Volumetric and Viscometric Behavior of the Binary System: (Hexan-1-ol + *p*-Xylene)

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Densities and viscosities for the binary mixtures of hexan-1-ol with *p*-xylene have been measured at a number of mole fractions at $T = (303.15, 313.15, \text{and } 323.15)$ K. The excess molar volumes and viscosity deviations have been calculated from the experimental results and have been fitted to the Redlich−Kister polynomial equation.

Introduction

Densities and viscosities of multicomponent solvent mixtures are required for the process design involving heat transfer, mass transfer, fluidity, and so forth as well as for the development of our understanding of molecular interactions in such systems.[1,2] In this work, which is a part of our ongoing research on the accumulation of the binary physical property data of organic liquid mixtures,[3–7] we are reporting the density and viscosity data of the binary mixtures of hexan-1-ol with *p*-xylene at $T = (303.15, 313.15, \text{and } 323.15)$ K. Among the two components of the studied binary mixtures, hexan-1-ol is an aliphatic polar solvent with strong self-associating nature via hydrogen bonding and van der Waals interactions, while *p*-xylene is a nonassociating solvent. Therefore, a favorable interaction with the hydroxyl group of hexan-1-ol is possibly due to the presence of aromatic rings with delocalized π-electrons in *p*-xylene,[8] and the experimental results will allow us to study the interactions. Excess molar volumes and viscosity deviations for the binary systems have been calculated from the experimental results and fitted to the Redlich−Kister polynomial equation[9] to estimate the binary coefficients and the standard deviations. The experimental and the derived data have been interpreted using some previous observations for the similar binary systems. The results are compared to those of binary systems of hexan-1-ol with *o*- and *m*-xylenes,[6,7] which were previously reported.

Experimental Section

Hexan-1-ol and *p*-xylene from Merck-Schuchard, Germany (0.98 mass fraction purity), were used without further treatment. The results of the measurements of their densities and viscosities at $T = (303.15, 313.15, \text{and } 323.15)$ K were in satisfactory agreement with the published values (Table 1). Hence, the materials were taken to be reasonably pure.

Table 1. Comparison of Experimental Densities, ρ, and Viscosities, η, of Pure Liquids with Literature Values at $T = (303.15, 313.15, \text{and } 323.15)$ K

		$\rho/\text{g}\cdot\text{cm}^{-3}$			$\eta/\text{mPa}\cdot\text{s}$		
liquid (s)	T/K	exptl	lit.	ref	exptl	lit.	ref
hexan-1-ol	303.15	0.8119	0.8120	20	3.829	3.84	20
			0.8121	21		3.769	21
			0.8115	22		3.861	22
	313.15	0.8046	0.8046	20, 21	2.879	2.90	20
			0.80428	23		2.89	24
	323.15	0.7975	0.7972	20	2.215	2.23	20
			0.7979	21		2.210	24
p-xylene	303.15	0.8524	0.8523	25	0.573	0.568	25
			0.85239	26		0.5762	26
			0.85235	27			
			0.8521	28			
	313.15	0.8439	0.8435	28	0.512	0.517	28, 29
			0.8440	29			
			0.8436	30			
	323.15	0.8352	0.8349	27	0.461	0.4599	27

All binary mixtures were prepared by mass on an analytical balance (B 204-S, Mettler Toledo, Switzerland) with uncertainty of ± 0.0001 g and operating in a drybox. Mixtures were completely miscible over the whole composition range. Caution was taken to prevent evaporation of the samples after preparation. The mole fraction of each mixture was obtained to an uncertainty of $\pm\, 1.0\cdot10^{-4}$. A transparent glass-walled thermostatic water bath was used. The bath temperature was controlled by the Thermo Haake DC10 controller (Thermo Fisher Scientific, MA, USA) and was monitored with a minimum−maximum thermometer (Brannan Thermometers, Cumberland, UK). The uncertainty in the temperature during the measurements was ± 0.05 K. A 10 mL bicapillary pycnometer and an A-type Ostwald viscometer, previously calibrated with redistilled water, were used to measure the densities and viscosities, respectively. The average uncertainties in the measured densities and viscosities were $\pm\, 0.0004\ \text{g}\cdot\text{cm}^{-3}$ and $\pm\, 0.005\ \text{mPa}\cdot\text{s}$, respectively. For all mixture compositions and pure solvents, triplicate measurements were performed, and the average of these values was considered in all calculations.

