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High-pressure densities of *n*-decane+*o*-xylene mixtures:

Measurement and modelling

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ABSTRACT

In this work, the liquid densities of *n*-decane/*o*-xylene mixtures were measured at four different component proportions, the mole fractions of *n*-decane are 0.2001, 0.4065, 0.5835, and 0.8041, respectively. The measurements were performed based on the high-pressure vibrating-tube densimeter, and the measured temperatures were from 283.15 K to 363.15 K and the pressures were from 0.1 MPa to 60 MPa. The Tammann-Tait equation was used to correlate the experimental densities, and the simplified Perturbed Associating Fluid Theory (sPC-SAFT) and Cubic Plus Associating (CPA) equation were used to predict the high-pressure densities of the mixtures with the binary interaction parameters. Derived properties, including isothermal compressibilities and isobaric thermal expansivities, were calculated from Tait equation, sPC-SAFT equation, and CPA equation, respectively. In addition, excess molar volumes of the considered mixtures were obtained and the effects of pressure and temperature on the excess molar volume were discussed.

KEYWORDS: *n*-decane; *o*-xylene; volumetric properties; high-pressure density; EOS

1. Introduction

In petroleum industry, in order to assess the amount of petroleum of reservoir, high-pressure densities of the fluids is an essential parameter. To carry out the experimental investigations on

the $P\rho T_x$ property of crude oil or the corresponding components is an important and critical issue. In addition, the derived properties from the densities of fluids can provide some new information on the molecular interactions. Furthermore, the knowledge of accurate $P\rho T_x$ data of mixtures is also valuable for the further investigation of equation of state.

The composition of crude oil is very complex, however, the main components are different hydrocarbons, such as alkanes, aromatics, cycloalkanes. Due to the scarce high-pressure densities of alkanes/aromatics mixtures in the literature, our group carried out a systematically investigation on it. Xylene is one of the typical aromatics and has three constitutional isomers, called *o*-xylene, *m*-xylene, and *p*-xylene. In our previous work¹, the high-pressure densities of *n*-decane/*p*-xylene mixtures have been reported. For the *n*-decane/*o*-xylene mixtures, only Chevalier et al.² reported its $P\rho T_x$ data at 298.15 K under atmospheric pressure.

In this work, the experimental system based on the vibrating-tube method which was established in our laboratory was used to measure the densities of *n*-decane/*o*-xylene system over four different composition ranges (the mole fractions of *n*-decane are 0.2001, 0.4065, 0.5835, and 0.8041) at pressures up to 60 MPa. The results were correlated based the modified Tammann-Tait equation, and the volumetric properties were derived. In addition, two equations of state, cubic plus association (CPA³) and simplified perturbed-chain statistical associating fluid theory (sPC-SAFT^{4,5}), were used to model the $P\rho T_x$ properties of the mixtures.

2. Experimental section

The samples of *n*-decane and *o*-xylene were supplied by Aladdin Chemistry without further purification. The information of the samples is shown in Table 1.

Table 1. Sample descriptions.

Chemical name	CAS	Source	Mass fraction purity	Purification method
---------------	-----	--------	----------------------	---------------------

<i>n</i> -decane	124-18-5	Aladdin Chemistry	≥ 0.99	none
<i>o</i> -xylene	95-47-6	Aladdin Chemistry	≥ 0.99	none

The mixtures were prepared using Mettler analytical balance (model: AB204-N, accuracy: 10^{-4} g). The uncertainty of the mole fraction for the mixtures was less than 2.0×10^{-4} . The $P\rho T_x$ property was measured up to 60 MPa and at temperatures between 283.15 and 363.15 K using *U*-shape vibrating-tube densimeter (Anton Paar DMA-HPM). The densimeter operated in a static mode following the procedure described by our previous work^{1,6-8}. The combined expanded uncertainty of the present measurements was within 0.001ρ with 0.95 confidence level.

