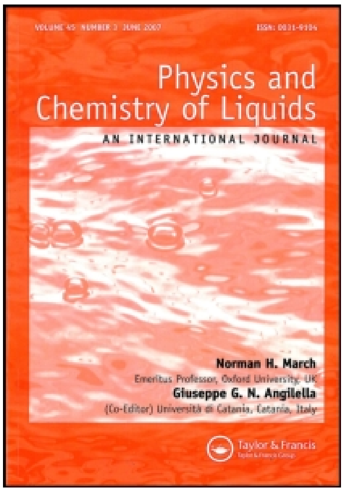

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Densities, speeds of sound, excess volumes and viscosities of binary mixtures of mtbe with tetralin and decalin at 303.15 k

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DENSITIES, SPEEDS OF SOUND, EXCESS VOLUMES AND VISCOSITIES OF BINARY MIXTURES OF MTBE WITH TETRALIN AND DECALIN AT 303.15 K

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Measurements of densities, speeds of sound, excess volumes and viscosities of binary mixture of methyl *tert*-butyl ether with tetralin and decalin are reported at 303.15 K over the entire range of composition. Excess volumes are measured using batch dilatometer technique. Sound speeds are obtained using ultrasonic interferometer. Densities are computed from excess volume data. Isentropic compressibilities are derived from density and sound speed data. Speeds of sound are evaluated on the basis of Jacobson's free length theory and Schaff's collision factor theory. The predicted values are in good agreement with the experimental results. The viscosity data are analysed on the basis of corresponding states approach. Excess volumes and deviation in isentropic compressibilities are negative and deviation in viscosities are positive over the entire composition range. The experimental results are discussed in terms of possible molecular interactions between unlike molecules.

Keywords: Excess volumes; Compressibilities; Viscosities; Methyl *tert*-butyl ether

1. INTRODUCTION

Several fuel oxygenates are used to enhance the octane rating of gasoline to improve air quality by reducing air pollution. Generally ethers and alkanols are added to gasoline as oxygenates to replace lead based anti-knock agents. Methyl *tert*-butyl ether (MTBE) has been used extensively as anti-knock agent. Recently many papers have appeared on thermodynamic properties of methyl *tert*-butyl ether with hydrocarbons [1–4]. To ensure fair trade of ether + gasoline mixtures the density data of the mixtures needs to be known accurately [4]. It is well known that the ultrasound technique has a wide range of applications such as in industry and in equipment testing. Molecular association in solution, correlation of sound speed with various parameters, isentropic compressibilities, free volume etc. can be studied by measurement of speeds of sound in liquid mixtures. As a part of our studies on thermodynamic and transport properties,

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this article reports excess volumes, sound speeds and viscosities of MTBE with bicyclic compounds, tetralin and decalin, over the entire range of composition at 303.15 K. A literature survey showed that no measurements on these properties have been previously reported for these mixtures. The aim of this work is to characterise the molecular interactions between branched chain ether with bicyclic compounds in terms of excess volume, deviation in isentropic compressibility and deviation in viscosity data. Further, the speeds of sound are evaluated on the basis of Jacobson's free length theory and Schaff's collision factor theory and the viscosity data are analysed on the basis of a corresponding states approach.

2. EXPERIMENTAL

The chemicals, tetralin and decalin, were supplied by Riedel (Germany) and MTBE was from Spectrochem Pvt. Ltd. (India) with guaranteed purity of 99.5% grade. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The purity of the components was checked by comparing the measured densities and boiling points of the components with literature [5–7]. The data are reported in Table I.

Excess volumes were measured with the dialatometer described by Reddy and Krishnaiah [8]. The experimental method was previously checked for the test system benzene + cyclohexane and results obtained showed a standard deviation of $\pm 0.004\,\mathrm{cm^3\,mol^{-1}}$. Four dialatometers with different capacities were used to cover the entire range of composition. The sound speeds of liquids and liquid mixtures were measured with a single crystal ultrasonic interferometer at a fixed frequency of 3 MHz, and the values were reproducible up to ± 0.1%. The viscosities of pure liquids and liquid mixtures were determined by a suspended Ubbelohde-type viscometer as in the earlier work described by Krishnaiah and Surendranath [9]. The estimated error in viscosity is ± 0.001 cp. All the measurements were made using a thermostatic bath maintained at 303.15 ± 0.01 K.

