

Correlations and Predictions of THF + 2-Alkanol Binary Mixtures Behaviour by PC-SAFT Model and Friction Theory

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In this article the behavior of tetrahydrofuran (THF) + 2-alkanol namely 2-propanol, 2-butanol, 2-pentanol, 2-hexanol and 2-heptanol binary mixtures through the density and viscosity measurements has been studied as a function of composition and within the temperature range of 293.15-313.15 K. The excess molar volume, isobaric thermal expansivity, partial molar volumes, and viscosity deviations have been calculated. For all binary mixtures, values of excess molar volume are positive and viscosity deviations are negative while increasing with the alkyl chain of the alcohol. The results provide information on the interactions among the molecules in the pure state as well as the binary liquid mixtures. The measured densities and viscosities have been applied to test the applicability of the PC-SAFT model and friction theory coupled with the Peng-Robinson-Stryjek-Vera equation of state.

Keywords: Density, Viscosity, PC-SAFT model, Friction Theory

INTRODUCTION

Thermophysical properties such as density and viscosity of pure liquids and their mixtures are important for chemical engineers in the design and optimization of industrial processes. The simultaneous investigations on the density and viscosity of mixtures may give an insight to the intermolecular interactions occurring in the liquid systems. Moreover, to estimate the mixture properties, such investigations are an introductory process for development of the equations [1]. THF has numerous applications in organic chemistry for the synthesis of new compounds and also a super solvent in many pharmaceutical procedures [2]. A literature survey of the thermodynamic properties of these binary mixtures shows that some investigated systems have been studied earlier [2-4], however, no data have been reported for densities and viscosities of THF with 2-pentanol, 2-hexanol and 2-heptanol. As a continuation of our research program on the alcohol containing mixtures behaviour [5-7], here, densities and viscosities for binary

mixtures of THF + 2-alkanols at $T = (298.15, 303.15, 308.15, 313.15)$ K are reported. Moreover, this work not only contributes to examine the compatibility of PC-SAFT model but also to correlate the viscosity of described systems by the friction theory.

EXPERIMENTAL

Chemicals (THF, 2-Propanol, 2-Butanol, 2-Pentanol, 2-Heptanol) were analytical grade, and purchased from Merck with stated level of purity greater than 99% of mass fraction and used as received without further purification. 2-Hexanol was supplied by Aldrich with mass purity >99%. The measured densities and viscosities for pure materials at $T = 298.15$ K are compared with their corresponding data in the literature, as shown in Table 1 [3,8-10]. The results show the measurements are in agreement with literature values and within the experimental uncertainties.

Density and viscosity measurements have been performed with an Anton-Paar SVM 3000 viscometer. The temperature of the measuring cell is controlled by a built-in thermo-electric heating and cooling thermostat. Prior to

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Table 1. Densities, ρ , and Viscosities, η , of Pure Components at $T = 298.15$ K and $P = 0.1$ MPa

Chemical Name	ρ (g cm ⁻³)		η (mPa s)	
	Exptl.	Lit.	Exptl.	Lit.
THF	0.8820	0.88237 ^a	0.51	0.530 ^b
		0.88209 ^a		0.470 ^a
2-Popanol	0.7809	0.78121 ^c	2.08	2.05 ^c
		0.7811 ^c		2.047 ^d
2-Butanol	0.8031	0.80291 ^c	3.03	2.99 ^c
		0.8031 ^c		3.117 ^d
2-Pentanol	0.8051	0.80514 ^c	3.42	3.41 ^c
		0.80542 ^c		3.47 ^d
2-Hexanol	0.8101	0.81032 ^c	4.10	4.14 ^c
		0.81019 ^c		3.98 ^d
2-Heptanol	0.8134	0.81333 ^c	5.3	5.228 ^c
		0.81327 ^c		4.99 ^d

Reference [3]. ^bReference [9]. ^cReference [10]. ^dReference [11].

each series of measurements, the apparatus was calibrated using doubly distilled degassed water and dry air at the atmospheric pressure. Pure fluids used in the binary mixtures were degasified before the preparation of the samples using an ultrasonic bath. The solutions were prepared by mass, using a digital balance (Mettler AE 163, Switzerland) with the precision ± 0.01 mg and stored in airtight stopped bottles to prevent evaporation of the samples. To minimize evaporation during the sample preparation, the less volatile component was charged first. The expanded uncertainty is 1×10^{-3} g cm⁻³ for density measurements and relative expanded uncertainty of viscosity measurements is 0.08.