Results and Discussion

Binary compositions of the mixtures of hexan-1-ol with *p*-xylene, the experimental densities and viscosities, excess molar volumes, V_m^E, and the viscosity deviations, $\Delta\eta$, at $T = (303.15, 313.15, \text{and } 323.15)$ K are summarized in Table 2. The V_m^E and $\Delta\eta$ values have been calculated using the following relations

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Table 2. Compositions, Experimental Densities, ρ, Excess Molar Volumes, V_m^E, Viscosities, η, and the Viscosity Deviations, $\Delta\eta$, for the Binary Mixtures of Hexan-1-ol with *p*-Xylene at T = (303.15, 313.15, and 323.15) K

Densities and Excess Molar Volumes of Hexan-1-ol (1) + *p*-Xylene (2)

	T/K = 303.15		T/K = 313.15		T/K = 323.15	
	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
x_1	$g\cdot cm^{-3}$	$cm^3\cdot mol^{-1}$	$g\cdot cm^{-3}$	$cm^3\cdot mol^{-1}$	$g\cdot cm^{-3}$	$cm^3\cdot mol^{-1}$
0.0000	0.8524	0.0000	0.8439	0.0000	0.8352	0.0000
0.0999	0.8478	0.0759	0.8393	0.0961	0.8305	0.1389
0.1999	0.8435	0.1090	0.8351	0.1335	0.8264	0.1873
0.2999	0.8394	0.1140	0.8311	0.1421	0.8226	0.1907
0.4001	0.8354	0.1041	0.8272	0.1355	0.8189	0.1783
0.4997	0.8314	0.0990	0.8233	0.1335	0.8152	0.1702
0.6000	0.8275	0.0756	0.8195	0.1129	0.8116	0.1430
0.7000	0.8236	0.0551	0.8157	0.0951	0.8080	0.1183
0.8000	0.8197	0.0357	0.8120	0.0626	0.8044	0.0942
0.8999	0.8158	0.0179	0.8083	0.0315	0.8009	0.0555
1.0000	0.8119	0.0000	0.8046	0.0000	0.7975	0.0000

Viscosities and Deviations of the Viscosity of Hexan-1-ol (1) + *p*-Xylene (2)

	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$
x_1	mPa·s	mPa·s	mPa·s	mPa·s	mPa·s	mPa·s
0.0000	0.573	0.000	0.512	0.000	0.461	0.000
0.0999	0.616	−0.077	0.544	−0.064	0.485	−0.054
0.1999	0.693	−0.145	0.605	−0.118	0.533	−0.098
0.2999	0.799	−0.214	0.689	−0.170	0.600	−0.138
0.4001	0.946	−0.279	0.802	−0.220	0.689	−0.175
0.4997	1.148	−0.332	0.956	−0.257	0.807	−0.203
0.6000	1.420	−0.371	1.156	−0.287	0.958	−0.224
0.7000	1.801	−0.365	1.433	−0.282	1.161	−0.222
0.8000	2.323	−0.296	1.806	−0.232	1.433	−0.185
0.8999	3.004	−0.162	2.295	−0.127	1.788	−0.105
1.0000	3.829	0.000	2.879	0.000	2.215	0.000

