Available online at www.sciencedirect.com

SCIENCE DIRECT

Thermochimica Acta 440 (2006) 43–50

thermochimica acta

www.elsevier.com/locate/tca

Excess volumes, densities, speeds of sound and viscosities for the binary systems of diisopropyl ether with hydrocarbons at 303.15 K

K.V.N. Suresh Reddy, G. Sankara Reddy, A. Krishnaiah*

Department of Chemistry, Sri Venkateswara University, Tirupati 517 502, India

Received 26 July 2005; received in revised form 6 October 2005; accepted 12 October 2005
Available online 14 November 2005

Abstract

Experimental results of excess volumes, speeds of sound and viscosities at 303.15 K are presented for the binary systems of diisopropyl ether with hexane, heptane, octane, isooctane, benzene, cyclohexane, tetralin and decalin over the entire range of composition. Isentropic compressibilities are calculated from speed of sound and density data. Speeds of sound are evaluated on the basis of Jacobson free length theory and Schaaffs collision factor theory. Further, the viscosity data was analysed on the basis of corresponding states approach and Grunberg and Nissan treatment. The experimental results are discussed in terms of molecular interactions between unlike molecules.

Keywords: Diisopropyl ether; Hydrocarbons; FLT theory; CFT theory; Corresponding states approach; Grunberg and Nissan treatment

1. Introduction

Thermodynamic and transport properties of mixtures containing fuel oxygenates are important as these fuel oxygenates are used to enhance the octane rating and reduce pollution. Methyl *tert*-butyl ether has been used extensively as an octane-enhancing additive. But it dissolves easily in water and causes health risk by contaminating drinking water [1–3]. In addition, it is resistant to microbial decomposition. Recently, it has been replaced by diisopropyl ether, which is environmentally benign. Treszczanowicz et al. [4] reported excess volumes for the binary system of diisopropyl ether with heptane at 298.15 K. Mahl et al. [5] reported excess volume data for the binary systems of diisopropyl ether with aromatic hydrocarbons at 308.15 K. Sharma et al. [6] reported isentropic compressibilities for the binary systems of diisopropyl ether with benzene and cyclohexane and Blanco et al. [7] reported excess volumes of diisopropyl ether + isooctane at 298.15 K. In continuation of our work on thermodynamic and transport properties of octane-enhancing additives [8–10], we report excess volumes, densities, speeds of sound, isentropic compressibilities, deviations in compressibility and deviations in viscosity for the binary systems of diisopropyl ether with hexane, heptane, octane, isooctane, benzene, cyclohexane, tetralin and decalin at 303.15 K. Further speeds of sound data are evaluated on the basis of Jacobson free length theory and Schaaffs collision factor theory. The viscosity data was analysed on the basis of corresponding states approach and Grunberg–Nissan treatment. The objective of this paper is to study the interactions between diisopropyl ether and hydrocarbons through excess volumes, deviations in isentropic compressibility and deviations in viscosity.

2. Materials and methods

All the chemicals, except diisopropyl ether, tetralin and decalin are supplied by S.D. Fine Chemicals Pvt. Ltd., Mumbai (India). Analytical grade diisopropyl ether supplied by E. Merk Ltd. (Mumbai, India) and tetralin and decalin supplied by Riedel (Germany) were used with out further purifications after gas chromatography failed to show any significant impurities. Other chemicals hexane, heptane, octane, isooctane, benzene and cyclohexane were purified through the methods described by Riddick et al. [11]. The purity of the samples were checked by comparing the measured boiling points and densities of the samples with those reported in the literature [11]. Experimental values were in agreement with literature values. The data is presented in Table 1.

---

* Corresponding author. Tel.: +91 9393621986; fax: +91 877 2249611.
E-mail address: abburikrish@yahoo.com (A. Krishnaiah).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.10.008

Table 1
Boiling points (T_{bp}) and densities (ρ) at 298.15 K of the pure components

Component	T_{bp} (K)		ρ (kg/m^3)	
	This work	Reference	This work	Reference
Diisopropyl ether	341.35	341.45	718.14	718.20
Hexane	341.85	341.89	654.90	654.81
Heptane	371.35	371.57	678.93	679.51
Octane	399.15	398.81	697.36	698.49
Isooctane	383.05	382.99	711.22	712.07
Benzene	353.15	353.20	873.64	873.70
Cyclohexane	353.95	353.87	773.98	773.89
Tetralin	464.25	464.85	965.89	966.20
Decalin	481.45	480.72	879.14	878.90

Excess volumes were measured by dilatometer described by Reddy et al. [12]. The experimental method was checked for the test system benzene + cyclohexane and the results showed a standard deviation of ±0.004 cm^3 mol^{-1}. Four dilatometers with different capacities were used to cover the entire range of composition. Densities of pure liquids were measured with bicapillary pycnometer described by Rao et al. [13]. These values are accurate to five parts in 10^5. The speeds of sound of the liquids and mixtures were measured with single crystal ultrasonic interferometer at a fixed frequency of 3 MHz, and the values were accurate to ±0.15%. The viscosities of pure liquids and liquid mixtures were determined by suspended Ubbelohde-type viscometer described by Krishnaiah et al. [14]. The measured viscosities were accurate to 0.001 cP. All the measurements were made using a thermostat bath maintained at 303.15 ± 0.01 K.

