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Excess Volumes, Densities, Speeds of Sound, and Viscosities for the Binary Systems of 1-Octanol with Hexadecane and Squalane at (298.15, 303.15 and 308.15) K

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Abstract Excess molar volumes, V_{m}^{E}, excess molar isentropic compressibilities, $K_{S,\text{m}}^{\text{E}}$, and deviations of the speeds of sound, u^{D}, from their ideal values u^{id} in an ideal mixture for binary mixtures of 1-octanol, $C_8H_{17}OH$, with hexadecane, $C_{16}H_{34}$, and squalane (2,6,10,15,19,23-hexamethyltetracosane), $C_{30}H_{62}$, at $T = (298.15, 303.15,$ and $308.15)$ K and at atmospheric pressure were derived from experimental density, ρ, and speed-of-sound data, u. Viscosity measurements were also carried out for the same mixtures. The Prigogine-Flory-Patterson (PFP) theory has been applied to analyze V_{m}^{E} of these systems. Furthermore, the apparent molar volumes, $\overline{V}_{\varphi,i}^{0}$ and apparent molar compressibility, $\overline{K}_{\varphi,i}^{0}$ of the components at infinite dilution have been calculated.

Keywords Apparent molar volume · Binary Mixtures · Density · Excess volumes · Hexadecane · Isentropic compressibility · 1-Octanol · PFP theory · Speed of sound · Squalane · Viscosity

1 Introduction

Physicochemical and thermodynamic investigations play an important role in understanding the nature and extent of patterns of molecular aggregation that exist in binary liquid mixtures and their sensitivities to variations in composition and the molecular structure of the pure components. Experimental data of excess thermodynamic properties of liquid mixtures provide useful information about molecular interactions

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and can be used to test thermodynamic models. In the present investigation, an attempt has been made to study binary mixtures of 1-octanol with hexadecane and squalane to understand the effect of the chain length and branching in alkanes on the excess thermodynamic properties.

The objective of the present work is to provide new experimental data on densities, viscosities, speeds of sound, and derived thermodynamic properties of ($C_8H_{17}OH$ + $C_{16}H_{34}$, or + $C_{30}H_{62}$) at $T = (298.15, 303.15, \text{and } 308.15)$ K and atmospheric pressure over the entire range of composition. As far as we know, there are not any literature data available for the studied binary mixtures at these temperatures. A literature review shows that the thermodynamic properties of binary mixtures containing alcohols with either $C_{16}H_{34}$ or $C_{30}H_{62}$ are not well known [1–5], whereas those for binary mixtures of hydrocarbons with $C_{16}H_{34}$ or $C_{30}H_{62}$ are available in the literature [6–18]. So it offers us a good opportunity to study the mixing behavior in such systems.

Components for this study were chosen with the intent of considering mixtures with molecules of significantly different molecular size, shape, and flow behavior. The examined alkanes also differ in molecular structure complexity as $C_{16}H_{34}$ is a linear alkane while $C_{30}H_{62}$ is branched having six symmetrically placed methyl groups along a twenty-four carbon atom backbone. Very useful properties of squalane are its very low coagulation point (−55 °C) and very high melting point (203 °C) making it very suitable for lubrication. On the basis of numerous clinical tests, it has been concluded that squalane is a bland vehicle, with the unusual ability to increase the rate, depth, and extent of penetration of topical agents from medicated ointments. Squalane is a natural emollient. Attempts have also been made to use squalane as a substitute for mineral oil in the treatment of tumors [19].

2 Experimental

2.1 Materials

The chemicals used in this work were of analytical grade. $C_8H_{17}OH$ was supplied by S.D. Fine Chemicals Ltd. whereas $C_{16}H_{34}$ was a Hi-media product and $C_{30}H_{62}$ was purchased from Acros. The stated purities (in mass%) are as follows: $C_8H_{17}OH$ (99.5 %), $C_{16}H_{34}$ (99 %), and $C_{30}H_{62}$ (99 %). Prior to experimental measurements, all liquids were stored in dark bottles over 0.4 nm molecular sieves to reduce water content, and were partially degassed with a vacuum pump under a nitrogen atmosphere. The estimated purities determined by gas chromatographic analysis were better than 99.5 mol % for all the liquid samples. Furthermore, the purities of the liquids were checked by comparing densities, ρ, viscosities, η, and speeds of sound, u, with corresponding literature values [11,14,20–30], as reported in Table 1.

2.2 Apparatus and Procedures

The densities, ρ, and speeds of sound, u, of pure liquids and their mixtures were simultaneously and automatically measured using an Anton Paar DSA 5000 instrument. As these parameters are extremely sensitive to temperature, the temperature was control-

Table 1 Experimental and literature values of densities, ρ, viscosities, η, and speeds of sound, u of pure liquid components at (298.15, 303.15, and 308.15) K

Liquids	T (K)	$\rho \times 10^{-3}$ (kg · m^{-3})		η (mPa · s)		u (m · s^{-1})	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
$C_8H_{17}OH$	298.15	0.821813	0.82181 [24]	7.508	7.498 [21]	1348.0	1348.0 [22]
	303.15	0.818796	0.8184 [21]	6.344	6.36 [25]	1330.8	1335.0 [23]
	308.15	0.815286	0.8150 [21]	5.363	5.38 [25]	1314.1	1314.27 [24]
$C_{16}H_{34}$	298.15	0.770456	0.77046 [26]	3.041	3.052 [27]	1338.6	1338.0 [14]
	303.15	0.766981	0.76655 [14]	2.706	–	1320.0	1320.0 [28]
	308.15	0.763520	0.7637 [29]	2.409	2.381 [29]	1301.7	1301.0 [14]
$C_{30}H_{62}$	298.15	0.805122	0.80513 [11]	28.257	28.254 [11]	1381.9	–
	303.15	0.801912	0.80188 [30]	22.087	–	1364.1	–
	308.15	0.798709	–	17.774	–	1346.5	–

led to ±0.001K by a built-in solid-state thermostat. Before each series of measurements, the apparatus was calibrated with double-distilled water and dry air. The estimated uncertainty in the density measurements is $\pm 2 \times 10^{-3}$ kg · m^{-3} and in the speed of sound is ± 0.1 m · s^{-1}. More details of the calibration and experimental procedures can be found elsewhere [31].

