



The effect of the naphthenic ring on the VLE of (carbon dioxide + alkane) mixtures



Sergiu Sima^a, Juan Manuel Milanese^b, Juan Ignacio Ramello^b, Martin Cismondi^{b,*}, Catinca Secuianu^{a,*}, Viorel Feroiu^a, Dan Geană^a

^a Department of Inorganic Chemistry, Physical Chemistry & Electrochemistry, Faculty of Applied Chemistry & Materials Science, University Politehnica of Bucharest, 1-7 Gh. Polizu Street, S1, 011061 Bucharest, Romania

^b IDTQ-Grupo Vinculado PLAPIQUI-CONICET, Facultad de Ciencias Exactas Físicas y Naturales, Universidad Nacional de Córdoba, Av. Vélez Sarsfield 1611, Ciudad Universitaria, X5016GCA Córdoba, Argentina

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ABSTRACT

Isothermal (vapour + liquid) equilibrium (VLE) data for the binary systems (carbon dioxide + cyclopentane) and (carbon dioxide + cyclohexane) were determined using a (static + analytical) method with phases sampling by rapid online sample injectors (ROLSI) coupled to a gas chromatograph (GC) for analysis.

The VLE behaviour for these systems was also analysed based on the PR and RKPR equations of state (EoS) and different available data from the literature, both critical and subcritical. It is clearly shown how CO₂ is more soluble and miscible with normal alkanes than with the corresponding cycloalkanes. Predictions based on the general correlation of available data in wide ranges of conditions suggest the appearance of double retrograde behaviour at least for (CO₂ + cyclohexane) mixtures with very low contents of the hydrocarbon in CO₂, being this phenomenon very much related to asymmetry of the system. The existence of this phenomenon has not been experimentally confirmed yet for these systems and should be explored.

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1. Introduction

Carbon dioxide (CO₂) capture and storage (CCS) is one of the major options for mitigation of greenhouse gases, as over 80% are CO₂ emissions produced by industrial and energy-related sources [1]. Many researchers focused on CCS, e.g. CO₂ capture technologies, separation technologies, transport, utilisation, geological storage, leakage, and monitoring [2]. In this context, the study of the phase behaviour of fluid mixtures of relevance for CCS is of fundamental importance. Among these relevant fluid mixtures are the (carbon dioxide + hydrocarbons) systems [3]. Although there are many experimental and theoretical studies on the (carbon dioxide + n-alkanes) series [4,5], some issues still need to be addressed, while other (carbon dioxide + hydrocarbon) systems are less investigated [6–8]. Therefore, we started a systematic study regarding other types of carbon dioxide + hydrocarbons mixtures than (CO₂ + n-alkanes). Previously [9], we compared different thermodynamic models to represent the high-pressure phase behaviour

* Corresponding authors.

E-mail addresses: mcismondi@efn.uncor.edu (M. Cismondi), c_secuianu@chim.upb.ro (C. Secuianu).

of (carbon dioxide + cycloalkane) systems. Particularly, in this study we measured new (vapour + liquid) equilibrium data for the (carbon dioxide + cyclopentane) at T = (323.15, 333.15, 344.65, and 353.15) K and pressures up to 100.3 bar, and (carbon dioxide + cyclohexane) binary systems at T = (323.15 and 353.15) K and pressures up to 110.2 bar. In addition to CCS, the new measurements can be also useful to the design of enhanced oil recovery (EOR) projects [10,11]. The (carbon dioxide + cyclopentane) system was previously investigated by Eckert and Sandler [12], Marathe and Sandler [13], and Shah *et al.* [14], who reported (vapour + liquid) equilibrium data at temperatures from (274.64 to 493.11) K and pressures up to 122 bar [9,15–16] and critical points, while the (carbon dioxide + cyclohexane) binary system has received much attention [15,16], as can be seen from table 1 where the experimental conditions (temperature, pressure range, number of experimental points, phase compositions) of the available information on the later system are summarised. However, experimental data measured at atmospheric pressure were not mentioned here. There are also several papers reporting critical data for the (carbon dioxide + cyclohexane) system [29–33]. Although reported in the literature are many isothermal results (see table 1) for this system, most of them report only the

TABLE 1
Literature VLE data for the {carbon dioxide (1) + cyclohexane (2)} binary system.

T/K	10 p_{range} /MPa	NEXP ^a	Observations ^b	References
273.15	7.67 to 30.57	7	$p-x_1$	[17]
273.16	5.39 to 29.79	5	$p-x_1$	[18]
278.16	6.86 to 29.40	5	$p-x_1$	[18]
283.15	8.73 to 38.56	7	$p-x_1$	[17]
283.16	8.13 to 33.41	5	$p-x_1$	[18]
288.16	7.44 to 41.16	5	$p-x_1$	[18]
293.00	39.0 to 53.3	10	$p-x_1$	[19]
293.15	9.20 to 58.10	16	$p-x_1, y_1$	[20]
298.15	10.34 to 52.77	7	$p-x_1$	[17]
298.16	7.54 to 42.82	5	$p-x_1$	[18]
303.00	45.90 to 64.10	10	$p-x_1$	[19]
303.15	9.70 to 66.60	10	$p-x_1, y_1$	[20]
303.15	10.91 to 58.05	7	$p-x_1$	[17]
308.15	33.0 to 70.0	6	$p-x_1$	[21]
313.00	52.10 to 75.60	9	$p-x_1$	[19]
313.15	10.0 to 82.20	10	$p-x_1, y_1$	[20]
313.15	8.90 to 61.90	9	$p-x_1$	[22]
313.45	24.10 to 70.60	8	$p-x_1, y_1$	[23]
313.50	8.60 to 36.10	7	$p-x_1$	[24]
318.15	33.30 to 72.50	5	$p-x_1$	[21]
323.00	58.40 to 87.40	8	$p-x_1$	[19]
323.15	10.70 to 86.50	9	$p-x_1, y_1$	[20]
323.30	28.30 to 75.50	8	$p-x_1, y_1$	[23]
333.00	65.10 to 97.50	7	$p-x_1$	[18]
333.15	34.60 to 86.00	6	$p-x_1$	[21]
333.15	10.80 to 81.70	9	$p-x_1$	[22]
343.15	33.80 to 96.70	7	$p-x_1$	[21]
344.26	68.70 to 109.70	16	$p-x_1, y_1$	[25]
348.20	19.79 to 90.0	6	$p-x_1$	[26]
352.70	26.40 to 49.80	7	$p-x_1$	[24]
353.15	12.70 to 100.20	9	$p-x_1$	[22]
366.00	102.0 to 119.70	3	$p-y_1$	[27]
366.50	51.91 to 128.0	7	$p-x_1, y_1$	[28]
373.20	28.41 to 99.95	7	$p-x_1$	[26]
392.00	30.90 to 56.40	8	$p-x_1$	[24]
410.80	17.18 to 144.41	3	$p-x_1, y_1$	[28]
410.90	34.44 to 138.14	9	$p-x_1, y_1$	[28]
423.20	34.03 to 104.28	7	$p-x_1$	[26]
473.15	13.38 to 129.70	8	$p-x_1, y_1$	[29]
483.15	15.71 to 122.60	8	$p-x_1, y_1$	[29]
493.15	18.24 to 115.51	5	$p-x_1, y_1$	[29]
503.15	20.97 to 106.90	7	$p-x_1, y_1$	[29]
513.15	24.32 to 97.27	6	$p-x_1, y_1$	[29]
523.15	28.27 to 84.10	6	$p-x_1, y_1$	[29]
533.15	31.71 to 69.91	5	$p-x_1, y_1$	[29]

^a Number of experimental points.^b p – experimental pressure, x_1 – mole fraction of the CO₂ in the liquid phase, y_1 – mole fraction of the CO₂ in the vapour phase.

composition of the liquid phase and not on the entire range of pressure, up to the critical point of the mixture.

Besides providing new data, the goal in this work is to analyse the fluid phase behaviour of (carbon dioxide + cycloalkane) mixtures, in comparison to the binaries with the corresponding normal alkanes, and at the same time to evaluate the capacity of equations of state to represent qualitatively and quantitatively these behaviours. For that objective, we chose the more common and probably important alkanes of this type, namely cyclopentane and cyclohexane. The models chosen for the study were the Peng–Robinson (PR) equation of state (EoS) [34], given its wide industrial application, and the more flexible three-parameters RKPR EoS [35]. In very recent works this latter model has been shown to be

capable of a very accurate representation of the phase behaviour for the more asymmetric alkane mixtures, where the classic two-parameter equations, e.g. SRK and PR, fail [36,37]. In addition, for the EOR applications the minimum miscibility pressure (MMP) calculations require EoS very accurate in the critical region [38].

