25.43
0.8904	1248.33	773.04	-19.64	-20.39	-20.97
0.9281	1233.23	801.75	-14.24	-14.65	-15.31
0.9646	1218.69	831.23	-8.03	-7.86	-8.35
0.9789	1212.83	843.46	-5.09	-4.84	-5.18
T=303.15K					
0.1374	1512.57	449.98	-4.13	-4.79	-4.33
0.2639	1463.21	490.42	-12.23	-11.43	-11.82
0.3806	1418.92	532.11	-19.02	-18.64	-19.18
0.4887	1381.26	573.27	-26.28	-25.11	-25.18
0.5891	1345.15	617.48	-30.42	-29.72	-29.27
0.6826	1310.80	664.73	-31.45	-31.54	-30.97
0.7699	1278.17	715.13	-29.28	-29.87	-29.67
0.8515	1247.00	769.13	-23.43	-24.24	-24.62
0.8904	1232.01	797.52	-19.09	-19.83	-20.44
0.9281	1217.33	826.85	-13.79	-14.33	-15.01
0.9646	1203.29	856.82	-7.85	-7.73	-8.23
0.9789	1197.66	869.19	-5.08	-4.77	-5.12
T=308.15K					
0.1374	1489.89	465.83	-2.87	-2.78	-2.37
0.2639	1437.74	510.27	-8.90	-9.21	-9.57
0.3806	1395.01	553.11	-16.43	-16.43	-16.91
0.4887	1356.88	596.91	-22.89	-22.58	-22.64
0.5891	1320.84	643.53	-26.44	-26.54	-26.13
0.6826	1287.45	692.43	-27.59	-27.65	-27.14
0.7699	1256.09	744.15	-25.83	-25.60	-25.41
0.8515	1226.02	799.64	-20.18	-20.26	-20.61
0.8904	1211.67	828.57	-16.13	-16.38	-16.92
0.9281	1197.92	858.11	-11.45	-11.69	-12.30
0.9646	1185.28	887.45	-6.94	-6.22	-6.68
0.9789	1179.38	900.81	-3.51	-3.82	-4.14
T=313.15K					
0.1374	1469.64	480.87	-2.19	-1.68	-1.30
0.2639	1417.57	527.27	-6.28	-7.20	-7.54
0.3806	1376.16	570.99	-12.98	-13.70	-14.16
0.4887	1339.89	615.01	-19.30	-19.39	-19.45
0.5891	1306.25	661.11	-23.47	-23.16	-22.78
0.6826	1274.58	709.87	-24.91	-24.37	-23.89
0.7699	1244.60	761.60	-23.30	-22.71	-22.53
0.8515	1216.22	816.52	-18.43	-18.06	-18.38
0.8904	1202.25	845.71	-14.23	-14.62	-15.13
0.9281	1189.31	874.82	-10.10	-10.45	-11.02
0.9646	1177.19	904.05	-5.82	-5.57	-6.00
0.9789	1172.13	916.51	-3.34	-3.42	-3.72

Table 5: Mole fraction of 1-propanol (x_1), experimental sound speed (u) isentropic compressibilities (κ_s), excess isentropic compressibilities (κ_s^E) and predicted excess isentropic compressibilities (Redlich-Kister eq.9 & Hwang eq.10) at T =298.15 K to 313.15 K for the binary mixtures of 1-propanol with Toluene, (o)chlorotoluene, (m)chlorotoluene, (p)chlorotoluene and Toluidine.