Kinematic viscosities $\nu (= \eta/\rho)$of the pure liquids and binary mixtures at all working temperatures and atmospheric pressure were determined with a modified Ubbelohde suspended-level viscometer. The viscometer was calibrated at all working temperatures before measurements. Other experimental details have been given in our earlier papers [31–33]. The flow time measurements were made using an electronic stopwatch with a readability of ±0.1 s. An average of four or five sets of flow times was taken for each liquid or liquid mixture. The measured values of kinematic viscosities (ν) were converted to dynamic viscosities (η) after multiplication by density. The estimated uncertainty for the viscosity measurements is ±0.003 mPa · s. A thermostatically controlled, well-stirred water bath whose temperature was controlled to ±0.01 K was used for the viscosity measurements.

The mole fraction of each mixture was obtained with an uncertainty of $\pm 1 \times 10^{-4}$ from the measured apparent masses of the components. All the measurements were performed on an Afcoset-ER-120A electronic balance. All masses were corrected for buoyancy. All molar quantities were based on the IUPAC relative atomic mass table [34].

3 Results and Discussion

The experimental results for the densities, ρ, speeds of sound, u, excess molar volumes, V_m^E, deviations u^D of the speeds of sound from the u^{id} values calculated for ideal mixtures, $K_{S,m}$, the products of the molar volume and the isentropic compressibility and their corresponding excess molar quantities $K_{S,m}^E$ at (298.15, 303.15, and 308.15) K are listed in Tables 2 and 3 while Table 4 reports the values of the viscosity, η, for both binary mixtures at the studied temperatures. The density, ρ, values have been

Table 2 Values of densities, ρ, speeds of sound, u, excess molar volumes, V_m^E, deviations in speeds of sound, u^D, molar isentropic compressibilities, $K_{S,\mathrm{m}}$, and excess molar isentropic compressibilities, $K_{S,\mathrm{m}}^\mathrm{E}$, for x_1 $C_8H_{17}OH + (1 - x_1)$ $C_{16}H_{34}$ at (298.15, 303.15, and 308.15) K

x_1	$\rho \times 10^{-3}$ $(\mathrm{kg \cdot m^{-3}})$	$V_\mathrm{m}^\mathrm{E} \times 10^6$ $(\mathrm{m^3 \cdot mol^{-1}})$	u $(\mathrm{m \cdot s^{-1}})$	u^D $(\mathrm{m \cdot s^{-1}})$	$K_{S,\mathrm{m}}$ $(\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}})$	$K_{S,\mathrm{m}}^\mathrm{E}$ $(\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}})$
$T = 298.15$ K						
0.0000	0.770456	0.0000	1338.6	0.00	212.89	0.00
0.0461	0.771581	0.0668	1337.0	−1.62	208.62	0.60
0.1039	0.773103	0.1320	1335.7	−2.99	202.99	1.10
0.1547	0.774574	0.1742	1334.7	−4.07	197.94	1.45
0.1944	0.775766	0.2079	1334.3	−4.54	193.89	1.61
0.2685	0.778197	0.2461	1333.7	−5.32	186.24	1.83
0.3383	0.780693	0.2735	1333.5	−5.75	178.91	1.92
0.4099	0.783479	0.2953	1333.3	−6.25	171.38	2.02
0.4981	0.787310	0.3013	1333.5	−6.54	161.96	2.00
0.6017	0.792441	0.2864	1334.2	−6.63	150.79	1.89
0.6927	0.797621	0.2533	1335.8	−5.98	140.77	1.61
0.7963	0.804426	0.1992	1338.5	−4.76	129.24	1.19
0.8445	0.808003	0.1635	1340.1	−4.04	123.84	0.97
0.8950	0.812077	0.1187	1342.2	−3.01	118.12	0.69
0.9529	0.817221	0.0563	1344.9	−1.78	111.56	0.37
1.0000	0.821813	0.0000	1348.0	0.00	106.12	0.00
$T = 303.15$ K						
0.0000	0.766981	0.0000	1320.0	0.00	220.92	0.00
0.0461	0.768090	0.0774	1318.4	−1.76	216.50	0.69
0.1039	0.769605	0.1542	1317.1	−3.19	210.67	1.25
0.1547	0.771039	0.2105	1316.1	−4.32	205.45	1.66
0.1944	0.772218	0.2519	1315.8	−4.74	201.22	1.82
0.2685	0.774630	0.3023	1315.3	−5.51	193.25	2.06
0.3383	0.777145	0.3312	1315.1	−6.01	185.63	2.17
0.4099	0.779937	0.3541	1314.9	−6.60	177.81	2.29
0.4981	0.783781	0.3630	1315.3	−6.80	167.98	2.25
0.6017	0.788911	0.3564	1316.2	−6.81	156.32	2.12
0.6927	0.794075	0.3343	1317.9	−6.17	145.91	1.84
0.7963	0.800846	0.2956	1320.9	−4.77	133.89	1.38
0.8445	0.804438	0.2597	1322.6	−3.99	128.26	1.14
0.8950	0.808561	0.2077	1324.9	−2.81	122.28	0.81
0.9529	0.813871	0.1160	1327.9	−1.33	115.38	0.39
1.0000	0.818796	0.0000	1330.8	0.00	109.68	0.00
$T = 308.15$ K						
0.0000	0.763520	0.0000	1301.7	0.00	229.25	0.00
0.0461	0.764586	0.0939	1299.9	−2.01	224.75	0.85
0.1039	0.766078	0.1786	1298.7	−3.55	218.67	1.42
0.1547	0.767495	0.2403	1297.7	−4.80	213.27	1.87
0.1944	0.768680	0.2789	1297.4	−5.35	208.87	2.04
0.2685	0.771077	0.3328	1296.9	−6.31	200.61	2.31
0.3383	0.773575	0.3629	1296.8	−6.96	192.67	2.42
0.4099	0.776383	0.3813	1296.8	−7.57	184.49	2.50
0.4981	0.780228	0.3875	1297.2	−7.98	174.27	2.48
0.6017	0.785346	0.3812	1298.4	−7.98	162.11	2.29
0.6927	0.790488	0.3618	1300.2	−7.41	151.27	2.00
0.7963	0.797284	0.3136	1303.4	−5.90	138.74	1.50
0.8445	0.800882	0.2747	1305.3	−4.95	132.86	1.22
0.8950	0.805017	0.2184	1307.8	−3.58	126.62	0.86
0.9529	0.810331	0.1238	1310.9	−1.78	119.43	0.43
1.0000	0.815286	0.0000	1314.1	0.00	113.46	0.00