3. RESULTS AND DISCUSSION

The experimental excess volumes (V^E) of the two binary systems are given in Table II and the dependence of V^E on mole fraction of MTBE is graphically represented in Fig. 1.

Isentropic compressibilities (k_s) are computed from the density (ρ) and sound speed (u) data using the equation,

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

TABLE I Densities at 298.15 K and boiling points of pure components

Components	*Density* (ρ) ($\mathrm{g\,cm^{-3}}$)		*Boiling point* (K)	
	Present work	*Literature*	*Present work*	*Literature*
MTBE	0.73554	0.73528	328.15	328.35
Tetralin	0.96589	0.96620	464.25	464.85
Decalin	0.87914	0.87890	481.45	480.72

TABLE II Data on mole fraction of MTBE (x_1), density (ρ), excess volume (V^E) and viscosity (η) for the binary systems of MTBE with tetralin and decalin at 303.15 K

x_1	V^E ($cm^3\,mol^{-1}$)	ρ ($g\,cm^{-3}$)	η_{exp} (cp)	η_{cal} (cp)	$\Delta ln\,\eta$ (cp)
MTBE (1) + tetralin (2)					
0.0000	0.000	0.95544	1.749	–	0.0000
0.1289	−0.370	0.93222	1.534	1.527	0.0756
0.1851	−0.512	0.92168	1.432	1.441	0.0983
0.2839	−0.729	0.90249	1.253	1.254	0.1235
0.3506	−0.849	0.88903	1.136	1.137	0.1334
0.4458	−0.970	0.86902	0.983	0.930	0.1425
0.5017	−1.015	0.85683	0.903	0.902	0.1474
0.6257	−1.020	0.82846	0.737	0.736	0.1447
0.7392	−0.892	0.80081	0.606	0.608	0.1314
0.8539	−0.613	0.77097	0.486	0.486	0.0958
0.9246	−0.356	0.75166	0.370	0.371	0.0591
1.0000	0.000	0.73021	0.349	–	0.0000
MTBE (1) + decalin (2)					
0.0000	0.000	0.86850	2.091	–	0.0000
0.1134	−0.202	0.85740	1.739	1.699	0.0186
0.1840	−0.297	0.84996	1.547	1.493	0.0278
0.2577	−0.376	0.84180	1.367	1.305	0.0364
0.3906	−0.471	0.82595	1.089	1.024	0.0469
0.4774	−0.502	0.81480	0.935	0.874	0.0501
0.5234	−0.508	0.80866	0.863	0.805	0.0515
0.6441	−0.489	0.79136	0.694	0.647	0.0500
0.7771	−0.396	0.77051	0.543	0.511	0.0425
0.8937	−0.232	0.75035	0.431	0.418	0.0240
1.0000	0.000	0.73021	0.349	–	0.0000