RESULTS AND DISCUSSION

Densities and Derived Properties

The experimental values of densities for binary mixtures

at various temperatures are listed in Table 2. Binary densities and viscosities decrease as a function of temperature and increase with increasing alcohols chain length. The volumetric properties are closely related with volume change of substance, such as density, partial molar volume, excess molar volume and expansibility. The excess molar volume can be calculated according to the following equation:

$$V_m^E = V_m - \sum_{i=1}^2 x_i V_{m,i} \quad (1)$$

where $V_{m,i}$ is the molar volume of component i and V is the volume of mixture. The values of V_m^E can be fitted by Redlich-Kister [11] type polynomial equation

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

Table 2. Densities, ρ , and Viscosities, η , for the Binary Mixtures as a Function of the Mole Fraction x_1 of THF at Pressure $p = 0.1 \text{ MPa}^a$

THF (1) + 2-Propanol (2)								
x_1	T/K = 298.15		T/K = 303.15		T/K = 308.15		T/K = 313.15	
	ρ (g cm^{-3})	η (mPa s)	ρ (g cm^{-3})	η (mPa s)	ρ (g cm^{-3})	η (mPa s)	ρ (g cm^{-3})	η (mPa s)
0	0.7809	2.08	0.7768	1.79	0.7724	1.56	0.7678	1.35
0.0808	0.7891	1.63	0.7847	1.44	0.7801	1.27	0.7753	1.12
0.1599	0.7970	1.27	0.7924	1.19	0.7878	1.07	0.7829	0.94
0.2404	0.8050	1.03	0.8004	1.02	0.7956	0.94	0.7906	0.82
0.3509	0.8161	0.87	0.8113	0.88	0.8062	0.83	0.8012	0.72
0.4400	0.8250	0.78	0.8201	0.79	0.8149	0.76	0.8098	0.66
0.5582	0.8369	0.70	0.8318	0.70	0.8266	0.67	0.8213	0.59
0.6497	0.8461	0.65	0.8410	0.63	0.8356	0.61	0.8302	0.53
0.7390	0.8552	0.60	0.8499	0.56	0.8444	0.56	0.8391	0.49
0.8492	0.8665	0.56	0.8611	0.50	0.8554	0.51	0.8500	0.44
0.9348	0.8753	0.53	0.8697	0.46	0.8641	0.47	0.8586	0.41
1	0.8820	0.51	0.8764	0.44	0.8707	0.43	0.8652	0.39
THF (1) + 2-Butanol (2)								
x_1	T/K = 298.15		T/K = 303.15		T/K = 308.15		T/K = 313.15	
	ρ (g cm^{-3})	η (mPa s)	ρ (g cm^{-3})	η (mPa s)	ρ (g cm^{-3})	η (mPa s)	ρ (g cm^{-3})	η (mPa s)
0	0.8031	3.03	0.7989	2.53	0.7946	2.12	0.7901	1.80
0.0831	0.8082	2.30	0.8038	1.88	0.7993	1.65	0.7949	1.30
0.1604	0.8132	1.79	0.8086	1.47	0.8040	1.30	0.7996	0.95
0.2417	0.8186	1.41	0.8140	1.22	0.8093	1.05	0.8047	0.74
0.3503	0.8262	1.15	0.8214	1.02	0.8166	0.88	0.8119	0.60
0.4440	0.8331	1.00	0.8282	0.90	0.8234	0.78	0.8185	0.53
0.5599	0.8421	0.85	0.8371	0.77	0.8321	0.69	0.8270	0.48
0.6491	0.8495	0.76	0.8443	0.69	0.8391	0.64	0.8340	0.45
0.7400	0.8573	0.68	0.8521	0.63	0.8468	0.58	0.8415	0.43
0.8485	0.8671	0.59	0.8617	0.54	0.8563	0.52	0.8509	0.42
0.9397	0.8758	0.54	0.8703	0.48	0.8648	0.47	0.8593	0.40
1	0.8820	0.51	0.8764	0.44	0.8707	0.43	0.8652	0.39

