Study of Excess Thermodynamic Parameters in Binary Liquid Mixtures of n-tetradecane with alkane-1-ol

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ABSTRACT

Viscosities, densities and speed of sound have been measured over the whole composition range for n-tetradecane with hexan-1-ol, heptan-1-ol, octan-1-ol, decan-1-ol and dodecan-1-ol at 298.15 K and atmospheric pressure along with the properties of the pure components. Excess molar volumes, Excess isentropic compressibility and viscosity deviations for the binary systems were calculated and fitted to Redlich–Kister equation to determine the fitting parameters and the root-mean square deviations. The Prigogine–Flory–Patterson (PFP) theory and its applicability in predicting V_m^E is tested. Furthermore, the theoretical values of speed of sound (u) and isentropic compressibility (ks) have also been estimated using the Prigogine–Flory–Patterson (PFP) theory with the van der Waals (vdW) potential energy model.

Keywords: Density; Viscosity; n-tetradecane; Alkane-1-ols; PFP theory.
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INTRODUCTION

The study of the thermodynamic properties of binary mixtures is significant for many purposes one of which is to obtain information on molecular features of the studied mixtures. There has been an increasing interest in the study of systems comprising of unlike components with interactions of varying type. The sign and magnitude of excess parameters have been used to investigate the interactions between the components of a system [1-3].The characterization of the mixtures through their thermodynamic and transport properties is considered one of the most extended and reliable ways to obtain information about the structure and interactions of mixed solvents.[4-5]

In the present paper ,we report the densities, viscosities, and speed of sound, of binary mixtures formed by for n-tetradecane with hexan-1-ol, heptan-1-ol, octan-1-ol, decan-1-ol and dodecan-1-ol at 298.15 K .From the experimental results we have obtained the corresponding Excess molar volumes ,Excess isentropic compressibility and viscosity deviations. Furthermore, estimation of Excess molar volumes and the isentropic compressibilities using the Prigogine-Flory-Patterson theory is provided and a comparison between the reported and estimated values has been performed.

MATERIALS AND METHODS

The sources and the mole fraction purities of the chemicals were: n-tetradecane (S.D. Fine Chemicals Pvt. Ltd. Mumbai, purity 99%), hexan-1-ol(S.D. Fine Chemicals Pvt. Ltd. Mumbai ,purity 99.2%), heptan-1-ol(S.D. Fine Chemicals Pvt. Ltd. Mumbai, purity 99.13%), octan-1-ol (S.D. Fine Chemicals Pvt. Ltd. Mumbai, purity 0.98.5), decan-1-ol (E-Merck, purity 99.6) and dodecan-1-ol (E-Merck, purity 99.7%) . All the chemicals were purified by fractional glass distillation in 1m long packed column. All samples were kept in tightly sealed bottles to minimize the absorption of atmospheric moistures and CO_2, and dried over 0.4 nm molecular sieves to reduced water content. Prior to measurement all liquid were partially degassed at low pressure. The binary mixtures were prepared by mass and kept in special airtight bottles. The weighing was done on a Metler balance with an accuracy of $\pm 1 \times 10^{-5}$ g. Care was taken to avoid evaporation and contamination during mixing. The probable error in mole fraction was estimated

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to be less than ±0.0001. The purity of the chemicals was determined using HP 6890 gas chromatography using FID detector .The water content was determined by a Karl Fischer method.

Densities of all mixtures were determined using single stem pycnometer made up of borosil glass, having total volume about 8 cm^3 with graduated stem of 0.05 cm^3 division and capillary with internal diameter of 0.1cm was chosen for the present work. The experimental techniques, operation mode and calibration have been previously described [6-8]. An average of triplicate measurement was taken in to account. The reproducibility of density estimate was found to be of the order ± 3x10-^{5} g/cm^3.

The measurement of dynamic viscosity of pure liquids and liquids mixtures were obtained with a calibrated ubbelohood suspended level viscometer .The detailed of the apparatus and procedure have been reported previously [6-8]. The flow time was measured with an accurate stopwatch with a resolution of 0.001 s. The reproducibility of viscosity results was found to be within ± 0.003mP s.

Ultrasonic velocities were measured by using single crystal ultrasonic interferometer model Mittal's F-81 at 2 MHz frequency. The detailed of the apparatus and procedure have been reported previously [6-8].The ultrasonic velocity data have accuracy of 0.03%.

A thermostatically controlled well-stirred water bath whose temperature was controlled to ±0.001 K was used for all measurement.

The purity of the purified chemicals was checked by comparing the measured densities, viscosities and speeds of sound with those reported in the literature. The measured values are included in table 1 along with literature values.

RESULTS

The Experimentally determined values of densities (ρ), viscosities (η) and ultrasonic velocities (u) for binary mixtures of n-tetradecane with hexan-1-ol, heptan-1-ol, octan-1-ol, decan-1-ol and dodecan-1-ol at 298.15K are presented in Table2.From the measured values of densities, excess molar volumes (V_m^E) were calculated using the following equation,

$$V_m^{E} = (x_1M_1+x_2M_2)/\rho_{12} - (x_1M_1/\rho_1)-(x_2 M_2 /\rho_2) \tag{1}$$

where ρ_{12} is the density of the mixture and x_1, M_1, ρ_1, and x_2, M_2, ρ_2 are the mole fraction, the molecular weight, and the density of pure components 1and 2, respectively.

The viscosity deviations ($\Delta\eta$) were calculated using the relationship

$$\Delta\eta/mPa.s=\eta_{12}-x_1\eta_1-x_2\eta_2 \tag{2}$$

Where η_{12} is the viscosity of the mixture and x_1 ,x_2 and η_1, η_2 are the mole fraction and the viscosity of pure components 1and 2, respectively.

