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P ρ *T* measurements and modelling of (*n*-decane+*m*-xylene) mixtures from
293.15 K to 363.15 K at pressures up to 60 MPa

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ABSTRACT

In this work, the experimental measurements for liquid densities of *n*-decane and *m*-xylene binary mixtures were performed over the entire composition range with a high-pressure vibrating-tube densimeter. The range of temperatures for the present measurements was from 293.15 K to 363.15 K and the pressures were up to 60 MPa. The combined expanded uncertainty of the density measurements is estimated to be 0.001ρ with 0.95 confidence. Experimental density values were correlated by the modified Tammann-Tait equation. The simplified Perturbed Associating Fluid Theory (sPC-SAFT) and Cubic Plus Associated (CPA) equations of state (EoS) were applied to predict the densities of *n*-decane and *m*-xylene and their mixtures. Reasonably results were observed between the experimental data and calculated results for the two equations, and the deviation is less than 0.48 % and 0.89 % with sPC-SAFT and CPA EoS, respectively. In addition, excess molar volumes were determined from the experimental density data as well as from sPC-SAFT and CPA models. The effects of pressure and temperature on the excess molar volume were also discussed.

KEYWORDS: *n*-decane, *m*-xylene, volumetric properties, high-pressure density, EOS

1. Introduction

Density data for hydrocarbons (for instance, *n*-alkanes, iso-alkanes, naphthenes and aromatics) and their mixtures at reservoir conditions are indispensable for accurate assessment of the recoverable petroleum amount within a reservoir. Furthermore, the knowledge of accurate $P\rho T_x$ data of mixtures is also needed for testing the performance of equations of state (EoS). The development of EoS is of particular significance as, when sufficiently accurate, they constitute a convenient way to obtaining results compared to the time-consuming measurements of gas-crude-oil reservoir-fluid samples.

There are limited density data of asymmetric hydrocarbon mixtures under high-pressure conditions in the open literatures. To the best of our knowledge, only Hamzehlouia *et al.*[1] reported densities of the *n*-decane/*m*-xylene binary mixtures at 308.15 K and 313.15 K under atmospheric pressure. As a continuation of our work to investigate $P\rho T_x$ properties of mixtures containing *n*-decane [2], the vibrating-tube densimeter is used here to provide experimental densities of *n*-decane/*m*-xylene binary system over the entire composition range at pressures up to 60 MPa and at temperatures from 293.15 K to 363.15 K. The obtained density data were correlated as a function of temperature and pressure with the modified Tammann-Tait equation. In addition, excess molar volumes were determined from the experimental densities. Moreover, the capabilities of two EoS, i.e. cubic plus association (CPA)[3] and simplified perturbed-chain statistical associating fluid theory (sPC-SAFT) [4,5] to calculate the densities and the excess molar volume were analysed.

2. Experimental

2.1 Samples

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

Table 1. Sample descriptions.

Chemicals	CAS	Source	Mass fraction purity	Purification method
<i>n</i> -decane	124-18-5	Aladdin Chemistry	≥ 0.99	None
<i>m</i> -xylene	108-38-3	Aladdin Chemistry	≥ 0.99	None

2.2 Experimental apparatus

The $P\rho T$ properties of the mixtures were measured with the Anton Paar vibrating-tube densimeter (DMA-HPM). Figure 1 shows the schematic diagram of the apparatus. Detailed descriptions of the system have been presented in our previous work [2,6-8]. The main parts of the densimeter consist of the measuring cell and interface module. When the vibrating-tube of the measuring cell is excited, the interface module can be used to obtain the oscillating period and the cell temperature simultaneously. A platinum resistance thermometer purchased from Fluke (model: Fluke 5608) was used to measure the sample temperature. The combined expanded uncertainty for temperature was smaller than 0.03 K ($k=2$, k denotes coverage factor). A manual piston pump supplied by HIP (model: 50-6-15) was applied for accurate measurement at high pressures, and the pressure was measured by a Paroscientific pressure transducer (model 410 K-101, 0.01% for full scale).