Table 2. Continued

THF (1) + 2-Pentanol (2)								
x_1	T/K = 298.15		T/K = 303.15		T/K = 308.15		T/K = 313.15	
	ρ (g cm ⁻³)	η (mPa s)	ρ (g cm ⁻³)	η (mPa s)	ρ (g cm ⁻³)	η (mPa s)	ρ (g cm ⁻³)	η (mPa s)
0	0.8051	3.42	0.8009	2.83	0.7969	2.35	0.7926	1.98
0.0810	0.8090	2.33	0.8047	1.87	0.8006	1.72	0.7963	1.45
0.1591	0.8130	1.68	0.8086	1.32	0.8044	1.24	0.8000	1.09
0.2402	0.8175	1.29	0.8130	1.01	0.8087	0.93	0.8041	0.88
0.3538	0.8244	1.01	0.8197	0.77	0.8152	0.74	0.8105	0.72
0.4388	0.8300	0.88	0.8253	0.67	0.8206	0.66	0.8159	0.65
0.5633	0.8393	0.74	0.8343	0.58	0.8294	0.57	0.8245	0.56
0.6504	0.8464	0.66	0.8414	0.52	0.8363	0.53	0.8313	0.51
0.7405	0.8544	0.59	0.8493	0.48	0.8441	0.50	0.8389	0.47
0.8498	0.8652	0.53	0.8598	0.45	0.8544	0.47	0.8492	0.43
0.9392	0.8749	0.511	0.8694	0.45	0.8638	0.45	0.8584	0.40
1	0.8820	0.51	0.8764	0.44	0.8707	0.43	0.8652	0.39
THF (1) + 2-Hexanol (2)								
x_1	T/K = 298.15		T/K = 303.15		T/K = 308.15		T/K = 313.15	
	ρ (g cm ⁻³)	η (mPa s)	ρ (g cm ⁻³)	η (mPa s)	ρ (g cm ⁻³)	η (mPa s)	ρ (g cm ⁻³)	η (mPa s)
0	0.8101	4.10	0.8061	3.41	0.8021	2.82	0.7980	2.22
0.0814	0.8131	2.82	0.8090	2.30	0.8048	1.87	0.8006	1.55
0.1595	0.816	2.04	0.8119	1.66	0.8077	1.35	0.8034	1.08
0.2407	0.8198	1.56	0.8154	1.28	0.8110	1.05	0.8067	0.83
0.3543	0.8255	1.26	0.8210	1.01	0.8165	0.84	0.8119	0.65
0.4393	0.8305	1.10	0.8258	0.89	0.8212	0.75	0.8165	0.58
0.5638	0.8387	0.93	0.8339	0.75	0.8290	0.63	0.8243	0.51
0.6508	0.8454	0.84	0.8404	0.68	0.8354	0.56	0.8305	0.47
0.7409	0.8532	0.73	0.8481	0.60	0.8429	0.50	0.8379	0.45
0.8503	0.8642	0.62	0.8588	0.52	0.8534	0.46	0.8481	0.41
0.9396	0.8744	0.55	0.8688	0.47	0.8633	0.43	0.8577	0.39
1	0.8820	0.51	0.8764	0.44	0.8707	0.43	0.8652	0.39

Table 2. Continued

THF (1) + 2-Heptanol (2)								
x_1	T/K = 298.15		T/K = 303.15		T/K = 308.15		T/K = 313.15	
	ρ (g cm ⁻³)	η (mPa s)	ρ (g cm ⁻³)	η (mPa s)	ρ (g cm ⁻³)	η (mPa s)	ρ (g cm ⁻³)	η (mPa s)
0	0.8134	5.30	0.8095	4.31	0.8057	3.53	0.8015	2.96
0.0760	0.8155	3.93	0.8115	3.13	0.8076	2.49	0.8033	2.08
0.1587	0.8182	2.88	0.8141	2.24	0.8100	1.76	0.8057	1.46
0.2398	0.8211	2.21	0.8169	1.77	0.8128	1.37	0.8083	1.13
0.3533	0.8260	1.74	0.8217	1.42	0.8173	1.09	0.8127	0.90
0.4383	0.8303	1.50	0.8259	1.25	0.8214	0.96	0.8167	0.79
0.5629	0.8379	1.20	0.8332	1.04	0.8286	0.80	0.8237	0.66
0.6499	0.8442	1.05	0.8394	0.90	0.8346	0.71	0.8297	0.59
0.7401	0.8519	0.88	0.8469	0.76	0.8419	0.63	0.8368	0.51
0.8493	0.8628	0.70	0.8577	0.60	0.8523	0.53	0.8471	0.43
0.9388	0.8734	0.58	0.8682	0.51	0.8625	0.47	0.8573	0.40
1	0.8820	0.51	0.8764	0.44	0.8707	0.43	0.8652	0.39

^a x_1 is the mole fraction of THF in the (THF + 2-alkanol) solutions. Standard uncertainties u are $u(T) = 0.02$, K, $u(x) = 0.0001$, $u(p) = 10$ kPa, the combined expanded uncertainty $U_c(\rho) = 1 \cdot 10^{-4}$ g cm⁻³ (0.95 level of confidence), and for viscosity the relative combined expanded uncertainty $U_r(\eta) = 0.04$ (0.95 level of confidence).

where x is the mole fraction of one component of mixture, A_k is the adjustable parameter, and k is the order of polynomial equation. V_m^E values for binary mixtures are reported in SI (supplementary Information) file along with the A_k and standard deviation values σ . The experimental values of excess molar volume for the binary system THF + 2-alkanol along with those obtained from the Redlich–Kister polynomial equation are shown in Fig. 1.

For all studied mixtures, excess molar volumes, V_m^E are positive and increase with increase of alkanols chain length. In the mixing of THF with 2-alkanols, chemical interaction such as the hydrogen bond between the hydroxyl group of the alcohol and the hydrogen acceptor oxygen of tetrahydrofuran forms, but donor capacity of hydroxyl group of the alcohol decreases when the alkyl chain length rises, so the specific interaction of OH-O becomes weaker.

Moreover, in the sterically hindered alcohols (alcohols with higher chain length), self-association relatively breaks easier. These effects lead to the positive V_m^E and rise of excess molar volumes by increasing the alcohol size. Comparisons between our data and reported values of other papers [2-4] are presented in SI (Supplementary Information) file. Also, values of excess molar volumes for binary mixtures of THF + 2-pentanol at various temperatures are shown in Fig. 2. As indicated in this picture, V_m^E increases with rise of temperature.

