Temperature and Composition Dependence of the Densities, Viscosities, and Speeds of Sound of Binary Liquid Mixtures of 1-Butanol with Hexadecane and Squalane

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Excess molar volumes, $V_m{}^E$, viscosity deviations, $\Delta\eta$, deviations in speed of sound, Δu, and isentropic compressibility, $\Delta\kappa_s$, for the binary mixtures of 1-butanol, C_4H_9OH with hexadecane, $C_{16}H_{34}$, and squalane (2,4,6,10,15,19,23-hexamethylteracosane), $C_{30}H_{62}$, at T = (298.15, 303.15, and 308.15) K and at atmospheric pressure were derived from experimental density, ρ, viscosity, η, and speed of sound, u, data. The calculated excess and deviation functions were further fitted to the polynomial relation to estimate the coefficients and standard errors. The Prigogine−Flory−Patterson (PFP) theory has been used to explain $V_m{}^E$, whereas PFP theory with the van der Waals (vdW) potential energy model has also been used for theoretical estimation of u and κ_s.

Introduction

In the present communication, an attempt has been made to generate data on density, viscosity, and speed of sound for the binary mixtures of 1-butanol, C_4H_9OH with hexadecane, $C_{16}H_{34}$, and squalane, $C_{30}H_{62}$, at T = (298.15, 303.15, and 308.15) K and at atmospheric pressure. From the experimental results, excess molar volumes, $V_m{}^E$, viscosity deviations, $\Delta\eta$, deviations in speed of sound, Δu, and isentropic compressibility, $\Delta\kappa_s$, have been evaluated to provide additional information on molecular interactions.

The previous investigation reveals that the excess thermodynamic properties of binary mixtures of $C_{16}H_{34}$ and $C_{30}H_{62}$ with hydrocarbons have been reported in several papers.[1–10] However, the mixing properties in 1-alkanol + $C_{16}H_{34}$, or + $C_{30}H_{62}$ are not well-known. As far as we know, very little literature[11–14] is available about the binary mixtures containing alkanols and $C_{16}H_{34}$, or $C_{30}H_{62}$. To our knowledge, no experimental values of ρ, η, and u have been reported in the literature for the binary mixtures of C_4H_9OH with $C_{16}H_{34}$, or $C_{30}H_{62}$ at different temperatures.

Experimental Section

Materials. The analytical grade C_4H_9OH 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 purity is as follows: C_4H_9OH (99.5 %), $C_{16}H_{34}$ (99 %), and $C_{30}H_{62}$ (99 %). The density, ρ, viscosity, η, and speed of sound, u, data of pure components are reported in Table 1 along with literature data.[6,9,15–29] The mole fraction of each mixture was obtained with an uncertainty of $\pm\ 1\cdot10^{-4}$ from the measured apparent masses of the components.[30]

Apparatus and Procedure. Densities, ρ, and speeds of sound, u, were measured using a digital vibrating tube density and speed of sound analyzer (Anton Paar DSA 5000) with a proportional temperature controller that kept the samples at the required temperature with an accuracy of 0.001 K. The apparatus was calibrated at the working temperatures with double-distilled water[31,32] and dry air. The uncertainty reported in density measurements is $\pm\ 2\cdot10^{-3}$ kg·m^{-3} and in speed of sound is $\pm$ 0.1 m·s^{-1}. More details of calibration and procedures can be found elsewhere.[30]

Viscosities, η, of pure liquids and binary mixtures at all working temperatures and atmospheric pressures were determined with a modified Ubbelohde suspended-level viscometer. The viscometer was calibrated at all working temperatures before measurements. The details have been given in our earlier papers.[30,33,34] The uncertainty in η measurements is $\pm$ 0.003 mPa·s.

Before the measurements began, the experimental technique was checked by determining $V_m{}^E$ and η of the mixture ($x_1C_6H_{12} + x_2C_6H_{14}$) at the temperatures (298.15, 303.15, and 308.15) K and u of the mixtures ($x_1C_6H_{11}CH_3 + x_2C_3H_7OH$) at (298.15, 303.15, and 308.15) K.[35,36] These data are compared well in general.

Results and Discussion

Density, ρ, speed of sound, u, excess molar volumes, $V_m{}^E$, deviation in speed of sound, Δu, and isentropic compressibility, κ_s, determined by means of the Laplace equation ($\kappa_s = \rho^{-1}u^{-2}$), and deviation in isentropic compressibility, $\Delta\kappa_s$, at (298.15, 303.15, and 308.15) K for ($C_4H_9OH + C_{16}H_{34}$) and ($C_4H_9OH + C_{30}H_{62}$) are reported in Tables 2 and 3, respectively. The uncertainties in the derived parameters such as $V_m{}^E$, Δu, and $\Delta\kappa_s$ due to the estimated uncertainty in ρ ($\pm\ 2\cdot10^{-3}$ kg·m^{-3}) and u ($\pm$ 0.1 m·s^{-1}) are $\pm\ 0.0007\cdot10^{-6}$ m^3·mol^{-1}, $\pm$ 0.1 m·s^{-1} and $\pm$ 0.1 m·s^{-1}, respectively.