Before the measurements, a method proposed by Lagourette *et al.* [9,10] was used to calibrate the apparatus. In order to convert oscillation period from measuring cell to density data more precisely, the parameters of the apparatus were obtained using water as the reference substance when considering ranges of temperature and pressure involved in this study. A Mettler analytical balance (model: AB204-N, accuracy: 10^{-4} g) was applied in the preparation process for the *n*-decane/*m*-xylene mixtures. The uncertainty of the mole fraction for the binary mixtures was estimated to be within 2.0×10^{-4} . Taking all uncertainties into consideration, the combined

expanded uncertainty of the density measurements was less than 0.001ρ with 0.95 confidence level.

Figure 1. Schematic diagram of the compressed-liquid densimeter. PP, manual piston pump; TC, temperature controller; TS, Pt100 temperature sensor; PS, pressure sensor; CFP, constant-flux pump; SC, sample cylinder; TP, Turbo pump; RVVP, rotary vane vacuum pump; TB, thermostatic bath; EU, mPDS-5 unit; DMM, digital multimeter; PC, personal computer.

3. Thermodynamic modelling

3.1 Equations of state

In this section, the CPA and sPC-SAFT EoS, used as tools for describing $P\rho T$ properties of samples considered, are introduced in brief. CPA is a convenient equation of state, proposed by Kontogeorgis et al.[3], which combines the simple cubic equation of state (SRK) [11] and an association term, the latter from the Wertheim theory [12-15], similar to that used in the well-known SAFT models [4,5,16-23]. Of particular note is that CPA reduces to SRK functionality when applied for non-associating compounds. This guarantees that CPA model maintains the merits of speed and reliability of classical cubic EoS for many compounds, e.g. those of relevance to the oil and gas industries. Besides that, the numerical implementation of the association term ensures that the computation time is not much higher than that of simple classical models, such as SRK and PR equation. The expression for CPA is shown below:

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

where ρ denotes the amount density ($\rho=1/V_m$). A detailed description of CPA can be found in the book by Kontogeorgis and Folas [24]. In this study, the association term is zero and thus CPA reduces to the SRK functionality but with parameters fitted to various properties, and not just vapour pressures and critical point, the latter method typically used in cubic EoS.

The simplified PC-SAFT equation of state used in the present work, written in terms of the Helmholtz energy, is given as the sum of an ideal gas contribution (a^{id}), a hard-chain contribution (a^{hc}), a dispersion contribution (a^{disp}), and an association contribution (a^{ass}),

$$a = a^{id} + a^{hc} + a^{disp} + a^{ass} \quad (2)$$

von Solms *et al.* [4] proposed a modification of PC-SAFT which simplifies it and somewhat reduces the computational times (compared to the original PC-SAFT⁵) without loss of accuracy. It should be noted that the parameters of simplified PC-SAFT used in this work are taken from Kontogeorgis and Folas [24], but for CPA the *m*-xylene parameters estimated by Oliveira *et al.* [25], shown in Table 2. More details about math calculation formula and physical significance of the model parameters for CPA and sPC-SAFT are available in Support Information.

Table 2. Pure CPA and sPC-SAFT component parameters of *n*-decane and *m*-xylene.

Model	parameters	<i>n</i> -decane	<i>m</i> -xylene
CPA	$0.1 a_0 / \text{MPa} \cdot \text{mol}^{-2}$	47.389 ²⁴	29.1 ²⁵
	b / mol^{-1}	0.17865 ²⁴	0.1091 ²⁵
	c_1	1.13243 ²⁴	0.88 ²⁵
	T_c / K	617.7 ²⁴	617.05 ²⁴
PC-SAFT	M	4.6627 ²⁴	3.1861 ²⁴
	$10\sigma / \text{nm}$	3.8384 ²⁴	3.7563 ²⁴
	$(\epsilon/\kappa) / \text{K}$	243.87 ²⁴	283.98 ²⁴

3.2 The modified Tammann-Tait equation

The experimental density data of *n*-decane, *m*-xylene and their binary mixtures were fitted by the modified Tammann-Tait equation, as shown below:

$$\rho(T, P) = \frac{\rho_0(T)}{1 - C \ln((B(T) + p) / (B(T) + P_0))} \quad (3)$$

$$\rho_0 = A_0 + A_1T + A_2T^2 + A_3T^3 \quad (4)$$

$$B(T) = B_0 + B_1T + B_2T^2 \quad (5)$$

where $\rho_0(T)$ denotes the density at reference pressure P_0 which is chosen to be 0.1 MPa. C is a temperature-independent fitting parameter. The expressions of deviations including *ARD* (average relative deviation), *MRD* (maximum relative deviation), *bias* (average deviation), and σ (standard deviation), are displayed below:

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

$$MRD / \% = \max \left(100 \left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \right| \right) \quad (7)$$

$$bias / \% = \frac{100}{N} \sum_{i=1}^N \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \quad (8)$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (\rho_i^{\text{exp}} - \rho_i^{\text{cal}})^2}{N - m}} \quad (9)$$

where ρ^{exp} denotes the experimental densities measured in this work, ρ^{cal} refers to the values obtained from eq. 3, N equal the number of data points, m is the parameter number of the modified Tait equation ($m = 8$).

