PHASE EQUILIBRIA CALCULATIONS FOR CARBON DIOXIDE + 2-PROPANOL SYSTEM

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The ability of different thermodynamic models to predict the phase behavior of carbon dioxide (1) + 2-propanol (2) binary system is tested. The models chosen are Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) cubic equations of state (EOS), coupled with classical van der Waals mixing rules (two-parameter conventional mixing rule, 2PCMR) mixing rules. A single set of binary parameters was used to predict the global phase behavior of the system for a wide range of pressure and temperature. Although the models used are simple, they are able to represent reasonably well the complex phase behavior of the system studied in this work.

Keywords: carbon dioxide; 2-propanol; high pressures; SRK; PR; phase behavior

1. Introduction

The knowledge of high-pressure phase behavior of carbon dioxide comprising mixtures is of interest in a variety of processes, well established or new applications of supercritical fluids, like extraction, particle formation, impregnation (wood preservation, polymers, catalysts, and textiles), leather, paper and textile treatment, dyeing, cleaning, reaction, chromatography, drying of aerogel, injection molding and extrusion, and electronic chip manufacturing [1-5].

Among them, the carbon dioxide + alcohols mixtures at high-pressures are of a particular importance in the design, simulation, and optimization of extraction processes, where the alcohols are commonly used as cosolvents [6].

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In the last years a series of studies [7-31] on the carbon dioxide + alcohols systems at high pressures was initiated at the Applied Thermodynamics Research Laboratory of University Politehnica of Bucharest. Recently, we started to explore the functional group effect in binary systems containing carbon. The first step is to analyze binary systems of carbon dioxide and several types of alcohol isomers.

The present paper investigates the influence of binary interaction parameters on the phase behavior of the carbon dioxide + 2-propanol binary mixture.

To the best of our knowledge, there are no experimental data proving the type of phase behavior for carbon dioxide + 2-propanol system, according to the classification of van Konynenburg and Scott [32]. However, the system seems to be type I or type II phase behavior, according to the classification of van Konynenburg and Scott [32]. In the *P–T* diagram [33], type I is characterized by a continuous liquid–vapor critical line connecting the critical points of the pure components, while type II phase behavior is very similar to type I but it has an additional liquid–liquid (LL) critical line ending in an upper critical endpoint (UCEP) where intersects a three-phase liquid–liquid–vapor (LLV) line.

All available data for the carbon dioxide + 2-propanol were collected and our database was updated. The critical data for the system reported in the literature are summarized in Table 1. The temperature and pressure ranges, the number of the experimental points and the type of vapor–liquid equilibrium (VLE) literature data collected are shown in Table 2.

Table 1

Literature critical data for CO_2 (1) +2-Propanol (2) binary system

T_{range}/K	P_{range}/MPa	NEXP[6]	Observations	References
306.20÷319.60	7.560÷8.810	8	VLE critical curve	[34]
306.60÷322.00	7.530÷9.090	8	VLE critical curve	[35]
313.15÷393.15	8.120÷13.350	5	VLE critical curve	[36]
344.04÷432.58	10.354÷12.933	3	VLE critical curve	[37]
304.25÷483.15	7.390÷7.900	16	VLE critical curve	[38]

*Number of experimental points

Table 2

Literature VLE data for CO_2 (1) + 2-Propanol (2) binary system

T/K	P_{range}/MPa	NEXP	Observations	Reference
293.25	0.680÷5.560	13	*P-x,y*	[7]
293.30	1.100÷5.100	5	*P-x,y*	[44]
298.00	5.280÷5.770	3	*P-x*	[49]
298.15	1.050÷6.070	10	*P-x,y*	[7]
298.15	3.290÷5.940	7	*P-x,y*	[41]
302.80	0.990÷3.970	4	*P-x*	[54]
303.15	3.160÷10.050	7	*P-x*	[53]
308.10	1.760÷7.450	7	*P-x*	[50]
308.15	1.960÷6.730	7	*P-x,y*	[40]
308.15	1.590÷7.150	5	*P-x,y*	[7]