The next step of this study is the examination of derivations of the isobaric thermal expansivity, α_p , excess thermal expansion, α^E and the partial molar volumes, $\bar{V}_{m,i}$ according to well-known thermodynamic relations [12,13]. Values of α_p and intervals among them increase with increasing temperature and differences between α_p values at

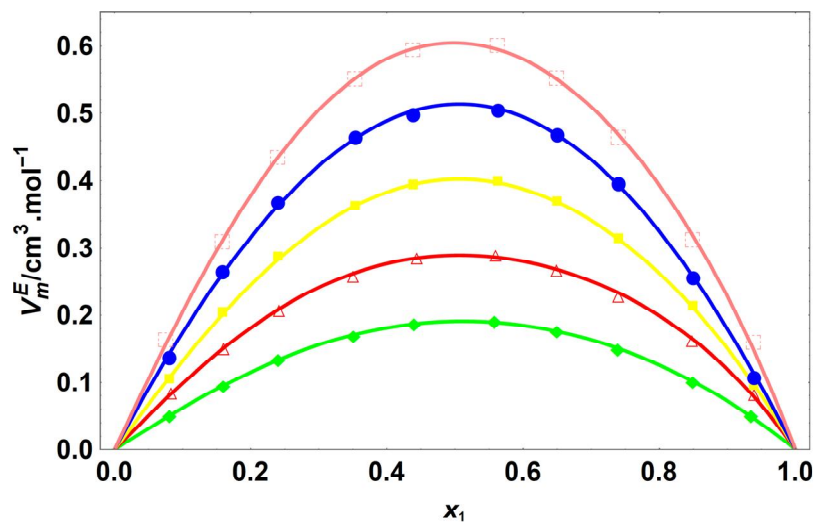


Fig. 1. Excess molar volumes V_m^E vs. mole fraction of THF for binary mixtures of THF with (♦) 2-PrOH, (Δ) 2-BuOH, (■) 2-PenOH, (●) 2-HexOH, (□) 2-HepOH at $T = 298.15$ K. The solid curves were calculated from Redlich-Kister type equation.

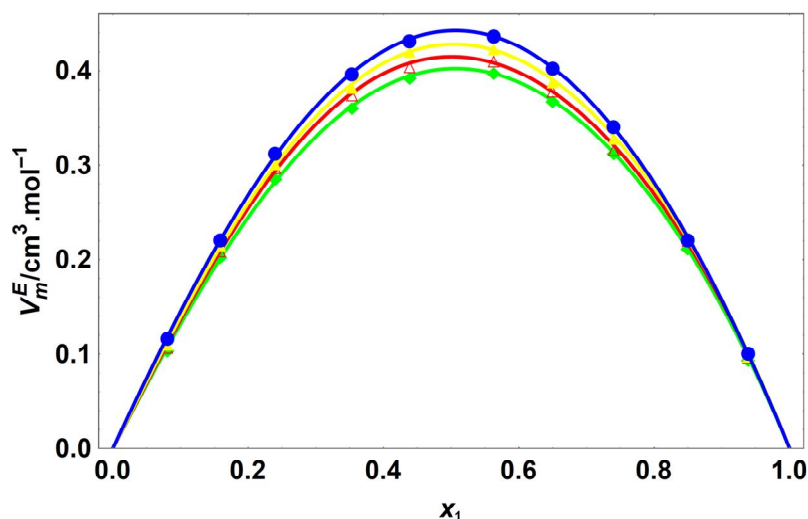


Fig. 2. Excess molar volumes V_m^E vs. mole fraction of THF for binary mixtures of THF with 2-PenOH at (♦) $T = 298.15$ K, (Δ) $T = 303.15$ K, (▲) $T = 308.15$ K, (●) $T = 313.15$ K. The solid curves were calculated from Redlich-Kister type equation.

various temperatures, and these values decrease with rise of the THF concentration in the mixture. Observed behaviour may be explained in terms of packing effects. Packing effects occur due to the accommodation of THF molecules

in the hydrogen-bonded structure of the alcohol. This phenomenon only can appear at high mole fraction of THF, since there must be enough THF to accommodate in the cavities (hydrogen-bonded structure) of alcohols. So, the

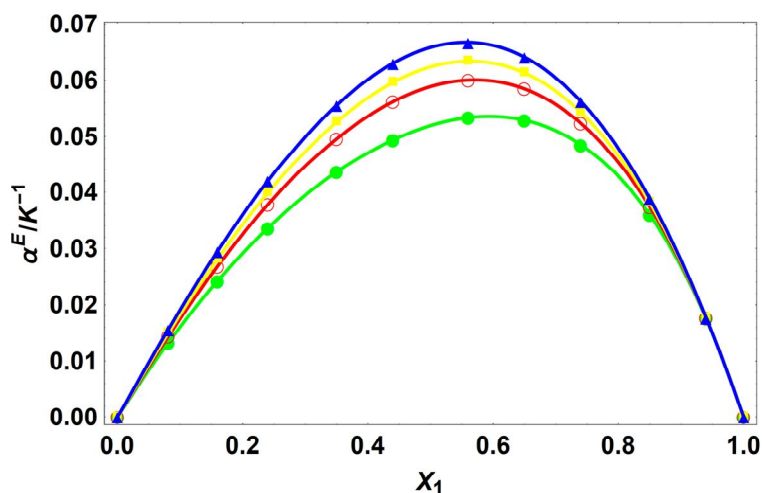


Fig. 3. Excess thermal expansion α^E vs. mole fraction of THF for binary mixtures of THF with 2-PenOH at (●) $T = 298.15$ K, (○) $T = 303.15$ K, (■) $T = 308.15$ K, (▲) $T = 313.15$ K. The solid curves were calculated from Redlich-Kister type equation.