2. Experimental

2.1. Materials

Carbon dioxide (mass fraction purity > 0.997) was provided by Linde Gaz Romania, Bucharest, Romania, cyclopentane (mass fraction purity > 0.98), and cyclohexane (mass fraction purity \geq 0.999) were Sigma–Aldrich products, as presented in table 2. The chemicals were used as supplied, except for drying of the cycloalkanes. Gas chromatographic analyses of the cycloalkanes were also performed and they confirmed the stated purity by the manufacturer.

2.2. Apparatus and procedure

The experimental setup was previously described in detail [39–42]. The main component of the experimental apparatus used in this work is the high-pressure visual cell with variable volume [39,40], coupled with a sampling and analysing system [41,42]. The sampling system consists of two high-pressure electromechanical sampling valves, namely the rapid on-line sampler injector (ROLSI™, MINES ParisTech/CEP-TEP – Centre énergétique et procédés, Fontainebleau, France [43]). The ROLSI valves are connected to the equilibrium visual cell and to a gas chromatograph (GC) through capillaries. The expansion chamber of the sampler injector is heated with a heating resistance so the liquid samples are rapidly vaporised. A linear resistor coupled to an Armines/CEP/TEP regulator is used to heat the transferring lines between ROLSI and the GC. The GC (Perichrom, France) is equipped with a thermal conductivity detector, TCD, and a HP-Plot/Q column 30 m long and 0.530 mm diameter. Helium is the GC carrier gas at a flow rate of 30 mL · min⁻¹. The setup is completed with a syringe pump Teledyne ISCO model 500D. As the working procedure is similar as in our previous studies [39–42], here it will be briefly described. Firstly, the entire internal loop of the apparatus including the equilibrium cell is rinsed several times with carbon dioxide. Then, a vacuum pump is used to evacuate the equilibrium cell. The cell is charged with the organic substance, which is previously degassed by using a vacuum pump and vigorously stirring. The lighter component (in this case CO₂) is filled with the syringe pump into equilibrium cell and the pressure is set to the desired value. Then the cell is heated to the experimental temperature. The mixture in the cell is stirred for a few hours to facilitate the approach to an equilibrium state. Then the stirrer is switched off, and about 1 h is allowed to pass until the coexisting phases are completely separated. Samples of the liquid and vapour phases are withdrawn by ROLSI and analysed with the GC. In order to check the repeatability, at least six samples of the liquid phase are normally analysed at the equilibrium temperature and pressure. The sample sizes being very small, the equilibrium pressure in the cell remains constant.

TABLE 2
Provenance and mass fraction purity of the materials.

Compound	Chemical formula	Source	Purification method	Minimum mass fraction purity
Carbon dioxide	CO ₂	Linde Gaz Romania	None	>0.997
Cyclopentane	C ₅ H ₁₀	Sigma–Aldrich	None	>0.980
Cyclohexane	C ₆ H ₁₂	Sigma–Aldrich	None	\geq 0.999

TABLE 3
Pure compound parameters for the RK-PR EoS (this work).

Compound	ID	$10 a_c/\text{MPa} \cdot \text{L}^2 \cdot \text{mol}^{-2}$	$b/\text{L} \cdot \text{mol}^{-1}$	δ_1	K
Carbon dioxide	CO ₂	3.7859	0.028696	1.500000	2.28138
n-Pentane	C5	20.2237	0.093631	1.957315	2.28763
n-Hexane	C6	26.4457	0.111805	2.057565	2.45609
Cyclopentane	Cyc5	18.9220	0.070011	3.000000	1.81752
Cyclohexane	Cyc6	24.4730	0.083709	3.000000	1.87108

TABLE 4
Experimental critical values selected for the objective function for the system {carbon dioxide (1) + alkane (2)}: critical temperature, T_c , critical pressure, p_c , and compressibility factor, z_c .

Compound	T_c/K	$10p_c/\text{MPa}$	$z_c(\text{CO}_2)$	References
n-Pentane	404.80	93.15	0.6687	Poettmann and Katz [46]
	368.40	99.28	0.7988	
n-Hexane	387.00	117.20	0.7800	Liu et al. [47]
	332.90	94.30	0.9350	
Cyclopentane	403.07	122.00	0.6520	Shah et al. [14]
	328.23	89.70	0.9110	
Cyclohexane	461.75	136.40	0.7040	Zhang et al. [33]
	322.75	90.50	0.9783	Zhang et al. [32]

TABLE 5
Experimental bubble point values selected for the objective function for the system {carbon dioxide (1) + alkane (2)}: temperature, T , pressure, p , liquid mole fraction of CO₂, x_{CO_2} .

Compound 2	T/K	$10p/\text{MPa}$	x_{CO_2}	Reference
n-Hexane	273.15	24.02	0.5341	Kaminishi et al. [17]
	283.15	29.23	0.5341	
Cyclohexane	273.15	25.60	0.4235	
	283.15	30.90	0.4235	

TABLE 6
Experimental (liquid + vapour) values selected for the objective function for the system {carbon dioxide (1) + alkane (2)}: temperature, T , pressure, p , mole fraction of CO₂ in the liquid and vapour phases, x_{CO_2} , y_{CO_2} .

Compound 2	T/K	$10p/\text{MPa}$	x_{CO_2}	y_{CO_2}	Reference
n-Pentane	277.60	22.39	0.4860	0.9846	Besserer and Robinson [48]
	310.15	38.63	0.4440	0.9510	
	333.15	51.65	0.4450	0.9190	Tochigi et al. [49]
	343.40	49.64	0.3790	0.8960	
	344.15	39.34	0.3030	0.8936	Besserer and Robinson [48]
	363.15	50.00	0.3170	0.8390	
	377.60	44.99	0.2550	0.7854	Besserer and Robinson [48]
	423.48	49.16	0.2010	0.5443	
	438.15	38.40	0.1050	0.3546	Leu and Robinson [52]
	n-Hexane	303.15	39.55	0.5060	0.9815
313.15		40.52	0.4450	0.9748	
313.15		58.19	0.6870	0.9850	Li et al. [54]
353.15		67.09	0.4860	0.9470	
353.15		91.49	0.6830	0.9300	
393.15		77.57	0.4330	0.8770	
Cyclopentane		276.64	18.62	0.2740	0.9830
	293.14	15.31	0.1560	0.9640	
	293.14	35.92	0.4790	0.9770	
	344.70	37.16	0.2130	0.9100	
	344.70	74.83	0.5080	0.9270	
	419.15	51.35	0.1680	0.6750	
	419.15	97.41	0.3820	0.7200	
	463.23	61.44	0.1540	0.4450	
Cyclohexane	293.14	29.00	0.2970	0.9902	Zhang and Zheng [20]
	293.15	47.26	0.7400	0.9943	
	323.15	35.60	0.2410	0.9818	
	323.15	66.10	0.5420	0.9858	
	410.90	51.51	0.2050	0.8593	Shibata and Sandler [28]
	410.90	120.56	0.5160	0.8636	
	503.15	70.93	0.1950	0.5000	Krichevskii and Sorina [29]
	523.15	60.80	0.1600	0.3230	

The calibration of the TCD for CO₂, cyclopentane, and cyclohexane is done by injecting known amounts of each component using gas chromatographic syringes. Calibration data are fitted to quadratic polynomials to obtain the mole number of the component versus chromatographic area. The correlation coefficients of the GC calibration curves were 0.999 for carbon dioxide, 0.999 for cyclopentane, and 0.998 for cyclohexane.

For the phase equilibrium compositions, the relative uncertainty of the mole fraction in the liquid and vapour phases was calculated using the procedure given by Scheidgen [44], equations (5–2, 5–3, 5–4, 5–6), p. 194–196. The average relative uncertainty was <2%. As usually in the literature [45], we report the mole fractions with four decimal places. The uncertainties of the measurements were estimated to be within 0.1 K for temperature. The platinum temperature probe connected to a digital indicator was calibrated against the calibration system Digital Precision Thermometer with PT 100 sensor (Romanian Bureau of Legal Metrology). The uncertainty of platinum probe is estimated to be within $T = \pm 0.1$ K using a similar procedure as described in [45]. The pressure transducer connected to a digital multimeter was calibrated at $T = 323.2$ K with a precision hydraulic dead-weight tester (model 580C, DH-Budenberg SA, Aubervilliers, France). The uncertainty of the pressures is estimated to be within ± 0.015 MPa using a similar

procedure as described in [48], for a pressure range between (0.5 and 20) MPa.

Critical points were also measured in this study, following the procedure described by Scheidgen [44]. Thus, the pressure in the equilibrium cell is increased by introducing CO₂ with the syringe pump at a fixed temperature. The transition from heterogeneous (two phases) to the homogeneous range is visually observed. Then, by slowly cooling ($T = 1$ to 3 K) the pressure in the cell decreases, and the inverse transition from homogeneous to heterogeneous range can be observed. The temperature and the pressure of the opalescence point are considered as critical data points. The composition of the critical point is obtained by sampling from the homogeneous mixture. The procedure is then repeated by introducing new amounts of CO₂ and slowly cooling.