313.00	0.720÷7.580	10	*P-x,y*	[47]
313.00	6.420÷7.420	3	*P-x*	[49]
313.10	2.280÷8.100	7	*P-x*	[50]
313.15	1.836÷8.137	11	*P-x*	[43]
313.15	6.000÷8.000	4	*P-y*	[43]
313.15	2.290÷7.770	8	*P-x,y*	[40]
313.15	4.130÷8.120	11	*P-x*	[36]
313.15	7.820÷8.120	2	*P-y*	[36]
313.15	1.210÷7.600	11	*P-y*	[46]
313.15	1.050÷7.720	16	*P-x*	[52]
313.15	1.230÷7.260	8	*P-x,y*	[41]
313.16	1.210÷7.770	13	*P-x*	[46]
313.20	2.100÷7.100	6	*P-x,y*	[44]
313.22	2.402÷7.788	9	*P-x,y*	[51]
313.70	1.280÷7.700	13	*P-y*	[42]
316.65	1.330÷8.380	11	*P-x,y*	[7]
316.75	5.860÷7.930	3	*P-x,y*	[39]
317.15	6.930÷8.060	3	*P-x,y*	[8]
323.07	2.660÷8.720	5	*P-x*	[50]
323.10	0.980÷5.940	6	*P-x*	[54]
323.15	1.520÷8.600	6	*P-x,y*	[7]
323.15	1.060÷9.080	10	*P-x,y*	[48]
323.16	1.110÷8.570	12	*P-x,y*	[46]
324.70	1.555÷8.905	8	*P-x,y*	[45]
324.99	1.640÷9.180	6	*P-x,y*	[45]
333.00	2.820÷9.720	5	*P-x*	[50]
333.03	2.577÷10.145	8	*P-x,y*	[51]
333.15	4.570÷10.160	9	*P-x*	[36]
333.15	9.530÷10.160	3	*P-y*	[36]
333.15	2.010÷8.910	11	*P-x,y*	[48]
333.15	4.220÷8.830	7	*P-x,y*	[41]
333.17	1.010÷9.560	20	*P-y*	[46]
333.20	2.100÷8.100	7	*P-x,y*	[44]
333.21	1.010÷9.080	17	*P-x*	[46]
333.70	1.300÷10.090	12	*P-y*	[42]
333.70	1.751÷9.447	10	*P-x,y*	[45]
333.82	1.025÷8.151	5	*P-x,y*	[45]
334.04	9.187÷10.354	5	*P-x,y*	[37]
334.95	1.380÷9.310	8	*P-x,y*	[39]
343.15	1.990÷9.970	10	*P-x,y*	[48]
344.23	2.030÷11.145	13	*P-x,y*	[37]
348.00	3.320÷11.350	5	*P-x*	[50]
348.25	1.801÷11.570	10	*P-x,y*	[51]
348.60	1.752÷10.448	5	*P-x,y*	[45]
353.15	5.420÷11.850	8	*P-x*	[36]
353.15	11.100÷11.850	3	*P-y*	[36]
353.15	5.130÷10.770	7	*P-x,y*	[48]

353.72	10.074÷12.210	7	*P-x,y*	[37]
354.45	5.860÷11.380	5	*P-x,y*	[39]
362.92	2.580÷12.423	9	*P-x,y*	[51]
373.15	6.070÷12.650	6	*P-x*	[36]
373.15	10.060÷12.650	5	*P-y*	[36]
373.18	10.490÷13.383	5	*P-x,y*	[37]
393.15	6.560÷13.350	5	*P-x*	[36]
393.15	13.000÷13.350	3	*P-y*	[36]
394.55	6.900÷12.4100	5	*P-x,y*	[39]
398.62	9.588÷13.788	5	*P-x,y*	[37]
413.45	5.028÷13.109	9	*P-x,y*	[37]
432.58	10.049÷12.933	6	*P-x,y*	[37]
443.46	3.334÷11.610	9	*P-x,y*	[37]

The literature data for the carbon dioxide + 2-propanol system were modeled with two cubic equations of state, namely the Peng–Robinson (PR) [55] and Soave–Redlich–Kwong (SRK) [56], coupled with classical van der Waals mixing rules. A single set of binary parameters was used to predict the global phase behavior of the system for a large range of pressure and temperature. Although the models are simple, they are able to represent correctly the complex phase equilibria of the system studied in this work.