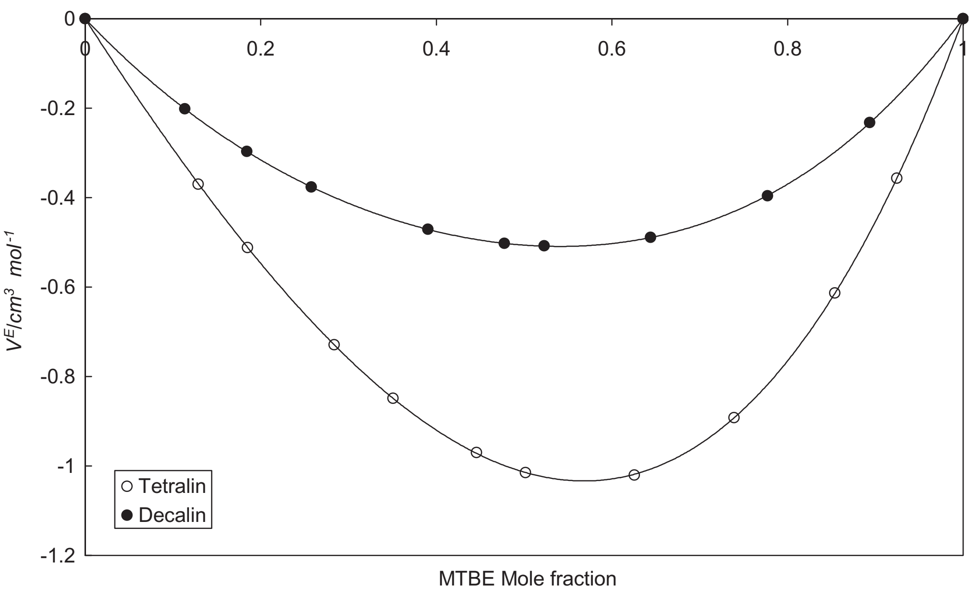

FIGURE 1 Plots of excess volume (V^E) *vs.* mole fraction of MTBE with tetralin and decalin at 303.15 K.

Densities of mixtures are computed from measured excess volume data from the following equation,

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1 + x_2 V_2 + V^{\mathrm{E}}} \tag{2}$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are the molecular weights, V_1 and V_2 are the molar volumes of MTBE and bicyclic compounds, respectively. Deviation in isentropic compressibility (Δk_s) was 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 sound speed (u), density (ρ), isentropic compressibility (k_s) and deviation in isentropic compressibility (Δk_s) are given in Table III as a function of volume fraction (ϕ), variation of the (Δk_s) with ϕ are shown in Fig. 2.

Sound speeds were evaluated on the basis of Jacobson's free length theory [10,11] and Schaff's collision factor theory [12,13], details of which are discussed by Reddy and Krishnaiah [14]. The ultrasonic speed in the mixture can be evaluated by the following equation described by Jacobson,

$$U_{\mathrm{mix}} = \frac{K}{L_{f,\mathrm{mix}}^{1/2}\ \rho_{\mathrm{mix}}} \tag{4}$$

TABLE III Volume fraction (ϕ_1) of MTBE, density (ρ), sound velocity (u_{exp}, u_{FLT}, u_{CFT}) and deviation in isentropic compressibility (Δk_s) for the binary systems of MTBE with tetralin and decalin at 303.15 K

ϕ_1	ρ ($\mathrm{g\,cm^{-3}}$)	U_{exp} ($\mathrm{m\,s^{-1}}$)	U_{FLT} ($\mathrm{m\,s^{-1}}$)	U_{CFT} ($\mathrm{m\,s^{-1}}$)	k_s ($\mathrm{Tpa^{-1}}$)	Δk_s ($\mathrm{Tpa^{-1}}$)
MTBE (1) + tetralin (2)						
0.0000	0.95544	1477	–	–	480	0.0
0.1143	0.93222	1430	1416	1420	525	−52.2
0.1653	0.92168	1406	1392	1396	549	−71.7
0.2569	0.90249	1365	1347	1352	595	−103.8
0.3201	0.88903	1337	1313	1322	629	−123.8
0.4123	0.86902	1298	1273	1279	683	−147.8
0.4676	0.85683	1274	1247	1251	719	−158.8
0.5932	0.82846	1219	1188	1196	812	−172.5
0.7118	0.80081	1165	1137	1140	920	−165.7
0.8360	0.77097	1104	1085	1086	1064	−127.4
0.9145	0.75166	1063	1048	1053	1177	−80.6
1.0000	0.73021	1014	–	–	1332	0.0
MTBE (1) + decalin (2)						
0.0000	0.86850	1404	–	–	584	0.00
0.0884	0.85740	1368	1360	1363	623	−26.90
0.1406	0.84996	1344	1330	1338	651	−41.90
0.2084	0.84180	1319	1300	1310	682	−57.40
0.3271	0.82595	1274	1251	1260	746	−82.20
0.4093	0.81480	1244	1215	1228	793	−96.80
0.4540	0.80866	1227	1201	1210	821	−101.90
0.5785	0.79136	1182	1151	1161	904	−111.90
0.7256	0.77051	1127	1100	1108	1022	−104.90
0.8644	0.75035	1072	1053	1059	1160	−70.24
1.0000	0.73021	1014	–	–	1332	0.00