Excess molar volumes, deviations in speed of sound, and deviations in isentropic compressibility were derived, respectively, from

$$V_m^E = \sum_{i=1}^{2} x_i M_i(\rho^{-1} - \rho_i^{-1}) \tag{1}$$

$$\Delta u = u - \sum_{i=1}^{2} \varphi_i u_i \tag{2}$$

$$\Delta\kappa_s = \kappa_s - \sum_{i=1}^{2} \varphi_i \kappa_{s,i} \tag{3}$$

where ρ_i, u_i, and $\kappa_{s,i}$ are the density, speed of sound, and isentropic compressibility of the pure component and ρ, u, and

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Table 1. Comparison of Experimental Density, ρ, Viscosity, η, and Speed of Sound, u, of Pure Liquids with Literature Data

		$\rho 10^{-3}$/kg·m^{-3}		η/mPa·s		u/m·s^{-1}	
components	T/K	exptl	lit.	exptl	lit.	exptl	lit.
C_4H_9OH	298.15	0.805907	0.80589[15]	2.573	2.571[16,17]	1240.5	1240.6[18]
	303.15	0.803155	0.8022[19]	2.275	2.276[20]	1226.5	1223.0[21]
	308.15	0.799249	0.79804[22]	1.981	1.981[23,24]	1209.8	1208.0[21]
$C_{16}H_{34}$	298.15	0.770456	0.77046[25]	3.041	3.052[26]	1338.6	1338.0[9]
	303.15	0.766981	0.76655[9]	2.706	–	1320.0	1320.0[27]
	308.15	0.763520	0.76312[9] 0.7637[28]	2.409	2.381[15]	1301.7	1301.0[9]
$C_{30}H_{62}$	298.15	0.805122	0.80513[6]	28.257	28.254[6]	1381.9	–
	303.15	0.801912	0.80188[15]	22.087	–	1364.1	–
	308.15	0.798709	-	17.774	–	1346.5	–

Table 2. Density, ρ, Excess Molar Volume, V_m^E, Speed of Sound, u, Deviation in Speed of Sound, Δu, Isentropic Compressibility, κ_s and Deviation in Isentropic Compressibility, $\Delta\kappa_s$, for ($x_1C_4H_9OH$ + $x_2C_{16}H_{34}$) at Several Temperatures

	$\rho\cdot 10^{-3}$	$V_m^E\cdot 10^6$	u	Δu	κ_s	$\Delta\kappa_s$
x_1	kg·m^{-3}	m^3·mol^{-1}	m·s^{-1}	m·s^{-1}	TPa^{-1}	TPa^{-1}
			298.15 K			
0.0000	0.770456	0.0000	1338.6	0.0	724.3	0.0
0.0899	0.770953	0.2024	1332.4	−3.3	730.7	3.9
0.1048	0.771053	0.2320	1331.2	−3.9	731.8	4.6
0.1516	0.771517	0.2786	1328.2	−5.2	734.7	6.0
0.2017	0.772074	0.3212	1324.9	−6.5	737.9	7.5
0.2494	0.772705	0.3435	1321.9	−7.5	740.6	8.6
0.3382	0.774083	0.3674	1315.8	−9.3	746.2	10.6
0.4147	0.775524	0.3701	1310.6	−10.2	750.7	11.5
0.5057	0.777651	0.3458	1303.9	−10.9	756.3	12.1
0.5845	0.779950	0.3026	1297.6	−11.0	761.5	12.0
0.6980	0.784249	0.2118	1287.4	−10.0	769.4	10.6
0.7945	0.789246	0.1046	1276.8	−8.1	777.2	7.9
0.8497	0.792847	0.0398	1269.5	−6.4	782.6	5.8
0.8963	0.796346	−0.0012	1262.7	−4.3	787.6	3.4
0.9530	0.801232	−0.0192	1252.3	−1.5	795.8	0.6
1.0000	0.805907	0.0000	1240.5	0.0	806.37	0.0
			303.15 K			
0.0000	0.766981	0.0000	1320.0	0.0	748.3	0.0
0.0899	0.767402	0.2391	1313.4	−3.9	755.5	4.8
0.1048	0.767499	0.2710	1312.2	−4.5	756.7	5.6
0.1516	0.767916	0.3371	1309.2	−5.9	759.8	7.4
0.2017	0.768482	0.3795	1305.8	−7.4	763.2	9.1
0.2494	0.769093	0.4108	1302.9	−8.3	765.9	10.2
0.3382	0.770439	0.4484	1296.9	−10.3	771.8	12.6
0.4147	0.771883	0.4531	1291.6	−11.5	776.7	13.9
0.5057	0.773952	0.4465	1285.5	−12.0	781.9	14.4
0.5845	0.776223	0.4110	1279.2	−12.2	787.3	14.7
0.6980	0.780452	0.3349	1269.2	−11.6	795.4	13.8
0.7945	0.785434	0.2289	1258.5	−10.4	803.9	12.2
0.8497	0.789093	0.1540	1251.4	−8.9	809.3	10.3
0.8963	0.792717	0.0952	1244.8	−6.9	814.2	7.9
0.9530	0.797973	0.0322	1235.8	−3.4	820.6	3.7
1.0000	0.803155	0.0000	1226.5	0.0	827.7	0.0
			308.15 K			
0.0000	0.763520	0.0000	1301.7	0.0	772.9	0.0
0.0899	0.763863	0.2650	1294.9	−4.0	780.7	5.3
0.1048	0.763961	0.2957	1293.8	−4.7	782.0	6.2
0.1516	0.764360	0.3652	1290.3	−6.5	785.8	8.6
0.2017	0.764874	0.4216	1287.3	−7.7	788.9	10.1
0.2494	0.765462	0.4561	1284.4	−8.7	791.9	11.4
0.3382	0.766796	0.4889	1278.2	−10.8	798.2	13.9
0.4147	0.768201	0.4966	1273.1	−11.9	803.1	15.3
0.5057	0.770240	0.4873	1266.9	−12.5	808.9	16.1
0.5845	0.772472	0.4509	1260.9	−12.6	814.1	16.2
0.6980	0.776653	0.3688	1251.1	−12.0	822.6	15.3
0.7945	0.781597	0.2545	1240.6	−10.5	831.3	13.5
0.8497	0.785172	0.1836	1233.7	−9.3	836.8	11.6
0.8963	0.788760	0.1212	1227.4	−7.2	841.6	8.8
0.9530	0.794054	0.0422	1218.5	−3.8	848.3	4.5
1.0000	0.799249	0.0000	1209.8	0.0	854.9	0.0