4. Results and discussion

4.1 Density data and correlations

Experimental density results of pure *m*-xylene and the binary mixtures of *m*-xylene and *n*-decane are shown in Table 3. For all samples, measurements of density were carried out along isotherms spaced at 10 K intervals from 293.15 K to 363.15 K in the pressure range from 0.1 to

60 MPa. Meanwhile, the density data were correlated as a function of both temperature and pressure using the modified Tammann-Tait equation.

Table 3. Experimental liquid densities ($\text{g}\cdot\text{cm}^{-3}$) for the n -decane(x) + m -xylene ($1-x$) mixture at various temperatures and pressures.

P/MPa	Density / ($\text{g}\cdot\text{cm}^{-3}$)							
	T/K							
	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15
	$x=0$							
0.1	0.8642	0.8550	0.8467	0.8377	0.8290	0.8200	0.8113	0.8022
1	0.8644	0.8554	0.8469	0.8386	0.8298	0.8211	0.8122	0.8033
3	0.8658	0.8575	0.8486	0.8402	0.8317	0.8230	0.8143	0.8055
5	0.8669	0.8588	0.8501	0.8419	0.8334	0.8250	0.8162	0.8076
10	0.8705	0.8623	0.8540	0.8459	0.8376	0.8294	0.8210	0.8124
15	0.8738	0.8658	0.8576	0.8498	0.8416	0.8336	0.8257	0.8176
20	0.8770	0.8690	0.8611	0.8536	0.8456	0.8379	0.8298	0.8218
25	0.8802	0.8722	0.8645	0.8570	0.8493	0.8417	0.8340	0.8260
30	0.8832	0.8753	0.8677	0.8604	0.8528	0.8455	0.8380	0.8302
35	0.8860	0.8782	0.8709	0.8637	0.8562	0.8492	0.8417	0.8342
40	0.8887	0.8810	0.8738	0.8669	0.8597	0.8525	0.8453	0.8381
50	0.8944	0.8867	0.8798	0.8730	0.8660	0.8591	0.8521	0.8452
60	0.8991	0.8920	0.8851	0.8788	0.8719	0.8650	0.8585	0.8520
	$x=0.2005$							
0.1	0.8251	0.8160	0.8081	0.7994	0.7911	0.7823	0.7739	0.7651
1	0.8254	0.8167	0.8084	0.8003	0.7919	0.7835	0.7748	0.7662
3	0.8268	0.8187	0.8101	0.8020	0.7938	0.7854	0.7771	0.7686
5	0.8280	0.8201	0.8117	0.8038	0.7956	0.7875	0.7791	0.7708
10	0.8317	0.8238	0.8157	0.8080	0.7999	0.7920	0.7840	0.7757
15	0.8351	0.8273	0.8194	0.8119	0.8041	0.7964	0.7887	0.7810
20	0.8383	0.8306	0.8229	0.8158	0.8081	0.8007	0.7930	0.7853
25	0.8415	0.8338	0.8264	0.8192	0.8119	0.8046	0.7972	0.7895
30	0.8445	0.8370	0.8297	0.8227	0.8154	0.8084	0.8012	0.7938
35	0.8473	0.8401	0.8330	0.8260	0.8189	0.8121	0.8050	0.7978
40	0.8501	0.8429	0.8359	0.8292	0.8224	0.8155	0.8086	0.8017
50	0.8558	0.8486	0.8419	0.8353	0.8287	0.8221	0.8154	0.8088