3. Experimental results and discussion

3.1 Densities and derived properties

The experimental densities of the studied mixtures were fitted with a modified Tammann-Tait equation^{9,10} using the MATLAB software. The expressions of the Tait equation are:

$$\rho(T, P) = \frac{\rho_0(T)}{1 - C \ln((B(T) + p) / (B(T) + P_0))} \quad (1)$$

$$\rho_0 = A_0 + A_1T + A_2T^2 + A_3T^3 \quad (2)$$

$\rho_0(T)$ is the density at reference pressure P_0 which is chosen to be 0.1 MPa here, C is a fitting parameter with temperature-independent, and $B(T)$ is correlated as third-order polynomial:

$$B(T) = B_0 + B_1T + B_2T^2 \quad (3)$$

The expressions of deviations between the calculated densities and those of experimental data, including *ARD* (average absolute relative deviation), *MRD* (maximum relative deviation), *bias* (average deviation), and σ (standard deviation), are displayed below:

$$ARD / \% = \frac{100}{N} \sum_{i=1}^N \left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \right| \quad (4)$$

$$MRD / \% = \max \left(100 \left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \right| \right) \quad (5)$$

$$bias / \% = \frac{100}{N} \sum_{i=1}^N \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \quad (6)$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (\rho_i^{\text{exp}} - \rho_i^{\text{cal}})^2}{N - m}} \quad (7)$$

where ρ^{exp} denotes the measured density data in this study, ρ^{cal} refers to the calculated values obtained from Eq. (1), N is the total number of data points, m is the parameter number of the equation (here $m = 8$).

Experimental densities of pure *o*-xylene and the mixtures of *o*-xylene and *n*-decane were shown in Table 2. Measurements in this work for the densities were carried out along isotherms at 10 K intervals from 283.15 K to 363.15 K in the pressure range from 0.1 to 60 MPa.

Table 2. Densities ($\text{g}\cdot\text{cm}^{-3}$) for the *n*-decane(x) + *o*-xylene (1- x) mixture at various temperatures and pressures.

P/MPa	T/K								
	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15
$x=0$									
0.1	0.8905	0.8797	0.8709	0.8627	0.8538	0.8451	0.8363	0.8278	0.8193
1.0	0.8908	0.8799	0.8716	0.8629	0.8546	0.8460	0.8372	0.8286	0.8203
3.0	0.8924	0.8814	0.8730	0.8645	0.8561	0.8478	0.8390	0.8306	0.8224
5.0	0.8935	0.8824	0.8744	0.8659	0.8577	0.8494	0.8409	0.8324	0.8243
10.0	0.8967	0.8859	0.8778	0.8696	0.8615	0.8533	0.8449	0.8369	0.8287
15.0	0.8990	0.8889	0.8811	0.8730	0.8652	0.8571	0.8490	0.8412	0.8336
20.0	0.9026	0.8920	0.8842	0.8763	0.8688	0.8609	0.8530	0.8451	0.8376
25.0	0.9053	0.8949	0.8873	0.8796	0.8720	0.8644	0.8566	0.8491	0.8415
30.0	0.9081	0.8978	0.8903	0.8827	0.8753	0.8678	0.8602	0.8528	0.8455
35.0	0.9109	0.9005	0.8931	0.8857	0.8784	0.8710	0.8637	0.8564	0.8493
40.0	0.9133	0.9031	0.8959	0.8884	0.8815	0.8743	0.8668	0.8598	0.8531
50.0	0.9182	0.9085	0.9012	0.8942	0.8873	0.8803	0.8732	0.8663	0.8598
60.0	0.9230	0.9131	0.9064	0.8992	0.8928	0.8860	0.8789	0.8725	0.8663
$x=0.2001$									
0.1	0.8435	0.8356	0.8266	0.8187	0.8101	0.8016	0.7929	0.7845	0.7759
1.0	0.8439	0.8359	0.8276	0.8190	0.8108	0.8025	0.7938	0.7853	0.7770
3.0	0.8454	0.8373	0.8291	0.8206	0.8125	0.8043	0.7958	0.7875	0.7793
5.0	0.8465	0.8385	0.8306	0.8222	0.8142	0.8060	0.7977	0.7894	0.7814