Table 3. Density, ρ, Excess Molar Volume, V_m^E, Speed of Sound, u, Deviation in Speed of Sound, Δu, Isentropic Compressibility, κ_s, and Deviation in Isentropic Compressibility, $\Delta\kappa_s$, for ($x_1C_4H_9OH$ + $x_2C_{30}H_{62}$) at Several Temperatures

	$\rho\cdot 10^{-3}$	$V^E_m\cdot 10^6$	u	Δu	κ_s	$\Delta\kappa_s$
x_1	kg·m^{-3}	m^3·mol^{-1}	m·s^{-1}	m·s^{-1}	TPa^{-1}	TPa^{-1}
			298.15 K			
0.0000	0.805122	0.0000	1381.9	0.0	650.4	0.0
0.0451	0.804881	0.1554	1379.5	−1.2	652.8	1.1
0.1077	0.804649	0.2909	1376.1	−2.8	656.3	2.6
0.1346	0.804573	0.3306	1374.8	−3.3	657.6	3.0
0.1888	0.804447	0.3889	1371.7	−4.6	660.6	4.1
0.2231	0.804377	0.4169	1369.7	−5.4	662.6	4.7
0.3059	0.804273	0.4566	1365.1	−6.7	667.2	5.6
0.4052	0.804097	0.4821	1358.8	−7.9	673.5	6.5
0.5039	0.803949	0.4930	1350.9	−9.6	681.6	7.6
0.6118	0.803817	0.4773	1340.5	−10.8	692.3	8.1
0.7056	0.803732	0.4430	1328.8	−11.3	704.7	8.1
0.7998	0.803836	0.3577	1312.5	−11.2	722.2	7.6
0.8546	0.803989	0.2951	1299.5	−10.7	736.5	7.0
0.9035	0.804336	0.2117	1284.3	−9.7	753.7	6.4
0.9669	0.805126	0.0861	1258.5	−5.1	784.2	3.3
1.0000	0.805907	0.0000	1240.5	0.0	806.4	0.0
			303.15 K			
0.0000	0.801912	0.0000	1364.1	0.0	670.2	0.0
0.0451	0.801658	0.1673	1361.7	−1.2	672.7	1.2
0.1077	0.801402	0.3211	1358.3	−2.9	676.3	2.9
0.1346	0.801318	0.3667	1356.5	−3.6	678.2	3.8
0.1888	0.801160	0.4449	1353.8	−4.9	681.1	4.7
0.2231	0.801070	0.4841	1351.8	−5.7	683.2	5.4
0.3059	0.800898	0.5429	1347.1	−7.1	688.1	6.6
0.4052	0.800714	0.5832	1340.8	−8.6	694.7	7.7
0.5039	0.800528	0.6048	1332.6	−10.7	703.5	9.5
0.6118	0.800347	0.5983	1322.5	−11.8	714.4	10.1
0.7056	0.800179	0.5784	1310.9	−12.5	727.3	10.5
0.7998	0.800194	0.4998	1294.8	−12.7	745.4	10.4
0.8546	0.800335	0.4290	1281.8	−12.5	760.4	10.4
0.9035	0.800708	0.3313	1266.8	−11.9	778.3	10.3
0.9669	0.801896	0.1404	1241.4	−7.6	809.2	7.2
1.0000	0.803155	0.0000	1226.5	0.0	827.7	0.0
			308.15 K			
0.0000	0.798709	0.0000	1346.5	0.0	690.6	0.0
0.0451	0.798397	0.2020	1343.0	−1.4	694.4	2.5
0.1077	0.798084	0.3845	1340.2	−3.0	697.6	3.7
0.1346	0.797991	0.4319	1338.9	−3.9	698.9	4.1
0.1888	0.797826	0.5065	1335.9	−5.2	702.3	5.3
0.2231	0.797731	0.5436	1333.9	−5.9	704.4	6.0
0.3059	0.797543	0.5979	1329.3	−7.4	709.6	7.3
0.4052	0.797320	0.6395	1322.8	−9.1	716.8	8.7
0.5039	0.797098	0.6569	1314.8	−11.1	725.7	10.4
0.6118	0.796857	0.6479	1304.6	−12.3	737.3	11.2
0.7056	0.796621	0.6244	1293.1	−13.0	750.8	11.4
0.7998	0.796558	0.5368	1277.1	−13.1	769.8	11.6
0.8546	0.796660	0.4555	1264.2	−12.9	785.4	11.5
0.9035	0.796979	0.3495	1249.1	−12.4	804.2	11.5
0.9669	0.798060	0.1478	1224.4	−7.7	835.8	7.8
1.0000	0.799249	0.0000	1209.8	0.0	854.9	0.0

κ_s denote corresponding mixture properties. x_i is the mole fraction, and φ_i is the volume fraction for the pure component.

The viscosity deviations are calculated from their linear dependence by using the relation

$$\Delta\eta = \eta - \sum_{i=1}^{2} x_i\eta_i \qquad (4)$$

where η and η_i are the viscosity of the mixture and pure component, respectively. The $\Delta\eta$ values are given in Table 4, and the uncertainty in $\Delta\eta$ is ± 0.003 mPa·s. The experimental results were fitted in the Redlich–Kister polynomial equation[37]

$$Y^{E} = x_1x_2\sum_{i=0}^{m-1} A_i(1-2x_1)^i \qquad (5)$$

where Y^E is any excess property or deviation; A_i is the polynomial coefficient; and m is the polynomial degree. When Y^E ($= V_m^E$, $\Delta\eta$), the composition is taken as mole fraction x_i, and for Y^E ($= \Delta u$, $\Delta\kappa_s$), the volume fraction φ_i is used. The standard deviation (σ) was calculated using

$$\sigma = \left[\sum (Y^{E}_{\text{exptl}} - Y^{E}_{\text{calcd}})/(n-m)\right]^{1/2} \qquad (6)$$

where n is the number of experimental data points. The coefficients A_i along with standard deviation (σ) are reported in Table 5.