3. Results and discussion

The experimental excess volume data at 303.15 K for the binary systems of diisopropyl ether with hexane, heptane, octane, isooctane, benzene, cyclohexane, tetralin and decalin are reported in Table 2. The dependency of V^E on mole fraction of diisopropyl ether is graphically represented in Fig. 1.The isenropic compressibilities (k_s) are computed from the density (ρ) and sound speed (u) data using the equation:

$$k_s = \frac{1}{u^2\rho} \tag{1}$$

Densities are computed from measured excess volume data from the following equation:

$$\rho = \frac{x_1M_1 + x_2M_2}{x_1V_1 + x_2V_2 + V^E} \tag{2}$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 the molecular weights and V_1 and V_2 are the molar volumes of diisopropyl ether and hydrocarbons, respectively. Deviation in isentropic compressibility (Δk_s) are calculated using the relation:

$$\Delta k_s = k_s - \phi_1 k_{s,1} - \phi_2 k_{s,2} \tag{3}$$

where $k_{s,1}$, $k_{s,2}$ and k_s are the isentropic compressibilities of pure components 1, 2 and mixtures, respectively, ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, respectively. Data on speed of sound (u), density (ρ), isentropic compressibility (k_s) and deviation in isentropic compressibility (Δk_s) are given in Table 3 and variation of Δk_s with volume fraction is shown in Fig. 2.

Sound speeds, evaluated on the basis of Jacobson free length theory [15–17] and Schaaffs collision factor theory [18–20], are given in Table 3. The details of the theories are discussed in our earlier publication [9]. The required parameters to evaluate the sound speeds are given in Table 4.

The viscosities of the pure components and mixtures are calculated using the equation:

$$\eta = k_v \rho t \tag{4}$$

where k_v is viscometer constant and ρ and t are the density and flow time, respectively. The densities of mixtures are calculated from Eq. (2). Deviation in viscosities ($\Delta\ln\eta$) of the mixtures are calculated using the following relation:

$$\Delta\ln\eta = \ln\eta_{mix} - x_1 \ln\eta_1 - x_2 \ln\eta_2 \tag{5}$$

where η_{mix} is the viscosity of the mixture, η_1 and η_2 are the viscosities of diisopropyl ether and hydrocarbons, respectively.

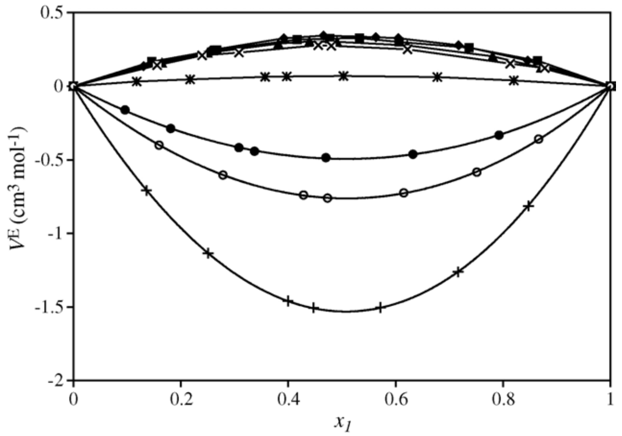

Fig. 1. Excess volume (V^E) vs. diisopropyl ether (DIPE) mole fraction (x_1) for the binary systems of DIPE with hexane (⧫), heptane (■), octane (▲), isooctane (×), benzene (●), cyclohexane (✱), tetralin (+) and decalin (○).

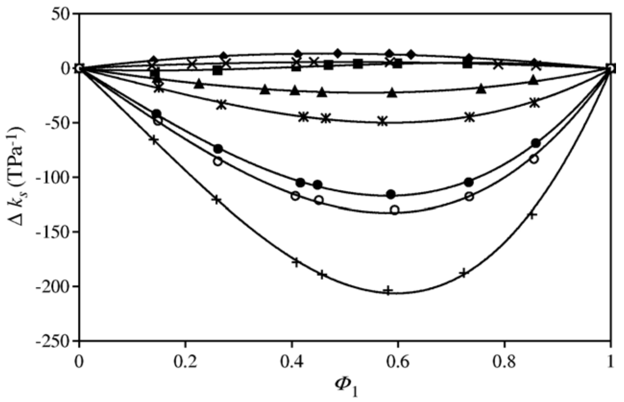

Fig. 2. Deviation in isentropic compressibility (Δk_s) vs. diisopropyl ether (DIPE) volume fraction (Φ_1) for the binary systems of DIPE with hexane (⧫), heptane (■), octane (▲), isooctane (×), benzene (●), cyclohexane (✱), tetralin (+) and decalin (○).