3. Modelling

The models chosen for this study were the Peng–Robinson (PR) EoS [34], given its wide industrial application, and the more flexible three-parameter RKPR EoS [35]. In very recent works [36,37] this latter model has been shown to be capable of a very accurate representation of the phase behaviour of the more asymmetric alkane mixtures, where typical two-parameter equations like SRK and PR fail. Classic van der Waals quadratic mixing rules were used in both cases. The pure compound parameters used in this work for the RKPR EoS are given in table 3.

With the goal of analysing the fluid phase behaviour of (CO₂ + cycloalkane) mixtures, in comparison to the binaries with the corresponding normal alkanes, and at the same time to evaluate the capacity of the chosen equations of state to represent qualitatively and quantitatively these behaviours, we performed a careful selection of literature data in wide ranges of conditions, for the binaries of CO₂ with n-pentane, n-hexane, cyclopentane, and cyclohexane. Such data, including critical points, bubble points, and VLE compositions, are resumed in tables 4–6.

A special objective function (OF), defined by Cismondi *et al.* [4] and used also in other publications [36,37], was used to optimise the interaction parameters for both models based on the data in tables 4–6 and following the same procedure. The optimum binary interaction parameters, k_{ij} and l_{ij} , together with the achieved minimum OF values are presented in table 7. The minimum OF values are similar for both models, and only for CO₂ + cyclohexane (the most asymmetric among the four systems studied, in terms of volatility) the difference is more important, in favour of the RKPR EoS.

4. Results and discussion

4.1. Predictions and comparison of phase behaviour (based on literature data)

Using the software GPEC, based on the algorithms and methods by Cismondi and Michelsen [55,56], predictions from both PR and RKPR models with parameters from tables 3 and 7 were obtained

TABLE 7
Optimised interaction parameters, k_{ij} , l_{ij} , and the corresponding minimum values for the objective function, for (CO₂ + alkane) systems, with the PR and RKPR EoS.

Compound 2	PR EoS			RKPR EoS		
	k_{ij}	l_{ij}	min OF	k_{ij}	l_{ij}	min OF
n-Pentane	0.1265	0.0022	2.0378	0.1335	-0.0170	2.2422
n-Hexane	0.1162	0.0018	1.6511	0.1220	-0.0283	1.5944
cyclopentane	0.1033	-0.0446	1.2804	0.1142	-0.0974	1.5135
cyclohexane	0.1251	-0.0276	3.2220	0.1308	-0.0861	2.7559

TABLE 8

VLE of the {carbon dioxide (1) + cyclopentane (2)} system at $T = (323.15, 333.15, 344.65, \text{ and } 353.15) \text{ K}^a$

p/MPa	x_1	y_1	p/MPa	x_1	y_1
$T/K = 323.15 \pm 0.1$					
1.02	0.0973	0.9280	5.00	0.4895	0.9816
2.02	0.1889	0.9609	6.01	0.6086	0.9770
3.01	0.2869	0.9742	7.01	0.7306	0.9633
4.02	0.3887	0.9798	8.02	0.8550	0.9562
$T/K = 333.15 \pm 0.1$					
1.01	0.0837	0.8920	6.01	0.5196	0.9800
2.01	0.1673	0.9387	7.01	0.6174	0.9812
3.00	0.2524	0.9604	8.01	0.7305	0.9617
4.02	0.3401	0.9756	9.03	0.8404	0.9376
5.00	0.4273	0.9793			
$T/K = 344.65 \pm 0.1$					
0.63	0.0442	0.7674	5.61	0.4278	0.9764
1.49	0.1107	0.8837	6.55	0.5067	0.9775
2.57	0.1998	0.9236	7.54	0.5920	0.9673
3.61	0.2763	0.9459	8.63	0.6869	0.9480
4.58	0.3526	0.9719	9.62	0.7775	0.9135
$T/K = 353.15 \pm 0.1$					
1.18	0.0796	0.8418	6.01	0.4191	0.9765
2.02	0.1419	0.8943	7.00	0.5026	0.9742
3.00	0.2127	0.9275	8.01	0.5866	0.9587
4.01	0.2822	0.9738	9.02	0.6567	0.9350
5.01	0.3558	0.9766	10.03	0.7341	0.8989

^a Standard uncertainties u are $u(T) = 0.1 \text{ K}$, $u(p) = 0.015 \text{ MPa}$, $u(x_1, y_1) = 0.005$.

for critical lines and isothermal p - x , y diagrams at different conditions. The Peng–Robinson pure compound parameters are the typical ones, *i.e.* obtained from critical temperature and pressure, and acentric factor of each compound.

Figures 1 and 2 show the predicted critical lines for the binary systems of CO₂ with both the paraffins and the corresponding naphthenes as number of carbons, namely the pentanes and hexanes respectively. It is well known that the (carbon dioxide + n-alkane) systems up to n-dodecane exhibit type II phase behaviour, the carbon dioxide + n-tridecane corresponds to type IV phase behaviour, while the mixtures of CO₂ with n-tetradecane or with longer n-alkanes exhibit type III phase

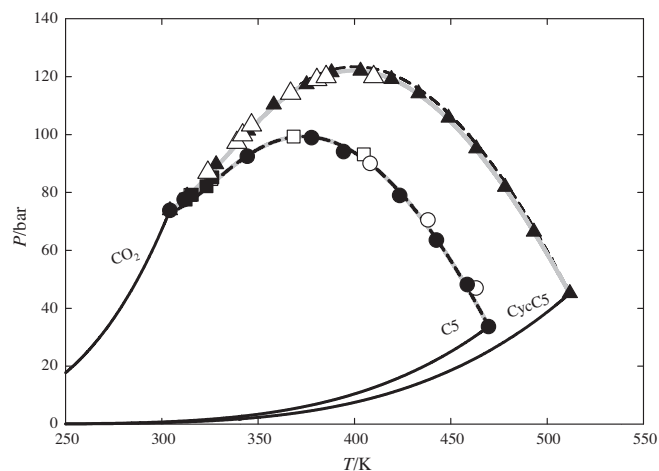


FIGURE 1. Predictions from interaction parameters in table 7, in comparison to literature data for critical lines in the CO₂ mixtures with n-pentane and cyclopentane. Solid black lines (—): vapour pressure curves; solid gray line (—): critical line predicted by RKPR EoS; dashed black lines (---): critical line predicted by PR EoS; empty squares (□): data by Poettmann and Katz [46]; black filled squares (■): data by Chen *et al.* [57]; empty circles (○): data by Leu and Robinson [52]; black filled circles (●): data by Cheng *et al.* [51]; black filled triangles (▲): data by Shah *et al.* [14]; empty triangles (△): critical data measured in this work.

behaviour [4]. Instead for the mixtures of CO₂ with cycloalkanes no experimental evidence was found regarding the type of phase behaviour. However, the carbon (dioxide + cyclopentane) and (carbon dioxide + cyclohexane) systems can be attributed to type I or type II phase behaviour, according to the classification of van Konynenburg and Scott [59] or the more recent one of Privat and Jaubert [60]. Type I is characterised by a continuous (liquid + vapour) critical curve ending in the critical points of the pure components, while type II has an additional (liquid + liquid) critical curve intersecting in an upper critical endpoint with a three phases (liquid + liquid + vapour) equilibrium curve stretching to lower temperatures.

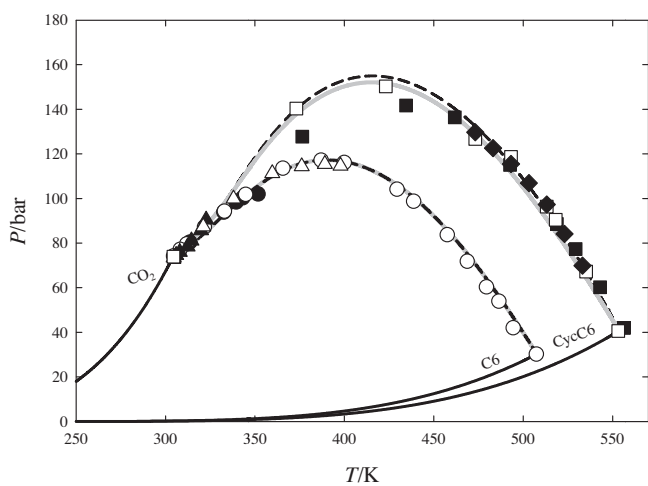


FIGURE 2. Predictions from interaction parameters in table 7 in comparison to literature data for critical lines in the CO₂ mixtures with n-hexane and cyclohexane. Solid black lines (—): vapour pressure curves; solid gray line (—): critical line predicted by RKPR EoS; dashed black lines (---): critical line predicted by PR EoS; empty squares (□): data by Sorina [30]; black filled squares (■): data by Zhang et al. [33]; empty circles (○): data by Liu et al. [47]; black filled circles (●): data by Choi and Yeo [58]; empty triangles (△): data by Leder and Irani [31]; black filled triangles (▲): data by Zhang et al. [33]; black filled rhombuses (◆): data by Krichevskii and Sorina [29].