Figure 1a, b depicts the variation of V_m^E with composition for ($C_4H_9OH + C_{16}H_{34}$) and ($C_4H_9OH + C_{30}H_{62}$), respectively. Both the systems show positive V_m^E values and also a positive $(\delta V_m^E/\delta T)_P$. The V_m^E values are more positive for ($C_4H_9OH + C_{30}H_{62}$) as compared to ($C_4H_9OH + C_{16}H_{34}$) due to the increasing chain length of alkane molecules. The observed positive V_m^E values can be interpreted as a result of disruption of alkanol multimers through the breaking of H-bonds since the multimers tend to have a smaller volume than the sum of their component parts. This may be offset to some extent by the effect of a branched structure of multimers on the standard volume of association. However, such compensation should be negligible in the dilute alkanol region where the degree of association is low and only small multimers (such as a dimer and trimer) are present. The disruption of alkanol aggregates is also more pronounced at low concentration, as the probability of contact and subsequent interactions with other unlike molecules (alkane in this case) is higher. This causes the shape of the V_m^E of (alkanol + alkane) to be asymmetric, with the maximum being shifted toward lower x_1 as observed in ($C_4H_9OH + C_{16}H_{34}$). On the other hand, the presence of nonspecific physical interactions between the real species present in the mixture (alkane molecules, alkanol monomers, and multimers) also contributes to the positive V_m^E. It appears that these terms comprise the major part of the positive contributions to V_m^E over much of the mole fraction range.

Table 4. Viscosity, η, and Viscosity Deviation, $\Delta\eta$, for the Binary Mixtures of ($x_1C_4H_9OH + x_2C_{16}H_{34}$) and ($x_1C_4H_9OH + x_2C_{30}H_{62}$) at Several Temperatures

	T = 298.15 K		T = 303.15 K		T = 308.15 K	
	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$
x_1	mPa·s	mPa·s	mPa·s	mPa·s	mPa·s	mPa·s
			$x_1C_4H_9OH + x_2C_{16}H_{34}$			
0.0000	3.041	0.000	2.706	0.000	2.409	0.000
0.0899	2.957	−0.042	2.600	−0.067	2.302	−0.068
0.1048	2.937	−0.055	2.582	−0.079	2.287	−0.076
0.1516	2.899	−0.071	2.546	−0.094	2.254	−0.090
0.2017	2.846	−0.100	2.515	−0.104	2.223	−0.099
0.2494	2.811	−0.113	2.478	−0.121	2.189	−0.112
0.3382	2.753	−0.129	2.432	−0.128	2.146	−0.118
0.4147	2.704	−0.143	2.394	−0.134	2.112	−0.120
0.5057	2.665	−0.139	2.344	−0.144	2.068	−0.125
0.5845	2.635	−0.133	2.306	−0.148	2.029	−0.130
0.6980	2.594	−0.121	2.256	−0.149	1.990	−0.120
0.7945	2.568	−0.101	2.223	−0.140	1.960	−0.109
0.8497	2.558	−0.085	2.218	−0.121	1.953	−0.091
0.8963	2.551	−0.070	2.219	−0.101	1.948	−0.078
0.9530	2.556	−0.039	2.228	−0.067	1.953	−0.048
1.0000	2.573	0.000	2.275	0.000	1.981	0.000
			$x_1C_4H_9OH + x_2C_{30}H_{62}$			
0.0000	28.257	0.000	22.087	0.000	17.774	0.000
0.0451	26.655	−0.444	20.877	−0.316	16.806	−0.256
0.1077	24.689	−0.802	19.417	−0.536	15.620	−0.453
0.1346	23.925	−0.875	18.855	−0.565	15.162	−0.486
0.1888	22.478	−0.930	17.780	−0.566	14.294	−0.498
0.2231	21.622	−0.905	17.138	−0.529	13.789	−0.462
0.3059	19.666	−0.735	15.643	−0.383	12.617	−0.326
0.4052	17.395	−0.455	13.900	−0.159	11.385	0.010
0.5039	15.106	−0.209	12.136	0.032	9.903	0.087
0.6118	12.474	−0.069	10.119	0.153	8.307	0.195
0.7056	10.056	−0.078	8.276	0.169	6.824	0.194
0.7998	7.573	−0.142	6.348	0.107	5.267	0.124
0.8546	6.128	−0.180	5.200	0.045	4.344	0.067
0.9035	4.873	−0.179	4.186	−0.001	3.527	0.022
0.9669	3.325	−0.098	2.912	−0.018	2.497	−0.007
1.0000	2.573	0.000	2.275	0.000	1.981	0.000