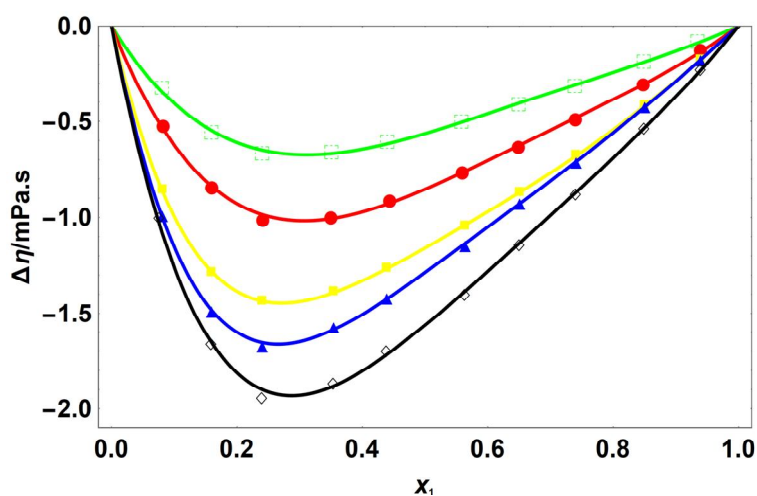


Fig. 4. Viscosity deviations $\Delta\eta$ vs. mole fraction of THF, for binary mixtures of THF with (□) 2-PrOH, (●) 2-BuOH, (■) 2-PenOH, (▲) 2-HexOH, (◇) 2-HepOH at $T = 298.15$ K. The solid curves were calculated from Redlich-Kister type equation.

packing effects occur at high concentration of THF. Partial molar volumes, $\bar{V}_{m,i}$, increase with increase of temperature. As the temperature of the solution is increased, contribution from the THF-alcohol binding is weakened and the partial molar volume of the THF molecules increases significantly. The positive values of α^E suggest that the expansivity of the

solution is greater than that for the pure liquid and means a smaller expansion of the pure liquid with increasing in the average intermolecular distance compared to the mixtures. Therefore, the solution structure breaks easier than the pure state due to the fact that there are weaker interactions in the mixture in comparison to pure state. This behaviour for

THF + 2-pentanol is presented in Fig. 3.

Dynamic Viscosities

Dynamic viscosities at various temperatures are reported in Table 2. In order to study the solvent-solute interactions, the deviation in viscosity ($\Delta\eta$) was calculated by the following relation

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \quad (3)$$

where η and η_i are the viscosity of mixture and pure components i , respectively. As for binary mixtures, the values of $\Delta\eta$ were fitted by Redlich-Kister-type polynomial equation and values of A_k and σ are reported in SI. Deviation in viscosity is negative for all studied mixtures and its absolute values for the binary mixtures fall in the following order: 2-heptanol > 2-hexanol > 2-pentanol > 2-butanol > 2-propanol. This behaviour indicates that specific interactions between THF + 2-alkanol decrease when the alcohol carbon chain length increases. Deviation in viscosity for binary mixtures at $T = 298.15$ K are shown in Fig. 4.

PC-SAFT Model

General definition for the residual Helmholtz energy in PC-SAFT [14,15] is explained by

$$a^{res} = a^{hc} + a^{disp} + a^{assoc} \quad (4)$$

The hard-sphere chain contribution is calculated as

$$a^{hc} = \bar{m}a^{hs} + \sum_i x_i(m_i - 1) \ln g_{ij}^{hs} \quad (5)$$

where \bar{m} is the mean segment number and g_{ij}^{hs} is the radial pair distribution function

$$g_{ij}^{hs} = \frac{1}{1-\zeta_3} + d_{ij} \frac{3\zeta_2}{(1-\zeta_3)^2} + d_{ij}^2 \frac{3\zeta_2^2}{(1-\zeta_3)^3} \quad (6)$$

Hardsphere contribution, a^{hs} is computed as

$$a^{hs} = \frac{1}{\zeta_0} \left[\frac{3\zeta_1\zeta_2}{1-\zeta_3} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln(1-\zeta_3) \right] \quad (7)$$