The excess isentropic compressibility, κ_s^E, were estimated by means of the equation,

$$\kappa_s^E=\kappa_s-\kappa_s^{id} \tag{3}$$

here κ_s is the isentropic compressibility and was calculated using the Newton- Laplace equation,

$$\kappa_s=(1/u^2\rho) \tag{4}$$

and κ_s^{id} is isentropic compressibility for the ideal mixtures was calculated by the following relation

$$\kappa_s^{id} = \sum \phi i[\kappa_{s,i} +TV^o_i(\alpha^o_i{}^2)/C_{p,i}] - [T(\sum x_iV^o_i) (\sum \phi_i \alpha^o_i)^2 / \sum x_iC_{p,i}] \tag{5}$$

ϕ_i is the volume fraction of the component and was defined by the relation

$$\phi_I=x_iV^o_i/(\sum x_iV^o_i) \tag{6}$$

V^o_i , α^o_i and $C_{p,i}$,are the molar volume, coefficient of thermal expansion, and molar heat capacity respectively, for pure component i. The values required were taken from literature [9]

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The values of V_m^E, $\Delta\eta$ and κ_s^E were fitted to Redlich Kister [10] type polynomial equation

$$Y = x_1 x_2 \sum_i^n a_i (x_1 - x_2)^i \tag{7}$$

The values coefficients a_is of eq. (7) were obtained by the method of least square along with their standard deviation. The standard deviation (σ) were computed using the following relation

$$\sigma(Y) = \left[\frac{\sum (Y_{expt} - Y_{calc})^2}{N - n} \right]^{1/2} \tag{8}$$

where N is the number of data points and n is the number of coefficients. The calculated values of the coefficients a_i along with the standard deviations (σ) are given in Table 3.

DISCUSSION

The variation in excess molar volumes, V_m^E with mole fraction of the binary mixtures of n-tetradecane with hexan-1-ol, heptan-1-ol, octan-1-ol, decan-1-ol and dodecan-1-ol are displayed in figure 1.The V_m^E curve for the mixture shows positive deviation over the entire composition range.

Generally V_m^E can be considered as arising from three types of interactions between component molecules of liquid mixtures [11-12](1) physical interactions consisting of mainly of dispersion forces or weak dipole-dipole interaction making a positive contribution, hereby the contraction volume and compressibility of the mixtures (2) chemical or specific interactions, which include charge transfer ,forming of H-bonds and other complex forming interactions ,resulting in a negative contribution (3) structural contribution due to differences in size and shape of the component molecules of the mixtures ,due to fitting of component molecules into each other's structure, hereby reducing the volume and compressibility of the mixtures , resulting in a negative contribution.

The large positive V_m^E values for above binary mixtures are attributed to the rupture of three-dimensional H-bonded network of alkanol due to the addition of solute, which is not compensated by the weak interactions between unlike molecules. The V_m^E values for binary mixtures of n-tetradecane with alkane-1-ol are in the order hexan-1-ol > heptan-1-ol > octan-1-ol> decan-1-ol > dodecan-1-ol .The differences in the values for V_m^E for these binary mixtures may be ascribed to the effect of chain length on degree of polymerization of alcohols in the pure state. In increase in chain length is expected to decrease the degree of polymerization in the pure state.

Figure 2 shows the variation of $\Delta\eta$ with mole fraction of the binary mixtures of binary mixtures n-tetradecane with hexan-1-ol, heptan-1-ol, octan-1-ol, decan-1-ol and dodecan-1-ol at T = 298.15K, shows negative deviation over the entire composition range.

The deviations viscosity is influenced by [13] (1) The difference in size and shape of the component molecules and the loss of dipolar association to a decrease in viscosity (2) specific interactions between unlike molecules such as H-bond formation and charge transfer complexes may cause for the increase in viscosity in mixtures rather than in pure component. The former effect produces negative in excess viscosity and latter   effect produces positive in excess viscosity. Positive values of $\Delta\eta$ are indicative of strong interactions whereas negative values indicate weaker interactions [14].

 The negative deviations in viscosity support the main factor of breaking of the self-associated alcohols and weak interactions between unlike molecules, decrease systematically with an increased in chain length of alkanol. With increasing in chain length of alcohols, hydrogen bonding interaction of n-tetradecane with alkanols is weaker due to decreased polarizability.The negative values viscosity deviation decreases in the following sequence: hexan-1-ol > heptan-1-ol > octan-1-ol> decan-1-ol > dodecan-1-ol.

The variation of k_s^E with composition of mixture of the binary mixtures of n-tetradecane with hexan-1-ol, heptan-1-ol, octan-1-ol, decan-1-ol and dodecan-1-ol at T = 298.15K are displayed in figure 3. The k_s^E curve for all the mixture show positive deviation over the entire composition range.

Kiyohara and Benson [15] have suggested that k_s^E is the resultant of several opposing effects. A strong molecular interaction through charge transfer, dipole induced dipole and dipole- dipole interactions, interstitial accommodation and orientation ordering lead to a more compact structure making k_s^E negative and breakup of the alkanol structures

tend to make k^Es positive[16]. The magnitudes of the various contributions depend mainly on the relative molecular size of the components.

The positive k^Es values for n-tetradecane with hexan-1-ol, heptan-1-ol, octan-1-ol, decan-1-ol and dodecan-1-ol signify decreasing dipole-dipole interaction due to decreasing proton donating ability with increasing chain length of alkan-1-ol. It also suggests the rupture of hydrogen bonded chain of the dipolar interaction between solute and alkanol exceed the intermolecular interaction through dipole-dipole and hydrogen bonding between n-tetradecane and alkanol molecules. The positive k^Es values for any pair of alkanol follow the order hexan-1-ol > heptan-1-ol > octan-1-ol> decan-1-ol > dodecan-1-ol.