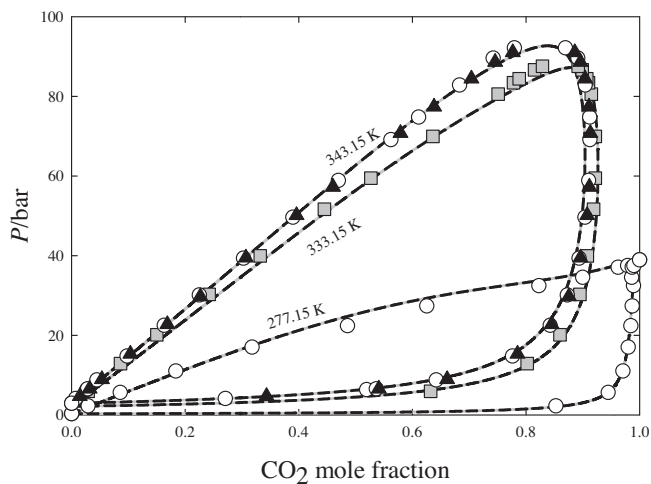


FIGURE 3. Predictions from interaction parameters in table 7, in comparison to literature VLE data for the system (CO₂ + n-pentane). Solid gray line (—): isothermal predictions using RKPR EoS; dashed black lines (---): isothermal predictions using PR EoS; empty circles (○): data by Besserer and Robinson [48]; black filled triangles (▲): data by Cheng et al. [51]; gray filled squares (□): data by Tochigi et al. [49].

In a recent paper [9] it was shown using a different modelling approach for the carbon dioxide + cyclopentane binary system that unique sets of binary interaction parameters for the PR and SRK [61] models can predict very well the (liquid + vapour) critical curve, but it also predicts an upper critical endpoint (UCEP) and a (liquid + liquid) critical curve, suggesting type II phase behaviour. It was also shown [9] that the single set of parameters for each model used leads to significantly higher errors in the bubble-point pressures compared with the correlations.

In this study, a very good agreement with different sets of data from the literature can be observed in general for all the systems and with both models. With the current modelling approach, both models also predict type II phase behaviour (see figures 1 and 2), but the UCEP is located at very low temperatures.

In the particular case of (CO₂ + cyclohexane), where there is a clear disagreement between two different sets of data in the maximum pressure region of the locus, it can be seen that predictions

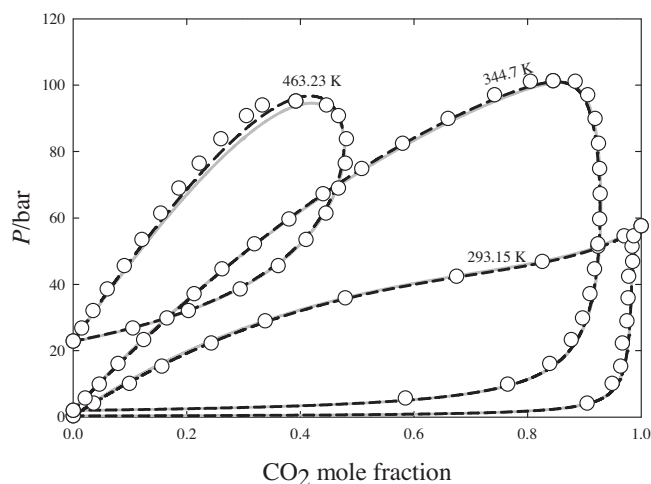


FIGURE 4. Predictions from interaction parameters in table 7, in comparison to literature VLE data for the system (CO₂ + cyclopentane). Solid gray line (—): isothermal predictions using RKPR EoS; dashed black lines (---): isothermal predictions using PR EoS; empty circles (○): data by Shah et al. [14].

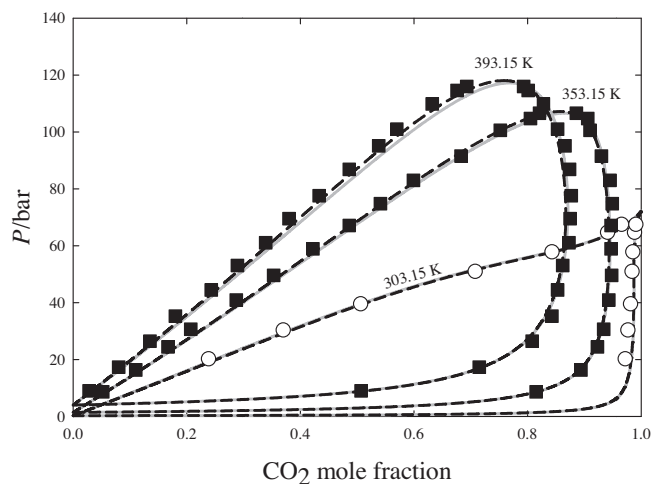


FIGURE 5. Predictions from interaction parameters in table 7, in comparison to literature VLE data for the system (CO₂ + n-hexane). Solid gray line (—): isothermal predictions using RKPR EoS; dashed black lines (---): isothermal predictions using PR EoS; empty circles (○): data by Wagner and Wichterle [53]; black filled squares (■): data by Li et al. [54].

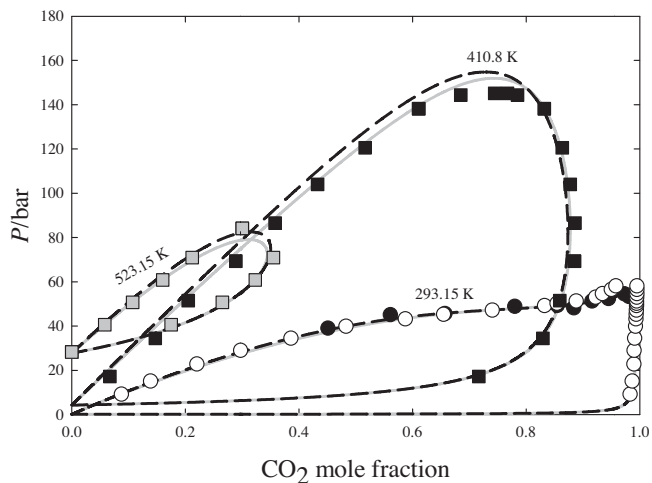


FIGURE 6. Predictions from interaction parameters in table 7, in comparison to literature data for the system (CO₂ + cyclohexane). Solid gray lines (—): isothermal predictions using RKPR EoS; dashed black lines (---): isothermal predictions using PR EoS; empty circles (○): data by Zhang and Zheng [20]; black filled circles (●): data by Esmelindro *et al.* [19]; black filled squares (■): data by Shibata and Sandler [28]; gray filled squares (◻): data by Krichevskii and Sorina [29].

TABLE 9

(Vapour + liquid) critical values for {carbon dioxide (1) + cyclopentane (2)} system: critical pressure, p , critical temperature, T , and critical mole fraction, x_1 .^a

p /MPa	T /K	x_1	p /MPa	T /K	x_1
8.69	323.85	0.9469	11.42	366.85	0.8519
9.72	338.95	0.9183	11.89	380.45	0.8118
9.98	341.95	0.9089	11.99	385.25	0.7958
10.32	346.55	0.8949	11.99	409.95	0.6663

^a Standard uncertainties u are $u(T) = 0.1$ K, $u(p) = 0.015$ MPa, $u(x_1) = 0.005$.

TABLE 10

VLE of the {carbon dioxide (1) + cyclohexane (2)} system at $T = (323.15$ and $353.15)$ K.^a

p /MPa	x_1	y_1	p /MPa	x_1	y_1
$T/K = 323.15 \pm 0.1$					
1.36	0.1088	0.9604	5.00	0.4189	0.9767
2.00	0.1567	0.9651	6.00	0.5191	0.9782
3.00	0.2364	0.9713	7.00	0.6342	0.9796
4.00	0.3406	0.9759	8.00	0.7754	0.9747
$T/K = 353.15 \pm 0.1$					
1.00	0.0652	0.8977	7.00	0.4469	0.9750
2.00	0.1321	0.9324	8.00	0.5192	0.9650
3.00	0.1958	0.9570	9.00	0.5855	0.9574
4.00	0.2523	0.9616	10.00	0.6573	0.9454
5.00	0.3167	0.9669	11.01	0.7353	0.9132
6.00	0.3834	0.9746			

^a Standard uncertainties u are $u(T) = 0.1$ K, $u(p) = 0.01$ MPa, $u(x_1, y_1) = 0.005$.