10.0	0.8500	0.8421	0.8341	0.8260	0.8182	0.8101	0.8020	0.7941	0.7860
15.0	0.8532	0.8453	0.8376	0.8296	0.8220	0.8141	0.8063	0.7986	0.7911
20.0	0.8562	0.8484	0.8408	0.8331	0.8258	0.8180	0.8104	0.8027	0.7952
25.0	0.8592	0.8515	0.8440	0.8364	0.8291	0.8216	0.8141	0.8068	0.7992
30.0	0.8621	0.8544	0.8470	0.8396	0.8324	0.8251	0.8178	0.8106	0.8034
35.0	0.8649	0.8572	0.8500	0.8427	0.8356	0.8284	0.8214	0.8143	0.8073
40.0	0.8675	0.8599	0.8528	0.8455	0.8388	0.8318	0.8247	0.8178	0.8111
50.0	0.8727	0.8654	0.8584	0.8514	0.8447	0.8380	0.8312	0.8244	0.8180
60.0	0.8775	0.8701	0.8635	0.8565	0.8504	0.8438	0.8369	0.8307	0.8245
$x=0.4065$									
0.1	0.8054	0.8001	0.7911	0.7835	0.7751	0.7667	0.7582	0.7499	0.7415
1.0	0.8061	0.8006	0.7923	0.7839	0.7759	0.7676	0.7591	0.7507	0.7427
3.0	0.8071	0.8020	0.7938	0.7855	0.7776	0.7695	0.7611	0.7530	0.7450
5.0	0.8088	0.8032	0.7954	0.7871	0.7794	0.7713	0.7632	0.7549	0.7471
10.0	0.8122	0.8068	0.7989	0.7911	0.7835	0.7756	0.7676	0.7598	0.7519
15.0	0.8154	0.8101	0.8025	0.7947	0.7874	0.7797	0.7719	0.7645	0.7571
20.0	0.8185	0.8133	0.8057	0.7982	0.7912	0.7836	0.7762	0.7687	0.7613
25.0	0.8215	0.8164	0.8090	0.8017	0.7945	0.7875	0.7799	0.7728	0.7655
30.0	0.8244	0.8195	0.8121	0.8049	0.7980	0.7908	0.7837	0.7767	0.7697
35.0	0.8272	0.8223	0.8152	0.8080	0.8011	0.7942	0.7874	0.7804	0.7737
40.0	0.8299	0.8250	0.8180	0.8109	0.8044	0.7976	0.7907	0.7839	0.7775
50.0	0.8352	0.8306	0.8236	0.8168	0.8103	0.8038	0.7973	0.7906	0.7845
60.0	0.8400	0.8352	0.8288	0.8220	0.8161	0.8097	0.8030	0.7969	0.7911
$x=0.5835$									
0.1	0.7790	0.7754	0.7663	0.7589	0.7507	0.7426	0.7342	0.7261	0.7178
1.0	0.7796	0.7759	0.7676	0.7594	0.7515	0.7434	0.7352	0.7269	0.7190
3.0	0.7809	0.7772	0.7691	0.7610	0.7532	0.7454	0.7373	0.7293	0.7213
5.0	0.7822	0.7784	0.7707	0.7626	0.7550	0.7472	0.7393	0.7312	0.7235
10.0	0.7858	0.7822	0.7743	0.7666	0.7592	0.7515	0.7439	0.7362	0.7283
15.0	0.7892	0.7855	0.7780	0.7703	0.7632	0.7557	0.7482	0.7409	0.7336
20.0	0.7924	0.7887	0.7812	0.7738	0.7670	0.7596	0.7525	0.7452	0.7379
25.0	0.7954	0.7918	0.7845	0.7774	0.7704	0.7633	0.7563	0.7493	0.7421
30.0	0.7983	0.7949	0.7876	0.7806	0.7739	0.7669	0.7601	0.7532	0.7464
35.0	0.8009	0.7977	0.7907	0.7838	0.7771	0.7703	0.7638	0.7570	0.7503
40.0	0.8036	0.8004	0.7935	0.7867	0.7803	0.7738	0.7671	0.7605	0.7542
50.0	0.8091	0.8060	0.7992	0.7926	0.7863	0.7800	0.7737	0.7672	0.7612
60.0	0.8138	0.8107	0.8043	0.7978	0.7921	0.7859	0.7794	0.7735	0.7678
$x=0.8041$									
0.1	0.7523	0.7476	0.7407	0.7335	0.7256	0.7177	0.7095	0.7017	0.6935
1.0	0.7530	0.7482	0.7421	0.7341	0.7264	0.7185	0.7105	0.7025	0.6947
3.0	0.7543	0.7495	0.7437	0.7357	0.7282	0.7205	0.7126	0.7049	0.6971
5.0	0.7555	0.7507	0.7453	0.7374	0.7300	0.7223	0.7147	0.7069	0.6994