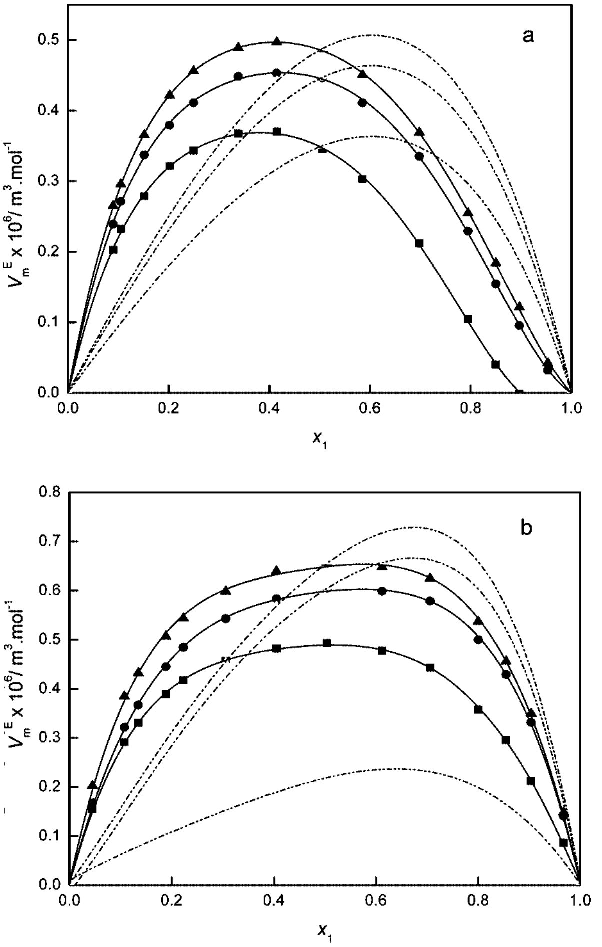

Figure 1. Excess molar volumes, V_m^E, at ■, 298.15 K; ●, 303.15 K; and ▲, 308.15 K for the binary mixtures of $x_1C_4H_9OH + x_2C_nH_{2n+1}$: (a) n = 16 and (b) n = 30. The solid curves have been derived from eq 5, and dotted (-----) curves are from the PFP theory.

The composition dependence of Δu vs φ_1 is shown in Figure 2a, b. The Δu values are negative for both the mixtures. A minima at $\varphi_1 \approx 0.3$ appears in Δu curves for ($C_4H_9OH + C_{16}H_{34}$), whereas for ($C_4H_9OH + C_{30}H_{62}$), almost a constant variation of Δu vs φ_1 is observed in the range of $0.25 \le \varphi_1 \le 0.7$. An increase in temperature makes Δu values more negative. Like V_m^E, $\Delta\kappa_s$ values (Figure 3a, b) are positive for both the mixtures. The trend observed in $\Delta\kappa_s$ is also similar to Δu but

Table 5. Coefficients of the Fitting Equation (Equation 5) and the Standard Deviations (σ) for ($x_1C_4H_9OH + x_2C_{16}H_{34}$) and ($x_1C_4H_9OH + x_2C_{30}H_{62}$) Binary Mixtures

binary mixture	T/K	Excess property	A_0	A_1	A_2	A_3	A_4	σ
$x_1C_4H_9OH + x_2C_{16}H_{34}$	298.15	$V^E\cdot10^6/m^3\cdot mol^{-1}$	1.3957	−0.6982	−0.2786	−1.3115		0.0034
		$\Delta u/m\cdot s^{-1}$	−35.9	31.2	−7.1	26.4	−22.6	0.1
		$\Delta\kappa_s/TPa^{-1}$	36.7	−41.8	3.5	−30.1	32.2	0.2
		$\Delta\eta/mPa\cdot s$	−0.560	0.096	−0.142	−0.343		0.003
	303.15	$V^E\cdot10^6\ /m^3\cdot mol^{-1}$	1.7823	−0.4240	0.2629	−1.1685		0.0034
		$\Delta u/m\cdot s^{-1}$	−43.9	20.7	−14.7	37.0	−25.1	0.2
		$\Delta\kappa_s/TPa^{-1}$	52.1	−27.4	13.2	−46.5	37.8	0.3
		$\Delta\eta/mPa\cdot s$	−0.574	−0.125	−0.384	−0.102	−0.392	0.004
	308.15	$V^E\cdot10^6\ /m^3\cdot mol^{-1}$	1.9445	−0.4972	0.4138	−1.0861		0.0027
		$\Delta u/m\cdot s^{-1}$	−45.2	21.9	−16.0	35.7	−31.9	0.2
		$\Delta\kappa_s/TPa^{-1}$	57.8	−29.9	13.4	−48.0	51.1	0.3
		$\Delta\eta/mPa\cdot s$	−0.506	−0.044	−0.253	0.037	−0.397	0.003
$x_1C_4H_9OH + x_2C_{30}H_{62}$	298.15	$V^E\cdot10^6\ /m^3\cdot mol^{-1}$	1.9699	0.0463	0.9550	−0.6938	0.4611	0.0029
		$\Delta u/m\cdot s^{-1}$	−43.8	12.9	−3.6	29.8	−47.0	0.3
		$\Delta\kappa_s/TPa^{-1}$	29.3	−11.2	1.5	−29.2	53.0	0.3
		$\Delta\eta/mPa\cdot s$	−0.862	4.069	−6.898			0.003
	303.15	$V^E\cdot10^6/m^3\cdot mol^{-1}$	2.4138	0.2180	1.3951	0.0307	0.6697	0.0034
		$\Delta u/m\cdot s^{-1}$	−50.6	6.5	−16.8	25.8	−45.8	0.3
		$\Delta\kappa_s/TPa^{-1}$	42.4	−1.8	15.4	−24.3	59.4	0.4
		$\Delta\eta/mPa\cdot s$	0.098	3.265	−3.697	0.522	−1.402	0.003
	308.15	$V^E\cdot10^6/m^3\cdot mol^{-1}$	2.6257	0.2292	1.5408	−0.4087	0.9894	0.0036
		$\Delta u/m\cdot s^{-1}$	−52.8	5.6	−16.6	31.5	−47.0	0.3
		$\Delta\kappa_s/TPa^{-1}$	47.4	0.2	11.3	−33.5	72.3	0.6
		$\Delta\eta/mPa\cdot s$	0.311	3.189	−4.043			0.003

opposite in sign. Positive deviations in $\Delta\kappa_s$ values suggest the presence of weak dispersive interactions among the component molecules in the mixture.