Table 2
Data on density (ρ), excess volume (V^E), viscosity (η) and deviations in viscosity ($\Delta\ln\eta$) for the binary mixtures of diisopropyl ether with hydrocarbons at 303.15 K

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	η_{Exp} (cP)	$\eta_{\mathrm{Eq.\,6}}$ (cP)	$\eta_{\mathrm{Eq.\,7}}$ (cP)	$\Delta\ln\eta$ (cP)
Diisopropyl ether + hexane						
0	0.65064	0	0.309	–	–	0
0.1305	0.65854	0.137	0.312	0.312	0.312	−0.0087
0.2555	0.66605	0.245	0.315	0.315	0.314	−0.0138
0.3920	0.67425	0.326	0.319	0.319	0.319	−0.0177
0.4661	0.67875	0.344	0.321	0.321	0.321	−0.0198
0.5633	0.68474	0.334	0.325	0.325	0.325	−0.0205
0.6050	0.68730	0.325	0.326	0.327	0.327	−0.0213
0.7173	0.69423	0.279	0.331	0.333	0.333	−0.0195
0.8460	0.70228	0.174	0.338	0.340	0.340	−0.0142
1	0.71197	0	0.350	–	–	0
Diisopropyl ether + heptane						
0	0.67438	0	0.387	–	–	0
0.1462	0.67894	0.167	0.385	0.378	0.376	0.0091
0.2667	0.68301	0.245	0.377	0.371	0.368	0.0004
0.4165	0.68823	0.316	0.365	0.364	0.361	−0.0164
0.4774	0.69047	0.324	0.359	0.362	0.359	−0.0267
0.5331	0.69254	0.327	0.356	0.360	0.357	−0.0302
0.6068	0.69543	0.301	0.352	0.357	0.354	−0.0345
0.7371	0.70057	0.261	0.346	0.354	0.352	−0.0364
0.8642	0.70586	0.173	0.345	0.351	0.350	−0.0271
1	0.71197	0	0.350	–	–	0
Diisopropyl ether + octane						
0	0.69256	0	0.477	–	–	0
0.1650	0.69472	0.158	0.464	0.453	0.450	0.0232
0.2501	0.69594	0.226	0.451	0.442	0.437	0.0224
0.3816	0.69804	0.295	0.429	0.424	0.419	0.0116
0.4395	0.69906	0.304	0.417	0.417	0.411	0.0020
0.4911	0.70005	0.302	0.404	0.410	0.405	−0.0142
0.6217	0.70269	0.278	0.381	0.394	0.389	−0.0319
0.7805	0.70626	0.203	0.360	0.375	0.372	−0.0392
0.8706	0.70852	0.126	0.354	0.364	0.362	−0.0284
1	0.71197	0	0.350	–	–	0
Diisopropyl ether + isooctane						
0	0.67991	0	0.455	–	–	0
0.1561	0.68368	0.143	0.441	0.436	0.435	0.0104
0.2397	0.68582	0.209	0.432	0.427	0.425	0.0107
0.3083	0.68771	0.228	0.422	0.419	0.418	0.0067
0.4565	0.69178	0.279	0.405	0.404	0.402	0.0033
0.4804	0.69283	0.275	0.400	0.400	0.399	−0.0028
0.6222	0.69750	0.250	0.380	0.386	0.384	−0.0151
0.8133	0.70444	0.154	0.360	0.367	0.366	−0.0189
0.8775	0.70687	0.124	0.355	0.361	0.360	−0.0167
1	0.71197	0	0.350	–	–	0
Diisopropyl ether + cyclohexane						
0	0.76914	0	0.793	–	–	0
0.1180	0.76038	0.032	0.666	0.671	0.666	−0.0781
0.2172	0.75357	0.047	0.589	0.590	0.589	−0.1192
0.3570	0.74466	0.063	0.513	0.503	0.513	−0.1436
0.3972	0.74223	0.066	0.494	0.483	0.494	−0.1471
0.5029	0.73613	0.069	0.452	0.440	0.451	−0.1513
0.6777	0.72683	0.063	0.403	0.393	0.403	−0.1230
0.8199	0.71996	0.039	0.373	0.369	0.373	−0.0820
1	0.71197	0	0.350	–	–	0
Diisopropyl ether + benzene						
0	0.86839	0	0.566	–	–	0
0.0962	0.84710	−0.161	0.542	0.543	0.542	0.0043
0.1813	0.82994	−0.287	0.522	0.523	0.522	0.0072
0.3084	0.80652	−0.417	0.492	0.493	0.493	0.0086
0.3375	0.80153	−0.442	0.486	0.486	0.486	0.0098
0.4703	0.77997	−0.486	0.456	0.457	0.456	0.0113

Table 2 (*Continued*)