10.0	0.7592	0.7545	0.7489	0.7414	0.7343	0.7268	0.7194	0.7119	0.7042
15.0	0.7626	0.7578	0.7527	0.7452	0.7382	0.7310	0.7238	0.7167	0.7097
20.0	0.7658	0.7611	0.7559	0.7488	0.7422	0.7350	0.7282	0.7211	0.7140
25.0	0.7690	0.7643	0.7592	0.7523	0.7456	0.7388	0.7320	0.7252	0.7182
30.0	0.7721	0.7672	0.7624	0.7555	0.7491	0.7424	0.7358	0.7292	0.7225
35.0	0.7749	0.7702	0.7655	0.7588	0.7523	0.7458	0.7395	0.7330	0.7266
40.0	0.7777	0.7729	0.7684	0.7617	0.7556	0.7493	0.7429	0.7366	0.7304
50.0	0.7823	0.7786	0.7740	0.7676	0.7616	0.7555	0.7495	0.7433	0.7374
60.0	0.7879	0.7832	0.7792	0.7728	0.7675	0.7615	0.7554	0.7497	0.7440

The combined expanded uncertainties U are $U_{c,r}(x) = 2.0 \times 10^{-4}$, $U_c(T) = 0.03$ K, $U_c(p) = 0.04$ MPa, and $U_c(\rho) = 0.001 \cdot \rho$ with a confidence level of 0.95.

The fitted parameters in the Tait equation, A_i , B_i and C , were listed in Table 3 along with the deviations (including ARD , MRD , $bias$ and σ). For the pure o -xylene, the ARD is 0.03 %, and for the mixtures at different fractions of n -decane, the ARD is less than 0.03 %.

Table 3. Parameters and deviations for density correlation for the n -decane(x) + o -xylene (1- x) mixture using Eqs. (1-3).

x	0.0000	0.2001	0.4065	0.5835	0.8041
$A_0/(\text{g} \cdot \text{cm}^{-3})$	2.0555	1.1430	0.1542	-0.2518	-0.4921
$A_1/(\text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-1})$	-0.0093	-0.0015	0.0071	0.0105	0.0123
$A_2/(\text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-2})$	2.54×10^{-5}	2.20×10^{-6}	-2.34×10^{-5}	-3.35×10^{-5}	-3.89×10^{-5}
$A_3/(\text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-3})$	-2.56×10^{-8}	-2.49×10^{-9}	2.30×10^{-8}	3.31×10^{-8}	3.83×10^{-8}
C	0.0867	0.0851	0.0848	0.0856	0.0864
B_0/MPa	434.1205	356.5168	316.8889	299.9300	309.6957
$B_1/(\text{MPa} \cdot \text{K}^{-1})$	-1.4900	-1.1525	-0.9861	-0.9187	-1.0115
$B_2/(\text{MPa} \cdot \text{K}^{-2})$	1.33×10^{-3}	9.26×10^{-4}	7.29×10^{-4}	6.55×10^{-4}	8.19×10^{-4}
$ARD/\%$	0.03	0.01	0.01	0.02	0.03
$MRD/\%$	0.09	0.05	0.05	0.07	0.08
$bias/\%$	-1.34×10^{-3}	-2.94×10^{-4}	-2.30×10^{-4}	-8.25×10^{-4}	1.95×10^{-3}
$\sigma/(\text{g} \cdot \text{cm}^{-3})$	3.11×10^{-4}	1.34×10^{-4}	5.02×10^{-5}	2.12×10^{-4}	2.50×10^{-4}

Here, we compared the experimental density data studied in this work and literature results. The deviations were given in Table 4. Detailed information of the literatures were also included in Table 4. Figure 1 (a) and (b) shows the deviations for the densities of o -xylene relative to those calculated results from Tait equation. It is obviously that experimental results of

this work are acceptable. The absolute average relative deviation between the literatures and calculations from Eq. 1 is less than 0.2 % except for the data of Wu et al.¹¹ However, the uncertainty reported by Wu et al. is 0.75 %, therefore, the experimental data reported by Wu et al. agree well with our results.