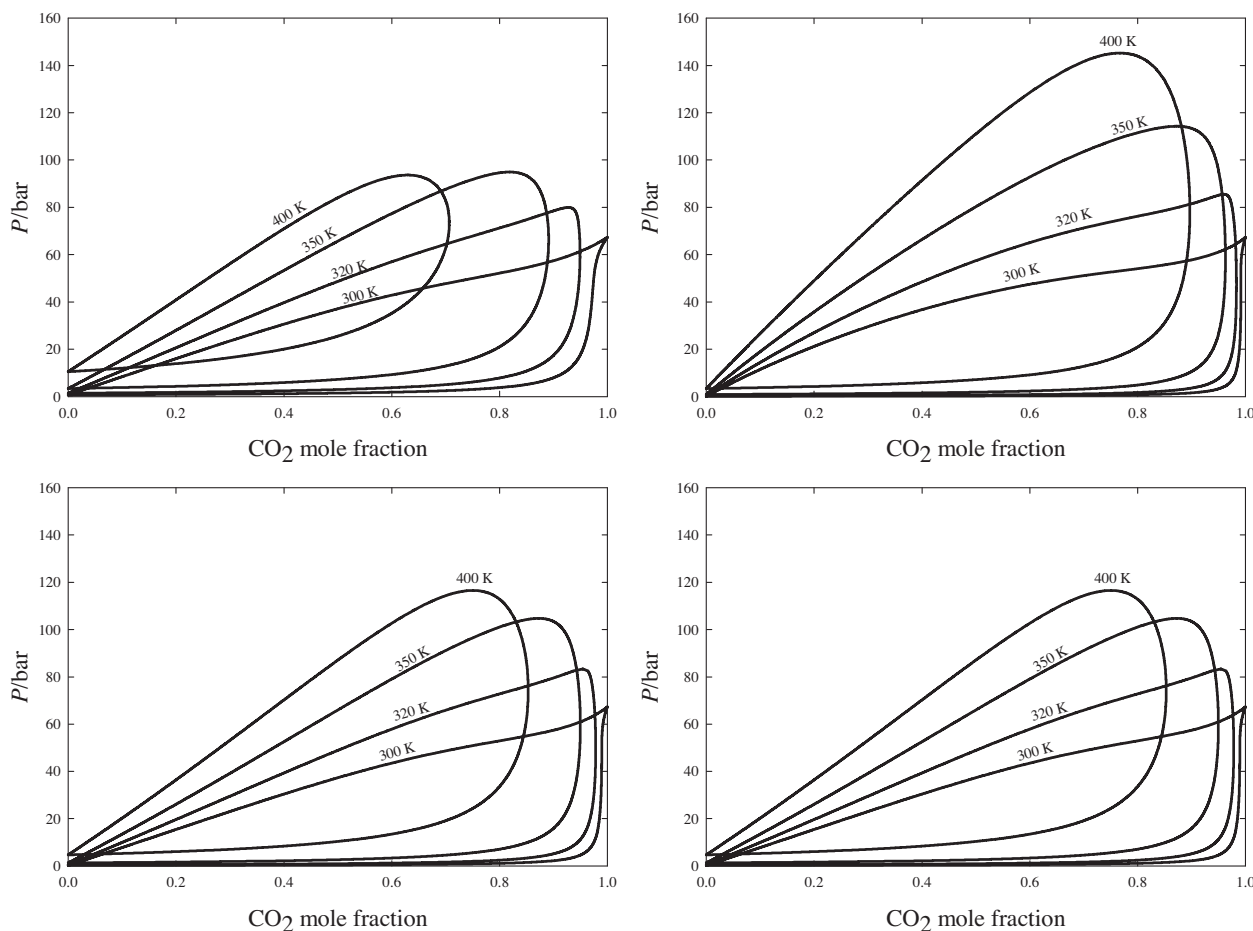


FIGURE 7. VLE behaviour resumed in four isotherms $T = \{(300, 320, 350, \text{ and } 400) \text{ K}\}$ for each of the four systems studied in this work. Predictions correspond to the RKPR EoS with parameters from tables 3 and 7.

agree with the critical points reported by Sorina [30] and not with those by Zhang *et al.* [33]. Practically the same level of general agreement is observed in figures 3–6 for subcritical VLE compositions, at different temperatures for each system. Predictions from

PR and RKPR are very similar in most cases and a systematic difference could only be found in figure 6 with cyclohexane, where PR seems to underestimate the CO₂ content, especially in the liquid phase and more clearly at $T = 410.8$ K. This observation is in agreement with, or could be expected from the better minimum achieved for the objective function with the RKPR in table 7, already mentioned in Section 3.

At a more basic and general level, from the critical lines in figures 2 and 3 it becomes evident that the binaries of CO₂ with cycloalkanes display larger ranges of immiscibility, especially in the higher temperature range, and that such difference is related to the higher critical temperatures and lower vapour pressure of these compounds in comparison to the corresponding normal alkanes with the same carbon number.

The same type of observation, but in terms of compositions, can be extracted from figure 7, when the already validated predictions of VLE from the RKPR EoS are now presented at the same temperatures for the different systems studied. As expected, the composition windows for phase separation at specified temperature and pressure are wider in the CO₂ systems with cycloalkanes. In other words, and more connected to possible applications in carbon capture and storage technologies, CO₂ is more soluble in normal alkanes than in cycloalkanes, and the difference becomes more pronounced at higher temperatures and pressures.

4.2. Measurements

(Vapour + liquid) equilibrium data for the (carbon dioxide + cyclopentane) system were measured in this work at $T = (323.15, 333.15, 344.65, \text{ and } 353.15)$ K up to 10.03 MPa and for the (carbon dioxide + cyclohexane) system at $T = (323.15 \text{ and } 353.15)$ K up to 11.01 MPa. Critical data were also measured for the (carbon dioxide + cyclopentane) system. The experimental data together with the corresponding uncertainties [62] are given in tables 8–10.

Critical points measured for the (carbon dioxide + cyclopentane) system were graphically compared in figure 1 with those of Shah *et al.* [14], as well as with the PR and RKPR predictions, and they are in good agreement. It should be remarked that the new data of this work were not used in the modelling optimisation

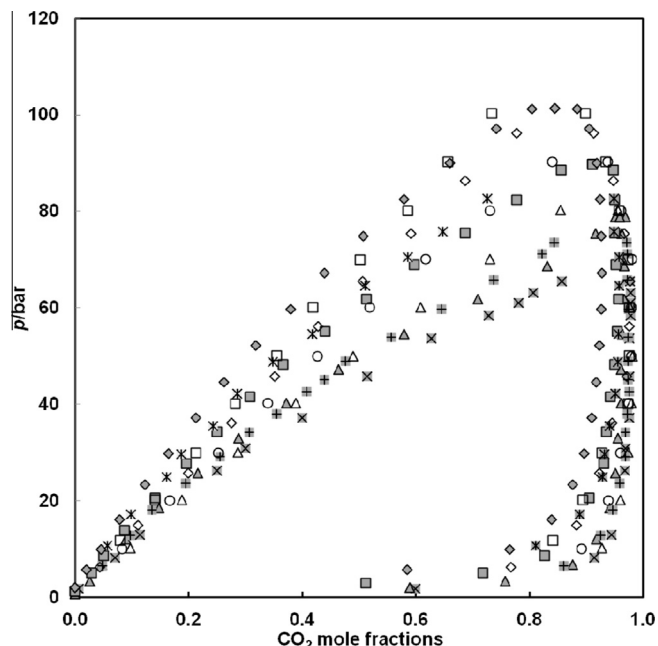


FIGURE 8. Comparison of measured and literature (vapour + liquid) equilibrium data for the (carbon dioxide + cyclopentane) system: gray filled \times (\boxtimes): isothermal VLE data at $T = 310.85$ K from Eckert and Sandler [12]; gray filled triangles (\blacktriangle): isothermal VLE data at $T = 313.08$ K from Shah *et al.* [14]; gray filled crosses (\boxtimes): isothermal VLE data at $T = 318.15$ K from Eckert and Sandler [12]; empty triangles (\triangle): isothermal VLE data at $T = 323.15$ K; gray filled squares (\blacksquare): isothermal VLE data at $T = 328.23$ K from Shah *et al.* [14]; empty circles (\circ): isothermal VLE data at $T = 333.15$ K; gray filled stars (\blackstar): isothermal VLE data at $T = 333.15$ K from Eckert and Sandler [12]; empty rhombuses (\diamond): isothermal VLE data at $T = 344.65$ K; gray filled rhombuses (\blacklozenge): isothermal VLE data at $T = 344.70$ K from Shah *et al.* [14]; empty squares (\square): isothermal VLE data at $T = 353.15$ K. All empty symbols represent new experimental values measured in this work.