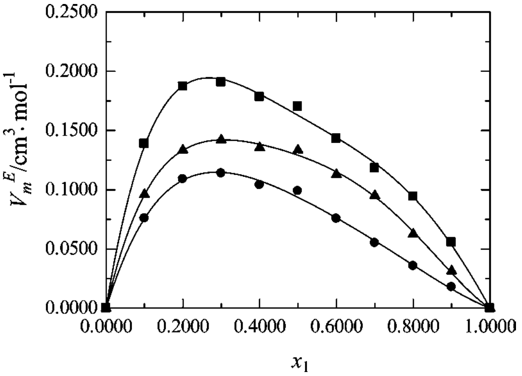

Figure 1. Excess molar volumes for hexan-1-ol (1) + *p*-xylene (2): ●, 303.15 K; ▲, 313.15 K; ■, 323.15 K.

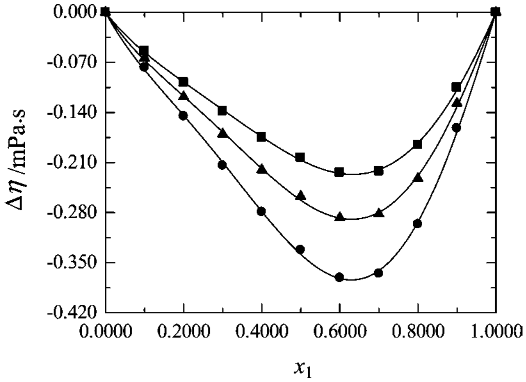

Figure 2. Viscosity deviations for hexan-1-ol (1) + *p*-xylene (2): ●, 303.15 K; ▲, 313.15 K; ■, 323.15 K.

$$V_m^E = [(x_1M_1 + x_2M_2)/\rho - \{(x_1M_1)/\rho_1 + (x_2M_2)/\rho_2\}] \tag{1}$$

$$\Delta\eta = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{2}$$

where x_1, M_1, ρ_1, and η_1 represent, respectively, mole fraction, molar mass, density, and viscosity of hexan-1-ol, and x_2, M_2, ρ_2, and η_2 are the corresponding quantities of *p*-xylene. ρ and η are the density and viscosity of the binary mixtures. The uncertainties in V_m^E and $\Delta\eta$ are found to be within ± 0.0001 $g\cdot cm^{-3}$ and ± 0.001 mPa·s, respectively.

The V_m^E profiles for the binary mixtures varying with the mole fraction of hexan-1-ol (x_1) at T = (303.15, 313.15, and 323.15) K are observed to be positive over the whole range of compositions (Figure 1). The V_m^E values increase sharply, reach a maximum, and then decrease gradually with the increase of hexan-1-ol mole fraction. The maxima are at about 0.3000 mol fraction. The magnitude of V_m^E values increases with the increase of temperature. The $\delta V_m^E/\delta T$ values for all temperatures are positive. The sign of V_m^E depends upon the resultant of the factors contributing to the expansion of volume and the factors contributing to the contraction of volume. The expansion of volume as indicated by the positive V_m^E values can be attributed to the fact that the total positive contributing factors outweigh the factors responsible for negative contributing effects, indicating weak interaction between the two components. Hexan-1-ol, like all other alcohols, has strongly associated molecules through H-bonding and was added to a nonassociating solvent, *p*-xylene, to prepare the binary mixtures. The initial sharp increase in V_m^E values in the hexan-1-ol low-concentration region may be due to the maximum or complete disintegration of associated molecules of hexan-1-ol in the solution containing the nonpolar component *p*-xylene. At the hexan-1-ol-rich region of the mixtures, maximum concentration of the alcohol remains in the associated state facilitating the partial or full accommodation of the *p*-xylene into the network of alcohol. These may be the causes of slow gradual decrease of V_m^E values at the hexan-1-ol-rich region. Lower V_m^E values obtained for hexan-1-ol with *p*-xylene than those reported for hexan-1-ol with *o*- and *m*-xylenes[6,7] indicate the probability of weaker interactions between the delocalized π-electrons of the *p*-xylene ring and the −OH group of hexan-1-ol besides the disruption of H-bonding.