Temperature	Redlich-Kister				Hwang			
	a_0	a_1	a_2	$\sigma(\kappa_s^E)$ TPa^{-1}	b_0	b_1	b_2	$\sigma(\kappa_s^E)$ TPa^{-1}
1-propanol(1) + Toluene(2)								
298.15K	-13.72	-75.62	2.147	0.170	-14.44	-87.16	92.89	0.468
303.15K	-11.04	-72.76	13.76	0.363	-15.63	-68.27	105.0	0.554
308.15K	-9.251	-69.86	26.97	0.678	-18.24	-47.21	119.1	0.781
313.15K	4.515	-59.08	11.24	0.308	0.768	-55.35	85.32	0.372
1-propanol(1) + (o)chlorotoluene(2)								
298.15K	-48.80	-103.1	-28.50	0.812	-39.30	-160.8	84.76	0.986
303.15K	-45.51	-97.92	-7.073	0.170	-43.15	-126.0	107.1	0.534
308.15K	-38.11	-83.74	14.24	0.626	-42.85	-80.71	118.7	0.773
313.15K	-27.08	-82.08	18.94	0.824	-33.39	-72.46	123.0	0.827
1-propanol(1) + (m)chlorotoluene(2)								
298.15K	-33.80	-89.06	-24.09	0.914	-25.77	-138.1	73.90	0.976
303.15K	-21.08	-82.48	-14.25	0.391	-16.33	-117.2	79.19	0.601
308.15K	-17.91	-76.13	5.355	0.297	-19.70	-83.49	97.77	0.511
313.15K	-10.39	-74.13	6.959	0.347	-12.71	-78.97	97.53	0.403
1-propanol(1) + (p)chlorotoluene(2)								
298.15K	-92.01	-100.8	-27.32	0.395	-82.90	-156.4	83.57	0.693
303.15K	-77.17	-86.80	-20.67	0.705	-70.28	-130.9	75.77	0.965
308.15K	-66.24	-71.38	3.645	0.876	-67.46	-80.12	89.84	0.965
313.15K	-57.77	-67.44	0.652	0.743	-57.99	-79.42	81.16	0.945
1-propanol(1) + Toluidine(2)								
298.15K	-114.1	-103.6	-22.85	0.682	-106.5	-153.8	92.87	0.876
303.15K	-102.9	-106.6	-28.10	0.748	-93.53	-164.4	89.44	0.942
308.15K	-92.52	-95.85	-0.770	0.334	-92.26	-115.1	113.1	0.618
313.15K	-79.64	-90.04	0.265	0.562	-79.73	-106.8	107.5	0.925

Table 6: Standard deviation $\sigma(\kappa_s^E)$ and values of constants (a_0, a_1, a_2; b_0, b_1, b_2) for Redlich-Kister, Eq. (9) and Hwang, Eq. (10) for the binary mixtures of 1-propanol with Toluene, (o)chlorotoluene, (m)chlorotoluene, (p)chlorotoluene and Toluidine.

The physical, chemical and structural effects operating among components of binary mixtures play a vital role in assessing the excess isentropic compressibility (κ_s^E)[xliii - xlv].The physical effects include weak dispersion forces producing positive (κ_s^E), where as the difference in size and shape of unlike molecules contributes for geometrical fitting of molecules, resulting into negative(κ_s^E)values[xlvi]. The chemical effects are due to breaking up of associate molecules present in the pure components, leading to positive (κ_s^E)values, while structural effects include specific interactions like strong hydrogen bonding, dipole–dipole interactions among component molecules leading to negative(κ_s^E)values.

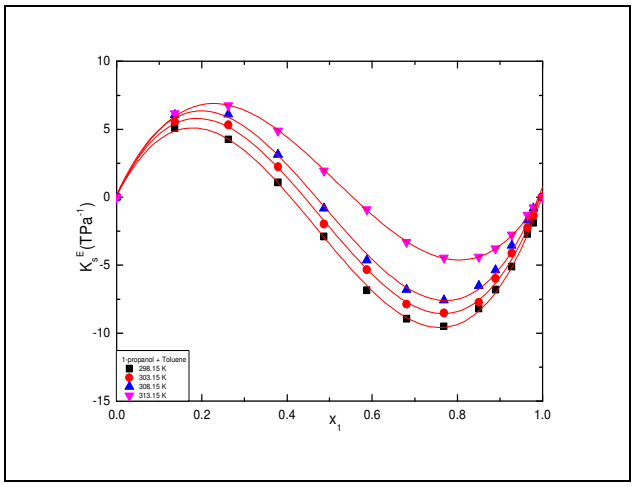

Figure 7: Variation of excess isentropic compressibility (K_s^E) for the binary liquid mixture of 1-propanol (1) with Toluene (2) at 298.15 K (■), 303.15 K (●), 308.15 K (▲) and 313.15 K(▼).