2. Modeling

Equations of state (EOS) models are the most common approach for the correlation and prediction of phase equilibria and properties of the mixtures. Frequently cubic EOSs are used for practical applications, though they have their known limitations [57].

Based on previous results [19-31] with mixtures containing carbon dioxide and alcohols, the PR and SRK EOSs coupled with classical van der Waals mixing rules (two parameter conventional, 2PCMR) were used to model the phase behavior of the studied system.

The Peng–Robinson [55] is described by the following equation:

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

where the two constants, *a* and *b*, are:

$$a = 0.45724\frac{R^2T_c^2}{P_c}\alpha(T) \tag{2}$$

$$b = 0.077796\frac{RT_c}{P_c} \tag{3}$$

$$\alpha(T_R,\omega)=\left[1+m_{PR}\left(1-T_R^{0.5}\right)\right]^2 \tag{4}$$

$$m_{PR}=0.37464-1.54226\omega-0.26992\omega^2 \tag{5}$$

The Soave–Redlich–Kwong [56] equation of state is:

$$P=\frac{RT}{V-b}-\frac{a(T)}{V(V+b)} \tag{6}$$

where the two constants, *a* and *b*, are:

$$a=0.42748\frac{R^2T_c^2}{P_c}\alpha(T) \tag{7}$$

$$b=0.08664\frac{RT_c}{P_c} \tag{8}$$

$$\alpha(T_R,\omega)=\left[1+m_{SRK}\left(1-T_R^{0.5}\right)\right]^2 \tag{9}$$

$$m_{SRK}=0.480-1.574\omega-0.176\omega^2 \tag{10}$$

The two parameter conventional mixing rules are given by:

$$a=\sum_i\sum_j x_i x_j a_{ij} \tag{11}$$

$$b=\sum_i\sum_j x_i x_j b_{ij} \tag{12}$$

where

$$a_{ij}=\sqrt{a_i a_j}\left(1-k_{ij}\right) \tag{13}$$

$$b_{ij}=\frac{b_i+b_j}{2}\left(1-l_{ij}\right) \tag{14}$$

The PR and SRK EOS were used to model predictively the phase behavior of the carbon dioxide + 2-propanol binary.

Table 3

Critical data (T_c, P_c) and acentric factor (ω) for pure components [58]

Compounds	T_c/K	p_c/MPa	ω
Carbon dioxide	304.21	7.383	0.22362
2-Propanol	508.30	4.764	0.66687

One set of parameters temperature independent for each EOS was used to predict VLE and critical curve. The set of binary parameters for each equation was calculated using the k_{12}–l_{12} method [16-17,19,57] to obtain the experimental value of the vapor–liquid critical pressure maximum (CPM) simultaneously with

the temperature of UCEP for the carbon dioxide + 2-butanol binary system [19]. The binary system carbon dioxide + 2-butanol is a type II phase diagram, according to the classification of van Konynenburg and Scott [32]. As Polishuk [57] has shown, the carbon dioxide + 2-butanol mixture is one of the most measured system, VLE data being available in a wide range of temperatures and pressure, as well as the critical curve, UCEP, and three phase LLV line.

We used these sets of binary interaction parameters obtained for carbon dioxide + 2-butanol to test the ability of the models to predict the phase behavior for the mixture containing the lighter component, 2-propanol.

The critical data and the acentric factors of the pure substances [58] used in the calculation are presented in Table 3.