7. Theoretical analysis
Prigogine–Flory–Patterson (PFP) theory
The Prigogine–Flory–Patterson (PFP) theory [17-19] has been commonly employed to estimate and analyze excess thermodynamic functions theoretically. This theory has been described in details by Patterson and co-workers [20]. According to PFP theory, V^E_m can be separated into three factors: (1) an interactional contribution, V^E_m *(int.)* (2) a free volume contribution, V^E_m *(fv)* and (3) an internal pressure contribution, V^E_m *(P*)*. The expression for these three contributions are given as V^E_m

$$V_m^E \quad (int) \quad = \quad [(\upsilon^{1/3}-1) \quad \upsilon^{2/3}\psi_1\theta_2/ \quad (4/3 \quad \upsilon^{-1/3}-1) \quad P_1{}^*\chi_{12} \tag{9}$$

$$V_m^E(fv)= \quad -[\upsilon_1- \quad \upsilon_2)^2(14/9 \quad \upsilon^{-1/3}-1) \quad \psi1\psi2]/ \quad [(14/9 \quad \upsilon^{-1/3}-1) \quad \upsilon] \tag{10}$$

$$V_m^E \quad (P^*) \quad = \quad [(\upsilon_1- \quad \upsilon_2) \quad (P_1{}^*+P_2{}^*) \quad \psi_1\psi_2)]/ \quad (P_1{}^*\psi_1+P_2{}^*\psi_2) \tag{11}$$

Thus, the excess molar volume V^E_m is given as

$$V_m^E / (x_1V_1+x_2V_2)= V_m^E (int)- V_m^E (fv)+ V_m^E (P^*) \tag{12}$$

Where ψ, θ and P* represent the contact energy fraction, surface site fraction, and Characteristic pressure, respectively, and are calculated as

$$\psi_1=(1-\psi_2)=\Phi_1P_1{}^*/(\Phi_1P_1{}^*+\Phi_2P_2{}^*) \tag{13}$$

$$\theta_2=(1-\theta1)=\Phi_2/[\Phi_1(V_2{}^*/V_1{}^*)] \tag{14}$$

$$P^*=T\upsilon^2\alpha/\kappa_T \tag{15}$$

The details of the notations and terms used in equations (9) - (14) may be obtained from the literature [17-20, 21, 22]. The other parameters pertaining to pure liquids and the mixtures are obtained from the Flory theory [9, 17] while α and κ_T values are taken from the literature [9]. Flory parameters of the pure compounds are given in table 4.The interaction parameter χ_{12} required for the calculation of V_m^E using PFP theory has been derived by fitting the V_m^E expression to the experimental equimolar value of V_m^E for each system under study.

The values of χ_{12}, θ_2, three PFP contributions interactional, free volume, and P* effect, and experimental and calculated (using PFP theory) V_m^E values at near equimolar composition are presented in table 5. Study of the data presented in table 5 reveals that the interactional and free volume contributions are positive, whereas P* contributions are negative for all the three systems under investigation. For these binary mixtures, it is only the interactional contribution which dominates over the remaining two contributions .The P* contribution, which depends both on the differences of internal pressures and differences of reduced volumes of the components, has little significance for the studied binary mixtures as compared to other two.

Furthermore, in order to check whether χ_{12}, derived from nearly equimolar V_m^E values can predict the correct composition dependence, V_m^E has been calculated theoretically using χ_{12} over the entire composition range. The theoretically calculated values are plotted in figure 1 for comparison with the experimental results. Figure 1 show that the PFP theory is quite successful in predicting the trend of the dependence of V_m^E on composition [23-25] for the present systems.

The theoretical values of the speed of sound, u and isentropic compressibility k_s, for both the liquid components and the liquid mixtures have been estimated using the van der Waals (vdW) potential energy model in the Prigogine–Flory–Patterson (PFP) theory. The relevant equations are given elsewhere [17-22]. The comparison between experimental and theoretically calculated values of speed of sound for the studied binary mixtures at T = 298.15 K has been graphically represented in figures 4. The experimental and the PFP estimates of both u and k_s with the vdW energy model for all the binary mixtures at equimolar composition are summarized in table 6.

In order to perform a numerical comparison of the estimation capability of the PFP theory, we calculated the standard percentage deviations (σ %) using the relation

$$\sigma \,\% = [\sum \{ \,100(\text{Expt-Theor})/\text{Expt}\} \,(n-1)]^{1/2} \tag{16}$$

Where n represents the number of experimental data points.

Table 1: Comparison of experimental densities (ρ), viscosities (η) and speeds of sound (u) of pure liquids with literature values.

pure liquids	$\rho \times 10^{-3}$ Kg m^{-3}		η mPa.s		u m.s^{-1}	
	Experimental	Literature	Experimental	Literature	Experimental	Literature
n-tetradecane	0.75913	0.75911[a]	2.081	2.077[a]	1311	1310[a]
Hexane-1-ol	0.81542	0.81540[b]	4.599	4.590[b]	1305	1306[b]
Heptane-1-ol	0.81873	0.81870[c]	5.726	5.724[c]	1331	1330[c]
Octane-1-ol	0.82161	0.82162[b]	7.365	7.363[b]	1351	1352[b]
Decane-1-ol	0.82632	0.82631[b]	11.792	11.790[b]	1388	1388[b]
Dodecane-1-ol	0.82830	0.82831[d]	16.136	16.134[d]	1452	1452[d]

[a]*Ref [9]*
[b]*Ref [12,27]*
[c]*Ref [26]*
[d]*Ref [13]*

Table 2: Densities (ρ), viscosities (η), speeds of sound (u), excess molar volumes(V^E,) viscosities deviations (Δη) and excess isentropic compressibilities (κ_s^E) of binary mixtures at T=298.15 K.