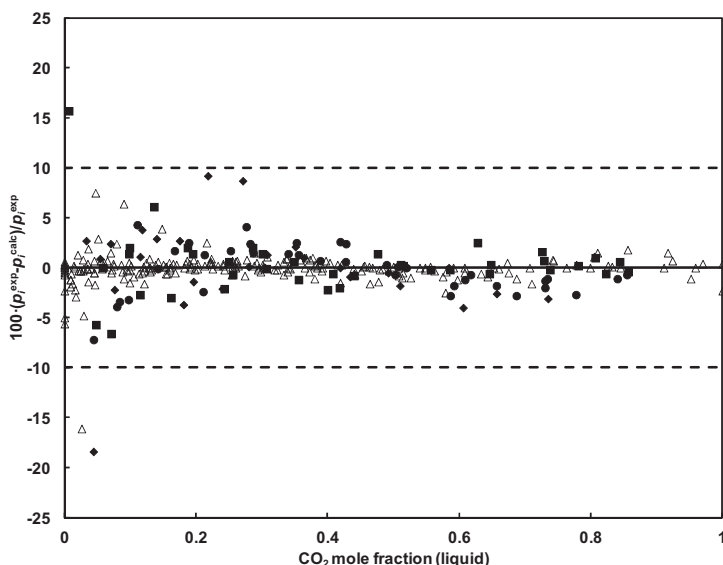


FIGURE 9. Deviations in calculated pressure of PR EoS/2PCMR correlations (regression of experimental data at each temperature from each data source separately) for the (carbon dioxide + cyclopentane) system: black filled circles (\bullet): new experimental data of this work; black filled squares (\blacksquare): Eckert and Sandler [12]; black filled rhombuses (\blacklozenge): Marathe and Sandler [13]; empty triangles (\triangle): Shah *et al.* [14].

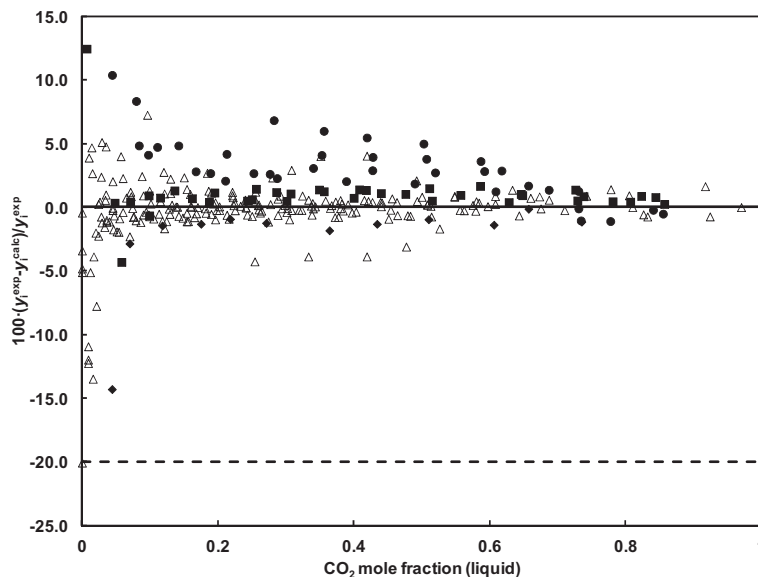


FIGURE 10. Deviations in vapour phase composition calculated with PR EoS/2PCMR (correlations) for the (carbon dioxide + cyclopentane) system: black filled circles (●): new experimental data of this work; black filled squares (■): Eckert and Sandler [12]; black filled rhombuses (◆): Marathe and Sandler [13]; empty triangles (Δ): Shah *et al.* [14].

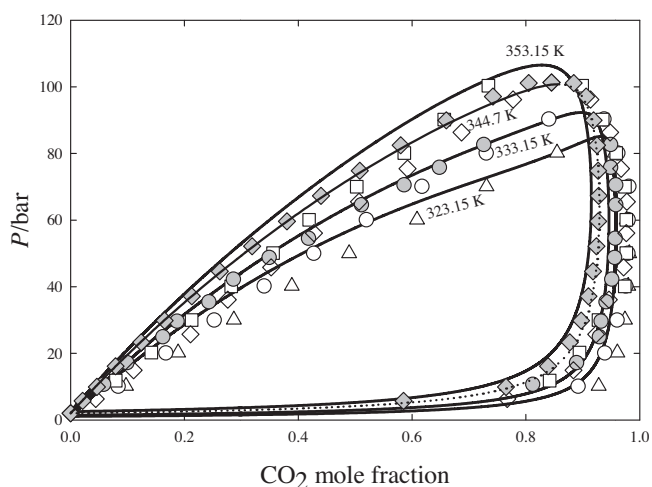


FIGURE 11. New VLE values measured in this work for (CO₂ + cyclopentane) (table 8, not used in the adjustment), in comparison to RKPR predictions with parameters from tables 3 and 7. Solid black lines (—): isothermal predictions using RKPR EoS; empty triangles (Δ): isothermal VLE data at $T = 323.15$ K; empty circles (○): isothermal VLE data at $T = 333.15$ K; empty rhombuses (◇): isothermal VLE data at $T = 344.65$ K; empty squares (□): isothermal VLE data at $T = 353.15$ K; gray filled circles (●): isothermal VLE data at $T = 333.15$ K from Eckert and Sandler [12]; gray filled rhombuses (◇): isothermic VLE data at $T = 344.70$ K from Shah *et al.* [14]. All empty symbols represent new experimental values measured in this work.

TABLE 11

Experimental critical and experimental (liquid + vapour) results of this work selected for the objective function for the system {carbon dioxide (1) + cyclopentane (2)}: critical temperature, T_c , critical pressure, p_c , critical composition, x_c , temperature, T , pressure, p , mole fraction of CO₂ in the liquid and vapour phases, x_{CO_2} , y_{CO_2} , and optimised interaction parameters, k_{ij} , l_{ij} , with the PR EoS.

T_c/K	$10p_c/MPa$	x_c	T/K	$10p/MPa$	x_{CO_2}	y_{CO_2}	PR EoS	
							k_{ij}	l_{ij}
323.85	86.9	0.9469	323.15	30.1	0.2869	0.9742	0.0788	0.0067
				60.1	0.6086	0.9770		
			333.15	30.0	0.2524	0.9604		
				70.1	0.6174	0.9812		
409.95	119.9	0.6663	344.65	25.7	0.1998	0.9236		
				65.5	0.5067	0.9775		
			353.15	30.0	0.2127	0.9275		
				70.0	0.5026	0.9742		

procedure presented in the previous section, so in this respect the calculations are pure predictions.

The new experimental values of this work for the (carbon dioxide + cyclopentane) system were compared with literature data in figure 8. Although the figure is pretty busy, it can be remarked that if we compare the new results with literature data at the same or nearest temperature (333.15, 344.65, and 344.70 K respectively), there are some differences. At the same pressure, the new values have a richer composition in CO₂ both in liquid and vapour phases than the data of Eckert and Sandler [12] or Shah *et al.* [14]. On the other hand, if we compare the new values of this work measured at $T = 323.15$ K with those of Eckert and Sandler [12] at $T = (310.85$ and $318.15)$ K and Shah *et al.* [14] at $T = 313.08$ K respectively, it can be noticed that our results are in agreement with those of Eckert and Sandler [12] at medium and large pressures, while the $T = 313.08$ K isotherm of Shah *et al.* [14] almost overlap the $T = 318.15$ K isotherm of Eckert and Sandler [12]. A similar observation can be made for the $T = 328.23$ K isotherm of Shah *et al.* [14] and $T = 333.15$ K isotherm of Eckert and Sandler [12]. It is difficult to conclude on the quality of the data, however it can be noted that the main difference between the three research groups who studied CO₂ + cyclopentane systems is experimental method, i.e. static-analytical in our case versus vapour recirculation system [14], or the type of chromatographic columns [12,14,41].