3. Results and Discussion

In a previous study [19], SRK/2PCMR and PR/2PCMR were used in a semi predictive approach generating for each model one set of binary interaction parameters that modeled the phase behavior (critical curves, LLV line, VLE data) for the carbon dioxide + 2-butanol binary system. The sets of binary interaction parameters are k_{12} = 0.020, l_{12} = –0.111 for SRK and k_{12} = 0.025, l_{12} = –0.108 for PR respectively.

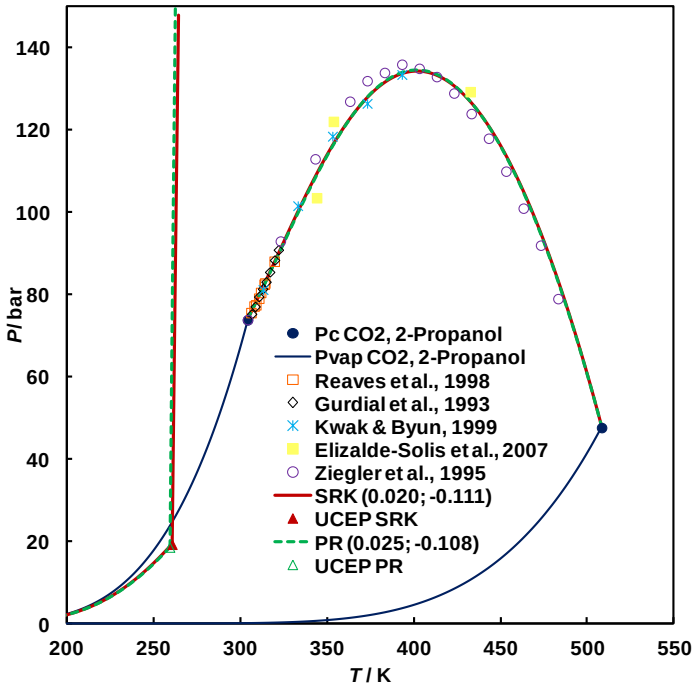

Fig. 1. *P*–*T* fluid phase diagram for carbon dioxide (1) + 2-propanol (2) system: symbols, literature data [34-38]; lines, prediction by SRK (solid tick lines) and PR (dashed tick lines) EOSs.

These parameters are used in the present study to predict the phase behavior of the carbon dioxide + 2-propanol system.

Firstly, we calculated the critical curve with both models. As can be seen in Fig. 1, both SRK and PR predict type II phase behavior, but the predicted UCEPs are located at very low temperatures. The vapor–liquid critical curves are remarkably well predicted by both EOS, though the parameters were obtained for the homologous member of the alkanols series. In Fig. 2 we plotted the critical pressures and temperatures against compositions. It can be easily noticed that the predictions are not very accurate and PR behaves slightly better that SRK.