ζ_n and d_i are defined as

$$\zeta_n = \frac{\pi}{6} \rho \sum_{i=1}^n x_i m_i d_i^n \quad (8)$$

$$d_i = \sigma_i \left[1 - 0.12 \exp\left(-\frac{3\varepsilon_i}{kT}\right) \right] \quad (9)$$

a^{dis} is calculated by

$$a^{dis} = -\pi\rho_{num} \left[2I_1 \sum_i \sum_j x_i x_j m_i m_j \sigma_{ij}^3 \frac{\varepsilon_{ij}}{k_B T} + mI_2 C \sum_i \sum_j x_i x_j m_i m_j \sigma_{ij}^3 \left(\frac{\varepsilon_{ij}}{k_B T} \right)^2 \right] \quad (10)$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (11)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} (1 - k_{ij}) \quad (12)$$

The ρ_{num} is the total number density of molecules. The terms I_1 and I_2 integrals can be approximated as power series in density and the coefficient C is given by

$$C = \left[1 + m \frac{8\eta - 2\eta^2}{(1-\eta)^4} + (1-m) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1-\eta)(2-\eta)]^2} \right]^{-1} \quad (13)$$

where

$$\eta = \frac{\pi}{6} \rho_{num} \sum x_i m_i d_i^3 \quad (14)$$

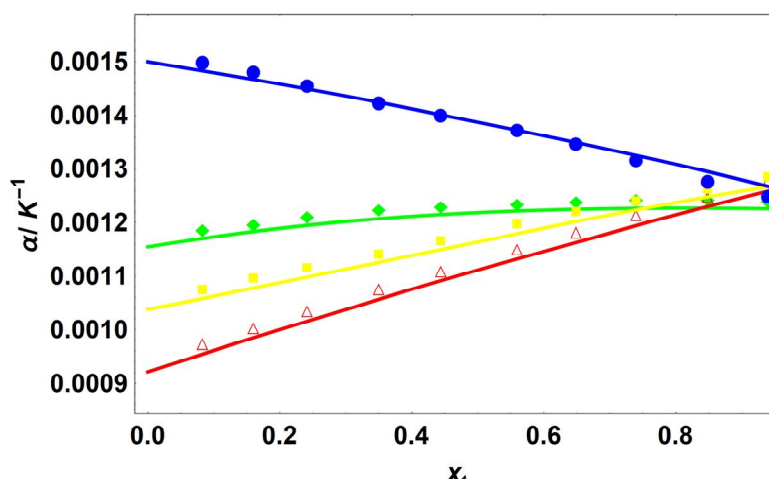
The association contribution is explained as:

$$a^{assoc} = \sum_{i=1} x_i \left[\sum_{A_i} \left(\ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{1}{2} M_i \right] \quad (15)$$

where M_i is the number of association sites on each molecule, and X^{A_i} is the mole fraction of molecules not bonded at site A in mixture:

Table 3. Binary Interaction Parameters k_{ij} for PC-SAFT Equation

Binary systems	k_{ij}
THF + 2-Propanol	0.065
THF + 2-Butanol	0.059
THF + 2-Pentanol	0.043
THF + 2-Hexanol	0.026
THF + 2-Heptanol	0.010

**Fig. 5.** Experimental and calculated isobaric thermal expansivity (α_p) of THF and 2-BuOH temperatures (Δ) 298.15 K, (\blacksquare) 303.15 K, (\blacklozenge) 308.15 K, (\bullet) 313.15 K. (—) PC-SAFT model.

$$X^A = \left[1 + \sum_j \sum_{B_j} \rho_j X^{B_j} \Delta^{A,B_j} \right]^{-1} \quad (16)$$

$$\kappa^{A,B_j} = \sqrt{\kappa^{A,B_i} \kappa^{A,B_j}} \left(\frac{\sqrt{\sigma_{ii} \sigma_{jj}}}{0.5(\sigma_{ii} + \sigma_{jj})} \right)^3 \quad (19)$$

Association strength Δ^{A,B_j} is approximated as:

$$\Delta^{A,B_j} = g_{ij}^{hs} \left[\exp(\varepsilon^{A,B_j} / kT) - 1 \right] (\sigma_{ij} \kappa^{A,B_j}) \quad (17)$$

The association energy ε^{A,B_j} and the association volume κ^{A,B_j} are calculated by [16]

$$\varepsilon^{A,B_j} = \frac{1}{2} (\varepsilon^{A,B_i} + \varepsilon^{A,B_i}) \quad (18)$$

In this paper, the PC-SAFT equation of state was used to correlate the volumetric properties of the binary mixtures. In the case of alcohols, five molecular parameters and for THF, three molecular parameters were fitted to experimental vapour pressures and densities. Obtained parameters for pure compounds are listed in the SI file. To reach a more accurate representation, the density values were used in a Levenberg-Marquardt algorithm regression for minimizing the objective function