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	η_{Exp} (cP)	$\eta_{Eq. 6}$ (cP)	$\eta_{Eq. 7}$ (cP)	$\Delta\ln\eta$ (cP)
0.6323	0.75656	−0.462	0.422	0.422	0.422	0.0101
0.7927	0.73584	−0.332	0.389	0.389	0.389	0.0070
1	0.71197	0	0.350	–	–	0
Diisopropyl ether + tetralin						
0	0.95544	0	1.749	–	–	0
0.1358	0.92602	−0.708	1.445	1.441	1.445	0.0279
0.2509	0.89997	−1.135	1.223	1.218	1.223	0.0459
0.3997	0.86495	−1.459	0.976	0.972	0.976	0.0599
0.4474	0.85343	−1.505	0.904	0.903	0.904	0.0600
0.5718	0.82279	−1.503	0.739	0.741	0.739	0.0580
0.7163	0.78622	−1.261	0.578	0.583	0.578	0.0447
0.8473	0.75228	−0.813	0.460	0.464	0.460	0.0287
1	0.71197	0	0.350	–	–	0
Diisopropyl ether + decalin						
0	0.86850	0	2.091	–	–	0
0.1596	0.84777	−0.400	1.586	1.579	1.586	0.0092
0.2785	0.83132	−0.603	1.289	1.280	1.289	0.0139
0.4286	0.80927	−0.739	0.989	0.981	0.989	0.0179
0.4734	0.80244	−0.760	0.913	0.906	0.913	0.0176
0.6153	0.77984	−0.724	0.706	0.703	0.706	0.0147
0.7514	0.75698	−0.584	0.553	0.550	0.553	0.0126
0.8663	0.73665	−0.359	0.448	0.446	0.448	0.0090
1	0.71197	0	0.350	–	–	0

Viscosities and deviations in viscosity are presented in Table 2 and deviations in viscosity as function of diisopropyl ether mole fraction are graphically represented in Fig. 3.

Further, the viscosities are analysed in terms of corresponding states approach and Grunberg and Nissan treatment. On the basis of corresponding states approach, Teja and Rice [21,22] proposed the following expression for the liquid mixture viscosity:

$$\ln(\eta_{mix}\xi_{mix}) = x_1 \ln(\eta_1\xi_1) + x_2 \ln(\eta_2\xi_2) \tag{6}$$

where $\xi = (V_c)^{2/3}/(T_c M)^{1/2}$; T_c, V_c and M are critical temperature, critical volume and molecular mass, respectively. The values of these parameters are evaluated by the procedure described by Krishnaiah and Viswanath [23]. The values of the interaction parameter (ε_{12}) used in this theory are given in Table 5.

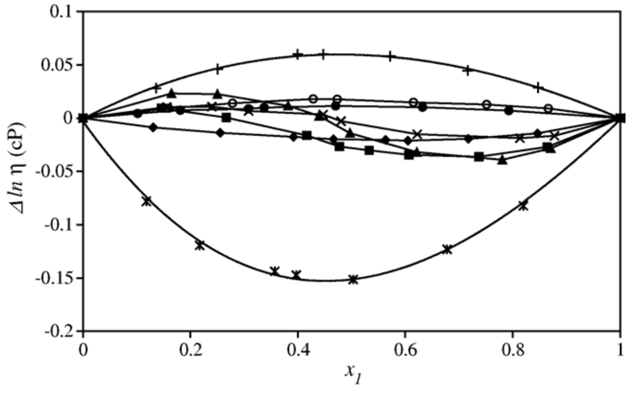

Fig. 3. Deviation in viscosity ($\Delta\ln\eta$) vs. diisopropyl ether (DIPE) mole fraction (x_1) for the binary systems of DIPE with hexane (◆), heptane (■), octane (▲), isooctane (×), benzene (●), cyclohexane (✱), tetralin (+) and decalin (○).

According to Grunberg and Nissan treatment [24], the low temperature viscosity for the mixture is given as

$$\ln\eta_m = x\ln\eta_1 + (1-x)\ln\eta_2 + x(1-x)d_{12} \tag{7}$$

where d_{12} is an interaction parameter, which is a function of chemical nature of the component and temperature. The value of d_{12} obtained from a fit of the above equation to the viscosity at $x = 0.5$, was used to compute the viscosities over the entire range of composition. The values of d_{12} are given in Table 5 and the values of viscosities based on these two theories are reported in Table 2.

Finally, the values of V^E, Δk_s and $\Delta\ln\eta$ for the binary systems are fitted to the following equation:

$$A = z_1 z_2[a_0 + a_1(z_1 - z_2) + a_2(z_1 - z_2)^2] \tag{8}$$

where z_1 and z_2 represent, respectively, the mole fractions with respect to V^E, $\Delta\ln\eta$ and volume fractions in case of Δk_s and A is the corresponding thermodynamic property. The values of the parameters, a_0–a_2 obtained by least square analysis are included in Table 6 along with the standard deviation. The values of standard deviation are calculated by the following equation:

$$\sigma(A) = \left[\frac{\Sigma(A_{cal} - A_{exp})^2}{n-p}\right]^{1/2} \tag{9}$$

where n is the number of experimental points and p is the number of parameters.