Table 4. Comparison between literature and calculated results from the Tait equation (Eq. (1-3)).

ref.	year	N	T/K	P/MPa	Measuring method	$u_r(\rho)$ /%	ARD/%
<i>o</i> -xylene							
Hales et al. ¹⁴	1972	14	293.15-490	0.1	magnetically controlled float	0.02	0.076
Serrano et al. ¹⁶	1990	7	273.15-303.15	0.1	pycnometer	none	0.127
Garg et al. ¹⁹	1993	72	318.15-373.15	0.1-10	vibrating-tube densimeter	0.04	0.075
Tahir et al. ¹²	1995	45	298.15-373.15	0.1-40	vibrating-tube densimeter	none	0.090
Chen et al. ¹⁵	2007	7	293.15-353.15	0.1	vibrating-tube densimeter	none	0.069
Yang et al. ²⁰	2007	7	298.15-353.15	0.1	vibrating-tube densimeter	0.02	0.030
Nain et al. ¹³	2008	7	288.15-318.15	0.1	pycnometer	0.02	0.057
Olmos et al. ¹⁸	2010	46	278.15-323.15	0.1	vibrating-tube densimeter	0.02	0.136
Behrooz et al. ¹⁷	2012	6	293.15-333.15	0.1	vibrating-tube densimeter	none	0.038
Zhang et al. ²¹	2013	5	288.15-328.15	0.1	vibrating-tube densimeter	0.02	0.084
Wu et al. ¹¹	2013	80	294.9-523.2	3.6-265	variable-volume cell	0.75	0.260
<i>n</i> -decane+ <i>o</i> -xylene							
Chevaller et al. ²	1990	5	298.15	0.1	vibrating-tube densimeter	none	0.095

“none” means the uncertainty was not given in the literatures.

Figure 1. Percentage deviations vs temperature (a) and pressure (b) for published data for *o*-xylene relative to those calculated from the Tait equation (Eq. (3-5)): ■, Tahir et al.¹²; ●, Nain et al.¹³; ▼, Hales et al.¹⁴; ▲, Chen

et al.¹⁵; ►, Serrano et al.¹⁶; □, Behroozi et al.¹⁷; Δ, Olmos et al.¹⁸; , Garg et al.¹⁹; ◁, Yang et al.²⁰; ▷, Zhang et al.²¹; ★, Wu et al.¹¹

For the *n*-decane + *o*-xylene mixtures, as aforementioned, only Chevalier et al.² reported the densities at 298.15 K and atmospheric pressure, the detailed information is also shown in Table 4. The deviation is 0.095 %, the data of Chevalier et al.² have an excellent agreement with our results.

In petroleum industry, the knowledge of the volumetric properties of hydrocarbon mixtures is essential. The derived volumetric properties include the coefficient of isobaric thermal expansivity, α_P , and the isothermal compressibility, κ_T . The expressions of the isobaric thermal expansivity and the isothermal compressibility are:

$$\alpha_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P$$

(8)

$$\kappa_T = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T$$

(9)

The above two coefficients were calculated based on the Tait equation here. The uncertainties, estimated through error propagation, are all within 5 %.

The variations of κ_T and α_P as a function of temperature and pressure are plotted separately in Figures 2 and 3 for *o*-xylene and *n*-decane, and in Figure 4 for their binary mixtures. It should be pointed out that the densities of *n*-decane which were used to calculate the derived properties were obtained from Ref [1]. For pure *o*-xylene, κ_T varies from $5.2 \times 10^{-4} \text{ MPa}^{-1}$ at 60 MPa and 283.15 K to $12.8 \times 10^{-4} \text{ MPa}^{-1}$ at atmospheric pressure and 363.15 K. For pure *n*-decane, it varies from $6.1 \times 10^{-4} \text{ MPa}^{-1}$ at 60 MPa and 283.15 K to $17.8 \times 10^{-4} \text{ MPa}^{-1}$ at atmospheric pressure and

363.15 K. Figure 2 shows, as is usual in hydrocarbons, that κ_T for the two pure components here decreases with pressure.