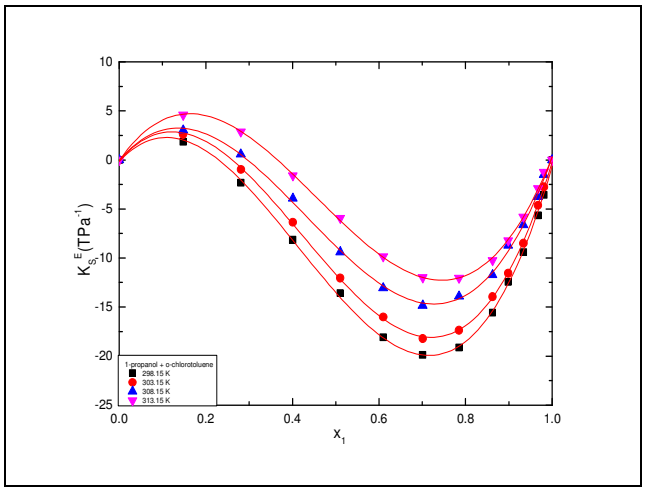

Figure 8: Variation of excess isentropic compressibility (K_s^E) for the binary liquid mixture of 1-propanol (1) with (o)chlorotoluene (2) at 298.15 K (■), 303.15 K (●), 308.15 K (▲) and 313.15 K(▼).

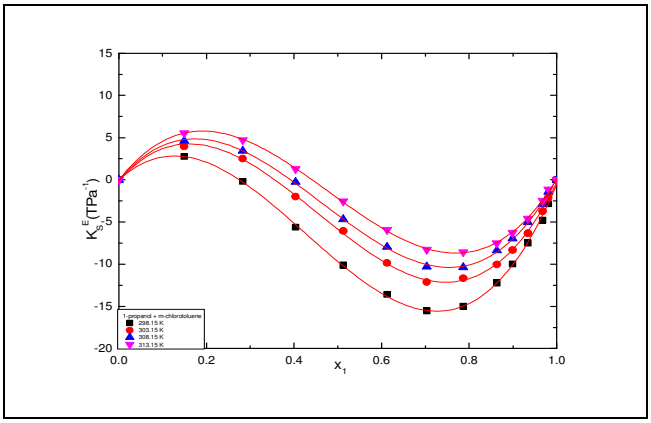

Figure 9: Variation of excess isentropic compressibility (K_s^E) for the binary liquid mixture of 1-propanol (1) with (m)chlorotoluene (2) at 298.15 K (■), 303.15 K (●), 308.15 K (▲) and 313.15 K(▼).

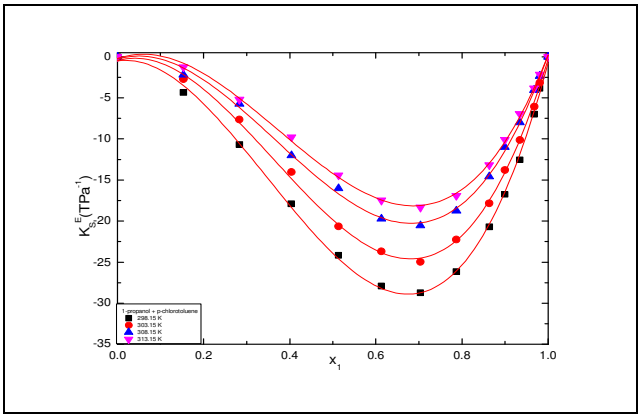

Figure10: Variation of excess isentropic compressibility (K_s^E) for the binary liquid mixture of 1-propanol (1) with (p)chlorotoluene (2) at 298.15 K (■), 303.15 K (●), 308.15 K (▲) and 313.15 K(▼).