The values of excess volumes were positive for the binary systems of diisopropyl ether with hexane, heptane, octane, isooctane, cyclohexane and negative with benzene, tetralin and decalin. The algebric values of V^E of the mixtures of diisopropyl

Table 3
Volume fraction (ϕ_1) of diisopropyl ether (DIPE), density (ρ), sound velocity (U_{Exp}, U_{FLT}, U_{CFT}) and deviation in isentropic compressibility (Δk_{s}) for the binary systems of diisopropyl ether with hydrocarbons at 303.15 K

ϕ_1	ρ (g cm^{-3})	U_{Exp} (ms^{-1})	U_{FLT} (ms^{-1})	U_{CFT} (ms^{-1})	k_{s} (TPa^{-1})	Δk_{s} (TPa^{-1})
Diisopropyl ether + hexane						
0	0.65064	1052.9	–	–	1386.3	0
0.1399	0.65854	1039.2	1038.9	1044.2	1406.1	6.9
0.2710	0.66605	1027.5	1026.6	1034.7	1422.1	10.9
0.4112	0.67425	1016	1014.0	1024.2	1436.7	12.7
0.4861	0.67875	1009.9	1007.8	1019.0	1444.5	13.7
0.5829	0.68474	1002.6	1000.5	1012.0	1452.8	13.1
0.6240	0.68730	999.6	997.7	1009.4	1456.1	12.7
0.7333	0.69423	992.4	990.5	1001.7	1462.5	9.1
0.8562	0.70228	984.4	982.9	992.1	1469.4	4.7
1	0.71197	974.9	–	–	1477.8	0
Diisopropyl ether + heptane						
0	0.67438	1110.5	–	–	1202.4	0
0.1419	0.67894	1090.7	1081.5	1096.1	1238.0	−3.4
0.2600	0.68301	1072.8	1063.7	1079.4	1272.1	−1.8
0.4081	0.68823	1050.6	1043.1	1058.3	1316.3	1.5
0.4688	0.69047	1041.8	1035.1	1050.1	1334.3	2.8
0.5244	0.69254	1033.9	1028.1	1042.4	1350.8	3.9
0.5985	0.69543	1023.9	1018.9	1032.8	1371.5	4.3
0.7303	0.70057	1006.9	1003.7	1015.0	1407.9	4.3
0.8601	0.70586	991.3	989.6	998.2	1441.6	2.3
1	0.71197	974.9	–	–	1477.8	0
Diisopropyl ether + octane						
0	0.69256	1152	–	–	1088.0	0
0.1467	0.69472	1125.5	1118.0	1128.7	1136.3	-8.9
0.2249	0.69594	1112.3	1102.2	1113.5	1161.4	−14.3
0.3493	0.69804	1090.5	1078.3	1090.0	1204.6	−19.5
0.4056	0.69906	1080.3	1068.0	1079.6	1225.7	−20.4
0.4564	0.70005	1071.7	1058.9	1070.4	1243.7	−22.2
0.5885	0.70269	1048.3	1036.7	1047.3	1294.9	−22.4
0.7558	0.70626	1018.9	1010.4	1019.2	1363.8	−18.7
0.8541	0.70852	1000.4	995.7	1003.3	1410.2	−10.7
1	0.71197	974.9	–	–	1477.8	0
Diisopropyl ether + isooctane						
0	0.67991	1060.8	–	–	1307.0	0
0.1364	0.68368	1047.6	1045.0	1052.8	1332.7	2.4
0.2122	0.68582	1040.4	1037.2	1045.4	1347.0	3.7
0.2757	0.68777	1034.5	1030.9	1039.4	1358.6	4.5
0.4086	0.69178	1022.6	1018.2	1027.3	1382.3	5.5
0.4413	0.69283	1019.7	1015.2	1024.3	1388.1	5.7
0.5845	0.69750	1007.5	1003.3	1012.1	1412.4	5.5
0.7882	0.70444	991.1	988.2	995.9	1445.1	3.5
0.8596	0.70687	985.6	983.3	990.5	1456.3	2.4
1	0.71197	974.9	–	–	1477.8	0
Diisopropyl ether + cyclohexane						
0	0.76914	1231	–	–	857.9	0
0.1494	0.76038	1187.4	1186.1	1205.7	932.7	−17.8
0.2670	0.75357	1157.7	1153.1	1179.4	990.0	−33.3
0.4215	0.74466	1117.9	1111.7	1142.5	1074.5	−44.6
0.4638	0.74223	1106.9	1100.8	1132.2	1099.6	−45.8
0.5704	0.73613	1080.7	1073.8	1104.9	1163.1	−48.4
0.7340	0.72683	1041.6	1034.4	1060.5	1268.1	−44.8
0.8569	0.71996	1011.6	1006.5	1025.0	1357.2	−31.6
1	0.71197	974.9	–	–	1477.8	0
Diisopropyl ether + benzene						
0	0.86839	1275.5	–	–	707.8	0
0.1452	0.84710	1232.1	1233.2	1253.6	777.6	−42.0
0.2610	0.82994	1201.5	1199.2	1227.7	834.6	−74.1
0.4157	0.80652	1159.2	1154.0	1189.2	922.7	−105.2
0.4483	0.80153	1148.4	1144.4	1180.5	945.9	−107.0