In the case of isobaric thermal expansivities α_p , the behavior with temperature is different from κ_T with pressure. For instance, α_p for *o*-xylene decreases firstly and then increases with increasing temperature. Within the considered T , P conditions, *n*-decane is more compressible than *o*-xylene but has similar expansive behaviors. Additionally, calculated results of κ_T and α_p from CPA and PC-SAFT EoS are also presented in Figure 2, the details would be further discussed in model section.

Figure 2. Isothermal compressibility obtained from Tait equation versus pressure at two temperatures. ■, 283.15 K; ●, 363.15 K. Solid line (blue) and dash-dot line (red) correspond to calculated κ_T from simplified PC-SAFT and CPA, respectively.

Figure 3. Isobaric thermal expansivities obtained from Tait equation versus temperature at two pressures. ■, 0.1 MPa; ●, 60 MPa. Solid line (blue) and dash-dot line (red) correspond to calculated α_p from simplified PC-SAFT and CPA, respectively.

In Figure 4, it is observed that the values α_p for the *n*-decane + *o*-xylene mixtures do not vary significantly with the composition at higher temperature, and the effect of pressure at high temperature can be negligible. However, κ_T (that slightly increases with increasing the mole fraction of *n*-decane) show near-linear relationship with the composition. In addition, κ_T for mixtures in all cases increase with temperature increasing and pressure decreasing, which is aligned with the fact already observed in Figure 2, where κ_T for both pure components exhibit similar tendencies.

Figure 4. Isothermal compressibilities and isobaric thermal expansivities for the mixture against mole fractions of *n*-decane. Calculated from Tait equation. ■, 0.1 MPa/283.15 K; □, 0.1 MPa/363.15 K; ●, 60 MPa/283.15 K; ○, 60 MPa/363.15 K. Solid lines correspond to polynomial fitting to guide the eyes.

3.2 Excess molar volumes

The excess molar volume (V^E) of the mixtures can be calculated:

$$V^E = \sum_i^n x_i M_i [1/\rho - 1/\rho_i] \quad (10)$$

where n is the component number, ρ_i , M_i and x_i are the densities, molar mass and mole fraction of pure component i , respectively.

The obtained V^E values were correlated by the Redlich-Kister equation²²:

$$V^E = x(1-x) \sum_{i=0}^n A_i (2x-1)^i \quad (11)$$

where A_i are the coefficients, x is the mole fraction of n -decane. The values of A_i as well as the standard deviations (σ) for the studied mixtures at different conditions are given in Table 5.

Table 5. Fitting parameters A_i of Eq. (11) and standard deviation σ for the selected pressures and temperatures for the mixture.

	$T=283.15$ K			$T=363.15$ K		
	0.1 MPa	30 MPa	60 MPa	0.1 MPa	30 MPa	60 MPa
$A_0 / \text{cm}^3 \cdot \text{mol}^{-1}$	0.870	0.731	0.640	2.409	2.147	2.027
$A_1 / \text{cm}^3 \cdot \text{mol}^{-1}$	-0.033	-0.044	-0.109	0.335	0.254	0.170
$A_2 / \text{cm}^3 \cdot \text{mol}^{-1}$	-0.294	-0.495	-0.571	0.991	0.747	0.499
$\sigma / \text{cm}^3 \cdot \text{mol}^{-1}$	0.01	0.02	0.03	0.04	0.02	0.01

For the n -decane/ o -xylene systems, the V^E values are all positive, which is indicative of a volume expansion upon mixing. The V^E values decrease with pressure increasing and temperature decreasing, as shown in Figure 5. As the temperature of the mixtures increases, the free volume of the molecular of the mixtures will be enlarged due to a more loosely molecular packing. Similarly, as the pressure of the mixtures increases, the molecular distance of the compounds will be shortened, resulted free volume decreasing, the values of V^E will be reduced.

Figure 5. Excess molar volume for the mixture against mole fractions of *n*-decane. At 283.15 K: ■, 0.1 MPa; ●, 30 MPa; ▲, 60 MPa. At 363.15 K: □, 0.1 MPa; ○, 30 MPa; △, 60 MPa. Solid lines correspond to Redlich-Kister fitting.