Table 3 Values of densities, ρ, speeds of sound, u, excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, deviations in speeds of sound, u^{D}, molar isentropic compressibilities, $K_{S,\mathrm{m}}$, and excess molar isentropic compressibilities, $K_{S,\mathrm{m}}^{\mathrm{E}}$ for $x_1\mathrm{C_8H_{17}OH} + (1 - x_1)\mathrm{C_{30}H_{62}}$ at (298.15, 303.15, and 308.15) K

x_1	$\rho \times 10^{-3}$ $(\mathrm{kg \cdot m^{-3}})$	$V_{\mathrm{m}}^{\mathrm{E}} \times 10^6$ $(\mathrm{m^3 \cdot mol^{-1}})$	u $(\mathrm{m \cdot s^{-1}})$	$u^{\mathrm{D}}(\mathrm{m \cdot s^{-1}})$	$K_{S,\mathrm{m}}(\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}})$	$K_{S,\mathrm{m}}^{\mathrm{E}}(\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}})$
$T = 298.15$ K						
0.0000	0.805122	0.0000	1381.9	0.00	341.57	0.00
0.0596	0.805175	0.1627	1379.9	−1.29	328.39	0.83
0.1053	0.805299	0.2389	1378.5	−2.15	318.11	1.30
0.1563	0.805499	0.2943	1376.9	−3.11	306.56	1.76
0.2092	0.805773	0.3244	1375.7	−3.58	294.29	1.95
0.2648	0.806107	0.3458	1374.2	−4.25	281.43	2.18
0.3404	0.806637	0.3643	1372.4	−4.78	263.75	2.30
0.3980	0.807105	0.3726	1370.8	−5.29	250.29	2.41
0.4799	0.807875	0.3813	1368.6	−5.73	231.01	2.42
0.5974	0.809279	0.3802	1364.9	−6.30	203.28	2.36
0.6988	0.810937	0.3509	1361.3	−6.41	179.18	2.14
0.8079	0.813477	0.2758	1356.9	−5.84	153.02	1.67
0.8519	0.814812	0.2350	1355.2	−5.02	142.34	1.36
0.8942	0.816384	0.1758	1353.2	−4.22	132.07	1.05
0.9474	0.818773	0.0969	1350.6	−2.63	119.08	0.59
1.0000	0.821813	0.0000	1348.0	0.00	106.12	0.00
$T = 303.15$ K						
0.0000	0.801912	0.0000	1364.1	0.00	353.36	0.00
0.0596	0.801944	0.1794	1362.1	−1.27	339.75	0.87
0.1053	0.802053	0.2667	1360.4	−2.44	329.28	1.54
0.1563	0.802234	0.3347	1359.3	−2.91	317.11	1.80
0.2092	0.802479	0.3819	1357.8	−3.69	304.58	2.16
0.2648	0.802799	0.4110	1356.4	−4.27	291.25	2.38
0.3404	0.803312	0.4375	1354.5	−4.92	273.01	2.56
0.3980	0.803775	0.4473	1352.9	−5.45	259.09	2.68
0.4799	0.804507	0.4572	1350.7	−5.91	239.16	2.72
0.5974	0.805920	0.4624	1347.1	−6.43	210.43	2.62
0.6988	0.807538	0.4431	1343.7	−6.39	185.46	2.35
0.8079	0.810008	0.3817	1339.5	−5.67	158.37	1.85
0.8519	0.811352	0.3346	1337.8	−4.88	147.32	1.53
0.8942	0.812920	0.2726	1335.9	−4.01	136.67	1.19
0.9474	0.815429	0.1625	1333.5	−2.26	123.16	0.64
1.0000	0.818796	0.0000	1330.8	0.00	109.68	0.00
$T = 308.15$ K						
0.0000	0.798709	0.0000	1346.5	0.00	365.57	0.00
0.0596	0.798711	0.1963	1344.1	−1.71	351.74	1.17
0.1053	0.798798	0.2944	1343.1	−2.19	340.57	1.52
0.1563	0.798947	0.3775	1341.5	−3.17	328.27	2.07
0.2092	0.799184	0.4245	1340.2	−3.77	315.22	2.35
0.2648	0.799487	0.4571	1338.7	−4.47	301.48	2.64
0.3404	0.799989	0.4810	1336.8	−5.15	282.62	2.83
0.3980	0.800439	0.4904	1335.3	−5.60	268.18	2.92
0.4799	0.801188	0.4969	1333.1	−6.09	247.56	2.94
0.5974	0.802536	0.4997	1329.5	−6.68	217.87	2.87
0.6988	0.804116	0.4784	1326.1	−6.71	192.04	2.60
0.8079	0.806567	0.4043	1322.1	−5.90	163.95	2.02
0.8519	0.807925	0.3503	1320.4	−5.17	152.51	1.67
0.8942	0.809463	0.2834	1318.7	−4.16	141.46	1.29
0.9474	0.811955	0.1666	1316.4	−2.41	127.46	0.71
1.0000	0.815286	0.0000	1314.1	0.00	113.46	0.00