60	0.8606	0.8539	0.8472	0.8412	0.8346	0.8281	0.8218	0.8156
$x=0.3999$								
0.1	0.7936	0.7846	0.7770	0.7686	0.7605	0.7520	0.7438	0.7352
1	0.7941	0.7856	0.7774	0.7695	0.7613	0.7531	0.7447	0.7364
3	0.7954	0.7874	0.7791	0.7713	0.7633	0.7551	0.7470	0.7388
5	0.7966	0.7890	0.7808	0.7731	0.7651	0.7572	0.7490	0.7410
10	0.8004	0.7925	0.7847	0.7773	0.7695	0.7618	0.7539	0.7459
15	0.8037	0.7962	0.7885	0.7812	0.7737	0.7661	0.7587	0.7512
20	0.8070	0.7995	0.7921	0.7851	0.7777	0.7705	0.7630	0.7556
25	0.8102	0.8027	0.7956	0.7886	0.7814	0.7743	0.7672	0.7598
30	0.8133	0.8059	0.7988	0.7921	0.7850	0.7782	0.7712	0.7641
35	0.8161	0.8090	0.8021	0.7953	0.7884	0.7819	0.7750	0.7681
40	0.8188	0.8118	0.8050	0.7986	0.7920	0.7853	0.7786	0.7720
50	0.8245	0.8175	0.8109	0.8047	0.7982	0.7919	0.7854	0.7791
60	0.8292	0.8227	0.8162	0.8105	0.8042	0.7978	0.7918	0.7858
$x=0.6030$								
0.1	0.7683	0.7593	0.7520	0.7439	0.7359	0.7276	0.7196	0.7113
1	0.7688	0.7605	0.7525	0.7447	0.7367	0.7287	0.7205	0.7125
3	0.7702	0.7623	0.7541	0.7465	0.7387	0.7307	0.7228	0.7149
5	0.7714	0.7639	0.7558	0.7483	0.7405	0.7328	0.7248	0.7171
10	0.7752	0.7675	0.7598	0.7526	0.7449	0.7375	0.7298	0.7220
15	0.7786	0.7712	0.7636	0.7566	0.7492	0.7418	0.7346	0.7274
20	0.7818	0.7744	0.7672	0.7604	0.7532	0.7462	0.7390	0.7317
25	0.7850	0.7778	0.7707	0.7638	0.7569	0.7500	0.7431	0.7359
30	0.7881	0.7809	0.7739	0.7674	0.7605	0.7539	0.7471	0.7402
35	0.7909	0.7841	0.7772	0.7706	0.7639	0.7576	0.7509	0.7443
40	0.7937	0.7869	0.7801	0.7739	0.7674	0.7610	0.7545	0.7482
50	0.7994	0.7926	0.7861	0.7799	0.7737	0.7676	0.7613	0.7552
60	0.8040	0.7978	0.7913	0.7858	0.7796	0.7734	0.7676	0.7618
$x=0.7998$								
0.1	0.7483	0.7394	0.7323	0.7244	0.7166	0.7084	0.7005	0.6923
1	0.7489	0.7408	0.7328	0.7252	0.7174	0.7094	0.7014	0.6935
3	0.7502	0.7424	0.7344	0.7270	0.7194	0.7115	0.7037	0.6959
5	0.7515	0.7440	0.7361	0.7288	0.7212	0.7136	0.7058	0.6982
10	0.7552	0.7477	0.7402	0.7331	0.7257	0.7183	0.7108	0.7030

15	0.7586	0.7514	0.7439	0.7371	0.7299	0.7226	0.7156	0.7085
20	0.7618	0.7547	0.7476	0.7410	0.7339	0.7270	0.7200	0.7128
25	0.7651	0.7580	0.7511	0.7444	0.7377	0.7309	0.7241	0.7170
30	0.7682	0.7612	0.7543	0.7479	0.7413	0.7347	0.7281	0.7214
35	0.7710	0.7643	0.7576	0.7512	0.7447	0.7384	0.7319	0.7254
40	0.7738	0.7671	0.7605	0.7544	0.7482	0.7418	0.7354	0.7293
50	0.7794	0.7728	0.7664	0.7604	0.7544	0.7485	0.7422	0.7363
60	0.7841	0.7780	0.7716	0.7663	0.7604	0.7542	0.7485	0.7429

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 correlation parameters of the modified Tammann-Tait equation, A_i , B_i and C , are listed in Table 4 along with the ARD , MRD , $bias$ and σ . Very good agreement between experimental and correlated densities is obtained. For the pure *m*-xylene, the ARD is 0.011 %. Additionally, the ARD is lower than 0.015 % for the binary mixtures. Density data of pure *n*-decane have been reported and discussed in our previous article¹. It can be noted that the maximum deviation does not exceed the experimental uncertainties.

