

Vapor-Liquid Equilibrium of CO₂/toluene, CO₂/n-decane and CO₂/toluene/n-decane: Experimental Measurements and Thermodynamic Modeling

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ABSTRACT

Experimental vapor-liquid equilibrium data are reported in the present work for binary systems CO₂/toluene and CO₂/n-decane as well as for the ternary system CO₂/toluene/n-decane. The measurements were carried out in a high-pressure variable volume cell used to perform phase transition measurements by visual synthetic method. All systems were measured at temperatures of (313.2 and 353.2) K with carbon dioxide composition ranging from 0.2 to 0.8 mole fraction. The equilibrium data for the binary systems were used to estimate the cross interactions parameters of the Peng-Robinson equation of state combined with the quadratic mixing rule. The cross interaction parameter for the binary toluene/n-decane was estimated from data available in the open literature. In order to evaluate the capability of the binary parameters in predicting the ternary vapor-liquid equilibrium data, binary parameters were used to calculate the bubble pressure of the ternary mixture. For all evaluated systems the Peng-Robinson model correlated well the bubble pressure data.

INTRODUCTION

The discovery of oil reservoirs in the pre-salt layer has opened new perspectives for the Brazilian economy. In deep waters, with high levels of carbon dioxide and subjected to high-pressures and temperatures, oil exploration in the pre-salt layer is a considerable technological challenge. In petroleum recovery, carbon dioxide can be used to improve oil production where CO₂ is used to displace oil from the reservoir. Therefore knowledge of phase equilibrium data for CO₂/hydrocarbon systems is essential for studying the thermodynamic behavior in these oil fields [1,2].

In petroleum research, n-decane is a reference paraffinic compound used to represent kerosene fractions [3] while toluene is a typical naphtha molecule [4]. In this context, experimental vapor-liquid equilibrium (VLE) data are reported in the present work for binary systems CO₂/toluene and CO₂/n-decane as well as for the ternary system CO₂/toluene/n-decane at temperatures of (313.2 and 353.2) K to simulate the thermodynamic behavior of kerosene and naphtha fractions. These substances are asymmetrical in shape, length and chemical nature.

There are several works in literature with VLE data for CO₂/toluene [5,6,7] and CO₂/n-decane [2,8,9] systems at temperatures close to those reported in this work. In the present work, the experimental procedure and apparatus were validated comparing measured CO₂/toluene VLE data at (313.2 and 353.2) K with those reported by Naidoo

et al. [7], Ng and Robinson [5] and Walther et al. [6]. For binary system toluene/n-decane Willman and Teja [10] reported VLE data at 373.5 K. No VLE data for CO₂/toluene/n-decane system available in the open literature is of our knowledge. The binary VLE data were used to estimate the cross interactions parameters of the Peng-Robinson [11] model combined with the quadratic mixing rule [11,12], allowing the correlation of binary and ternary mixture data.

MATERIALS AND METHODS

Experimental section

The suppliers and weight fraction purities of the chemicals used in the study are shown in table 1. All chemicals were used without further purification. The vapor-liquid equilibrium measurements were carried out in a high-pressure variable volume cell used to perform phase transition measurements by visual static synthetic method. The high-pressure equilibrium apparatus was previously described in Rocha et al. [13].

Table 1: Suppliers and purity of chemicals used in the study.

Chemical	Supplier	Purity (mass fraction)	Purification Method
CO ₂	Linde Gases	>0.999	No further
Toluene	Tedia Company	>0.995	purification
n-Decane	Vetec Química Fina	>0.99	

The mixtures were prepared weighting a desired mass of each pure hydrocarbon using an analytical balance (Mettler Toledo AR2140) with a precision of $\pm 1 \cdot 10^{-4}$ g. The estimated uncertainty in the mole fractions was $\pm 2 \cdot 10^{-4}$.