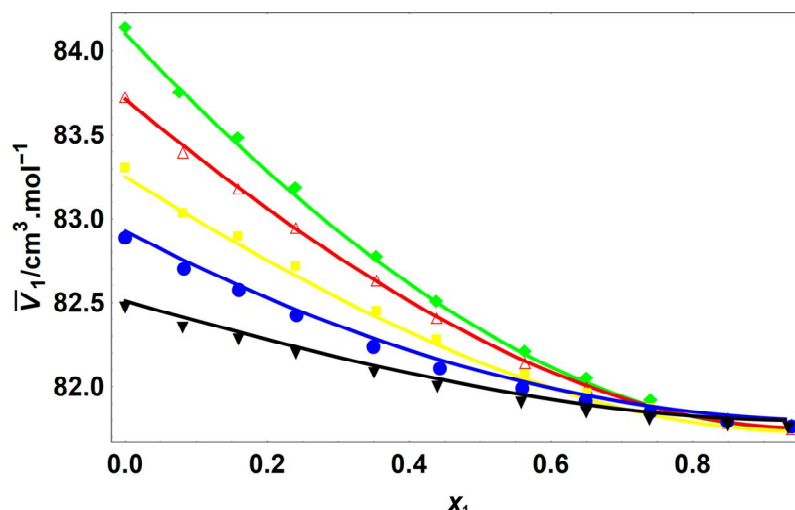


Fig. 6. Experimental and calculated partial molar volumes ($\bar{V}_{m,1}$) of THF with (\blacktriangle) 2-PrOH, (\bullet) 2-BuOH, (\blacksquare) 2-PenOH, (\triangle) 2-HexOH, (\blacklozenge) 2-HepOH at $T = 298.15$ K. (—) PC-SAFT.

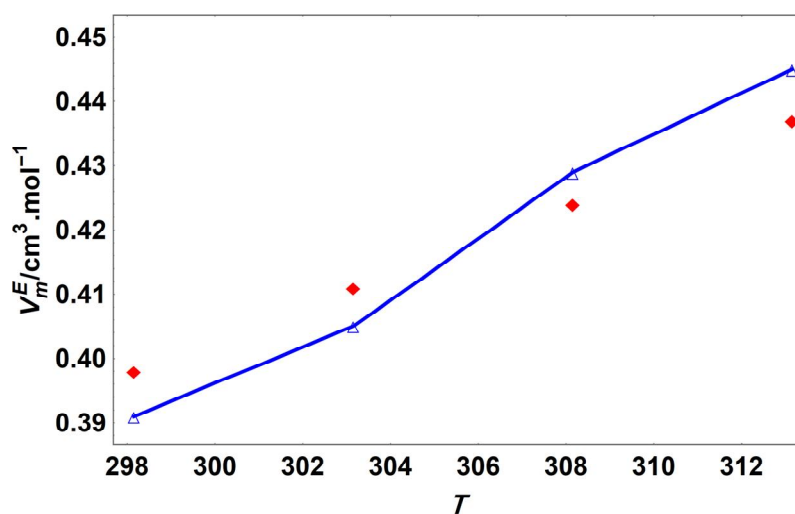


Fig. 7. Excess molar volumes for THF + 1-PenOH binary mixtures at mole fraction $x_1 = 0.5600$. (\blacksquare) experimental data, (\triangle) PC-SAFT model.

$$F = \sum_{i=1}^{N^{\text{exp}}} \left(\frac{\Omega_i^{\text{exp}} - \Omega_i^{\text{calc}}}{\Omega_i^{\text{exp}}} \right)^2 \quad (20)$$

where Ω is the density and N^{exp} is the total number of experimental points. The only binary interaction parameter in the PC-SAFT model, k_{ij} , was fitted to the experimental data and reported in Table 3. Also Figs. 5 and 6 indicate that

the PC-SAFT equations is a powerful expression to correlate the thermal expansivity and partial molar volumes of mixtures with only one binary interaction parameter covering the whole temperature ranges. Also PC-SAFT was used to correlate the excess molar volumes, however, outcomes indicate that obtained values are not satisfactory enough as indicated in Fig. 7. In short, although this model

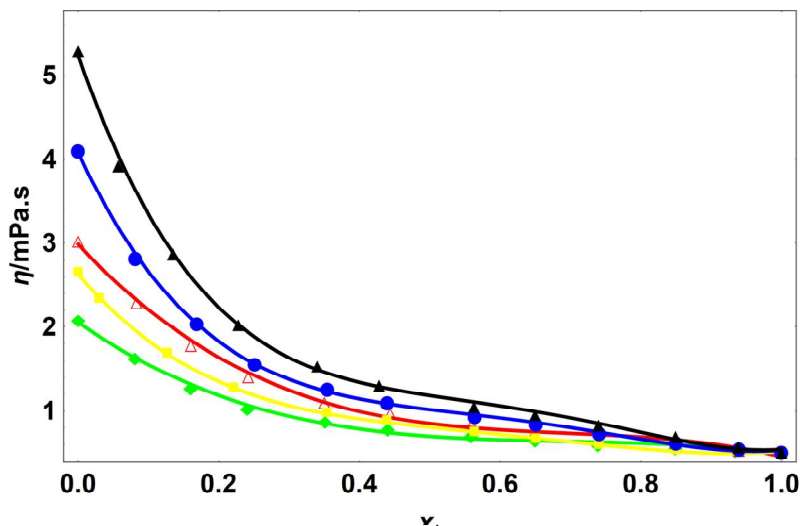


Fig. 8. Experimental and calculated viscosities of THF with (♦) 2-PrOH, (■) 2-BuOH, (Δ) 2-PenOH, (●) 2-HexOH, (▲) 2-HepOH at $T = 298.15$ K. (—) friction theory

appears to be adequate for calculation of thermal expansion coefficient and partial molar volume of binary mixtures, but to reach a better description of the excess molar volumes more complex mixing rules are required.