Figure 5 also shows that the excess molar volumes of the studied system are small in absolute value. For example, at the mole fraction $x_{\text{decane}}=0.5$, the maximum values are 0.22 $\text{cm}^3 \cdot \text{mol}^{-1}$ at 283.15 K and 0.1 MPa and 0.6 $\text{cm}^3 \cdot \text{mol}^{-1}$ at 363.15 K and 0.1 MPa, respectively. The small magnitude of V^E may be attributed to the small difference of the dispersion forces between the two components in the mixtures¹.

4. Model section

4.1 CPA and sPC-SAFT model

Two advanced EoSs, namely CPA and sPC-SAFT, are used here to describe the volumetric properties of the system. CPA equation, proposed by Kontogeorgis et al.³, combines the SRK equation and an association term^{23–26}, which is shown below:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2} \frac{RT}{V_m} \left(1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (12)$$

where the density ρ is $1/V_m$. The detailed information about CPA equation was given in the literature²⁷.

The sPC-SAFT equation is the sum of different contribution, including an ideal gas contribution, a^{id} , a hard-chain contribution, a^{hc} , a dispersion contribution, a^{disp} , and an association contribution, a^{ass} . The expression is

$$a = a^{id} + a^{hc} + a^{disp} + a^{ass} \quad (13)$$

The expressions of different contribution have been given by von Solms et al.⁴ The parameters in the CPA and sPC-SAFT equation used in the study substances are taken from

Kontogeorgis and Folas²⁷, except for CPA parameters of the *o*-xylene, it was provided by Oliveira et al.²⁸ Table 6 gives the summary of the parameters.

Table 6. Pure CPA and sPC-SAFT component parameters of *n*-decane and *o*-xylene used in this work.

Model	parameters	<i>n</i> -decane	<i>o</i> -xylene
CPA	$a_0 / \text{bar} \cdot \text{mol}^{-2}$	47.389	29.2
	b / mol^{-1}	0.17865	0.1086
	c_1	1.13243	0.88
	T_c / K	617.7	631
PC-SAFT	m	4.6627	3.1362
	$\sigma / \text{\AA}$	3.8384	3.76
	ε / K	243.87	291.05

4.2 Vapor pressures and fitted k_{ij}

When the CPA and sPC-SAFT equation was used to model the density of the *n*-decane/*o*-xylene mixture, the binary interaction parameter of the two substances should be known previously. Yang et al.²⁹ reported the vapor-liquid equilibria results of the *n*-decane/*o*-xylene mixture. Figure 6 shows a VLE comparison between Yang's data and the prediction results from both equations with binary interaction parameters. In Figure 6, we also include the calculated results when the binary interaction parameter is zero. The *ARD* for VLE data is given in Table 7.

Figure 6. *T*-*x*-*y* phase equilibrium diagram for the *n*-decane (1) + *o*-xylene (2) system at 20 kPa. blue line, calculated liquid and vapor compositions from sPC-SAFT ($k_{ij}=0.0032$, dash dot line; $k_{ij}=0$, solid line); red line,

calculated liquid and vapor compositions from CPA ($k_{ij}=-0.0628+1.6371\times 10^{-4}T$, dash dot line; $k_{ij}=0$, solid line).

Table 7. Average absolute deviation for VLE data for the studied system.

Model	$k_{ij}=k_{ija}+k_{ijb}T$		$ \Delta T /K$	$ARD^y/\%$
	k_{ija}	k_{ijb}	Yang et al. ⁴⁰	
CPA	0	0	1.07	7.02
CPA	-0.0019	0	0.22	3.67
CPA	-0.0628	1.6371×10^{-4}	0.11	2.50
sPC-SAFT	0	0	0.45	2.78
sPC-SAFT	-0.0035	0	0.08	0.75

The VLE calculated results show that the sPC-SAFT equation is better than CPA equation for the *n*-decane/*o*-xylene system, and for both equations, the calculative precision of VLE is improved via introducing k_{ij} . For CPA equation, to further strengthen the predictive accuracy here, the binary interaction parameters were considered as a function of temperature, as shown in Table 7. In the case, the smaller deviations of temperature at bubble point and vapor composition can be found. It should be pointed out that, when regressed the binary interaction parameter, the objective function used in this work is

$$f_{\min} = \sum_i^{N_p} |P_i^{\text{exp}} - P_i^{\text{cal}}| + \sum_i^{N_T} |T_i^{\text{exp}} - T_i^{\text{cal}}| + \sum_i^{N_y} |y_i^{\text{exp}} - y_i^{\text{cal}}| \quad (14)$$

where T and y are bubble temperature and composition of vapor phase, respectively. The subscript N is the total number of experimental points.