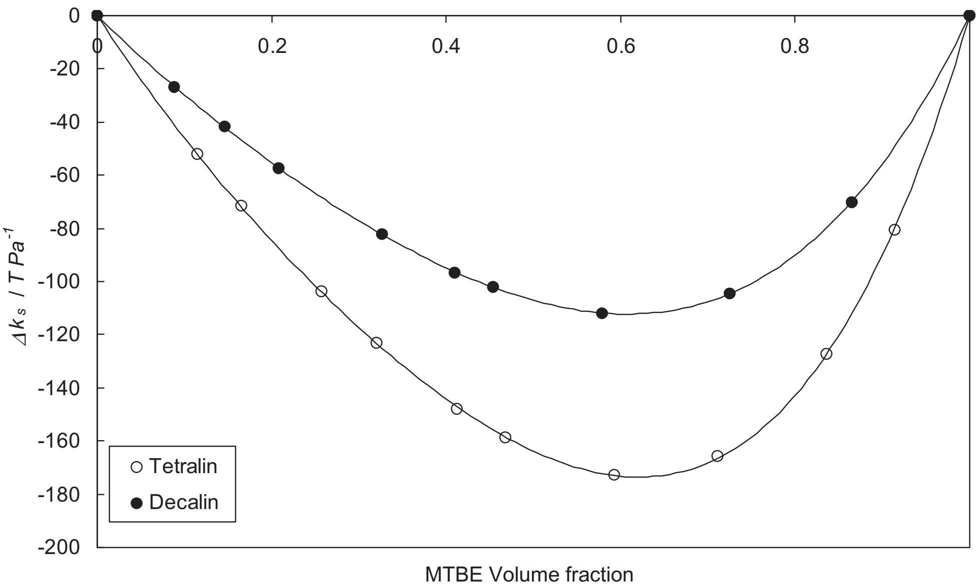

FIGURE 2 Plots of deviation in compressibility (Δk_s) *vs*. volume fraction of MTBE with tetralin and decalin at 303.15 K.

where K is a constant which is temperature dependent [11] and independent of the nature of the liquid. ρ_{mix} is the density of the mixture. $L_{f,\text{mix}}$ is the intermolecular free length of the mixtures and can be evaluated using the following equation [15],

$$L_{f,\text{mix}} = \frac{2[V_m - (x_1 V_1^0 + x_2 V_2^0)]}{x_1 Y_1 + x_2 Y_2} \tag{5}$$

According to the collision factor theory the sound speeds of the mixtures are calculated by using the following equation

$$u_{\text{mix}} = u_\infty [x_1 S_1 + x_2 S_2] \frac{[x_1 B_1 + x_2 B_2]}{V_m} \tag{6}$$

The values of sound speed of the mixtures predicted on the basis of the two theories are given in Table III. All the parameters required in these two theories were calculated as discussed earlier [14] and are reported in Table IV.

The viscosities of the mixtures were calculated using the equation,

$$\eta = k_v \cdot \rho \cdot t \tag{7}$$

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

$$\Delta \ln \eta = \ln \eta_{\text{mix}} - x_1 \ln \eta_1 - x_2 \ln \eta_2 \tag{8}$$

TABLE IV Molar volume (V), Molar volume at absolute zero (V_o), 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_o ($cm^3\,mol^{-1}$)	V_a ($cm^3\,mol^{-1}$)	L_f (Å)	Y	S	r_m (Å)
MTBE	120.72	91.03	29.690	0.728	81.574	1.547	2.710
Tetralin	138.37	117.41	20.956	0.437	95.908	1.879	2.998
Decalin	159.18	135.03	24.147	0.482	100.195	1.863	3.102