The mixture of interest is transferred to the equilibrium cell with a funnel. The equilibrium cell is sealed and primary vacuum (low vacuum) is rapidly produced in the system to minimize the presence of air. Carbon dioxide was added to the reaction vessel with a syringe pump (Teledyne ISCO 260D). The syringe pump was thermostatically controlled by bath to maintain the temperature at 288.2 K and operated in constant pressure mode at 100 bar. At these conditions the density of CO₂ is 0.89010 g/cm³ [14]. Therefore, the mass of CO₂ transferred from the syringe pump to the high-pressure equilibrium cell can be quantified.

The equilibrium cell is wrapped with a heating tape and the system is heated to the desired temperature and pressurized until the gas and hydrocarbons form a single phase, by displacing the cell's steel piston with the syringe pump loaded with carbon dioxide as hydraulic fluid. The equilibrium cell is rested for 15 minutes, time necessary for equilibrium establishment, then the pressure is slowly decreased until incipient formation of a new phase, characterized by the appearance of small vapor bubbles in the cell.

Modeling

In thermodynamics an equation of state is a relation between state variables [15]. Cubic equations are the simplest equations able to represent the behavior of both liquids and vapors [16]. The Peng-Robinson (PR) model (Equation (1)) is a cubic equation of state that combines simplicity and accuracy and can be used to predict the vapor

pressure and volumetric behavior of single-component and multicomponent systems [11]:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (1)$$

where P is pressure, R is the universal gas constant, T is temperature and V is the molar volume. The parameters b and a are defined as (Equations (2)-(6)):

$$b = 0.07780 \frac{RT_c}{P_c} \quad (2)$$

$$a = a_c \alpha(T, \omega) \quad (3)$$

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (4)$$

$$\alpha(T, \omega) = \left[1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}} \right) \right] \quad (5)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (6)$$

where P_c is critical pressure, T_c is critical temperature and ω the acentric factor. The physical property information (P_c , T_c and ω) used for the pure components is taken from Poling et al. [17] and are presented in table 2.

Table 2: Pure component parameters for Peng-Robinson model.

Component	P_c /bar	T_c /K	ω
CO ₂	73.74	304.12	0.225
Toluene	41.08	591.75	0.264
n-Decane	21.10	617.70	0.490

For mixtures the following quadratic mixing rules (Equations (7)-(8)) were used [11,12]:

$$a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (7)$$

$$b = \sum_{i=1}^n x_i b_i \quad (8)$$

where n indicates the number of components in mixture and k_{ij} is a binary interaction parameter. To a good approximation, k_{ij} is considered independent of temperature, pressure and composition. In general, k_{ij} must be obtained from some experimental information about the binary interaction [12,18].

The deviations between experimental and calculated values of bubble pressure were calculated as follows (Equation (9)):

$$\text{Deviation} = BP^{exp} - BP^{calc} \quad (9)$$

where BP is the bubble pressure, superscripts $calc$ and exp stand for calculated and experimental, respectively.

The root-mean-square deviation (RMSD) was calculated using Equation (10):

$$\text{RMSD} = \sqrt{\frac{\sum_{i=1}^n (BP_i^{exp} - BP_i^{calc})^2}{n}} \quad (10)$$

where i indicates an experimental point and n indicates the number of experimental points.

The least squares method has been used to fit the values of the binary interaction parameters in order to minimize the following objective function (Equation (11)):

$$\text{Fobj} = \sum_{i=1}^n (BP_i^{exp} - BP_i^{calc})^2 \quad (11)$$

RESULTS

Tables 3 and 4 presents a comparison between physical properties of CO₂, toluene and n-decane obtained in this work and from the literature. Density at atmospheric pressure was obtained using an automatic digital densimeter (Anton Paar DMA 4500) calibrated with air and bi-distilled water and presenting an estimated standard uncertainty of $2 \cdot 10^{-5}$ g/cm³. The refractive index was measured using a ABBE refractometer. The refractometer was calibrated by measuring the refractive index of bi-distilled water and ethanol. The uncertainty in refractive index measurements is 0.0002. Saturation pressure of pure CO₂ was measured in the high-pressure equilibrium apparatus. The standard uncertainty in the temperature is 0.1 K and 1 bar for pressure [13]. There is a very good agreement between our data and those from literature.

