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Experimental and modeling study of diisopropyl ether and 2-alkanol; PC-SAFT model and free volume theory

Simin Ahmadi[a], Mohammad Almasi[b,*]

[a] Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
[b] Department of Applied Chemistry, Faculty of Science, Malayer University, Malayer 65174, Iran

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ABSTRACT

In the present study, with the aim to discover the governing interactions in binary mixtures containing diisopropyl ether and short-range 2-alkanol (from 2-propanol to 2-hexanol), experimental values of density and viscosity at temperature range 293.15 K–323.15 K were reported. From these data, values of excess molar volume, partial molar volume, and viscosity deviation for mentioned systems were calculated. Findings show that strong interactions occur among unlike molecules while increasing in the carbon chain length of 2-alkanol, reinforces the interactions. Also, the perturbed-chain SAFT (PC-SAFT) equation of state was implemented to study the density and partial molar volume of binary mixtures. Combination of this model with Free Volume Theory was applied for prediction of binary viscosities. Maximum deviation in AAD for density correlation regarding PC-SAFT model was 1.21%, and for viscosity calculation was 2.19%.

1. Introduction

Diisopropyl ether (DIPE) is a colorless liquid and soluble in organic solvents. It is used as an extracting solvent to remove polar organic compounds from aqueous solutions such as phenols and acetic acid. Oil-based materials are dissolved in it, so it is the base of many dyes and resins. Oxygenated compounds like ethers and alcohols are becoming ever more crucial in fuel industries. The addition of fuel oxygenates to gasoline increases combustion temperature and promotes engine efficiencies, So that lower levels of carbon monoxide and unburned hydrocarbons are released in the air. Presently Ethyl tert-butyl ether governs the market. Nevertheless, due to the problems such as insufficient supply, tendencies have increased toward the heavier ethers such as DIPE. Therefore, from the industrial point of view, mixtures containing ethers and alkanols are of great significance since they are involved in the gasoline production process, improving the combustion and reducing emissions [1,2]. Accordingly, the study of molecular interactions and structural arrangements such as hydrogen bonds, non-specific or dispersive forces in these binary mixtures has great importance. For this reason, in the present study, as a continuation of our previous work focusing on interactions between alcohols and different functional groups [3–10], binary mixtures containing DIPE with 2-alkanol were selected. A survey in scientific literature demonstrates that previously, values of densities for binary mixtures of DIPE with 2-propanol and 2-butanol were published [2,11–16]. But no reports are available for binary viscosities or some binary densities. Also, the capability of PC-SAFT theory to correlate densities and partial molar volume of binary mixtures was investigated. Then, combination of this model with free volume theory (FVT) was used to correlate and predict binary viscosities.

2. Experimental section

All materials, except 2-hexanol, were purchased from Merck with purities higher than 99% and used as purchased. 2-Hexanol was obtained from Sigma-Aldrich Company and used without further purifications. Pure component specifications are presented in SI, Table S1, and comparison of experimental densities and viscosities with literature are shown in [14–33] Table 1. Maximum of deviation between our densities and literature values was 0.2% and for viscosity data was 5%. An automatic viscometer, namely SVM 3000, was used for measuring the density and viscosity. A thermoelectric thermostat controls the dependency of density and viscosity to temperature. Before measuring, the distilled water and dry air were used to calibrate the apparatus. Stabinger viscometer measures viscosity with the highest accuracy over the wide range of temperature and pressure while corrects the viscos-

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* Corresponding author.
E-mail address: m.almasi@malayeru.ac.ir (M. Almasi).

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Table 1
Densities, ρ and viscosities, η for pure components at various temperatures and pressure 0.1 MPa[a.]