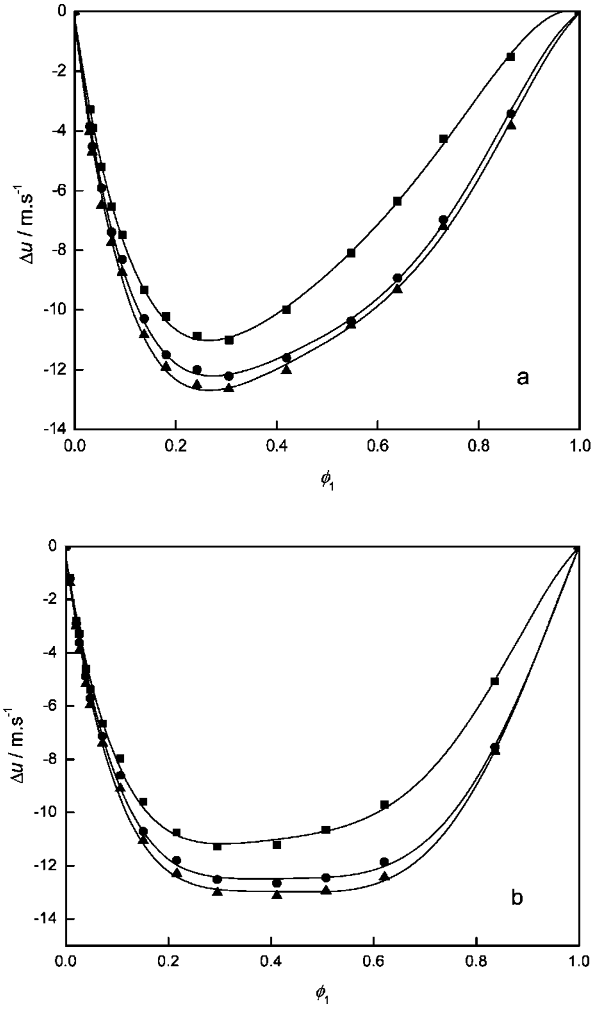

Figure 2. Deviation in speed of sound, Δu, at ■, 298.15 K; ●, 303.15 K; and ▲, 308.15 K for the binary mixtures of $x_1C_4H_9OH + x_2C_nH_{2n+1}$: (a) $n = 16$ and (b) $n = 30$. The solid curves have been derived from eq 5.

The variation of $\Delta\eta$ vs x_1 is given in Figure 4a, b. The $\Delta\eta$ values are negative ($C_4H_9OH + C_{16}H_{34}$), while W-shaped behavior is observed for ($C_4H_9OH + C_{30}H_{62}$). The W-shaped

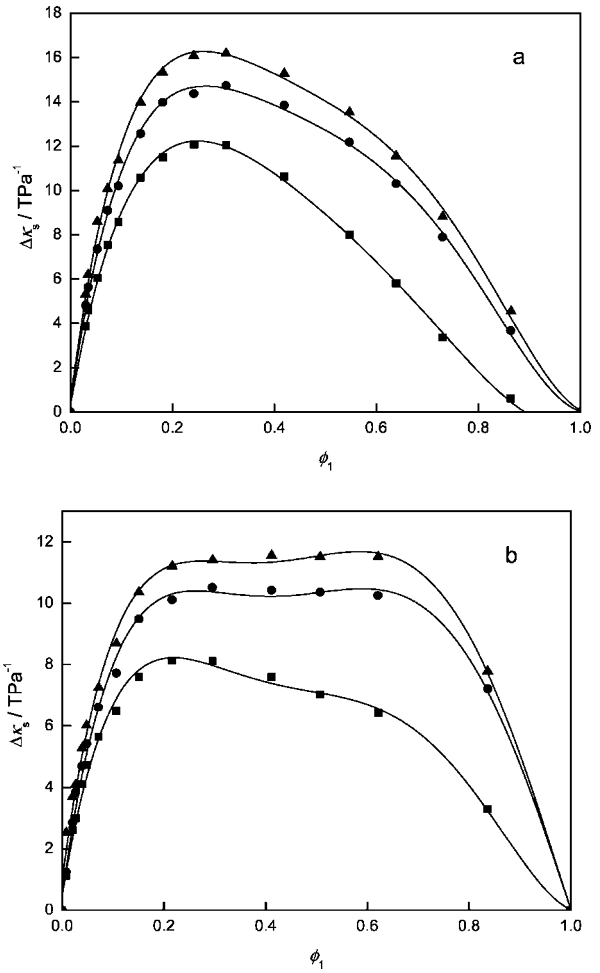

Figure 3. Deviation in isentropic compressibility, $\Delta\kappa_s$, at ■, 298.15 K; ●, 303.15 K; and ▲, 308.15 K for the binary mixtures of $x_1C_4H_9OH + x_2C_nH_{2n+1}$: (a) $n = 16$ and (b) $n = 30$. The solid curves have been derived from eq 5.

Table 6. Characteristic Parameters for the Pure Components at Several Temperatures Used in PFP Theory Calculations

components	T/K	$\alpha\cdot10^3$ $\mathrm{K^{-1}}$	κ_T $\mathrm{TPa^{-1}}$	C_P $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$\tilde{v}$	$\tilde{T}$	$V^*\cdot10^6$ $\mathrm{m^3\cdot mol^{-1}}$	$10^6\,P^*$ $\mathrm{J\cdot m^{-3}}$	T^* K
C_4H_9OH	298.15	0.932[44]	942.0[44]	177.12[22]	1.2336	0.0548	74.5581	448.89	5441
	303.15	0.939[39]	949.0[39]	178.88[22]	1.2388	0.0556	74.5007	460.30	5451
	308.15	0.952[a]	998.3[b]	180.60[22]	1.2444	0.0565	74.5263	455.07	5455
$C_{16}H_{34}$	298.15	0.887[a]	861.8[b]	501.60[47]	1.2241	0.0532	240.1106	459.80	5600
	303.15	0.894[a]	905.0[45]	504.30[c]	1.2287	0.0540	240.2808	452.14	5613
	308.15	0.900[a]	917.0[46]	507.15[46]	1.2332	0.0547	240.4950	459.95	5630
$C_{30}H_{62}$	298.15	0.758[10]	740.0[10]	904.00[48]	1.1958	0.0484	439.1806	436.41	6162
	303.15	0.764[10]	750.0[10]	904.75[48]	1.2000	0.0491	439.3787	444.56	6169
	308.15	0.770[10]	760.0[10]	905.83[48]	1.2043	0.0499	439.5793	452.80	6176

[a] Derived from our measured densities. [b] Calculated from $\kappa_T = 1/(\rho u^2) + TV\alpha^2/C_p$. [c] Estimated using group additivity.