Table 4 Values of viscosity, η, for x_1 $C_8H_{17}OH$ + $(1-x_1)$ $C_{16}H_{34}$ and x_1 $C_8H_{17}OH + (1-x_1)$ $C_{30}H_{62}$ at (298.15,303.15, and 308.15) K

x_1	η(mPa · s) $T = 298.15\,K$	η(mPa · s) $T = 303.15\,K$	η(mPa · s) $T = 308.15\,K$
x_1 $C_8H_{17}OH + (1-x_1)$ $C_{16}H_{34}$			
0.0000	3.041	2.706	2.409
0.0461	3.073	2.748	2.402
0.1039	3.089	2.741	2.399
0.1547	3.096	2.728	2.406
0.1944	3.107	2.728	2.419
0.2685	3.175	2.773	2.473
0.3383	3.290	2.881	2.561
0.4099	3.472	3.041	2.688
0.4981	3.768	3.307	2.896
0.6017	4.223	3.681	3.218
0.6927	4.714	4.086	3.554
0.7963	5.384	4.663	4.008
0.8445	5.757	4.992	4.251
0.8950	6.219	5.383	4.540
0.9529	6.860	5.883	4.944
1.0000	7.508	6.344	5.363
x_1 $C_8H_{17}OH + (1-x_1)$ $C_{30}H_{62}$			
0.0000	28.257	22.087	17.774
0.0596	24.176	19.207	15.495
0.1053	21.924	17.587	14.212
0.1563	20.118	16.254	13.144
0.2092	18.812	15.257	12.342
0.2648	17.878	14.504	11.734
0.3404	16.974	13.743	11.129
0.3980	16.377	13.237	10.724
0.4799	15.418	12.450	10.122
0.5974	13.555	11.008	9.007
0.6988	11.514	9.441	7.786
0.8079	9.294	7.693	6.416
0.8519	8.533	7.093	5.937
0.8942	7.963	6.624	5.572
0.9474	7.526	6.288	5.310
1.0000	7.506	6.344	5.363

used to calculate excess molar volumes using the following equation:

$$V_{\mathrm{m}}^{\mathrm{E}} = \sum_{i=1} x_i M_i (\rho^{-1} - \rho_i^{*-1}) \tag{1}$$

where ρ and ρ_i^* are the density of the mixture and the density of pure component i; x_i and M_i represent, respectively, the mole fraction and molar mass of component i in a mixture.

The speed of sound, u, is related to the isentropic compressibility, κ_S, by the Laplace equation,

$$\kappa_S = -V_{\mathrm{m}}^{-1}(\delta V_{\mathrm{m}}/\delta P)_S = (\rho u^2)^{-1} = V_{\mathrm{m}}(M u^2)^{-1} \tag{2}$$

where V_m is the molar volume and M is the molar mass of the mixture. To achieve agreement with the other thermodynamic quantities, it is appropriate to shift from the volume-intensive κ_S to the molar-intensive quantity $K_{S,m}$ [35,36],

$$K_{S,\mathrm{m}} = -(\delta V_\mathrm{m}/\delta P)_S = V_\mathrm{m}\kappa_S = \Sigma x_i M_i/(\rho u)^2 \tag{3}$$

where $K_{S,m}$ is the molar isentropic compressibility.

The excess molar isentropic compressibility $K^{\mathrm{E}}_{s,\mathrm{m}}$ is calculated by the following equation:

$$K^{\mathrm{E}}_{S,\mathrm{m}} = K_{S,\mathrm{m}} - K^{\mathrm{id}}_{S,\mathrm{m}} \tag{4}$$

where $K^{\mathrm{id}}_{s,\mathrm{m}}$ is defined by the approach developed by Benson and Kiyohara [37];

$$K^{\mathrm{id}}_{s,\mathrm{m}} = \Sigma x_i[K^*_{S,i} - TA^*_{P,i}\{(\Sigma x_i A^*_{P,i}/\Sigma x_i C^*_{P,i}) - (A^*_{P,i}/C^*_{P,i})\}] \tag{5}$$

where $A^*_{P,i}$ is the product of the molar volume V^*_i and the isobaric expansibility $\alpha^*_{P,i}$, $C^*_{P,i}$ is the molar isobaric heat capacity, and $K^*_{S,i}$ is the product of the molar volume V_i and the isentropic compressibility κ_S of the pure liquid component i.

The deviations of the speeds of sound from their values in an ideal mixture were calculated from [38,39]

$$u^{\mathrm{D}} = u - u^{\mathrm{id}} \tag{6}$$

In so far as the Newton-Laplace equation is valid, the ideal speeds of sound u^{id} may be expressed correctly in terms of the thermodynamic properties of an ideal mixture:

$$u^{\mathrm{id}} = (V^{\mathrm{id}}_\mathrm{m})^{1/2}(K^{\mathrm{id}}_{S,\mathrm{m}} \sum_i \phi_i \rho^*_i)^{-1/2} \tag{7}$$

where ϕ_i is the volume fraction of component i.