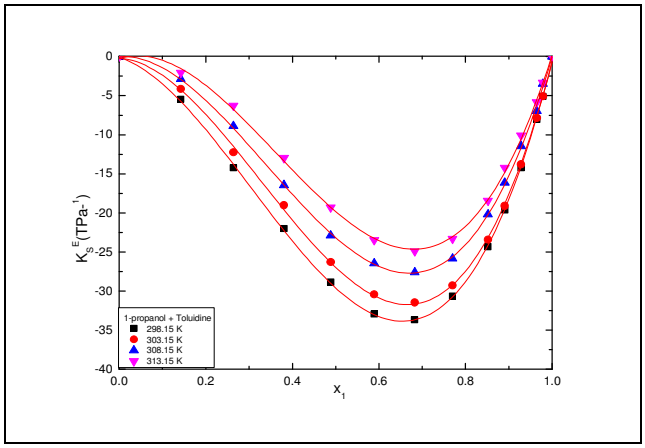

Figure11: Variation of excess isentropic compressibility (K_s^E) for the binary liquid mixture of 1-propanol (1) with Toluidine (2) at 298.15 K (■), 303.15 K (●), 308.15 K (▲) and 313.15 K(▼).

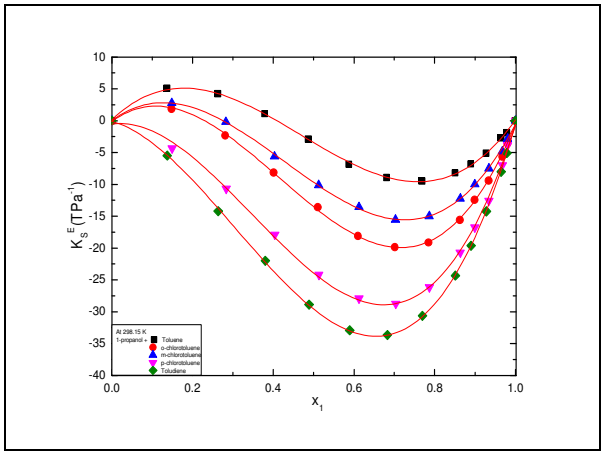

Figure 12: Variation of excess isentropic compressibility (K_s^E) for the binary liquid mixture of 1-propanol (1) with Toluene (■),(o)chlorotoluene(●),(m)chlorotoluene(▲), (p)chlorotoluene(▼) and Toluidine(♦) at 298.15 K .

A perusal of excess isentropic compressibility (κ_s^E)plots fig.7 to 12 show that physical and chemical effects prevail initially in the binary mixture of 1-propanol with toluene, o-chlorotoluene,m-chlorotoluene. The more negative deviation in the mixtures of 1-propanol with o-chlorotoluene, m-chlorotoluene, when compared to 1-propanol with toluene mixture may be due to dipole- dipole interactions with the introduction of chloro group in the toluene molecule while in 1-propanol with p-chlorotoulene binary mixture structural effects dominates leading to inversion in sign which could be attributed to the presence of electron repelling -CH_3 group in para position in chlorotoluene molecule increasing the π electron density on the ring and making the chloro group more negative and contributing for more dipole-dipole interactions between electron seeking hydrogen atom of –OH group of 1-propanol and chloro group of p-chlorotoluene when compared to toluene, o-chlorotoluene, m-chlorotoluene molecules. In the binary mixture of 1-propanol with toluidine the more negative deviations could be attributed due to prevailing hydrogen bonding between associated molecules. More over excess isentropic compressibities (κ_s^E) of these binary mixtures also shift towards to less negative side with increase of temperature (298.15 K-313.15 K) similar to excess volume data.The algebraic (κ_s^E)values of 1-propanol with toluene, isomeric chlorotoluenes and toluidine will adapt the following order:
Toluidine<p-chlorotoluene < o-chlorotoluene < m-chlorotoluene < Toluene.