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	$\chi_{12}\cdot10^6$ $\mathrm{J\cdot m^{-3}}$	$V_m^E\cdot10^6/\mathrm{m^3\cdot mol^{-1}}$ exptl	PFP	calculated contributions V_m^E (int.)	V_m^E (fv)	V_m^E (ip)
$x_1C_4H_9OH + x_2C_{16}H_{34}$	298.15	19.32	0.3489	0.3490	0.3592	−0.0038	−0.0065
	303.15	23.02	0.4456	0.4457	0.4448	−0.0043	0.0051
	308.15	25.11	0.4861	0.4862	0.4948	−0.0053	−0.0034
$x_1C_4H_9OH + x_2C_{30}H_{62}$	298.15	28.62	0.4925	0.2210	0.5286	−0.0705	0.0343
	303.15	33.94	0.6035	0.6027	0.6339	−0.0725	0.0421
	308.15	38.33	0.6564	0.6568	0.7277	−0.0777	0.0064

curves have two regions of negative curvature separated by a region of a positive one. This is a consequence of two opposite contributions: a positive contribution to $\Delta\eta$ (the so-called nonrandom contribution) transferring into a parabolic negative curve (the so-called random contribution). As can be seen in Figure 4b, the randomness, being predominant from $x_1 = 0$ to 0.3 and 0.75 to 1, results from the disruption of the molecular

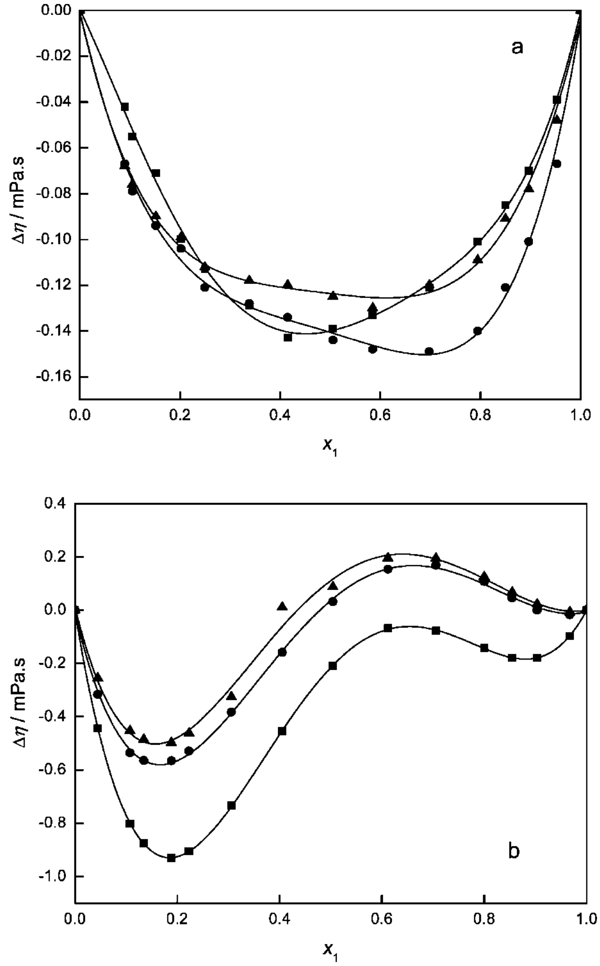

Figure 4. Viscosity deviations, $\Delta\eta$, at ■, 298.15 K; ●, 303.15 K; and ▲, 308.15 K for the binary mixtures of $x_1C_4H_9OH + x_2C_nH_{2n+1}$: (a) $n = 16$ and (b) $n = 30$. The solid curves have been derived from eq 5.

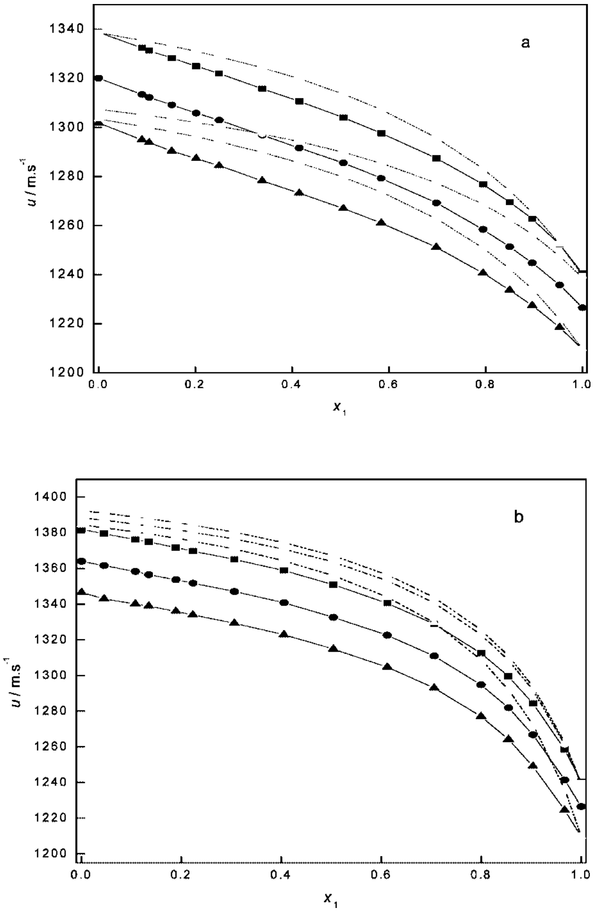

Figure 5. Variation of speed of sound, u, at ■, 298.15 K; ●, 303.15 K; and ▲, 308.15 K for the binary mixtures of $x_1C_4H_9OH + x_2C_nH_{2n+1}$: (a) $n = 16$ and (b) $n = 30$. The dotted (-----) curves have been derived from the PFP theory.