The $\Delta\eta$ values for the binary mixtures of hexan-1-ol with *p*-xylene are negative throughout the whole range of mole fraction. Figure 2 illustrates the trend of $\Delta\eta$ values as a function of the binary compositions at T = (303.15, 313.15, and 323.15) K with a minima at around 0.6000 mol fraction of alcohol. Molecular interactions between the components of the mixture determine the viscometric behavior of a solvent mixture. The negative $\Delta\eta$ values observed for the hexan-1-ol and *p*-xylene system can be described by the dominance of dispersion force compared to the induced dipole−dipole interactions which correspond to a system containing an associated component.[10] It is anticipated that the associated structure of hexan-1-ol via H-bonding undergoes disruption when added to *p*-xylene forming monomeric, oligomeric, or small-scaled multimeric species, which experience much less resistance to flow, resulting in the negative viscosity deviations. An increase of temperature leads to an increase in $\Delta\eta$; i.e., $\delta\eta/\delta T$ is positive. Skewed curves with minima in the hexan-1-ol high-concentration region may be due to the so-called interstitial accommodation effect. The *p*-xylene molecules occupy the void spaces within the hexan-1-ol network structures which may result in more compact and well-shaped flowing species with favorable geometric fitting. Therefore, the frictional resistance is reduced remarkably, and

Table 3. Coefficients, A_i, of the Redlich−Kister Equation (Equation 3), Expressing V_m^E (cm^3·mol^{-1}) and $\Delta\eta$ (mPa·s), and Standard Deviation, σ, for the Binary Mixtures of Hexan-1-ol with *p*-Xylene at T = (303.15, 313.15, and 323.15) K

T/K	A_0	A_1	A_2	A_3	σ
Correlated Results for Excess Molar Volumes of Hexan-1-ol (1) + *p*-Xylene (2)					
303.15	0.3746	0.3220	0.2129	0.1423	0.0026
313.15	0.5167	0.2282	0.2833	0.3601	0.0024
323.15	0.6511	0.3702	0.6326	0.3272	0.0037
Correlated Results for Viscosity Deviations of Hexan-1-ol (1) + *p*-Xylene (2)					
303.15	−1.3531	1.0008	−0.0358	−0.6278	0.0042
313.15	−1.0506	0.7411	−0.0823	−0.4537	0.0037
323.15	−0.8258	0.5440	−0.1365	−0.2822	0.0025

$\Delta\eta$ decreases sharply. The $\Delta\eta$ values for the hexan-1-ol and *p*-xylene binary system have higher magnitudes than those observed for hexan-1-ol with *o*- and *m*-xylenes.[6,7]

The composition dependence of V_m^E or $\Delta\eta$ can be represented by a Redlich−Kister[9] type equation

$$\delta = x_1 x_2 \sum_{i=0}^{n} A_i (1 - 2x_1)^i \qquad (3)$$

where δ refers to V_m^E or $\Delta\eta$, and x_1 and x_2 are the mole fractions of hexan-1-ol and *p*-xylene. The variables A_i are the equation coefficients, which are obtained by fitting the equation to the experimental values with a least-squares regression method (Table 3). Data processing and analyses are performed with LAB Fit[11] and LSM[12] curve-fitting programs. Sma4 for windows[13] are used for graphical representation of data.

Excess molar volumes (V_m^E) for the hexan-1-ol and *p*-xylene system were reported by Rodriguez-Nuñez et al.[14] at 298.15 K. The V_m^E values observed at 298.15 K were relatively small, showing a negative−positive trend in the profile, whereas the trend of V_m^E profiles is positive over the entire range of binary compositions at T = (303.15, 313.15, and 323.15) K.

There are reports on the volumetric behavior of *p*-xylene with different alkanols[15–19] other than hexan-1-ol. However, no literature data are available with which to compare the present results for hexan-1-ol with *p*-xylene at T = (303.15, 313.15, and 323.15) K.

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