Table 4. Parameters and deviations for density correlation for the *n*-decane(*x*) + *m*-xylene (1-*x*) mixture using eq. 3-5.

<i>x</i>	0.0000	0.2005	0.3999	0.6030	0.7998
$A_0/(\text{g} \cdot \text{cm}^{-3})$	1.427	1.332	1.313	1.296	1.299
$A_1/(\text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-1})$	-3.7916×10^{-3}	-3.3082×10^{-3}	-3.4518×10^{-3}	-3.5324×10^{-3}	-3.7852×10^{-3}
$A_2/(\text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-2})$	9.2139×10^{-6}	7.7827×10^{-6}	8.2425×10^{-6}	8.4796×10^{-6}	9.3459×10^{-6}
$A_3/(\text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-3})$	-9.6678×10^{-9}	-8.1718×10^{-9}	-8.5934×10^{-9}	-8.7648×10^{-9}	-9.6959×10^{-9}
C	0.087	0.085	0.085	0.086	0.086
B_0/MPa	462.324	427.948	422.521	389.033	384.184
$B_1/(\text{MPa} \cdot \text{K}^{-1})$	-1.7188	-1.6148	-1.6253	-1.4602	-1.4535
$B_2/(\text{MPa} \cdot \text{K}^{-2})$	1.7048×10^{-3}	1.6307×10^{-3}	1.6773×10^{-3}	1.4615×10^{-3}	1.4671×10^{-3}
$ARD/\%$	0.011	0.010	0.012	0.013	0.014
$MRD/\%$	0.049	0.043	0.055	0.070	0.085
$bias/\%$	-2.17×10^{-6}	-1.86×10^{-6}	-2.55×10^{-6}	-2.96×10^{-6}	-3.58×10^{-6}
$\sigma/(\text{g} \cdot \text{cm}^{-3})$	1.32×10^{-4}	1.16×10^{-4}	1.29×10^{-4}	1.35×10^{-4}	1.44×10^{-4}

4.2 Comparison and discussion

Table 5 shows the comparisons between the experimental data (from literature) of pure *m*-xylene and the results from the Tammann-Tait equation reported in this research. Detailed information of the literature data is also included in Table 5 (references, the number of data points N , the relative uncertainty $u_r(\rho)$, and temperature and pressure ranges). Only the literature data within the temperature and pressure range of this work were considered.

Table 5. Comparison between literature and calculated results from the Tait equation (Eq. (3-5)).

ref.	year	N	T /K	P /MPa	$u_r(\rho)$ /%	ARD /%
<i>m</i> -xylene						
Takagi <i>et al.</i> ³³	1981	21	303.15	0.1-200	none	0.152
Yokoyama <i>et al.</i> ²⁶	1990	5	298.15	0.1-40	0.57	0.264
Garg <i>et al.</i> ³⁰	1993	72	318.15-373.15	0.1-10	0.04	0.030
Taravillo <i>et al.</i> ³²	1994	152	229.95-298.15	0.14-110	0.03	0.107
Tahir <i>et al.</i> ⁹	1995	45	298.15-363.15	0.1-40	none	0.075
Chang <i>et al.</i> ²⁸	1995	42	298.15-343.15	0.1-20	0.1	0.026
Chang <i>et al.</i> ²⁹	1996	21	333.15-413.15	0.1-30	0.01	0.165
Caudwell <i>et al.</i> ³¹	2009	81	298.15-473.15	0.1-198.5	0.2	0.134
Wu <i>et al.</i> ²⁷	2013	87	295.7-522.9	3.8-262.7	0.75	0.111
<i>n</i> -decane + <i>m</i> -xylene						
Hamzehlouia ²	2012	24	308.15, 313.15	0.1	none	0.420

For *m*-xylene, Figure 2(a) and 2(b) give the deviations for published densities relative to those calculated through the Tammann-Tait equation as a function of temperature and pressure, respectively. It is shown that experimental data in this work is reasonable and feasible. All the values are distributed evenly and there are no obvious trends with temperature and pressure. Meanwhile, the deviations are mostly within 0.2 % except for the data by Yokoyama *et al.* [26]. However, their reported relative uncertainty is 0.57 %, therefore, good agreement with our results can be concluded.