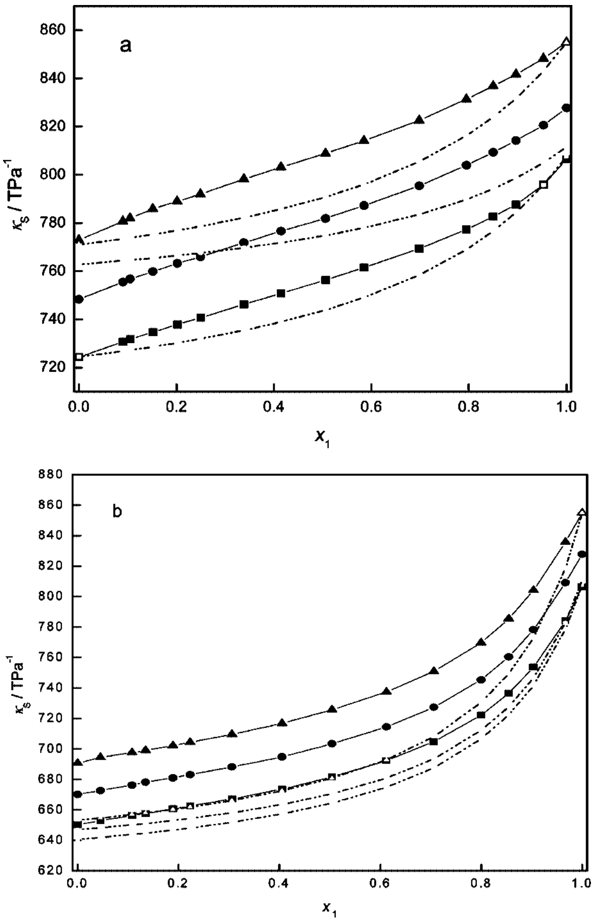

Figure 6. Variation of isentropic compressibility, κ_s, at ■, 298.15 K; ●, 303.15 K; and ▲, 308.15 K for the binary mixtures of $x_1C_4H_9OH + x_2C_nH_{2n+1}$: (a) $n = 16$ and (b) $n = 30$. The dotted (-----) curves have been derived from the PFP theory.

order of the dilute component; i.e., the molecules of the dilute component are separated and randomly distributed in the component of higher concentration. However, for range from $x_1 = 0.3$ to $x_1 = 0.75$, a positive contribution to $\Delta\eta$ is observed (nonrandomness) that results from the possible attractive van der Waals molecular interactions: attractions between permanent dipoles, between permanent and induced dipoles, and dispersive interactions. The viscosity of a mixture strongly depends on the entropy of the mixture and is related to the liquid structure and enthalpy. Thus, $\Delta\eta$ are functions of interactions as well as the size and shape of the participating molecules.[38] It is also clear from Figure 4b that the W-shape becomes less pronounced at higher temperatures. Thus, broadly speaking, the molecular interactions analyzed earlier on the basis of relative magnitude of V_m^E and $K_{S,m}^E$ are also consistent with viscosity behavior.

Theoretical Analysis. The Prigogine−Flory−Patterson (PFP) theory has been applied to predict and correlate the V_m^E, whereas the PFP theory with the van der Waals (vdW) potential energy model is used for theoretical estimation of u and κ_s of these systems. The relevant equations are given elsewhere.[39–47] Table 6 contains characteristic parameters for the pure components at several temperatures used in PFP theory calculations. Table 7 reports interaction parameter, χ_{12}, and the calculated and experimental values of V_m^E at $x_1 = 0.5$. Figures 1a, b, 5a, b, and 6a, b show the comparison between the experimental and calculated V_m^E, u, and κ_s values. It is clear from the figures that PFP cannot predict the experimental data quite satisfactorily. This is not surprising as PFP theory does not consider all the possible interactions taking place in the liquid mixture. The experimental and calculated values of u and κ_s at $x_1 = 0.5$ are given in Table 8 along with the standard percentage deviations (σ %).

Table 8. Comparison of Experimental and Calculated Values of the Speeds of Sound, u, and Isentropic Compressibility, κ_s, of Binary Mixtures at $x_1 = 0.5$ and Standard Percentage Deviation

	T	u/m·s^{-1}			κ_s/TPa^{-1}		
binary mixtures	K	exptl	vdW	σ %	exptl	vdW	σ %
$x_1C_4H_9OH + x_2C_{16}H_{34}$	298.15	1304.4	1313.9	0.5	756.2	743.6	1.1
	303.15	1285.8	1290.1	0.7	781.7	774.7	1.4
	308.15	1267.4	1280.1	0.7	808.4	790.5	1.6
$x_1C_4H_9OH + x_2C_{30}H_{62}$	298.15	1351.1	1367.8	0.9	681.6	664.8	2.0
	303.15	1333.1	1363.5	2.1	702.9	670.9	4.2
	308.15	1315.3	1355.9	2.8	725.2	680.8	5.5

Conclusions

This paper reports new measurements of density, speed of sound, and viscosity at (298.15, 303.15, and 308.15) K over the entire range of mixture compositions for $C_4H_9OH + C_{16}H_{34}$ or, $+ C_{30}H_{62}$ systems. The values of excess molar volumes and isentropic compressibility show positive deviations, whereas a negative trend is observed for viscosity deviations and deviations in speed of sound for the studied binary systems. These parameters provide support for the existence of weak dispersive interactions among the component molecules in the mixtures. Further, the applicability of PFP theory for the excess molar volumes in the studied systems has also been checked, and it is found that the results are not satisfactory. It concludes that there is a strong self-association between alcohol molecules which prevent the alcohol−alkane interactions.

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