Figure 1a, b depicts variations of excess molar volumes for both binary systems at (298.15, 303.15, and 308.15) K, along with the smoothed $V^{\mathrm{E}}_\mathrm{m}$ values using the Redlich-Kister equation [40]. As observed in Fig 1a, b, the excess molar volumes are positive over the entire composition range for both binary mixtures investigated, with a maximum at $x_1 = 0.5$ for $C_8H_{17}OH$ with $C_{16}H_{34}$, whereas $C_8H_{17}OH + C_{30}H_{62}$ excess molar volumes are almost constant in the range $0.25 \leq x_1 \leq 0.7$. The positive excess molar volume can be attributed to the weak dispersive interactions between unlike molecules. The $V^{\mathrm{E}}_\mathrm{m}$ values increase with increasing alkyl chain length of alkanes as well as with an increase in temperature.

The composition dependence of $K^{\mathrm{E}}_{S,\mathrm{m}}$ for both the studied binary mixtures over the entire range of composition is shown in Fig 2a, b. The curves for $K^{\mathrm{E}}_{S,\mathrm{m}}$ are positive and symmetrical with the position of the maximum at $x_1 \approx 0.5$. The behavior of $K^{\mathrm{E}}_{S,\mathrm{m}}$ is consistent with that of $V^{\mathrm{E}}_\mathrm{m}$ for these systems. These values of $K^{\mathrm{E}}_{s,\mathrm{m}}$ may be visualized in terms of the strength of interactions operating between the components of any given system. The positive values of $K^{\mathrm{E}}_{s,\mathrm{m}}$ for a given system mean that the mixture

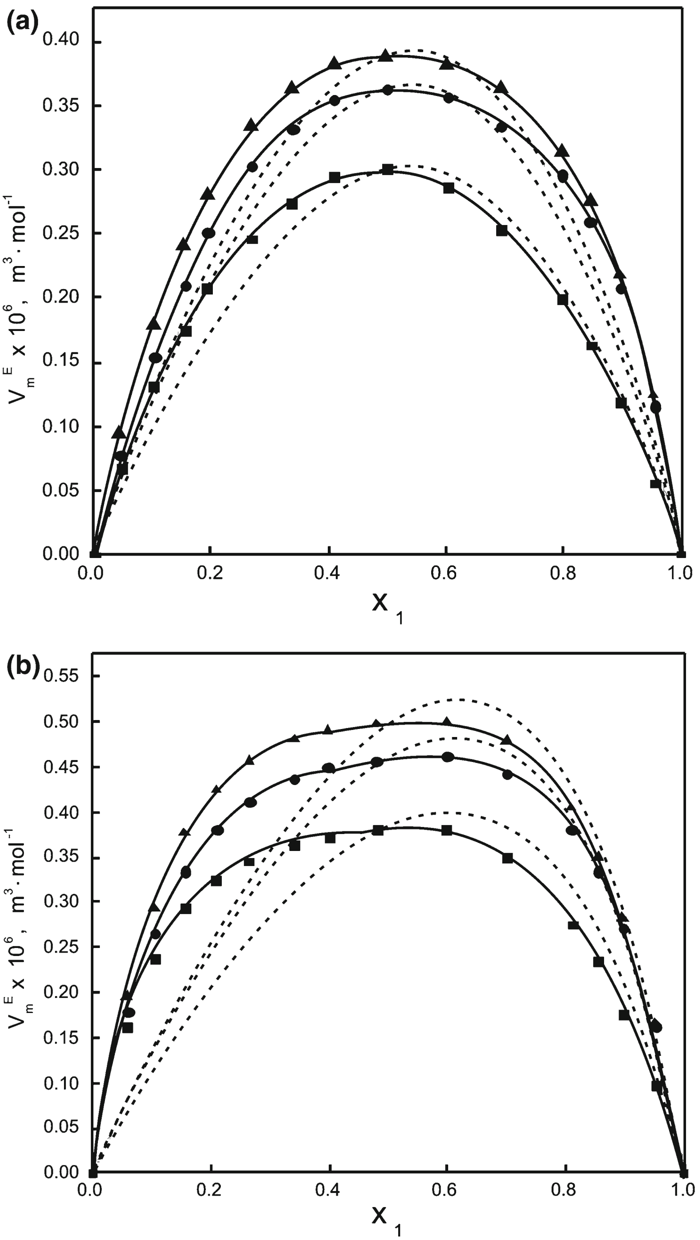

Fig. 1 Excess molar volumes, V_m^E at 298.15 K (■); 303.15 K (•); and 308.15 K (▲) for binary mixtures of $x_1C_8H_{17}OH + x_2C_nH_{2n+1}$; (**a**) $n = 16$ and (**b**) $n = 30$. Solid curves have been derived using Redlich-Kister equation and dotted (----) curves from PFP theory