3.3. Analysis of Speed of Sound

The measured speed of sound (u) data was analyzed in terms of collision factor theory (CFT) and free length theory (FLT). The details of process and calculation of theories were considered from earlier literature[vi, xlvii].The corresponding equations that are required for analysis of speed of sound are:
Schaaff's collision factor theory (CFT)[xlviii]

$$u_m = u_\infty \frac{\left(\sum_{i=1}^{n} \mathrm{X_i} S_i\right)\left(\sum_{i=1}^{n} \mathrm{X_i} B_i\right)}{V u_m} \quad (12)$$

where u_∞= 1600 m s^{-1}, S_i and B_i are the space filling factor and the actual volume of the molecule per mole of pure component in the mixture, respectively.
Jacobson's free length theory (FLT)[xlix-l].

$$u_m = \frac{\mathrm{K}}{L_{f,m}\rho_m{}^{1/2}} \quad (13)$$

where K is the Jacobson's constant and $L_{f,m}$ is the intermolecular free length of the binary mixture.
The outcome of these theories were correlated in terms of relative root mean deviation by using the following eq.14[xxvi, xliv],and the values were incorporated in table.7

$$RMSD = \frac{1}{n}\sum_{i=1}^{n}\left[\left[\frac{u_{exp}-u_{pred}}{u_{exp}}\right]^2\right]^{1/2} \quad (14)$$

RMSD	298.15K	303.15K	308.15K	313.15K
1-propanol (1) + Toluene (2)				
CFT	0.002	0.005	0.002	0.006
FLT	0.004	0.005	0.005	0.006
1-propanol (1) + (o)chlorotoluene (2)				
CFT	0.009	0.011	0.008	0.011
FLT	0.006	0.007	0.009	0.01
1-propanol (1) + (m)chlorotoluene (2)				
CFT	0.008	0.011	0.008	0.011
FLT	0.007	0.009	0.009	0.010
1-propanol (1) + (p)chlorotoluene (2)				
CFT	0.009	0.012	0.009	0.012
FLT	0.003	0.005	0.007	0.008
1-propanol (1) + Toluidine (2)				
CFT	0.003	0.004	0.003	0.004
FLT	0.015	0.016	0.019	0.019

Table 7: RMSD data of speed of sound (u) for the binary mixtures of 1-propanol with Toluene, (o)chlorotoluene, (m)chlorotoluene, (p)chlorotoluene and Toluidine at T =298.15 K, 303.15, 308.15 K and 313.15 K from CFT and FLT Models.

4. Conclusion

The density (ρ), speed of sound (u), excess volume (V^E), excess isentropic compressibility (κ_s^E) data for the binary mixtures of 1-propanol with toluene, isomeric chlorotoluenes and toluidine have been determined at T= (298.15K to 313.15K). In the present study, for these binary mixtures a similar trend was observed in the excess properties at all temperatures over the wide composition range. It is observed that these excess properties show a deviation from more positive to negative with the introduction of chloro group and

amino groups in toluene molecule and this deviation may be attributed due to prevailing dipole-dipole interaction, and hydrogen bonding existing between 1-propanol and isomeric chlorotoluenes, toluidine molecules respectively, overcoming the chemical effects (dispersive forces) between 1-propanol and toluene. Further the experimental excess properties data were found to decrease with the increase of temperature. The excess properties data were fitted to Redlich–Kister and Hwang equations, the results obtained were found to be in good agreement with the experimental data. The CFT and FLT theoretical models used for analyzing the ultrasonic sound speed data were also found to be in good agreement.

5. References

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