4.3 Density predictions

Figure 7 gives the density comparison between the calculated results of the two equations and the experimental data. Figure 8 shows the deviation distributions between the calculated results and those of the measurements of pure substances and mixtures at $x_{\text{decane}}=0.4065$. For the mixtures, the binary interaction parameters were used. The densities of pure *n*-decane were obtained from our previously work¹. For the calculated densities, different trends were observed

for the CPA and sPC-SAFT equation, respectively. Meanwhile, the calculated density data of the mixtures using sPC-SAFT equation are lower than the measurements at low pressures, and then become higher at high pressures. However, the densities are underestimated by the CPA equation in almost all the cases. The *ARD* between the densities calculated from sPC-SAFT and CPA and measurement results of the mixtures are 0.46 % and 1.34 %, respectively.

Figure 7. Comparison of experimental density data (symbols) for the mixture with calculated densities from CPA and sPC-SAFT EoS. ■, 283.15 K; ●, 293.15 K; ▲, 303.15K; ▼, 313.15 K; ◆, 323.15 K; ◀, 333.15 K; ▶, 343.15 K; □, 353.15 K; ○, 363.15 K; solid line, calculated liquid densities from simplified PC-SAFT; dashed line, calculated liquid densities from CPA.

Figure 8. Relative deviations of our experimental data from results with both models for *o*-xylene, *n*-decane and their binary mixture ($x_{\text{decane}}=0.4065$) as a function of pressure. *O*-xylene: ■, 283.15 K; ●, 323.15 K; ▲, 363.15K; *n*-decane: ◆, 283.15 K; ◀, 323.15 K; ▶, 363.15K; Mixture: □, 283.15 K; ○, 323.15 K; Δ, 363.15K.

In this work, we also calculated the isothermal compressibility and the isobaric thermal expansivity using CPA and sPC-SAFT equation, respectively. The results were compared with those calculated from Tait equation, as shown in Figure 2 and 3. For the isothermal compressibility k_T , similar trends were observed between the results from sPC-SAFT or CPA equation and the results from Tait equation. The ARDs obtained were 12.52 % and 28.46 % for CPA and sPC-SAFT, respectively. For the isobaric thermal expansivity α_p , the calculated results of sPC-SAFT equation were better than the results of CPA equation. The ARDs were 31.40 % and 7.89 % for CPA and sPC-SAFT, respectively. Actually, most EoS, including cubic EoS and SAFT-type EoS, cannot give accurate results when applied to the derivative properties, such as isothermal compressibility and isobaric thermal expansivity. As pointed out by Lafitte et al.³⁰, the difficulty to model the derivative properties might be attribute to the incorrect choice of intermolecular potential function. Although many researchers try to modify the SAFT equation

to enhance the calculation performance of the derivative properties^{30,31}, further intensively investigation of the equation should be carried out in the future.

5. Conclusion

The densities of *n*-decane/*o*-xylene mixtures are reported in this work at the temperature from 283.15 K to 363.15 K and at pressures up to 60 MPa. The experimental results were correlated as Tait equation and the coefficients of the equation were obtained. The V^E of the mixtures were determined and shows positive in all cases, moreover, the V^E values decrease with pressure increasing and temperature decreasing. The derived properties of isothermal compressibilities and isobaric thermal expansivities were obtained from Tait equation, CPA equation and sPC-SAFT equation, respectively. The calculated results were discussed in detail. In addition, densities were predicted with CPA and sPC-SAFT EoSs, and the *ARD* between the experimental data and calculated results is 1.34 % and 0.46 % with fitted binary interaction parameter, respectively. And the sPC-SAFT EoS is suitable to calculate the densities of *n*-decane/*o*-xylene mixtures.

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Notes

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