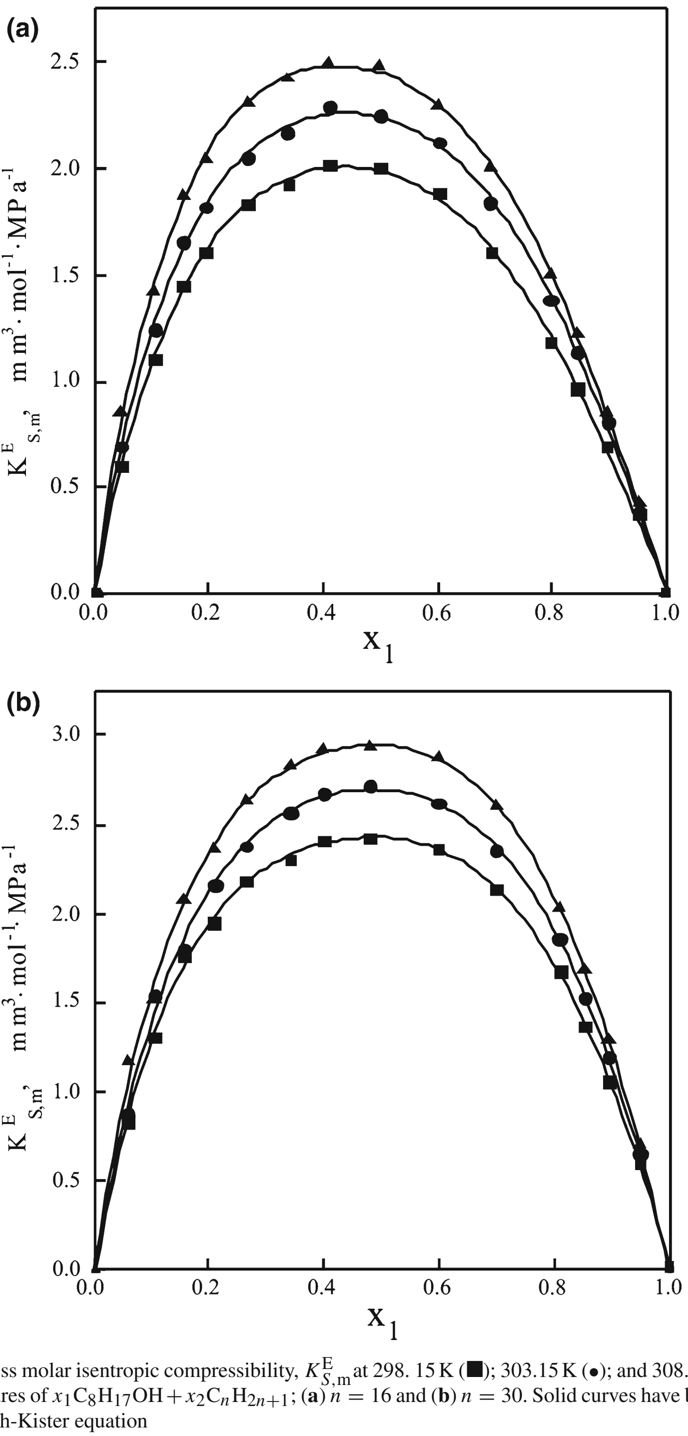

Fig. 2 Excess molar isentropic compressibility, $K^{\mathrm{E}}_{S,\mathrm{m}}$ at 298. 15 K (■); 303.15 K (●); and 308.15 K (▲) for binary mixtures of $x_1\mathrm{C_8H_{17}OH} + x_2\mathrm{C}_n\mathrm{H}_{2n+1}$; (**a**) $n = 16$ and (**b**) $n = 30$. Solid curves have been derived using Redlich-Kister equation

is more compressible than the corresponding ideal mixture, suggesting that there may be volume expansion resulting from the presence of weak dispersive interactions in these mixtures.

The opposite behavior was observed for deviations of the speed of sound, u^{D}, from their ideal values, u^{id}, over the whole composition range as shown in Fig. 3a, b at all three temperatures under study. The negative trend in u^{D} is observed for both binary mixtures with minima at $x_1 \approx 0.6$ for $C_8H_{17}OH + C_{16}H_{34}$ and at $x_1 \approx 0.7$ for $C_8H_{17}OH + C_{30}H_{62}$. As the temperature increases, u^{D} decreases with the same dependences and systematic variations.

The apparent molar compressibility ($\varphi_{k,1}$) of a solute component (1) in a solution, defined [41,42] in terms of mole fraction, is calculated from the relation

$$\varphi_{k,1} = \kappa_s \varphi_{V,1} + x_2 M_2 (\kappa_s - \kappa^*_{S,2})/x_1 \rho^*_2 \tag{8}$$

where

$$\varphi_{v,1} = M_2 (x_2/x_1 \rho^*_2 \rho)(\rho^*_2 - \rho) + M_1/\rho \tag{9}$$

and ρ^*_2, x_2, and $\kappa^*_{s,2}$ are the density, mole fraction, and isentropic compressibility of the solvent; M is the relative molar mass of the solvent mixture; x_1, M_1, and $\varphi_{v,1}$ are the mole fraction, relative molar mass, and apparent molar volume of the solute component; and ρ and κ_S are the density and isentropic compressibility of the solution mixture.

The limiting values of apparent molar volumes and apparent molar compressibilities were calculated by linear extrapolation and are denoted as $\varphi^0_{v,i}$, i.e., the infinite dilution molar volume, and $\varphi^0_{k,i}$, i.e., the infinite dilution molar isentropic compressibility. At infinite dilution, $\varphi^0_{v,i} = \overline{V}^0_{\varphi,i}$ and $\varphi^0_{k,i} = \overline{K}^0_{\varphi,i}$, where $\overline{V}^0_{\varphi,i}$ is the partial molar volume and $\overline{K}^0_{\varphi,i}$ is the partial molar isentropic compressibility at infinite dilution. A comparison of $\overline{K}^0_{\varphi,1}$ values with the corresponding molar isentropic compressibility $K^*_{s,1}$ (where $K^*_{s,1}$ can be considered as the partial molar compressibility of the solute when dissolved in itself, i.e., pure liquid) shows positive deviations (ΔK) for both binary mixtures. This can be analyzed in terms that the molecular volume of the solute molecules is affected and that the molecules are in a force field different to that for the pure liquid state. The observed positive ΔK values indicate that the partial molar isentropic compressibility of $C_8H_{17}OH$ increases when dissolved in alkanes. Hall and Sile [43] analyzed these deviations in terms of structural and geometrical compressibility. Similarly higher $\overline{V}^0_{\varphi,i}$ values of $C_8H_{17}OH$ in alkanes than the corresponding molar volume, i.e., positive ΔV, indicate that volume expansion is taking place with the addition of alkanes in $C_8H_{17}OH$ due to the rupture of H-bonding in $C_8H_{17}OH$. This provides support to the conclusions drawn earlier from other experimental data.