Figure 2. Percentage deviations vs temperature (a) and pressure (b) for published data for *m*-xylene relative to those calculated from the Tait equation (Eq. (3-5)): $\square$ Wu *et al.*²⁷; $\circ$ Chang *et al.*^{28,29}; Δ , Yokoyama *et al.*²⁶; ∇ , Garg *et al.*³⁰; $\diamond$, Caudwell *et al.*³¹; $\blacksquare$ Tahir *et al.*⁹; $\bullet$ Taravillo *et al.*³²; $\blacktriangle$ Takagi *et al.*³³

Very few density values for (*n*-decane + *m*-xylene) mixtures are available in the literature. The only available densities were measured by Hamzehlouia *et al.* [1] at 308.15 K and 313.15 K under atmospheric pressure. Due to the difference between the mole fractions of samples in literature and those in our work, an interpolation method is applied for facilitating the comparison. The *ARD* is 0.42 %, indicates that the deviation between the data of Hamzehlouia *et al.* [2] and our calculated values is acceptable if we take the possible source of error in the interpolation method into consideration.

4.3 Density predictions

Here, we used the CPA equation and simplified PC-SAFT equation to calculate the densities of the (*n*-decane + *m*-xylene) mixtures. The binary interaction parameter k_{ij} were firstly obtained from the vapour-liquid equilibrium (VLE) data of the mixtures [34,35]. The objective function is

$$f_{\min} = \sum_i^{N_P} |P_i^{\exp} - P_i^{\text{cal}}| + \sum_i^{N_T} |T_i^{\exp} - T_i^{\text{cal}}| + \sum_i^{N_y} |y_i^{\exp} - y_i^{\text{cal}}| \quad (10)$$

where P , T and y are vapour pressure, bubble temperature and composition of vapour phase, respectively. N is the total number of experimental points. The k_{ij} values are shown in Table 6.

Figures 3 and 4 contain comparisons of VLE values between the literature and the predictions from the two models with binary interaction parameters. Data used for comparison are reported by Yang *et al.* [34] and Willman *et al.* [35]. The results, which denote $k_{ij}=0$, from pure component parameters are also included here. The *ARD* for isobaric and isothermal VLE data with k_{ij} set to zero and fitted k_{ij} are listed in Table 6.

Figure 3. P - x - y phase equilibrium diagram for the n -decane (x) + m -xylene ($1-x$) system³⁵ at 373.5 K (■ □), 383.6 K (● ○), 393.7 K (▲ △). Solid line, calculated liquid and vapour compositions from simplified PC-SAFT ($k_{ij}=0.0032$, black line; $k_{ij}=0$, red line); dashed line, calculated liquid and vapour compositions from CPA ($k_{ij}=1.9243 \times 10^{-4}$, black line; $k_{ij}=0$, red line).

Figure 4. T - x - y phase equilibrium diagram for the n -decane (x) + m -xylene ($1-x$) system at 20 kPa³⁴. Solid line, calculated liquid and vapour compositions from simplified PC-SAFT ($k_{ij}=0.0032$, black line; $k_{ij}=0$, red line); dashed line, calculated liquid and vapour compositions from CPA ($k_{ij}=1.9243 \times 10^{-4}$, black line; $k_{ij}=0$, red line).

From Table 6, it can be seen that CPA performs slightly better than sPC-SAFT for the studied binary system. Meanwhile, introducing k_{ij} would not improve calculation precision of CPA to a large extent. It is important to note that the ARD value in Table 6 are average relative deviation between calculations and experimental temperature, pressure, and vapour compositions at bubble point including isobaric and isothermal VLE data, respectively. The VLE behaviour of this binary system within the considered temperature and pressure range is represented satisfactory by both sPC-SAFT and CPA equations of state with interaction parameters. No temperature dependence of k_{ij} is included.

Table 6. Average relative deviation for isobaric and isothermal VLE data using $k_{ij}=0$ and fitted k_{ij} for binary system of n -decane(x) + m -xylene ($1-x$).