Friction Theory (f-Theory)

In order to evaluate the viscosities of pure materials and binary mixtures, the friction theory [17] coupled with the Peng-Robinson-Stryjek-Vera [18] equation of state was applied. In the friction theory viscosity η is separated in two contributions

$$\eta = \eta_0 + \eta_f \quad (21)$$

where η_0 is the dilute gas viscosity term and η_f arises from the friction between layers. The η_f can be expressed as follows

$$\eta_f = \kappa_r p_r + \kappa_a p_a + \kappa_{rr} p_r^2 \quad (22)$$

where κ_a , κ_r , and κ_{rr} are the temperature dependent friction coefficients, p_a and p_r are the van der Waals attractive and repulsive pressure terms of the fluid. PRSV EOS was

applied in this work to calculate the pressure terms. The dilute gas viscosity is given by [19]:

$$\eta_0 = 40.785 \frac{\sqrt{M_w T}}{v_c^{2/3} \Omega^*} F_c \quad (23)$$

Ω^* is the reduced collision integral, and F_c is an empirical factor defined as

$$F_c = 1 - 0.275 \omega + 0.059035 \mu_r^4 + \chi \quad (24)$$

where ω is the acentric factor, χ is a correction factor and μ_r is the dimensionless dipole moment. For THF, the dilute gas viscosity was calculated by a simple accurate equation [20]:

$$\eta_0 = d_0 + d_1 T_r^{0.25} + d_2 T_r^{0.5} + d_3 T_r^{0.75} \quad (25)$$

where T_r is the reduced temperature and d_i is the adjustable parameter. The extension to mixtures follows from the properties of the pure components. The dilute gas limit mixture contribution may be approximated using the following mixing rule

$$\eta_0 = \exp \left[\sum_{i=1}^n x_i \ln(\eta_{0,i}) \right] \quad (26)$$

where, x_i is the mole fraction of compound “ i ” in the mixture. The mixing rules for the friction coefficients are given by

$$\kappa_r = \sum_{i=1}^n z_i \kappa_{r,i} \quad (27)$$

$$\kappa_a = \sum_{i=1}^n z_i \kappa_{a,i} \quad (28)$$

$$\kappa_{rr} = \sum_{i=1}^n z_i \kappa_{rr,i} \quad (29)$$

For the friction coefficients mixing rules, z_i is a mass weighted fraction. In PRSV EOS the regular van der Waals mixing rules have been used with a binary interaction parameter $\kappa_{ij} = 0.074$ optimized against the viscosity data. Parameters for mixtures are calculated based on pure substances. The obtained AAD are within the experimental uncertainty. A comparison of the correlated viscosities using f -theory with the experimental data is shown in Fig. 8. Correlated values are satisfactory, taking into account that they are obtained in conjunction with a simple cubic EOS.

CONCLUSIONS

Densities and viscosities for binary mixtures of THF and 2-alkanols are presented in this paper. Excess molar volumes are positive and viscosity deviations are negative over the whole composition range. The ability of the PC-SAFT equations of state to reproduce the volumetric behavior of binary mixtures at various temperatures was tested. Also the friction theory, in combination with the Peng-Robinson-Stryjek-Vera equation, was evaluated to describe the viscosities of pure components and binary mixtures. This model has been shown to provide satisfactory results for correlating the viscosity data.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://>

List of Symbols

- MM = Weighted molecular weight average
- MW _{i} = Molecular weight of component i
- p_a = Attraction pressure
- p_r = Repulsion pressure
- z = Mass-weighted fraction of component
- η = Total viscosity
- η_0 = Dilute gas viscosity
- η_f = Friction viscosity
- η_r = Reduced viscosity
- κ_a = Linear attractive viscous friction coefficient
- κ_r = Linear repulsive viscous friction coefficient
- κ_{rr} = Quadratic repulsive viscous friction coefficient
- A = Helmholtz energy
- a_0 = segment molar Helmholtz energy (seg), per mole of segments
- d = temperature-dependent segment diameter
- k = Boltzman's constant
- m = effective number of segments within the molecule
- m^{00} = volume occupied by 1 mol of molecules in a closed packed arrangements
- m = number of association sites on molecule
- T = temperature, K
- u_0/k = temperature-independent dispersion energy of interaction between segments
- v^{00} = temperature-independent segment volume, ml mol⁻¹ of
- X^A = monomer mole fraction (mole fraction of molecules *not* bonded at site A)
- κ^{AB} = volume of interaction between sites A and B

Δ^{AB} = "strength of interaction" between sites A and B

ϵ^{AB} = association energy of interaction between sites A and B

σ = Lennard-Jones segment diameter

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