Values of ΔV and ΔK for $C_{16}H_{34}$ or $C_{30}H_{62}$ in $C_8H_{17}OH$ are also higher at the infinitely dilute state as compared to their corresponding molar volumes. This fact signifies that $C_{16}H_{34}$ or $C_{30}H_{62}$ are also less close packed in the mixtures than in their pure states as the addition of $C_8H_{17}OH$ disrupts the orientational order present in

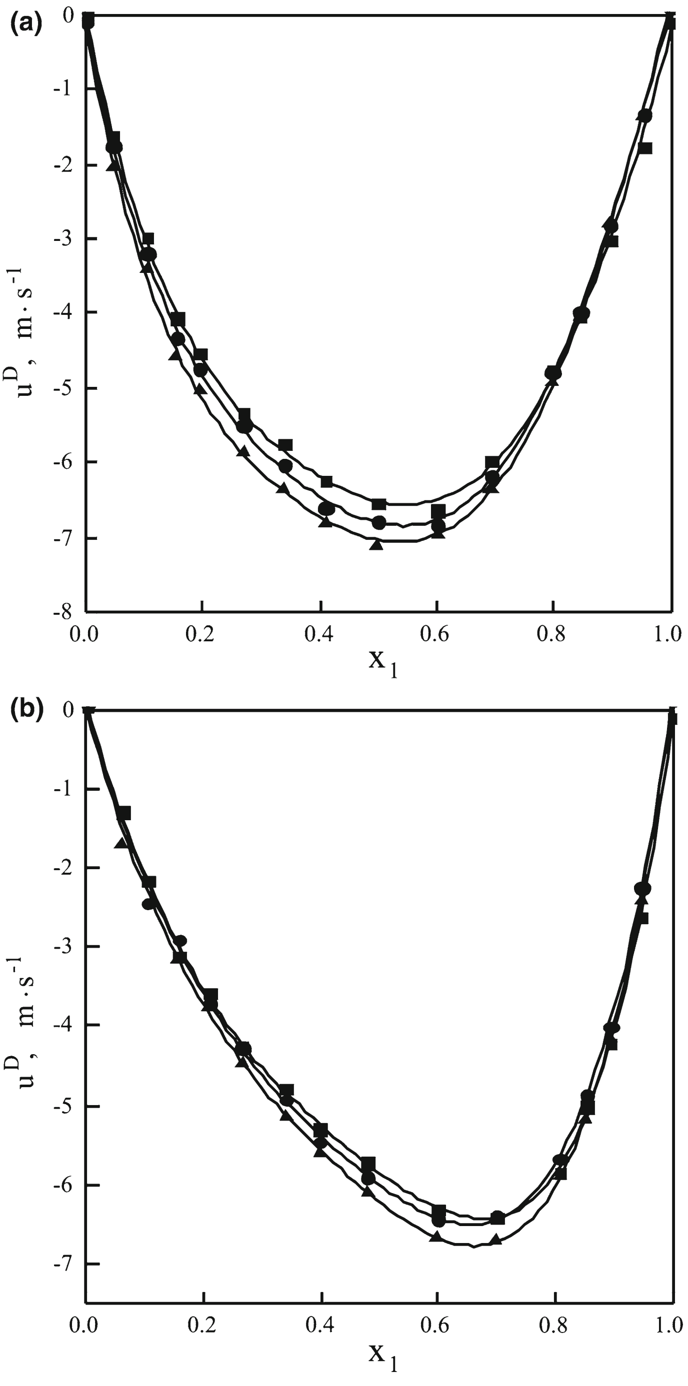

Fig. 3 Deviation in speeds of sound, u^D at 298.15 K (■); 303.15 K (•); and 308.15 K (▲) for binary mixtures of $x_1C_8H_{17}OH + x_2C_nH_{2n+1}$; (**a**) $n = 16$ and (**b**) $n = 30$. Solid curves have been derived using Redlich-Kister equation

Table 5 Values of partial molar volumes and partial molar isentropic compressibilties at infinite dilution at (298.15, 303.15, and 308.15) K

Binary mixture	$T\,(K)$	$V_1^* \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$\overline{V}^0_{\varphi,1} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$V_2^* \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$\overline{V}^0_{\varphi,2} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$\overline{K}^0_{\varphi,1}$ ($\text{mm}^3 \cdot \text{mol}^{-1} \cdot \text{MPa}^{-1}$)	$\overline{K}^0_{\varphi,2}$ ($\text{mm}^3 \cdot \text{mol}^{-1} \cdot \text{MPa}^{-1}$)
$C_8H_{17}OH + C_{16}H_{34}$	298.15	158.47	160.00	293.91	295.18	121.00	221.73
	303.15	159.05	160.81	295.24	297.82	125.97	231.01
	308.15	159.74	161.86	296.58	299.30	133.72	240.27
$C_8H_{17}OH + C_{30}H_{62}$	298.15	158.47	161.52	525.17	527.14	121.73	353.33
	303.15	159.05	162.38	527.27	530.56	127.44	367.04
	308.15	159.74	163.39	529.38	532.76	135.86	380.73

these long-chain alkane molecules. Partial molar volumes and partial molar isentropic compressibilities at infinite dilution for both components are listed in Table 5.