x1	$\rho \times 10^{-3}$ kg.m^{-3}	$V^E \times 10^6$ m^3.mol^{-1}	η mPa.s	$\Delta\eta$ (mPa.s)	u m.s^{-1}	$\square_s^E$ TPa^{-1}
		n-tetradecane(1)+ hexane-1-ol (2)				
0.0000	0.81542	0.000	4.594	0.000	1305	0.000
0.0555	0.80852	0.125	4.157	-0.297	1298	11.099
0.1000	0.80386	0.169	3.799	-0.544	1296	15.979
0.1555	0.79861	0.219	3.367	-0.836	1293	21.370
0.1999	0.79481	0.254	3.049	-1.043	1291	25.109
0.2554	0.79049	0.293	2.693	-1.259	1289	29.089
0.2999	0.78735	0.320	2.45	-1.390	1288	31.706
0.3554	0.78375	0.347	2.202	-1.499	1287	34.273
0.3999	0.78111	0.364	2.047	-1.542	1286	35.763
0.4554	0.77807	0.378	1.906	-1.543	1285	36.918
0.5000	0.77583	0.385	1.831	-1.507	1285	37.278
0.5553	0.77326	0.387	1.776	-1.422	1285	37.022
0.5998	0.77135	0.383	1.757	-1.329	1286	36.253
0.6555	0.76913	0.371	1.755	-1.191	1287	34.577
0.6998	0.76749	0.357	1.765	-1.070	1288	32.686
0.7553	0.76559	0.331	1.785	-0.910	1290	29.607
0.7998	0.76417	0.305	1.806	-0.777	1292	26.574
0.8556	0.76251	0.264	1.841	-0.603	1295	22.064
0.8999	0.76129	0.226	1.881	-0.451	1298	17.914
0.9556	0.75991	0.150	1.965	-0.227	1302	11.995
1.0000	0.75914	0.000	2.082	0.000	1311	0.000
		n-tetradecane(1)+ heptane-1-ol (2)				
0.0000	0.81873	0.000	5.726	0.000	1331	0.000
0.0555	0.81246	0.083	5.128	-0.396	1327	5.322
0.1000	0.80797	0.123	4.667	-0.695	1324	9.209
0.1555	0.80280	0.167	4.130	-1.029	1320	13.744
0.1999	0.79899	0.199	3.735	-1.262	1317	17.054
0.2555	0.79458	0.234	3.281	-1.513	1313	20.738
0.2995	0.79133	0.257	2.955	-1.679	1311	23.252
0.3555	0.78750	0.280	2.585	-1.845	1308	25.871
0.3999	0.78467	0.295	2.327	-1.941	1306	27.458
0.4555	0.78137	0.306	2.048	-2.018	1303	28.798
0.5000	0.77891	0.311	1.861	-2.042	1302	29.327
0.5554	0.77603	0.310	1.674	-2.027	1301	29.289
0.5998	0.77388	0.305	1.562	-1.977	1300	28.690

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0.6555	0.77135	0.291	1.469	-1.867	1300	27.216
0.6998	0.76945	0.275	1.433	-1.742	1300	25.465
0.7554	0.76722	0.248	1.437	-1.535	1301	22.556
0.7999	0.76555	0.220	1.480	-1.329	1302	19.670
0.8555	0.76358	0.178	1.584	-1.022	1304	15.378
0.8999	0.76210	0.138	1.708	-0.737	1305	11.443
0.9554	0.76036	0.081	1.915	-0.328	1308	5.897
1.0000	0.75914	0.000	2.082	0.000	1311	0.000

n-tetradecane(1)+ octane-1-ol (2)

0.0000	0.82162	0.000	7.365	0.000	1351	0.000
0.0555	0.81578	0.065	6.650	-0.763	1346	4.782
0.0999	0.81149	0.097	6.106	-0.981	1341	8.024
0.1555	0.80646	0.133	5.470	-1.300	1337	11.698
0.1998	0.80268	0.159	4.998	-1.571	1333	14.311
0.2554	0.79824	0.186	4.452	-1.746	1329	17.167
0.2998	0.79490	0.204	4.051	-1.957	1326	19.110
0.3555	0.79095	0.223	3.594	-2.098	1322	21.103
0.3999	0.78798	0.234	3.266	-2.210	1319	22.331
0.4554	0.78447	0.243	2.900	-2.360	1316	23.399
0.4999	0.78181	0.246	2.642	-2.499	1314	23.874
0.5555	0.77866	0.246	2.365	-2.569	1312	23.975
0.5998	0.77628	0.242	2.180	-2.598	1310	23.654
0.6554	0.77345	0.231	1.991	-2.442	1309	22.735
0.7000	0.77129	0.219	1.876	-2.310	1308	21.574
0.7555	0.76874	0.198	1.778	-2.100	1307	19.582
0.8000	0.76680	0.177	1.734	-1.800	1306	17.546
0.8555	0.76448	0.146	1.724	-1.600	1306	14.434
0.9000	0.76272	0.116	1.751	-1.220	1307	11.479
0.9553	0.76063	0.074	1.829	-1.074	1307	7.212
1.0000	0.75914	0.000	2.082	0.000	1311	0.000

n-tetradecane(1)+ decane-1-ol (2)