Table 3: Comparison between saturation pressure for CO₂ obtained in this work and from literature.

Temperature/K	Pressure/bar	
	This work	Literature
301.5	69.3	69.5 [14]

Table 4: Comparison between pure components density and refractive index for toluene and n-decane obtained in this work and from literature.

Temperature/K	Density/(g/cm ³)		Refractive Index	
	This work	Literature	This work	Literature
293.2	0.86662	Toluene	1.4976	1.4970 [22]
		0.86683 [19]		
293.2	0.73006	0.866733 [20]	1.4120	1.41234 [21]
		n-Decane		
		0.73012 [21]		

Table 5 presents detailed results of VLE data obtained in this work for binary systems CO₂/n-decane and CO₂/toluene at temperatures of (313.2 and 353.2) K. All observed phase transitions showed a bubble pressure behavior.

Table 5: Experimental bubble pressures for binary systems [CO₂/n-decane] and [CO₂/toluene], at T = (313.2 and 353.2) K.

CO ₂ (1)/n-decane(2)				CO ₂ (1)/toluene(2)			
T/313.2 K		T/353.2 K		T/313.2 K		T/353.2 K	
P/bar	x_1	P/bar	x_1	P/bar	x_1	P/bar	x_1
21.5	0.2114	29.2	0.2114	24.2	0.1999	33.9	0.1999
39.6	0.4005	57.0	0.4005	42.9	0.3996	66.3	0.3996
58.1	0.5986	87.5	0.5986	56.5	0.5995	94.9	0.5995
73.9	0.7997	127.2	0.7997	70.3	0.8001	124.1	0.8001

For CO₂/toluene, figure 1 shows that the experimental bubble pressures are in good agreement with those from literature [5,6,7] at (313.2 and 353.2) K. Figure 1 also presents the calculated values with Peng-Robinson model for these systems. The calculated sets of data are in good agreement with the experimental data.

For CO₂/n-decane, figure 2 shows experimental bubble pressures compared to those from literature [2,8,9] at (313.2 and 353.2) K as well as the calculated values with Peng-Robinson model. Again, the calculated sets of data are in good agreement with the experimental data.

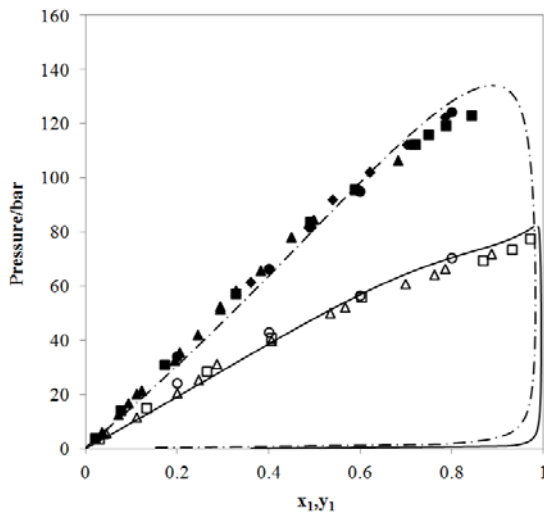


Figure 1: VLE data for CO₂(1)/toluene(2): ○, (313.2 K), ●, (353.2 K), this work; △, (311.15 K), ▲, (353.15 K), Naidoo et al. [7]; □, (311.3 K), ■, (352.6 K), Ng and Robinson [5]; ◆, (352.0 K), Walther et al. [6]. Lines were calculated with PR model using coefficients given in table 6, at: —, 313.2 K; - - -, 353.2 K.