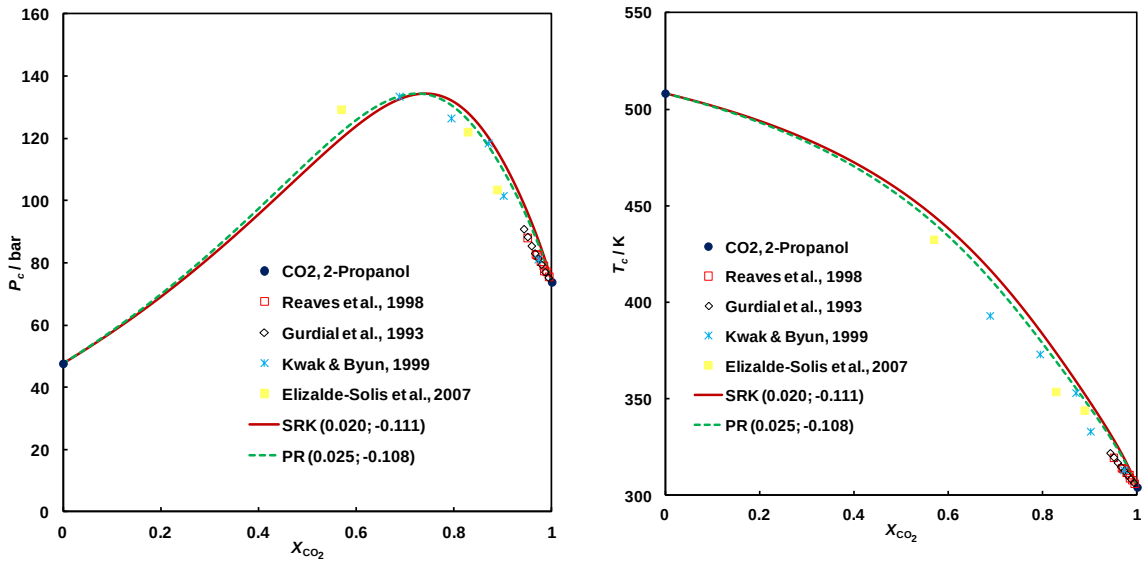

Fig. 2. *P*–*x* and *T*–*x* projections of the phase diagram for carbon dioxide (1) + 2-propanol (2) system: symbols, literature data [34-37]; lines, prediction by SRK (solid tick lines) and PR (dashed tick lines) EOSs.

The sets of binary parameters were then used to predict all available VLE data in the temperature range of 293.25 K to 443.46 K. The experimental data were compared with SRK and PR predictions in Figs. 3-9. It can be noticed a high degree of scatter among literature data, especially at 313 and 333 K that are reported in a large number. The predictions by SRK and PR are relatively good in the entire temperature range and they are better as temperature increases. This behavior is in agreement with the predictions of the critical curves from Figs. 1 and 2. For temperatures smaller than the maximum critical one, the bubble-pressure curves are underestimated by both SRK and PR, though the critical points are very well predicted (Figs. 3-6). As the temperature increases, the both liquid and vapor phases are better predicted (Figs. 7-9), but the critical points are slightly underestimated.

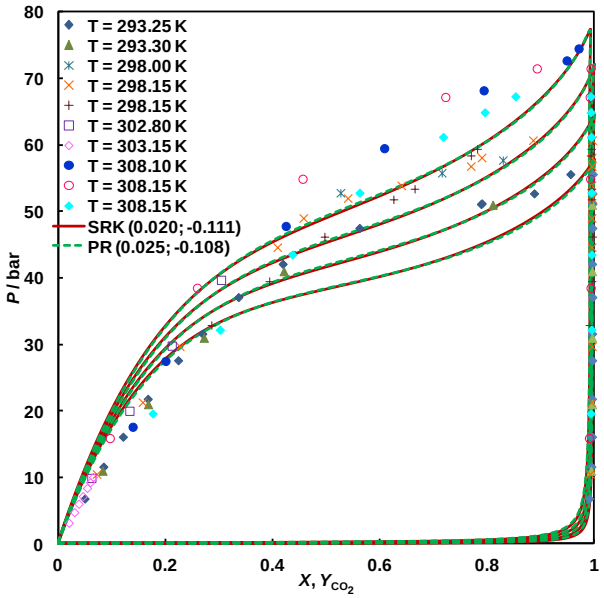

Fig. 3. Comparison of literature VLE data [7,44,49,7,41,54,53,50,40,7] and predictions by SRK (solid tick lines) and PR (dashed tick lines) EOSs for carbon dioxide (1) + 2-propanol (2) system.