0.0000	0.82632	0.000	11.792	0.000	1388	0.000
0.0555	0.82112	0.051	10.350	-0.903	1379	4.464
0.0998	0.81716	0.080	9.460	-1.363	1373	7.068
0.1554	0.81239	0.112	8.418	-1.864	1366	9.968
0.1998	0.80872	0.133	7.644	-2.207	1361	11.990
0.2555	0.80429	0.156	6.746	-2.565	1355	14.155
0.3000	0.80088	0.171	6.085	-2.794	1350	15.586
0.3555	0.79678	0.184	5.325	-3.014	1344	17.008
0.4000	0.79362	0.192	4.771	-3.136	1340	17.850
0.4555	0.78981	0.198	4.144	-3.224	1336	18.534
0.5000	0.78685	0.199	3.692	-3.245	1332	18.786
0.5556	0.78329	0.196	3.188	-3.209	1328	18.733
0.5998	0.78055	0.191	2.834	-3.133	1325	18.397
0.6555	0.77722	0.181	2.447	-2.979	1322	17.604
0.6998	0.77465	0.170	2.184	-2.812	1319	16.681
0.7555	0.77153	0.152	1.908	-2.547	1317	15.148
0.7999	0.76912	0.135	1.730	-2.293	1315	13.634
0.8555	0.76619	0.111	1.559	-1.925	1312	11.368
0.8998	0.76393	0.089	1.462	-1.591	1311	9.266
0.9555	0.76118	0.057	1.389	-1.123	1309	6.253
1.0000	0.75914	0.000	2.082	0.000	1311	0.000

n-tetradecane(1)+ dodecane-1-ol (2)

0.0000	0.82830	0.000	16.136	0.000	1452	0.000
0.0554	0.82370	0.050	14.469	-0.888	1436	5.130
0.0998	0.82015	0.072	13.294	-1.439	1426	7.226
0.1554	0.81578	0.095	11.914	-2.038	1415	9.529
0.2000	0.81235	0.111	10.879	-2.446	1406	11.119
0.2555	0.80814	0.127	9.677	-2.868	1396	12.778
0.2999	0.80485	0.138	8.784	-3.137	1388	13.849
0.3555	0.80078	0.148	7.747	-3.391	1379	14.869
0.3999	0.79761	0.154	6.986	-3.529	1372	15.427
0.4554	0.79370	0.158	6.112	-3.622	1364	15.805
0.4999	0.79062	0.159	5.473	-3.635	1358	15.851
0.5554	0.78685	0.156	4.753	-3.576	1351	15.588
0.5999	0.78388	0.151	4.234	-3.471	1346	15.120
0.6554	0.78024	0.142	3.657	-3.267	1340	14.216
0.6998	0.77737	0.133	3.250	-3.049	1335	13.236
0.7554	0.77385	0.117	2.809	-2.709	1330	11.689
0.8000	0.77107	0.102	2.508	-2.384	1326	10.191
0.8554	0.76767	0.081	2.196	-1.916	1321	8.007
0.8999	0.76500	0.060	1.995	-1.492	1318	5.999
0.9554	0.76171	0.032	1.804	-0.903	1313	3.172
1.0000	0.75914	0.000	2.082	0.000	1311	0.000

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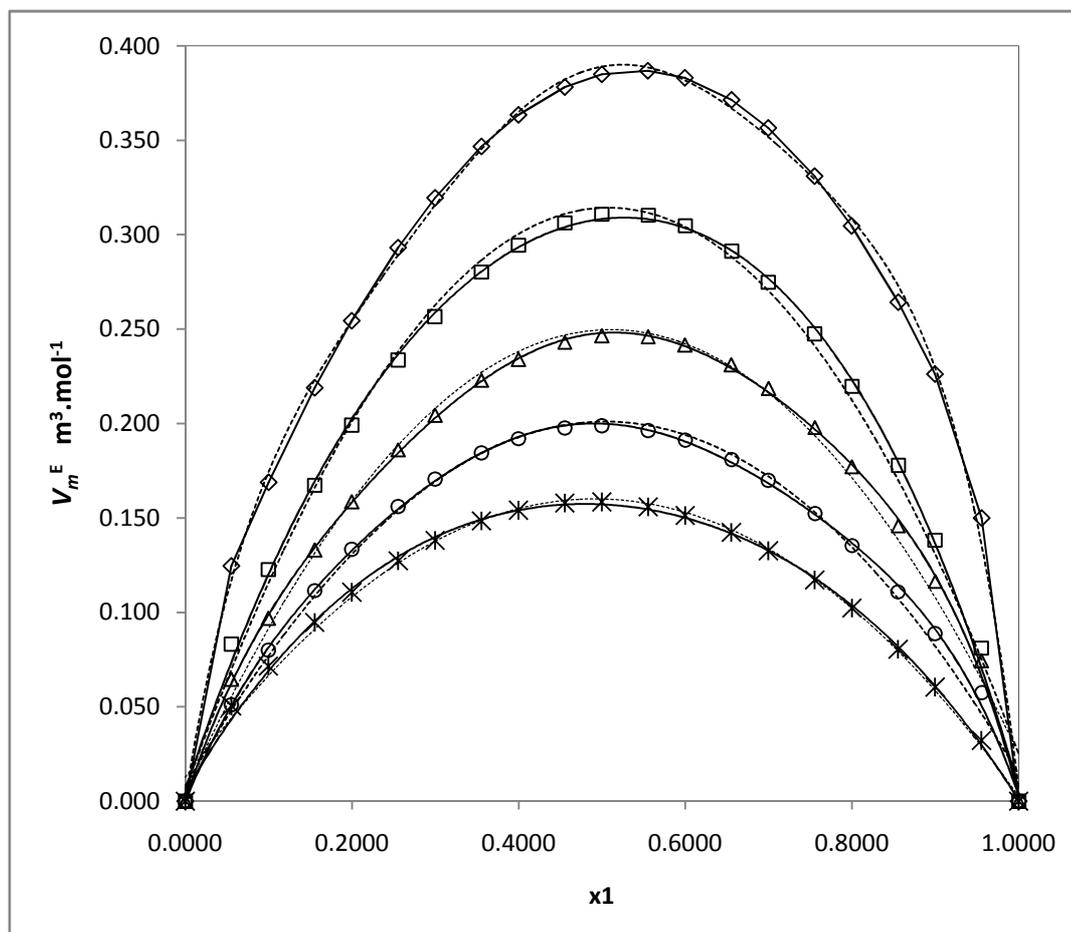
Figure 1. Plot of excess molar volumes (V_m^E) against mole fraction of n-tetradecane with (◊)) hexane-1-ol; (□) heptane-1-ol; octane-1-ol (Δ); decane-1-ol (o) and dodecane-1-ol (*) at T = 298.15 K. The corresponding dotted (- - - - -) curves have been derived from PFP theory.