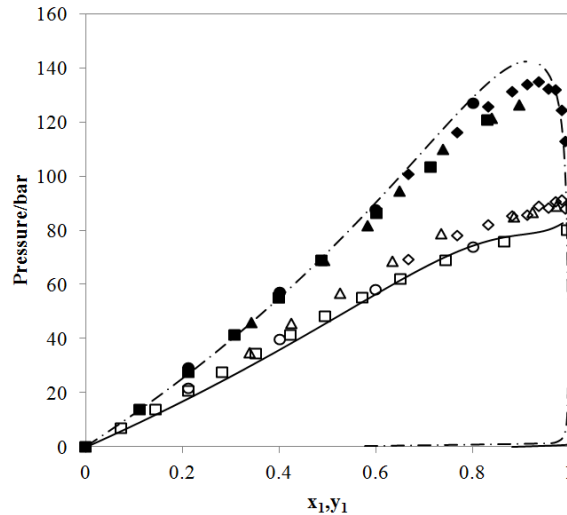


Figure 2: VLE data for CO₂(1)/n-decane(2): ○, (313.2 K), ●, (353.2 K), this work; △, (319.11 K), ▲, (344.74 K), Jiménez-Gallegos et al. [2]; □, (310.9 K), ■, (344.3 K), Reamer and Sage [8]; ◇, (318.1 K), ◆, (348.1 K), Zamudio et al. [9]. Lines were calculated with PR model using coefficients given in table 6, at: —, 313.2 K; - - -, 353.2 K.

The fitted values for the binary interaction parameters are summarized in table 6. The bubble pressure data obtained in this work were used to estimate the binary interaction parameters for systems CO₂/toluene and CO₂/n-decane. For system toluene/n-decane the bubble pressure data reported by Willman and Teja [10] at 373.5 K were used.

Figure 3 presents a comparison between experimental VLE data obtained from Willman and Teja [10] at 373.5 K and calculated values with Peng-Robinson model for toluene/n-decane system. As one can see, the proposed model correlated well the experimental data.

Table 6: Binary interaction parameters for Peng-Robinson model.

Binary system	k_{12}
CO ₂ (1)/toluene(2)	0.0789
CO ₂ (1)/n-decane(2)	0.0951
toluene(1)/n-decane(2)	-0.0176

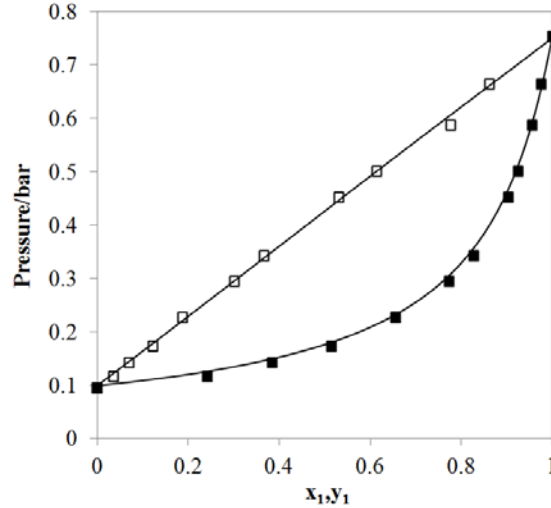
**Figure 3:** VLE data for toluene(1)/n-decane(2) at 373.5 K: ■, Willman and Teja [10]. Dark and open symbols denote the vapor and liquid phases, respectively. Lines were calculated with PR model using coefficients given in table 6 at 373.5 K.

Table 7 presents detailed results of VLE data obtained in this work for system CO₂/toluene/n-decane at temperatures of (313.2 and 353.2) K. Again, all observed phase transitions showed the same behavior of a bubble point transition.

Table 7: Experimental bubble pressures for ternary system [CO₂(1)/toluene(2)/n-decane(3)], at T = (313.2 and 353.2) K.