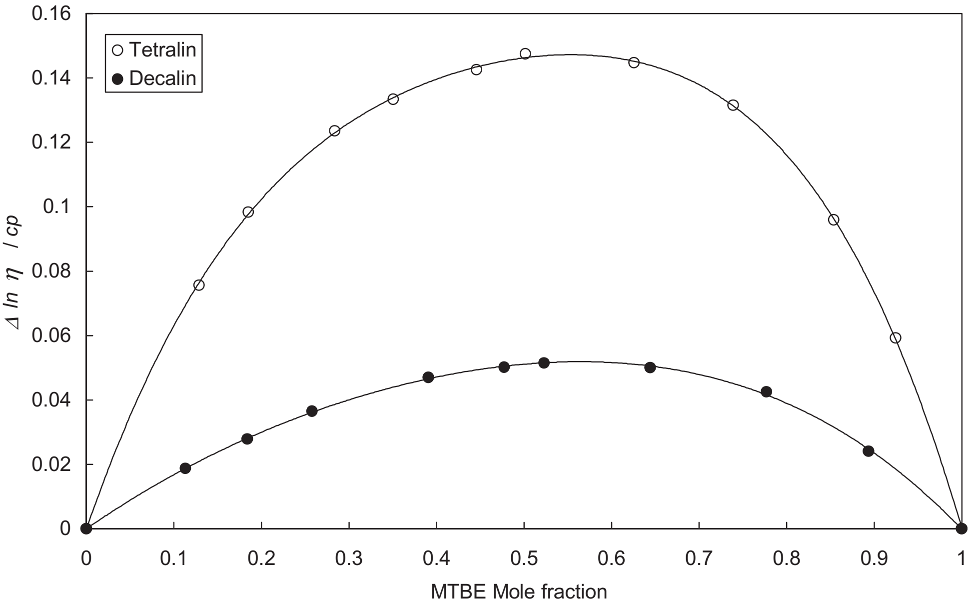

FIGURE 3 Plots of deviation in viscosity ($\Delta \ln \eta$) *vs.* mole fraction of MTBE with tetralin and decalin at 303.15 K.

where η_{mix} is the viscosity of the mixture, η_1 and η_2 are the viscosities of MTBE and bicyclic compounds respectively.

On the basis of a corresponding state treatment, Teja and Rice [16,17] proposed the following expression for liquid mixture viscosity

$$\ln(\eta_{mix}\,\xi_{mix}) = x_1 \ln(\eta_1 \xi_1) + x_2 \ln(\eta_2 \xi_2) \tag{9}$$

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 were evaluated by the procedure described by Krishnaiah and Viswanath [18]. The viscosities were obtained from Eq. (9) along with experimental viscosities, which are given in Table II. Deviations in viscosity *versus* MTBE mole fraction are plotted in Fig. 3.

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

$$A = z_1 z_2 [a_0 + a_1(z_1 - z_2) + a_2(z_1 - z_2)^2] \tag{10}$$

TABLE V Values of the parameters of Eq. (10) and standard deviation at 303.15 K

A^E	a_0	a_1	a_2	$\sigma(A)$
MTBE (1) + tetralin (2)				
V^E ($cm^3 mol^{-1}$)	−4.0548	−1.1297	−0.1324	0.006
Δk_s (Tpa^{-1})	−655.2	−307.4	−162.7	2.7
$\Delta \ln \eta$ (cp)	0.5846	0.0745	0.2726	0.004
MTBE (1) + decalin (2)				
V^E ($cm^3 mol^{-1}$)	−2.0257	−0.279	−0.3237	0.003
Δk_s (Tpa^{-1})	−428	−180.06	−76.12	2.1
$\Delta \ln \eta$ (cp)	0.2052	0.0456	0.0252	0.003

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 corresponding property. The values of parameters a_0, a_1 and a_2, obtained by least square analysis, are included in Table V along with standard deviation. The values of standard deviation are calculated by the following equation,

$$\sigma(A) = \left[\frac{\sum (A_{\mathrm{cal}} - A_{\mathrm{exp}})^2}{n - p} \right]^{1/2} \tag{11}$$

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

Excess volumes and deviations in isentropic compressibilities are negative over the entire composition range in both the systems. The values are more negative in the system, MTBE + tetralin than that of MTBE + decalin. The negative values indicate more effective packing in mixture compared to pure components. More negative values for MTBE + tetralin may be attributed to the relatively strong interaction between MTBE and tetralin due to the presence of π-electrons in tetralin. Similar trend is reported by Sharma *et al.* [3] wherein the V^E values are more negative for MTBE + aromatic hydrocarbon (benzene) compared to MTBE + alicyclic compound (cyclohexane). The compact packing of the components in mixtures compared to the pure components as result of n–π interaction is also supported by the positive values of the deviations in viscosity.

A comparison of experimental and computed speeds of sound data in Table III indicate that both free length theory and collision factor theory are capable of predicting the sound speed data in mixtures within ±2%. However, the values predicted on the basis of collision factor theory are in relatively good agreement with the experimental values compared to those of free length theory. The data included in Table II show that there is a good agreement between experimental and calculated viscosity data for the system MTBE + tetralin compared to MTBE + decalin.

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