4 Prigogine-Flory-Patterson Theory

V_m^E values were also correlated by means of the PFP theory. The following equations hold for the studied systems:

$$V_\text{m}^\text{E}/(x_1 V_1^* + x_2 V_2^*) = V_\text{m}^\text{E}(\text{int.}) + V_\text{m}^\text{E}(\text{fv}) + V_\text{m}^\text{E}(P^*) \tag{10}$$

where

$$V_\text{m}^\text{E}(\text{int.}) = [(\tilde{v}^{1/3} - 1)\tilde{v}^{2/3}\Psi_1\theta_2\chi_{12}]\big/[((4/3)\tilde{v}^{-1/3} - 1)P_1^*] \tag{11}$$

$$V_\text{m}^\text{E}(\text{fv}) = -[(\tilde{v}_1 - \tilde{v}_2)^2((14/9)\tilde{v}^{-1/3} - 1)\Psi_1\Psi_2]\big/[((4/3)\tilde{v}^{-1/3} - 1)\tilde{v}] \tag{12}$$

$$V_\text{m}^\text{E}(\text{ip}) = [(\tilde{v}_1 - \tilde{v}_2)(P1^* - P_2^*)\Psi_1\Psi_2]\big/(P_2^*\Psi_1 + P_1^*\Psi_2) \tag{13}$$

where $\tilde{v}_i$ and $\tilde{v}$ are the reduced volumes of the pure components and mixture, respectively. V_i^* is the characteristic volume of component i, P_i^* is the characteristic pressure of pure component i, and Ψ_i is the molecular contact energy fraction. All these quantities can be deduced from the molar volume, V_i, isobaric heat capacity, C_P^*, isobaric thermal expansivity, α_P^*, and isothermal compressibility, κ_T, values of the pure components using Flory's formalisms given elsewhere [44–46]; they are listed in Table 6.

The interaction parameter, χ_{12}, can be evaluated if values of the excess molar enthalpies are known. Because these values are not available for these binary systems, it is a common practice to use χ_{12} as the only adjustable parameter to fit the experimental V_m^E values to Eq. 10. The χ_{12} thus obtained by the least-squares method over

Table 6 Characteristic parameters for the pure components at several temperature used in PFP theory calculations

Components	T (K)	α_P^* ($\mathrm{kK^{-1}}$)	C_P^* ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)	$\tilde{v}$	$\tilde{T}$	$V^* \times 10^6$ ($\mathrm{m^3 \cdot mol^{-1}}$)	$P^* \times 10^6$ ($\mathrm{J \cdot m^{-3}}$)	T^* (K)
$C_8H_{17}OH$	298.15	0.8270 [20]	308.39 [47]	1.2111	0.0511	130.8427	473.40	5837
	303.15	0.8644 [47]	313.60 [47]	1.2223	0.0530	130.1205	486.68	5724
	308.15	0.8803 [47]	320.12 [47]	1.2289	0.0540	129.9807	493.91	5702
$C_{16}H_{34}$	298.15	0.887[a]	501.60 [48]	1.2241	0.0532	240.1106	459.80	5600
	303.15	0.894[a]	504.30[b]	1.2287	0.0540	240.2808	452.14	5613
	308.15	0.900[a]	507.15 [49]	1.2332	0.0547	240.4951	459.95	5631
$C_{30}H_{62}$	298.15	0.7575 [15]	904.00 [50]	1.1958	0.0484	439.1806	436.41	6162
	303.15	0.7638 [15]	904.75 [50]	1.2000	0.0491	439.3787	444.56	6169
	308.15	0.7700 [15]	905.83 [50]	1.2043	0.0499	439.5793	452.80	6176

[a] Derived from our measured densities

[b] Estimated using group additivity

the whole composition range for each system and temperature represents the intermolecular interactions between components of mixtures. The values of χ_{12} at different temperatures are listed in Table 7 as well as the three PFP contributions to V_m^E, the calculated and experimental values of V_m^E at $x_1 = 0.5$. A perusal of Table 7 reveals that for $C_8H_{17}OH + C_{16}H_{34}$ or + $C_{30}H_{62}$ systems, the interaction contribution is positive and increases with temperature.

It is also clear from Table 7 that the contributions due to an interaction term seems to play a dominant role in determining the sign and magnitude of V_m^E because it is larger than the other two contributions for both systems under study at all working temperatures. Figure 1a, b shows a comparison between the excess molar volumes determined experimentally and calculated using PFP theory. It may be observed that the PFP theory reproduces the main features of the experimental data by using only one fitted parameter adjusted to describe V_m^E for the $C_8H_{17}OH$ + alkanes (C_{16}, C_{30}) mixtures. For $C_8H_{17}OH + C_{30}H_{62}$, some deviations are observed in the dilute region of $C_8H_{17}OH$ but this is not surprising, considering that the PFP theory does not consider all the possible interactions existing in the mixture.

Table 7 PFP interaction parameter, χ_{12}, and calculated values of the three contributions from the PFP theory with experimental excess molar volumes at $x_1 = 0.5$

Binary mixtures	T (K)	$\chi_{12} \times 10^6$ ($\mathrm{J \cdot m^{-3}}$)	$V_m^E \times 10^6$ ($\mathrm{m^3 \cdot mol^{-1}}$)		Calculated contributions		
			Experimental	PFP	V_m^E(int.)	V_m^E(fv)	V_m^E(ip)
$C_8H_{17}OH + C_{16}H_{34}$	298.15	12.18	0.3003	0.3003	0.3271	−0.0108	−0.0160
	303.15	13.76	0.3624	0.3625	0.3852	−0.0027	−0.0201
	308.15	14.19	0.3891	0.3892	0.4019	−0.0012	−0.0130
$C_8H_{17}OH + C_{30}H_{62}$	298.15	11.90	0.3830	0.3830	0.3375	−0.0188	0.0643
	303.15	13.75	0.4602	0.4602	0.3960	−0.0396	0.1038
	308.15	14.99	0.4994	0.4994	0.4376	−0.0481	0.1099

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