T/313.2 K			T/353.2 K		
P/bar	x_1	x_2	P/bar	x_1	x_2
19.3	0.1997	0.4026	27.5	0.1997	0.4026
38.3	0.3999	0.3019	57.2	0.3999	0.3019
55.5	0.6007	0.2009	89.5	0.6007	0.2009
68.9	0.7993	0.1015	123.1	0.7993	0.1015
16.9	0.1890	0.2602	24.6	0.1890	0.2602
39.0	0.4016	0.1920	59.1	0.4016	0.1920
55.5	0.5933	0.1305	89.4	0.5933	0.1305
70.2	0.8002	0.0679	125.1	0.8002	0.0679
27.4	0.2993	0.4634	41.8	0.2993	0.4634
42.4	0.4598	0.3573	67.7	0.4598	0.3573
58.2	0.6504	0.2312	99.0	0.6504	0.2312
67.7	0.8003	0.1334	125.5	0.8003	0.1334

The deviations in bubble pressure between experimental and calculated values for all systems are shown in figures 4 and 5. The calculated RMSD was of 2.6 bar, which is higher than the experimental standard uncertainty for pressure, estimated as 1

bar. As one can see, for temperatures of (313.2 and 353.2) K the calculated data sets using the Peng-Robinson model with quadratic mixing rules provided positive deviations when carbon dioxide composition was lower than 0.5 mole fraction and negative deviations for higher compositions of CO₂. The calculated data sets for ternary system shows a tendency to superestimate the bubble pressure, especially at compositions close to the critical point of this mixture. This could be to the fact that only one binary interaction parameter, independent of temperature, pressure and composition could not represent all system non-ideality.

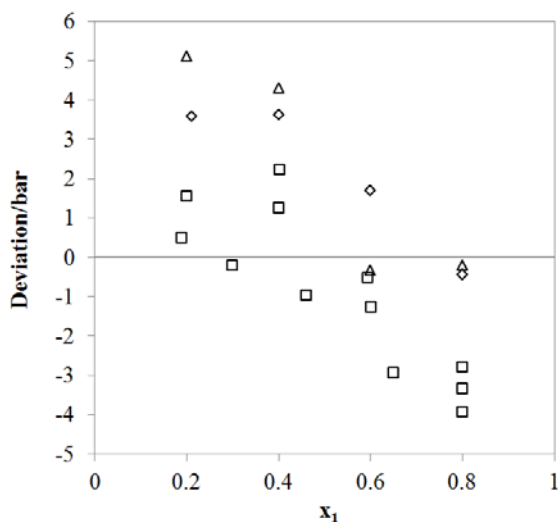


Figure 4: Deviations between experimental and calculated bubble pressures at 313.2 K: ◇, CO₂(1)/n-decane(2); △, CO₂(1)/toluene(2); □, CO₂(1)/toluene(2)/n-decane(3).

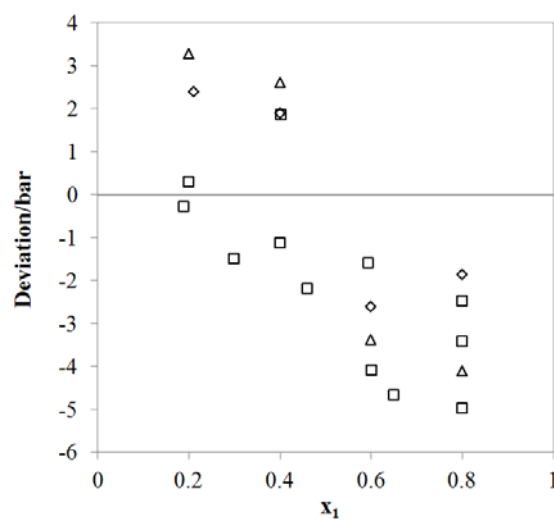


Figure 5: Deviations between experimental and calculated bubble pressures at 353.2 K: ◇, CO₂(1)/n-decane(2); △, CO₂(1)/toluene(2); □, CO₂(1)/toluene(2)/n-decane(3).

CONCLUSION

In this work we have experimentally determined bubble pressure data for the binary systems CO₂/toluene and CO₂/n-decane and for the ternary system CO₂/toluene/n-decane. Data are reported at T = (313.2 and 353.2) K with carbon dioxide composition ranging from 0.2 to 0.8 mole fraction. The experimental results were compared to those available in open literature showing a good agreement.