Compound	T (K)	ρ (g.cm^{-3})		η (mPa·s)	
		expt.	Lit.	expt.	Lit.
DIPE	293.15	0.7233	0.71789 [14], 0.7235 [16], 0.723509 [17]	0.332	0.3340 [17]
	298.15	0.7183	0.7183 [16], 0.718289 [17]	0.319	0.3178 [17]
	303.15	0.7130	0.713032 [17]	0.304	0.3001 [17]
	308.15	0.7076	0.707727 [17]	0.290	0.2857 [17]
	313.15	0.7025	0.7024 [16], 0.702378 [17]	0.274	0.2723 [17]
	318.15	0.6968		0.261	
	323.15	0.6919		0.246	
2-propanol	293.15	0.7854 [18–24]	0.78535 [25], 0.78525 [30]	2.42 [18–24]	2.414 [25], 2.3621[30]
	298.15	0.7811[18–24]	0.77950 [14], 0.78110 [25]	2.08 [18–24]	2.070 [25]
	303.15	0.7768 [18–24]	0.77712 [25], 0.77678 [30]	1.80 [18–24]	1.785 [25], 1.7694 [30]
	308.15	0.7724 [18–24]	0.77232 [25]	1.56 [18–24]	1.546 [25]
	313.15	0.7680 [18–24]	0.76879 [25], 0.76897 [30]	1.36 [18–24]	1.347 [25], 1.3297 [30]
	318.15	0.7634 [18–24]	0.76397 [25]	1.19 [18–24]	1.76 [25]
	323.15	0.7588 [18–24]	0.75882 [25]	1.05 [18–24]	1.033 [25]
2-butanol	293.15	0.8067 [18–24]	0.8067 [16],	3.67 [18–24]	
	298.15	0.8027 [18–24]	0.8026 [16], 0.802682 [26]	3.04 [18–24]	3.074 [26]
	303.15	0.7984 [18–24]	0.798374 [26], 0.7993 [31]	2.54 [18–24]	2.552 [26], 2.527 [31]
	308.15	0.7941 [18–24]	0.793881 [26]	2.13 [18–24]	2.144 [26]
	313.15	0.7898 [18–24]	0.7896 [16], 0.789487 [26]	1.80 [18–24]	1.818 [26], 1.801 [31]
	318.15	0.7852 [18–24]	0.784988 [26]	1.54 [18–24]	1.558 [26]
	323.15	0.7806 [18–24]		1.33 [18–24]	
2-pentanol	293.15	0.8093 [18–24]	0.80938 [32]	3.97 [18–24]	4.174 [32]
	298.15	0.8053 [18–24]	0.8055 [27], 0.80535 [32]	3.32 [33,10]	3.45 [27], 3.398 [32]
	303.15	0.8012 [18–24]	0.8010 [27], 0.80124 [32]	2.81 [33,10]	2.77 [27], 2.820 [32]
	308.15	0.7970 [18–24]	0.7969 [27], 0.79705 [32]	2.37 [33,10]	2.32 [27], 2.336 [32]
	313.15	0.7927 [18–24]	0.7926 [27], 0.79278 [32]	1.99 [33,10]	1.92 [27], 1.990 [32]
	318.15	0.7884 [18–24]		1.66 [33,10]	
	323.15	0.7840 [18–24]		1.39 [33,10]	
Compound	T (K)	ρ (g.cm^{-3})		η (mPa·s)	
2-hexanol		expt.	lit.	expt.	lit.
	293.15	0.8142	0.8142 [28]	5.15	
	298.15	0.8101	0.8102 [28]	4.10	
	303.15	0.8061	0.8062 [28]	3.29	3.23 [29]
	308.15	0.8021	0.80221 [28]	2.71	
	313.15	0.7984	0.7980 [28]	2.28	2.29 [29]
	318.15	0.7945		1.93	
	323.15	0.7901	0.7901 [29]	1.64	1.64 [29]

[a] Standard uncertainties are $u(T)$ = 0.02 K, $u(x)$ = 0.001, $u(p)$ = 10 kPa, expanded uncertainty for density is $U(\rho)$ = 0.001 g·cm^{-3} and relative expanded uncertainty for viscosity is $U_r(\eta)$ = 5%.

ity errors on density. To measure the density and viscosity, mixtures are provided precisely before use on an analytical balance (Mettler AE 163) with the precision 0.01 mg. The expanded uncertainty for density is 1×10^{-3} g·cm^{-3}, and the relative expanded uncertainty for viscosity is 5%. The uncertainty in the mole fraction is 1×10^{-3}. Effect of impurity was considered in the mole fraction uncertainty.

3. Results and discussion

3.1. Density and excess molar volume

Experimental densities and viscosities for studied systems are reported in Table 2. Excess molar volume, V_m^E was calculated by

$$V_m^E = V - \sum_i x_i V_i \tag{1}$$

where V is volume of the mixture, V_i and x_i are the volume and mole fraction of component i respectively. V_m^Edata were correlated as a function of mole fraction employing Redlich–Kister polynomial [34]

$$V_m^E = x_1(1 - x_1)\sum_{k=0}^{N} A_k(1 - 2x_1)^k \tag{2}$$

A_k represents adjustable coefficients, and x_1 is the DIPE mole fraction. Excess molar volumes are shown in Table 3, and A_k were reported in SI, Table S2. Standard deviation was calculated as follows

$$\sigma = \sqrt{\frac{1}{n-p}\sum_{i=1}^{N}\left(V_{\exp}^E - V_{cal}^E\right)^2} \tag{3}$$

The subscripts exp and *cal* indicate experimental and calculated values. Standard deviations are reported in SI, Table S2. Fig. 1 states $V_m^E$for all binary mixtures at T = 298.15 K along with solid lines calculated by Redlich–Kister polynomial. Values of $V_m^E$are negative over the entire concentration range and demonstrate that strong interactions occur in mixtures. Looking to the structure of DIPE, figured out that, this molecule has a small dipole due to the difference of electronegativity between carbon and oxygen. The dipole moment of carbon and oxygen do not cancel out each other, so the molecule has a net dipole moment and is therefore weakly polar. Dispersion forces as London type, result from short dipoles induced by fluctuations in the electron shell of molecules, are also present in the mixtures and are responsible for the weak interactions between the alkyl chain of 2-alkanol and the weakly polar ether molecules. Furthermore, hydrogen bonding between OH groups of 2-alkanol and oxygen of ether is possible. Because the ether oxygen can act as hydrogen bond acceptor facing with the hydrogen bond donors like OH of alcohols. This behavior also explains that DIPE is soluble in alkanol despite its low polarity. The values of $V_m^E$for DIPE + 2-alkanol mixtures are becoming more