Table 3 (*Continued*)

ϕ_1	ρ (g cm^{-3})	U_{Exp} (ms^{-1})	U_{FLT} (ms^{-1})	U_{CFT} (ms^{-1})	k_{s} (TPa^{-1})	Δk_{s} (TPa^{-1})
0.5862	0.77997	1108.5	1103.0	1140.1	1043.3	−115.8
0.7329	0.75656	1064.1	1058.3	1091.0	1167.3	−104.8
0.8591	0.73584	1022.2	1019.4	1042.6	1300.5	−68.7
1	0.71197	974.9	–	–	1477.8	0
Diisopropyl ether + tetralin						
0	0.95544	1477	–	–	479.7	0
0.1402	0.92602	1396.1	1399.9	1417.9	554.0	−65.6
0.2578	0.89997	1342.5	1341.6	1361.5	616.5	−120.6
0.4085	0.86495	1276.3	1267.2	1287.6	709.7	−177.7
0.4564	0.85343	1253.0	1244.7	1264.1	746.2	−189.0
0.5807	0.82279	1191.8	1180.8	1200.9	855.6	−203.7
0.7236	0.78622	1119.7	1107.8	1126.7	1014.4	−187.5
0.8520	0.75228	1054.2	1044.1	1059.1	1196.1	−134.0
1	0.71197	974.9	–	–	1477.8	0
Diisopropyl ether + decalin						
0	0.86850	1404	–	–	584.1	0
0.1478	0.84777	1329	1328.7	1345.3	667.8	−48.3
0.2606	0.83132	1282.3	1272.4	1294.9	731.5	−85.4
0.4064	0.80927	1220.1	1204.1	1230.5	830.0	−117.2
0.4507	0.80244	1199.7	1184.9	1211.3	865.8	−121.1
0.5935	0.77984	1141.3	1124.7	1149.9	984.4	−130.0
0.7340	0.75698	1084.9	1069.0	1090.3	1122.3	−117.7
0.8554	0.73665	1035.8	1026.8	1040.2	1265.2	−83.3
1	0.71197	974.9	–	–	1477.8	0

ether with hydrocarbons fall in the order:

$$\text{hexane} > \text{heptane} > \text{octane} > \text{isooctane} > \text{cyclohexane} > \text{benzene} > \text{decalin} > \text{tetralin}$$

This trend would seem to indicate more organised packing effect in mixtures containing bicyclic compounds and benzene than other hydrocarbons. The excess volumes were negative in mixtures containing tetralin, decalin and benzene. The values were more negative with tetralin (aromatic) when compared to decalin (alicyclic), this may be due to the specific interactions present between oxygen atom of ether and π electrons of aromatic hydrocarbons. V^{E} values were negative with benzene when compared to cyclohexane. This reflects stronger specific interactions present between branched chain ethers and aromatic hydrocarbons through n–π (aromatic) interactions. In the case of normal hydrocarbons V^{E} decreases with increase in chain length of *n*-alkanes. The same trend was observed by Rodriguez et al. [25] in case of methyl *tert*-butyl ether with alkanes.

The deviations in isentropic compressibility (Δk_{s}) for the binary systems of diisopropyl ether follow the order:

$$\text{hexane} > \text{heptane} > \text{isooctane} > \text{octane} > \text{cyclohexane} > \text{benzene} > \text{decalin} > \text{tetralin}$$

The deviation in isentropic compressibility is approximately proportional to strength of interactions between dissimilar molecules in the mixture. In case of aromatic hydrocarbons, negative deviations in isentropic compressibility indicate that the mixture is tends to become a closed packed structure and hence less compressible. In case of normal hydrocarbons and cyclic alkanes, the deviations in compressibility were greater than those of aromatic hydrocarbons. It may be due to the presence of π electrons in aromatic hydrocarbons. This further supports the

Table 4
Molar volume (V), molar volume at absolute zero (V_0), available volume (V_{a}), free length (L_{f}), surface area (Y), collision factor (S) and average molecular radius (r_{m}) of the pure liquid components at 303.15 K