Table 3: Coefficients ai of equation (7) and corresponding standard deviation (σ) of equation (8).

System	a0	a1	a2	a3	σ
n-tetradecane +hexane-1-ol					
V^E/(m^3.mol^{-1})	1.4029	0.388	1.465	0.3526	0.024
$\Delta\eta$/(mPa.s)	-5.977	0.905	0.644	-0.548	0.005
κ_s^E (TPa-1)	-9.562	6.625	7.215	6.875	1.425
n-tetradecane +heptane-1-ol					
V^E/(m^3.mol^{-1})	1.195	0.069	0.502	0.100	0.009
$\Delta\eta$/(mPa.s)	-8.224	-0.426	0.534	0.407	0.013
κ_s^E (TPa-1)	-1.168	1.208	-2.856	5.231	0.398
n-tetradecane +octane-1-ol					
V^E/(m^3.mol^{-1})	1.403	-2.680	5.111	-2.265	0.076
$\Delta\eta$/(mPa.s)	-8.188	0.295	-1.332	-2.314	0.003
κ_s^E (TPa-1)	9.415	-10.125	5.124	1.801	2.963
n-tetradecane +decane-1-ol					
V^E/(m^3.mol^{-1})	0.765	-0.100	0.352	0.359	0.007
$\Delta\eta$/(mPa.s)	-12.120	2.216	-8.645	-7.604	0.185
κ_s^E (TPa-1)	7.082	-6.523	4.123	4.321	1.085
n-tetradecane +dodecane-1-ol					
V^E/(m^3.mol^{-1})	-0.560	4.623	1.756	1.036	0.675
$\Delta\eta$/(mPa.s)	-14.096	1.801	-4.432	-4.409	0.095
κ_s^E (TPa-1)	-14.520	1.802	6.304	-4.423	1.491

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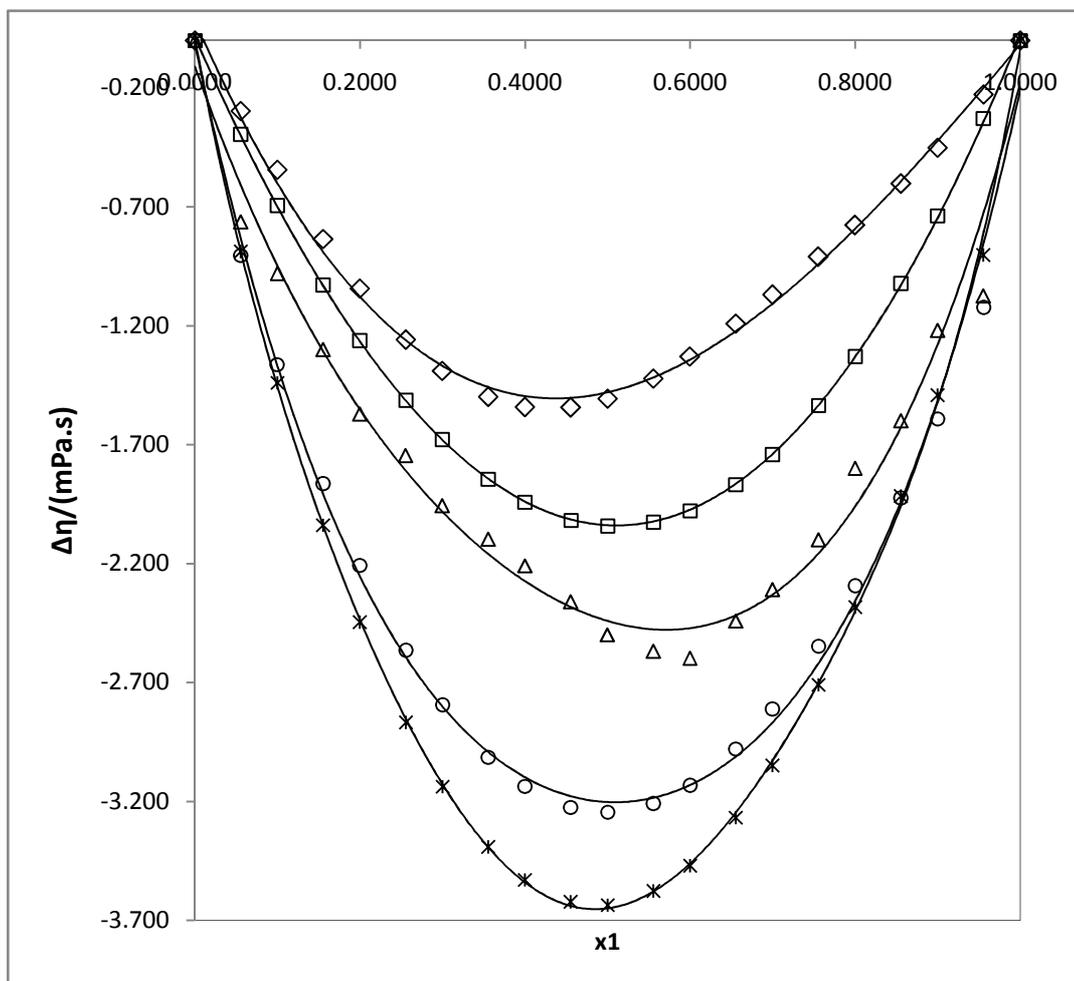
Figure 2. Plot of deviation in viscosity (Δη) against mole fraction n-tetradecane with (◊)) hexane-1-ol; (□) heptane-1-ol; octane-1-ol (Δ); decane-1-ol (o) and dodecane-1-ol (*) at T = 298.15 K.