The experimental data of binary systems were used to estimate the cross interaction parameters for the Peng-Robinson model allowing the correlation of binary and ternary mixture data. Although the proposed model with only one cross interaction parameter independent of temperature, pressure and composition for each binary mixture failed to correlate the experimental bubble pressure dependency with composition, as a qualitative model the Peng-Robinson equation correlated well the bubble pressure data for all evaluated systems.

REFERENCES

- [1] CHOU, G.F., FORBERT, R.R., PRAUSNITZ, J.M., J. Chem. Eng. Data, Vol. 35, **1990**, p. 26
- [2] JIMÉNEZ-GALLEGOS, R., GALICIA-LUNA, L.A., ELIZALDE-SOLIS, O., J. Chem. Eng. Data, Vol. 51, **2006**, p. 1624
- [3] WANG, Q.D., FANG, Y.M., WANG, F., LI, X.Y., Proceedings of the Combustion Institute, Vol. 34, **2013**, p. 187

- [4] SILVA, A.A., REIS, R.A., PAREDES, M.L.L., J. Chem. Eng. Data, Vol. 54, **2009**, p. 2067
- [5] NG, H.J., ROBINSON, D.B., J. Chem. Eng. Data, Vol. 23, **1978**, p. 325
- [6] WALTHER, D., PLATZER, B., MAURER, G., J. Chem. Thermodynamics, Vol. 24, **1992**, p. 387
- [7] NAIDOO, P., RAMJUGERNATH, D., RAAL, J.D., Fluid Phase Equilibria, Vol. 269, **2008**, p. 104
- [8] REAMER, H.H., SAGE, B.H., J. Chem. Eng. Data, Vol. 8, **1963**, p. 508
- [9] ZAMUDIO, M., SCHWARZ, C.E., KNOETZE, J.H., J. of Supercritical Fluids, Vol. 59, **2011**, p. 14
- [10] WILLMAN, B., TELA, A.S., J. Chem. Eng. Data, Vol. 30, **1985**, p. 116
- [11] PENG, D.Y., ROBINSON, D.B., Ind. Eng. Chem. Fundam., Vol. 15, **1976**, p. 59
- [12] CHUEH, P.L., PRAUSNITZ, J.M., Ind. Eng. Chem. Fundam., Vol. 6, **1967**, p. 492
- [13] ROCHA, I.C.C., FIALHO, R.L., MARQUES, J.J., DARIVA, C., PESSOA, F.L.P., J. Chem. Thermodynamics, Vol. 65, **2013**, p. 11
- [14] LEMMON, E.W., MCLINDEN, M.O., FRIEND, D.G., NIST Chemistry WebBook, Num. 69, **Accessed January 9, 2014**, <http://webbook.nist.gov>
- [15] PERROT, P., A to Z of Thermodynamics, **1998**
- [16] SMITH, J.M., VAN NESS, H.C., ABBOTT, M.M., Introdução à Termodinâmica da Engenharia Química, 7a Edição, **2007**
- [17] POLING, B.E., PRAUSNITZ, J.M., O'CONNELL, J.P., The Properties of Gases and Liquids, 5th Edition, **2001**
- [18] ZUDKEVITCH, D., JOFFE, J., AIChE Journal, Vol. 16, **1970**, p. 112
- [19] HALES, J.L., TOWNSEND, R., J. Chem. Thermodynamics, Vol. 4, **1972**, p. 763
- [20] SOMMER, D., KLEINRAHM, R., SPAN, R., WAGNER, W., J. Chem. Thermodynamics, Vol. 43, **2011**, p. 117
- [21] PAREDES, M.L.L., REIS, R.A., SILVA, A.A., SANTOS, R.N.G., SANTOS, G.J., RIBEIRO, M.H.A., XIMANGO, P.B., J. Chem. Thermodynamics, Vol. 45, **2012**, p. 35
- [22] NAIN, A.K., J. Chem. Eng. Data, Vol. 53, **2008**, p. 850