Model	k_{ij}	$ \Delta T /K$	$ARD^y/\%$	$ARD^p/\%$	$ARD^v/\%$
		Yang <i>et al.</i> ³⁴		Willman <i>et al.</i> ³⁵	
CPA	0	0.197	0.56	2.11	5.38
CPA	1.9243×10^{-4}	0.185	0.54	2.12	5.37
sPC-SAFT	0	0.482	2.21	2.00	5.70
sPC-SAFT	0.0032	0.118	0.94	1.89	5.48

Figure 5 gives the density comparisons between the calculated results from CPA and sPC-SAFT models using the binary interaction parameter k_{ij} and the experimental data. It can be seen that CPA and sPC-SAFT show different trends of density predictions with changing temperature, pressure and composition. For sPC-SAFT, the prediction results are lower than the experimental data at low pressures and become higher at high pressures in all cases. However, CPA provides relatively low values with increasing pressure and decreasing temperature. In addition, it must be pointed out that, the difference between both models widens as the composition of n -decane increases. The ARD for the mixtures of n -decane and m -xylene are 0.48 % and 0.89 % with sPC-SAFT and CPA, respectively. It can be concluded sPC-SAFT has a better overall performance on

density predictions of the compounds considered, although CPA performs better under higher temperatures (for example at 363.15 K).

Figure 5. Comparison of experimental density data for the *n*-decane + *m*-xylene mixture with calculated densities from CPA and sPC-SAFT EoS. ■ 293.15 K; ● 303.15 K; ▲ 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 ($k_{ij}=0.0032$); dashed line, calculated liquid densities from CPA ($k_{ij}=1.9243 \times 10^{-4}$). Data for pure *n*-decane in (f) are from the previous work¹.

4.4 Excess molar volume

Excess molar volume (V^E) of the *n*-decane/*m*-xylene mixtures were calculated from the experimental data using the following expression:

$$V^E = \sum_i^n x_i M_i [1/\rho - 1/\rho_i] \quad (11)$$

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

The Redlich-Kister [36] polynomial was applied for the correlation of the excess molar volumes:

$$V^E = x(1-x) \sum_{i=0}^n A_i (2x-1)^i \quad (12)$$

where x denotes the mole fraction of *n*-decane, and A_i are the fitting parameters. The values of coefficients A_i and the standard deviations (σ) for the selected temperature and pressure conditions are presented in Table 7.

Table 7. Fitting parameters A_i of Eq. (12) and standard deviation σ for the selected pressures and temperatures for the *n*-decane(x) + *m*-xylene (1- x) mixtures.

	$T = 293.15 \text{ K}$	$T = 333.15 \text{ K}$	$T = 363.15 \text{ K}$	$T = 363.15 \text{ K}$	$T = 363.15 \text{ K}$
	$P = 0.1 \text{ MPa}$	$P = 0.1 \text{ MPa}$	$P = 0.1 \text{ MPa}$	$P = 30 \text{ MPa}$	$P = 60 \text{ MPa}$
$A_0 / \text{cm}^3 \cdot \text{mol}^{-1}$	1.740	2.043	2.207	2.042	1.960
$A_1 / \text{cm}^3 \cdot \text{mol}^{-1}$	-0.146	0.038	0.308	0.470	0.554
$A_2 / \text{cm}^3 \cdot \text{mol}^{-1}$	-0.931	-0.545	0.109	-0.377	-0.746
$\sigma / \text{cm}^3 \cdot \text{mol}^{-1}$	0.01	0.02	0.07	0.09	0.12

For the studied systems, the V^E values of *n*-decane/*m*-xylene mixtures are positive over the entire composition range and they increase with increasing temperature. On the other hand, as the pressure raising, the value of excess molar volume decreases, as shown in Figures 6 and 7. The increasing in the excess molar volume with increasing temperature is a result of the higher thermal expansivity of the mixtures compared to pure compounds, which results in a higher increase in the molar volume of the mixtures compared to pure compounds. This may be due to a

more loosely molecular packing, an enlargement of the free volume and Brownian motions. As the mixtures are compressed, the distance between the compounds will shorten and free volume will decrease, leading to reduction in the values of V^E .

Figure 6. Excess molar volume for the *n*-decane (*x*) + *m*-xylene (1-*x*) mixtures at 0.1 MPa and different temperatures. ■ 293.15 K; ● 333.15 K; ▲ 363.15 K. The red line denotes fitted results from Eq. (12). Dash-dot line (blue) and dashed line (black) correspond to predicted excess molar volume from sPC-SAFT and CPA, respectively.