Table 4: Flory parameters of the pure compounds at T=298.15 K.

Components	$10^6 V^*/(m^3 mol^{-1})$	$10^6 P^*(J.m^{-3})$	T*/K
n-dodecane	183.77	455	5290
Hexane-1-ol	102.682	460	5663
Heptane-1-ol	117.52	469	5762
Octane-1-ol	102.682	466	5872
decane-1-ol	158.549	478	5906
dodecane-1-ol	186.1	486	5956

Table 5: Calculated values of the three contributions to the excess molar volume from the PFP theory with interaction parameter at T=298.15 K.

Component	$\chi_{12}x10^6$ (J.m^{-3})	$V^E \times 10^6 (m^3.mol^{-1})$ at x=0.5		Calculated contribution		
		Experimental	PEP	$V^E \times 10^6$ (int)	$V^E \times 10^6$ (fv)	$V^E \times 10^6$ (p*)
n-tetradecane +hexane-1-ol	27.66	0.385	0.384	0.8361	0.004	-0.007
n-tetradecane +heptane-1-ol	13.29	0.311	0.31	0.4297	0.015	-0.132
n-tetradecane +octane-1-ol	9.33	0.246	0.247	0.2876	0.006	-0.0352
n-tetradecane +decane-1-ol	8.76	0.199	0.199	0.306	0.036	-0.0677
n-tetradecane +dodecane-1-ol	6.12	0.159	0.158	0.3853	0.04	-0.1794

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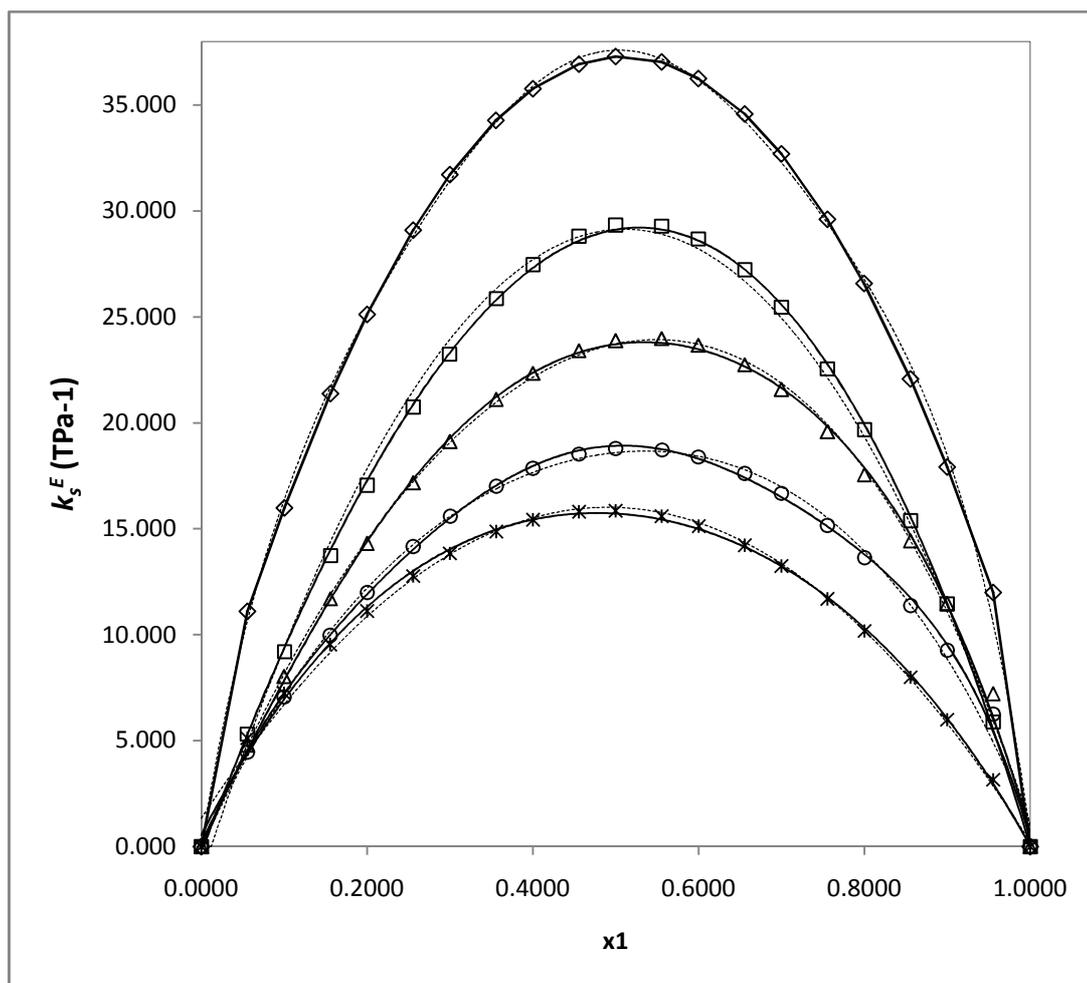
Figure 3. Plot of excess isentropic compressibility (κ_s^E) against mole fraction n-tetradecane with (◊)) hexane-1-ol; (□) heptane-1-ol; octane-1-ol (Δ); decane-1-ol (o) and dodecane-1-ol (*) at T = 298.15 K. The corresponding dotted (- - - - -) curves have been derived from PFP theory.