Component	V (cm^3 mol^{-1})	V_0 (cm^3 mol^{-1})	V_{a} (cm^3 mol^{-1})	L_{f} (Å)	Y	S	r_{m} (Å)
DIPE	143.51	108.51	35.00	0.767	91.274	1.340	2.959
Hexane	132.45	100.82	31.65	0.743	85.190	1.463	2.873
Heptane	148.59	116.04	32.34	0.691	93.479	1.487	3.02
Octane	164.94	131.25	33.69	0.659	102.19	1.502	3.154
Isooctane	168.01	131.54	36.45	0.721	101.06	1.429	3.141
Benzene	89.95	71.28	18.66	0.530	70.307	1.718	2.549
Cyclohexane	109.44	86.23	23.20	0.585	79.384	1.658	2.722
Tetralin	138.37	117.41	20.95	0.437	95.908	1.879	2.998
Decalin	159.18	135.03	24.147	0.482	100.19	1.863	3.102

Table 5
Values of interaction parameters (ε_{12}, d_{12}) and average absolute deviation (AAD) for the binary systems of diisopropyl ether (DIPE) with hydrocarbons at 303.15 K

DIPE with	ε_{12}	AAD	d_{12}	AAD
Hexane	0.921	0.001	−0.078	0.001
Heptane	0.928	0.005	−0.111	0.004
Octane	1.009	0.005	−0.054	0.006
Isooctane	0.997	0.004	−0.020	0.004
Benzene	1.085	0.001	0.046	0.001
Cyclohexane	0.411	0.007	−0.593	0.004
Tetralin	1.218	0.004	0.271	0.005
Decalin	0.997	0.005	0.065	0.001

explanation for V^E given above. In case of normal hydrocarbons, the deviations in compressibility decreases with increase in the carbon number of *n*-alkanes. Table 3 shows that the sound speed values decrease with increasing ether concentration, and corresponding values of L_f, which are used in FLT theory decreases for all the binary systems, as a results of mixing of the component liquids. This observation is in accordance with the views proposed by Eyring and Kincaid [26]. Though FLT and CFT theories are based on different concepts, they are capable of predicting the sound speed data with maximum deviation of 2.9%.

Table 6
Values of the parameters of Eq. (8) and standard deviations at 303.15 K

Property	a_0	a_1	a_2	σ (property)
Diisopropyl ether (1) + hexane (2)				
V^E (cm^3 mol^{-1})	1.3743	0.0730	−0.1955	0.004
Δk_s (TPa^{-1})	53.2	−11.9	−11.9	0.7
$\Delta \ln \eta$ (cP)	−0.0819	0.0596	−0.1088	0.008
Diisopropyl ether (1) + heptane (2)				
V^E (cm^3 mol^{-1})	1.2879	0.0689	0.180	0.007
Δk_s (TPa^{-1})	11.9	32.6	−37.8	0.6
$\Delta \ln \eta$ (cP)	−0.1060	−0.2	0.0632	0.001
Diisopropyl ether (1) + octane (2)				
V^E (cm^3 mol^{-1})	1.2218	−0.0155	−0.1571	0.004
Δk_s (TPa^{-1})	−95.3	−13.7	20.3	2.7
$\Delta \ln \eta$ (cP)	−0.0473	−0.3177	0.2087	0.003
Diisopropyl ether (1) + isooctane (2)				
V^E (cm^3 mol^{-})	1.0837	−0.0191	0.0399	0.008
Δk_s (TPa^{-1})	19.6	−0.7	−6.4	0.9
$\Delta \ln \eta$ (cP)	−0.0163	−0.1588	0.0242	0.003
Diisopropyl ether (1) + benzene (2)				
V^E (cm^3 mol^{-1})	−1.9684	−0.0955	0.0797	0.006
Δk_s (TPa^{-1})	−458.5	−152.9	3.4	1.7
$\Delta \ln \eta$ (cP)	0.0428	−0.0025	0.0068	0.001
Diisopropyl ether (1) + cyclohexane (2)				
V^E (cm^3 mol^{-1})	0.2750	−0.0111	0.0237	0.003
Δk_s (TPa^{-1})	−192.0	−76.2	−17.0	1.3
$\Delta \ln \eta$ (cP)	−0.5923	0.1225	−0.1088	0.001
Diisopropyl ether (1) + tetralin (2)				
V^E (cm^3 mol^{-1})	−6.1183	−0.2208	−0.1392	0.005
Δk_s (TPa^{-1})	−786.7	−345.1	−32.8	2.3
$\Delta \ln \eta$ (cP)	0.2412	−0.0176	−0.0250	0.001
Diisopropyl ether (1) + decalin (2)				
V^E (cm^3 mol^{-1})	−3.0564	−0.1001	−0.0531	0.005
Δk_s (TPa^{-1})	−510.1	−186.7	−41.2	2.3
$\Delta \ln \eta$ (cP)	0.0682	0.0018	0.0084	0.001

The deviations in viscosity for the binary systems diisopropyl ether with hydrocarbons follow the order:

$$\text{tetralin} > \text{decalin} > \text{benzene} > \text{octane} > \text{isooctane} > \text{heptane} > \text{hexane} > \text{cyclohexane}$$