In addition, the deviations in calculated pressure and vapour phase composition for each point show that all values reported

in this work and most of the data from literature are in within the limits to declare the results as being thermodynamically consistent [63], as shown in figures 9 and 10. The model chosen to correlate the new and literature data is the PR EoS with classical quadratic mixing rules (two-parameter conventional mixing rule, 2PCMR). The deviations in calculated pressure and vapour phase composition were calculated with the equations:

$$\Delta P_i(\%) = 100 \cdot (P_i^{\text{exp}} - P_i^{\text{calc}})/P_i^{\text{exp}}, \quad (1)$$

$$\Delta y_i(\%) = 100 \cdot (y_{1,i}^{\text{exp}} - y_{1,i}^{\text{calc}})/y_{1,i}^{\text{exp}}. \quad (2)$$

The optimised binary interaction parameters corresponding to the fittings by PR/2PCMR, made for the consistency test, are not given in this study, as for literature data [12–14] are shown in a recent paper [9], together with the values of average absolute deviations in bubble-point pressures (AADP, %) and the average absolute deviations in the vapour-phase compositions (AADY, %). It can be noted that the average values of the optimised binary interaction parameters for the isotherms reported in literature [12–14] are $k_{12} = 0.1182$ and $l_{12} = -0.0397$ [9], similar with those calculated in this work (see table 7). The main contribution of this modelling approach is that using minimum selected experimental information, *i.e.* for the carbon dioxide + cyclopentane system (see tables 4 and 6) one experimental point from each $T = (276.64$ and $463.23)$ K isotherms, and two experimental points from each $T = (293.14, 344.70,$ and $419.15)$ K isotherms respectively, as well as only two experimental critical points, the entire phase diagram is described.

It is obvious that the reliability of the method is related to the experimental values used. Therefore, when only literature data were used, as there are some differences between the experimental results of the three groups (see figure 8), it is expected that the predictions for the new values are not very good. The new values of this work for the (carbon dioxide + cyclopentane) were compared with the RKPR predictions (parameters from table 7) in figure 11. Taking into account that in the OF no experimental point from the new measured sets was used, the predictions are realistic.

Therefore, we calculated a new set of parameters by the same procedure as explained in the modelling section, but using only few experimental data of this work. The binary interaction

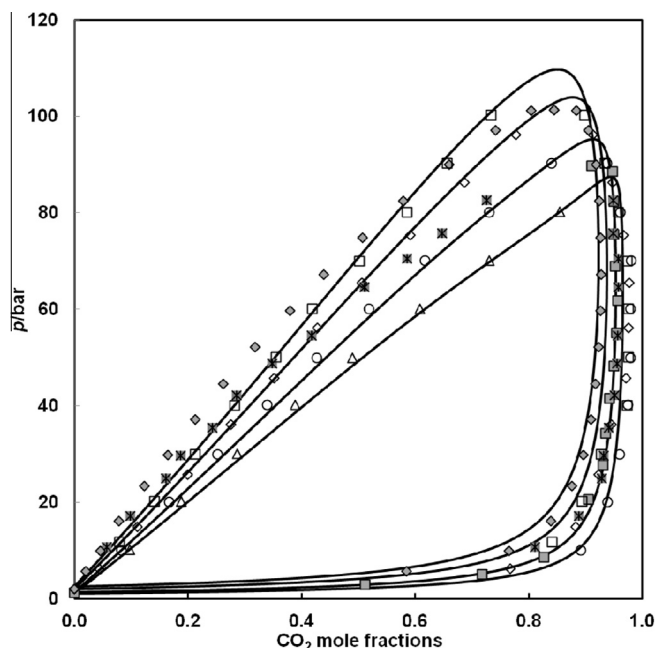


FIGURE 13. New VLE data measured in this work for CO_2 + cyclopentane, in comparison to PR predictions with parameters from table 11: solid black lines (—): isothermal predictions using PR EoS; empty triangles (Δ): isothermal VLE data at $T = 323.15$ K; empty circles (\circ): isothermal VLE data at $T = 333.15$ K; gray filled stars (\blacksquare): isothermal VLE data at $T = 333.15$ K from Eckert and Sandler [12]; empty rhombuses (\diamond): isothermal VLE data at $T = 344.65$ K; gray filled rhombuses (\blacklozenge): isothermal VLE data at $T = 344.70$ K from Shah *et al.* [14]; empty squares (\square): isothermal VLE data at $T = 353.15$ K. All empty symbols represent new experimental data measured in this work.

parameters for (CO_2 + cyclopentane) system and the selected experimental points in the objective function are given in table 11.

In figure 12 are shown the deviations in calculated pressures for the PR/2PCMR with the new set of parameters from table 11. It can be easily observed that the deviations are smaller for the new values and much higher for the literature data.

The new values of this work are compared with the PR EoS predictions (parameters from table 11) in figure 13, where a good

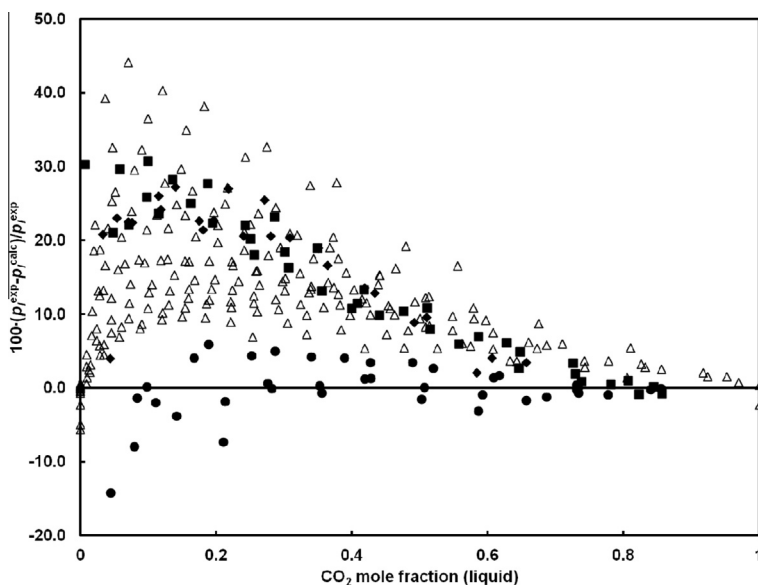


FIGURE 12. Deviations in calculated pressure with PR EoS/2PCMR ($k_{12} = 0.0788$; $l_{12} = 0.0067$) for the (carbon dioxide + cyclopentane) system: black filled circles (\bullet): new experimental data of this work; black filled squares (\blacksquare): Eckert and Sandler [12]; black filled rhombuses (\blacklozenge): Marathe and Sandler [13]; empty triangles (Δ): Shah *et al.* [14].

agreement can be observed, while the predictions for literature data are less accurate, opposite to the situation presented in figure 11.

The results for the (carbon dioxide + cyclohexane) system are discussed in the following section. The new data determined in the present work for the (carbon dioxide + cyclohexane) system are compared with literature data at the same and/or nearest temperature, as well with the RKPR predictions (parameters from table 7) in figure 14. It can be observed that the new data agree very well with the literature ones and reasonably well with the predictions. However, if we plot, similarly to the (carbon dioxide + cyclopentane) system, the deviations in pressure for the

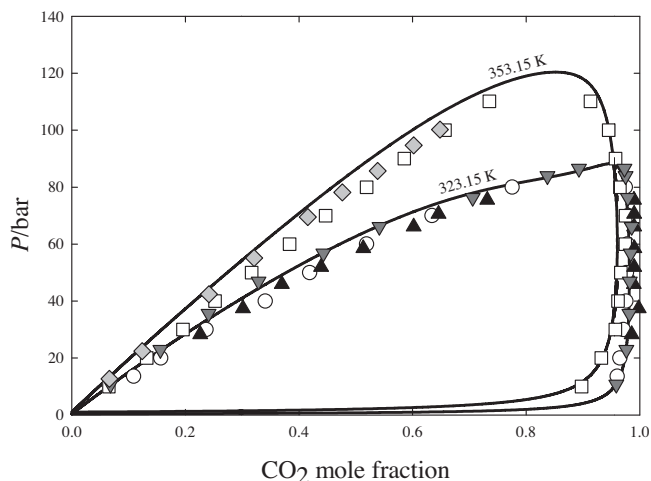


FIGURE 14. New VLE data measured in this work for CO₂ + cyclohexane (table 10, not used in the adjustment), in comparison to RKPR predictions with parameters from tables 3 and 7. Solid black lines (—): isothermal predictions using RKPR EoS; empty circles (○): isothermal VLE data at $T = 323.15$ K; empty squares (□): isothermal VLE data at $T = 353.15$ K; black filled triangles (▲): isothermal VLE data at $T = 323.15$ K from Feng *et al.* [23], inverted gray filled triangles (▼): isothermal VLE data at $T = 323.3$ K from Zhang and Zheng [20], gray filled rhombuses (◇): isothermal VLE data at $T = 353.15$ K from Al-Sahhaf *et al.* [22]. All empty symbols represent new experimental data measured in this work.

new data and all available literature data, it can be seen (figure 15) that are some literature data [18] outside acceptable margins of deviations [63]. In addition, when the vapour phase composition deviations are plotted (figure 16), for the new data measured in this work for the (carbon dioxide + cyclohexane) system and literature data which reported the composition of the vapour phase (see table 1), it can be noticed that most of the data have reasonable errors, and, excepting one literature point, are within the limits [63].