Table 6: Comparison of experimental and calculated values of the speed of sound u, and isentropic compressibility, ks of binary mixtures at x1 = 0.5, and standard percentage deviation at T=298.15 K.

Binary Mixture	$u(m\ s^{-1})$			Ks (TPa^{-1})		
	Experimental	vdw	σ%	Experimental	vdw	σ%
n-tetradecane +hexane-1-ol	1285	1285	0.000	7.82	7.81	0.36
n-tetradecane +heptane-1-ol	1302	1301	0.005	7.55	7.56	0.524
n-tetradecane +octane-1-ol	1312	1314	0.005	7.42	7.4	0.26
n-tetradecane +decane-1-ol	1332	1332	0.006	7.23	7.23	0.009
n-tetradecane +dodecane-1-ol	1358	1358	0.000	6.88	6.89	0.007

CONCLUSION

Densities, speeds of sound, and viscosities for the binary liquid mixture n-tetradecane with hexan-1-ol, heptan-1-ol, octan-1-ol, decan-1-ol and dodecan-1-ol of 288.15 K over the whole range of compositions. The positive V_m^E, $k^E s$ and negative values $\Delta\eta$ for the mixtures suggest that the rupture of hydrogen bonded chain of the dipolar interaction between solute and alkan-1-ol exceed the intermolecular interaction through dipole-dipole and hydrogen bonding between n-tetradecane and alkan-1-ol molecules. This behavior is characteristic for systems containing an associated component.

PFP theory is quite successful in predicting the trend of the dependence of V_m^E on composition for the present systems.

REFERENCES

[1] P. Venkatesu, D. Venkatesulu, M.V. Prabhakara Rao; *J. Indian Council of Chemists,* **1996**, 12, 30.

[2] R. Mehra, H. Sajnani; *Phys. Chem. Liq.* **2000,** 38,683.

[3] R. Mehra, H. Sajnani; *Phys. Chem. Liq.***2001**, 39, 581.

[4] I.L. Acevedo, G.C. Pedrosa, E.L. Arancibia, M. Katz; *J. Solution Chem*. **2001**, 30, 1029–1037.

[5] B. Giner, I. Gasc´on, H. Artigas, F.M. Royo, C. Lafuente;. *J. Phys. Chem B.* **2005,**109, 23096–23102.

[6] A. R. Mahajan, S.R. Mirgane, S B. Deshmukh; *Mat. Sci. Res. India*, **2007,** 4(2), 345-552.

[7] A. R. Mahajan, S.R. Mirgane, S B. Deshmukh; *Mat. Sci. Res. India*, **2007,** 4(2), 373-378.

[8] A.Pal,R. Bhardwaj ; *Indian J chem*. **2002,**41A, 706-711.

[9] A.Riddick , W.B.Bunger, T.K.Sakano ;Techniques of Chemistry, Organic Solvents, Physical Properties and Methods of Purifications, vol. II, John Wiley & Sons, New York, **1986**.

[10] O.Redlich, A.T.Kister; *Ind. Eng. Chem*. **1948**, 40, 345-348.

[11] A.J.Treszczanowicz, G.C.Benson; *J. Chem. Thermodyn. ,* **1978,** 10, 967-974.

[12] A.Ali, A. Nain, V.Sharma, S.Ahmed; Indian *J pure appl phys,* **2004,** 42,666-673.

[13] R.Mehra, M.Pancholi.; *Indian J. phys*, **2006,** 80 253-263.

[14] Yang, Changsheng, Xu Wei, Peisheng Ma;*J. Chem. Eng. Data*, **2004,** 49, 1794–1801.

[15] O.Kiyohara, G.C.Benson; *J.Chem.Thermodyn*, **1979**, 11,861-873.

[16] R.D.Rai, R.Shukla,A.K.Shukla, J.D.Pandey; *J.Chem.Thermodyn.*,**1989**, 21,125-129.

[17] P.J.Flory; *J. Am. Chem. Soc*. **1965**, 87, 1833–1838.

[18] A.Abe, P.J.Flory; J. *Am. Chem. Soc*. **1965**, 87, 1838–1846.

[19] I.Prigogine; Molecular Theories of Solutions, North-Holland Publishing Company, Amsterdam, **1957**.

[20] D.Patterson, G.Delmas; Discuss*. Faraday Soc*. **1970**, 49, 98–105.

[21] A.T.Rodriguez., D.Patterson ;*J. Chem. Soc., Faraday Trans*. **1982**,278,501–523.

[22] T.M.Aminabhavi, K.Banerjee, R.H.Balundgi ,*Indian J. Chem*. **1999**,38A ,768–777.

[23] V.D.Bhandarkar,G.R.Bedare,V.D.Muley,B.M.Suryawanshi; *Advances in Applied Science Research*. **2011**,2(4) ,378-347.

[24] S O.P.Chimankar,R.S.Shriwas,S.Jajodia,V.A.Tabhane ; *Advances in Applied Science Research*. **2011**,2(3) ,500-508.

[25] O.P.Chimankar,R.S.Shriwas,V.A.Tabhane; *Advances in Applied Science Research*. **2010**,1(3),78-85.

[26] S.K.Thakur,S.Chouhan, *Advances in Applied Science Research*. **2011**,2(2) ,208-217.

[27] S.S.Patil,S.R.Mirgane,B.R.Arbad; *Advances in Applied Science Research*. **2012**,3(4) ,2378-1387.