Deviations in viscosity displayed positive values for the binary systems of diisopropyl ether with tetralin and benzene, which further support the n–π (aromatic) interactions between the lone pair on the oxygen of diisopropyl ether and the π electrons in the aromatic ring. In case of the *n*-alkanes, the deviations in viscosity increases with increasing carbon number and the deviations in viscosity with octane shows more sigmoid shape than isooctane. The order of $\Delta \ln \eta$ in the above mixtures is approximately anti-parallel to that observed in excess volumes and deviations in isentropic compressibility. The data included in Table 5 indicate that the interaction parameters (ε_{12}) obtained from corresponding states approach are parallel to deviation in viscosity ($\Delta \ln \eta$). In Grunberg–Nissan treatment, the interaction parameter (d) is an approximat measure of strength of interactions between dissimilar molecules. From the data included in Table 5, it may be concluded that both the equations of corresponding states approach and Grunberg–Nissan equations are capable of representing the bahaviour of these systems.

4. Conclusions

From the present study, it may be concluded, that the values of V^E decreases if aliphatic is replaced by alicyclic and alicyclic is replaced by aromatic hydrocarbons. A similar phenomenon is observed in case of deviation in compressibility (Δk_s), which is in complete agreement with the conclusions reached for the excess volumes.

The results obtained in this study reveal, that strong negative values of V^E for diisopropyl ether with aromatic hydrocarbons can only be explained by assumption of strong n–π interactions present between the dissimilar molecules.

A comparison of experimental and computed speeds of sound data in Table 3 indicates that both free length theory and collision factor theory are capable of predicting the sound speed data in mixtures with maximum deviation of ±2.9%. The viscosity values computed on the basis of corresponding states approach and Grunberg and Nissan treatment were in good agreement with the experimental values with an average absolute deviation of 0.007.

Acknowledgement

The authors are grateful to University Grants Commission, New Delhi, India for the financial support to carryout this work.

References

[1] F. Belpoggi, M. Soffritte, C. Maltoni, Toxicol. Ind. Health 11 (1995) 1–31.

[2] D.W. Layton, W.J. Pitz, J.I. Daniels, S. Carle, R.M. Maxwell, K.L. Carroll, Prepr. Ext. Abstr. ACS Natl. Meet Am. Chem. Soc. Div. Environ. Chem. 40 (1) (2000) 294–297.

[3] E.J. Chang, Prep. Pap. Am. Chem. Soc. Div. Fuel Chem. 39 (1994) 330–336.

[4] A. Treszczanowicz, Thermochim. Acta 160 (1990) 253–259.

[5] B.S. Mahl, R. Malhotra, Z.S. Kooner, J. Chem. Thermodyn. 14 (1982) 855–858.

[6] S.C. Sharma, B. Rani, D. Kaur, M. Syngal, Acustica 81 (2) (1995) 186–189.

[7] S.T. Blanco, J.M. Embid, S. Otin, J. Chem. Thermodyn. 26 (1994) 23–28.

[8] K.V.N.S. Reddy, D.H.L. Prasad, A. Krishnaiah, J. Chem. Eng. Data 49 (2004) 1546–1549.

[9] K.V.N.S. Reddy, P.S. Rao, A. Krishnaiah, Phys. Chem. Liq. 42 (2004) 561–568.

[10] K.V.N.S. Reddy, D.H.L. Prasad, A. Krishnaiah, Fluid Phase Equilibr. 230 (2005) 105–108.

[11] J.A. Riddick, W.B. Bunger, Techniques of Chemistry, vol. 2, 3rd ed., Wiley-Inter Science, New York, 1970.

[12] K.V.R. Reddy, K. Rambabu, T. Devarajulu, A. Krishnaiah, J. Chem. Eng. Data 40 (1995) 124–127.

[13] M.V.P. Rao, P.R. Naidu, Can. J. Chem. 52 (1974) 788–790.

[14] A. Krishnaiah, K.N. Surendranath, J. Chem. Eng. Data 41 (1996) 1012–1014.

[15] B. Jacobson, J. Chem. Phys. 20 (1952) 927–928.

[16] B. Jacobson, Actachem. Scand. 5 (1951) 1214–1216.

[17] B. Jacobson, Actachem. Scand. 6 (1952) 1485–1498.

[18] W. Schaaffs, Z. Physik. 114 (1939) 110–115.

[19] W. Schaaffs, Z. Physik. 115 (1940) 69–76.

[20] W. Schaaffs, Acustica 33 (1975) 272–276.

[21] A.S. Teja, P. Rice, Chem. Eng. Sci. 36 (1981) 7–10.

[22] A.S. Teja, P. Rice, Ind. Eng. Chem. Fundam. 20 (1981) 77–81.

[23] A. Krishnaiah, D.S. Viswanath, J. Chem. Eng. Data 36 (1991) 317–318.

[24] L. Grunberg, A.H. Nissan, Nature 164 (1949) 799–800.

[25] A. Rodriguez, J. Canosa, J. Tojo, J. Chem. Eng. Data 44 (1999) 666–671.

[26] H. Eyring, J.F. Kincaid, J. Chem. Phys. 6 (1938) 620–629.