Figure 7. Excess molar volume for *n*-decane (*x*) + *m*-xylene (1-*x*) mixtures at 363.15 K and different pressures. ■ 0.1 MPa; ● 30 MPa; ▲ 60 MPa. The red line denotes fitted results from Eq. (12). Dash-dot line (blue) and dashed line (black) correspond to predicted excess molar volume from sPC-SAFT and CPA, respectively.

Further, the values of the excess molar volume for the mixtures studied in this work have been predicted by sPC-SAFT and CPA EoS. The results are also shown graphically in Figures 6 and 7. The comparison reveals that, within the considered T , P range, the estimated excess molar volume from both models are positive and reasonably accurate and the predictions show a uniform trend with changing temperatures and pressures. Generally, better results were obtained with CPA model. Meanwhile, not only predictions from CPA are bigger than those from sPC-SAFT and fitted values, but also the deviation between results from CPA and fitted values would be larger as mole fraction of n -decane increases. According to another expression of excess molar volume as shown in Eq. (S25) in the Supporting Information, together with bigger molar volume for pure n -decane through CPA, it may cause errors to cancel out rather cascade. Furthermore, it is not difficult to Figure out why the two models appears to provide precise values of density but less accurate values for the excess molar volume. In general, excess volume is a quite small value corresponds to the difference between two large close numbers (molar volume of the mixture, molar volume of the ideal mixture) and thus any small deviations in those molar volumes may lead to serious deviations in excess volume. Detailed discussion and analysis can be found in Supporting Information.

The experimental excess molar volumes of n -decane/ m -xylene mixtures have been reported by Alonso *et al.*[37] at 298.15 K under atmospheric pressure. Because we do not measure the density data at 298.15 K, for comparative purposes, the corresponding excess molar volumes are derived from the fitting densities through Tait equation. Figure 8 shows the comparison between our results and Alonso's data. Similar variant trends of excess molar volumes were observed. However, there exists relatively large deviations between this work and literatures, and the maximum deviation located near $x=0.5$.

Figure 8. Excess molar volume for *n*-decane (*x*) + *m*-xylene (1-*x*) mixtures at 298.15 K under atmospheric pressure. ■ calculated data from this work; ● experimental data from Alonso *et al.*³⁷. The red line denotes fitting results from Eq. (12). Dash-dot line (blue) and dashed line (black) correspond to the predictive results from sPC-SAFT and CPA, respectively.

5. Conclusion

High-pressure liquid densities are reported for *m*-xylene and *n*-decane/*m*-xylene mixtures over the entire composition range from 293.15 K to 363.15 K and at pressures up to 60 MPa. The experimental densities were fitted with the modified Tammann-Tait equation with absolute relative deviation in comparison with available literature data less than 0.2% in most cases. Densities of the studied system were predicted with CPA and sPC-SAFT EoS with *ARD* of 0.89 % and 0.48 %, respectively. Furthermore, the excess molar volume of the studied mixtures is positive over the entire range studied, becoming more positive as temperature is increasing and as pressure is decreasing. Both CPA and sPC-SAFT EoS can give reasonable description for V^E , however, more precise results were obtained with CPA in this study.

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Notes

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ABBREVIATIONS

CPA, cubic plus association; sPC-SAFT, simplified perturbed-chain statistical associating fluid theory; EoS, equation of state; HTHP, high temperature and high pressure; DMA-HPM, Anton Paar vibrating-tube densimeter; SRK, Soave-Redlich-Kwong; PP, manual piston pump; TC, temperature controller; TS, Pt100 temperature sensor; PS, pressure sensor; CFP, constant-flux pump; SC, sample cylinder; TP, Turbo pump; RVVP, rotary vane vacuum pump; TB, thermostatic bath; EU, mPDS-5 unit; DMM, digital multimeter; PC, personal computer; *AAD*, average absolute deviation); *MRD*, maximum relative deviation; *bias*, average deviation; σ , standard deviation; VLE, vapour liquid equilibrium.

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Highlights

- High pressure density data of *n*-decane and *m*-xylene mixtures were reported.
- The sPC-SAFT and CPA EoSs were applied to predict the densities of *n*-decane and *m*-xylene and their mixtures.
- The effects of pressure and temperature on the excess molar volume were discussed.