Regarding the modelling results of the new results with the parameters from table 7, it can be concluded that a reasonable agreement is observed, at least in figure 14 for the system with cyclohexane. It should be stressed out that new data were not considered among the few points used in the OF, and in this respect the calculations are predictions. Regarding the systematic differences observed in figure 11 with cyclopentane (lower contents of CO₂ are predicted for both phases in comparison to measurements) it would be difficult to conclude up to which extent they could be due to the quality of the other sets of data taken from the literature for the parameters optimisation, to the limitations of the global correlation based on the RKPR EoS and/or to possible problems in the measurements.

4.3. Analysis of the possibility of double retrograde behaviour

Double retrograde behaviour (DRB) has been studied both experimentally and theoretically by various different research groups during the last two decades (an updated review can be found in [64]). Ramello *et al.* [64] have shown the usefulness of computed cricondenbar (CCB) and cricondentherm (CCT) lines, given that the first ones allow for a direct detection of prediction of the isobaric DRB phenomenon, while the latter ones play the same role for isothermal DRB [64].

From figure 17 it can be deduced that isothermal DRB is predicted by the RKPR EoS and parameters from this work, for all the systems studied except the most miscible and less asymmetric one, *i.e.* (CO₂ + *n*-pentane).

On the other hand, isobaric DRB, which is normally less frequent, would be present only for the system with cyclohexane (the more asymmetric and less miscible one) as it can be deduced

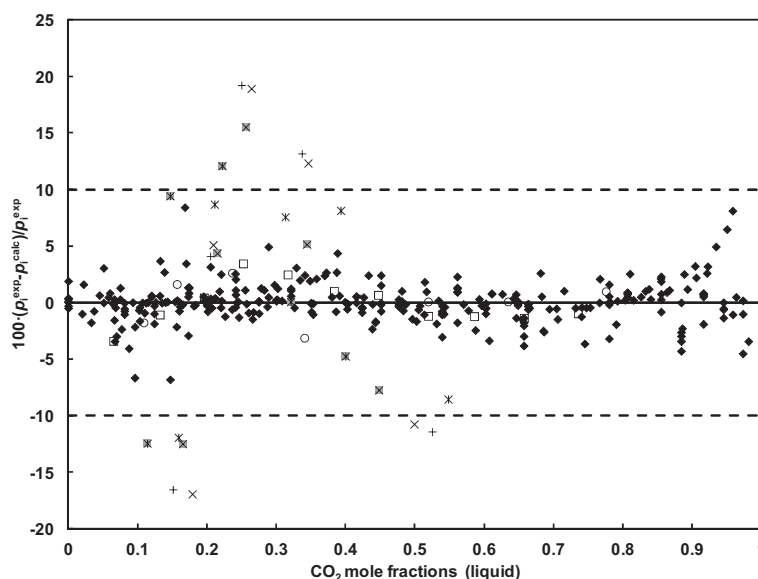


FIGURE 15. Deviations in calculated pressure with PR EoS/2PCMR (correlations) for the (carbon dioxide + cyclohexane) system: empty circles and squares (○, □): new experimental data of this work; black filled rhombuses (◆): all literature isothermal data from table 1, except reference [18]; all other symbols (+, ×, *, #): Gainar [18].

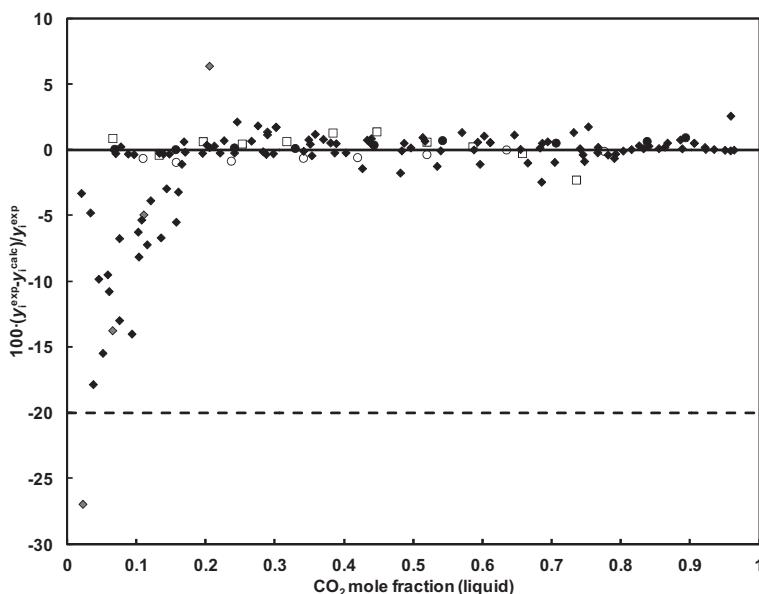


FIGURE 16. Deviations in vapour phase composition calculated with PR EoS/2PCMR (correlations) for the (carbon dioxide + cyclohexane) system: empty circles and squares (\circ , \square): new experimental data of this work; black filled rhombuses (\blacklozenge): all literature isothermal data from table 1 presenting vapour phase compositions; gray filled rhombuses (\blacklozenge): Krichevskii and Sorina [29].

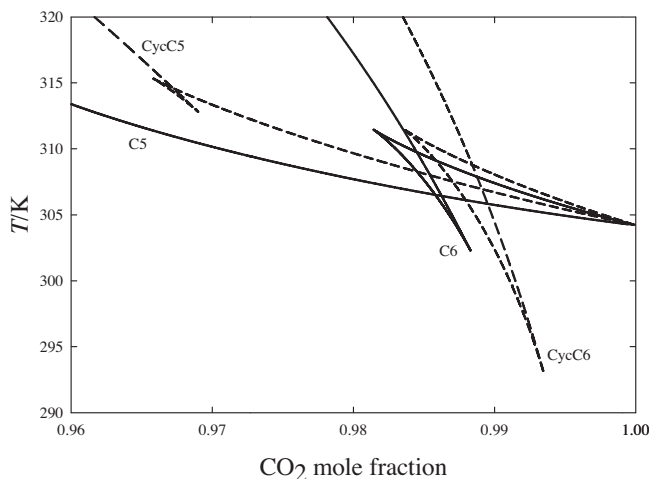


FIGURE 17. Cricondentherm (CCT) lines, predicted by the RKPR EoS, with parameters from tables 3 and 7. Dashed lines (— —): cyclic alkanes; solid lines (—): normal alkanes.

from the cricondenbar (CCB) lines in figure 18, but only in a very narrow composition range. The presence of these phenomena should be confirmed by experimental studies.

5. Conclusions

New (vapour + liquid) equilibrium results were determined for (carbon dioxide + cyclopentane) at $T = (323.15, 333.15, 344.65, \text{ and } 353.15) \text{ K}$ and pressures up to 10.03 MPa, and (carbon dioxide + cyclohexane) binary systems at $T = (323.15 \text{ and } 353.15) \text{ K}$ and pressures up to 11.02 MPa, using a visual high-pressure static-analytic setup. Critical points were also measured for the carbon dioxide + cyclopentane system up to 11.99 MPa.

The phase behaviour of the carbon dioxide + n-alkanes (+1-pentane, +1-hexane) and the corresponding cycloalkanes (+cyclopentane, +cyclohexane) was predicted with the RKPR and PR EoS.

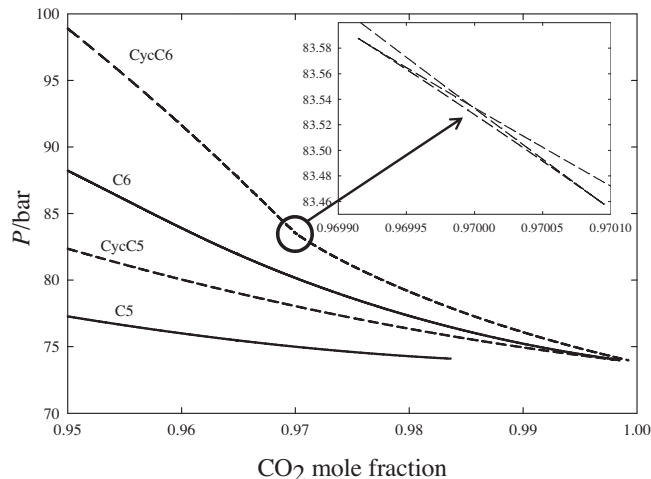


FIGURE 18. Cricondenbar (CCB) lines, predicted by the RKPR EoS, with parameters from tables 3 and 7. Dashed lines (— —): cyclic alkanes; solid lines (—): normal alkanes.

Double retrograde behaviour is predicted by RKPR model, but it should be confirmed by experiments.

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