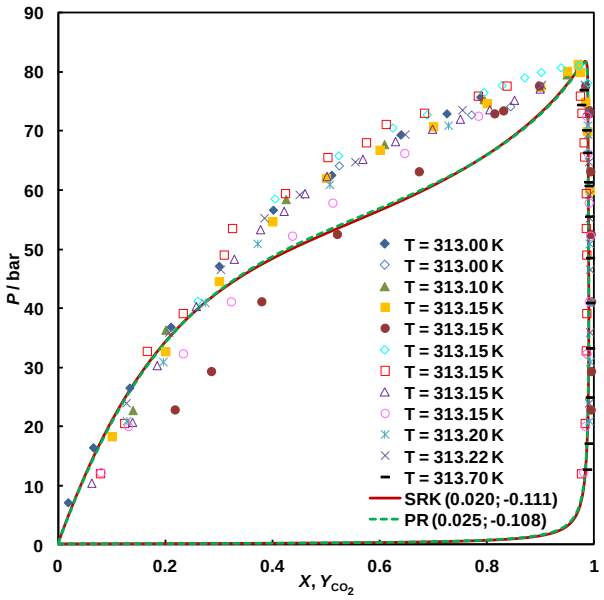

Fig. 4. Comparison of literature VLE data [47,49,50,43,40,36,46,52,46,44,51,42] and predictions by SRK (solid tick lines) and PR (dashed tick lines) EOSs for carbon dioxide (1) + 2-propanol (2) system.

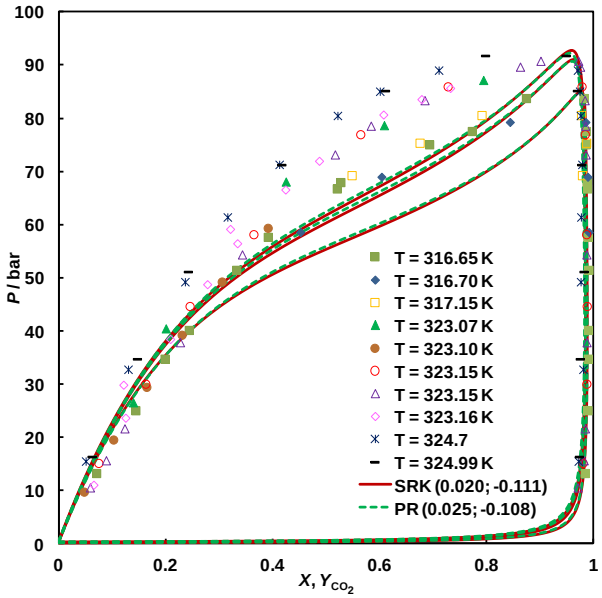

Fig. 5. Comparison of literature VLE data [7,39,8,50,54,7,48,46,45,45] and predictions by SRK (solid tick lines) and PR (dashed tick lines) EOSs for carbon dioxide (1) + 2-propanol (2) system.

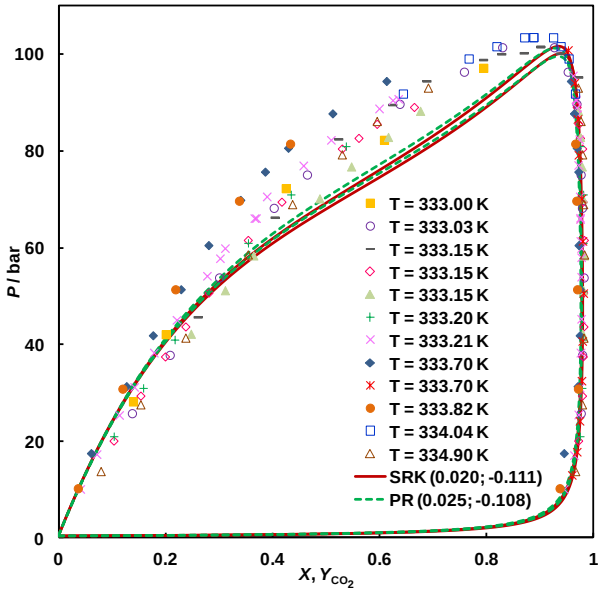

Fig. 6. Comparison of literature VLE data [50,51,36,48,41,46,44,46,42,45,45,37,39] and predictions by SRK (solid tick lines) and PR (dashed tick lines) EOSs for carbon dioxide (1) + 2-propanol (2) system.

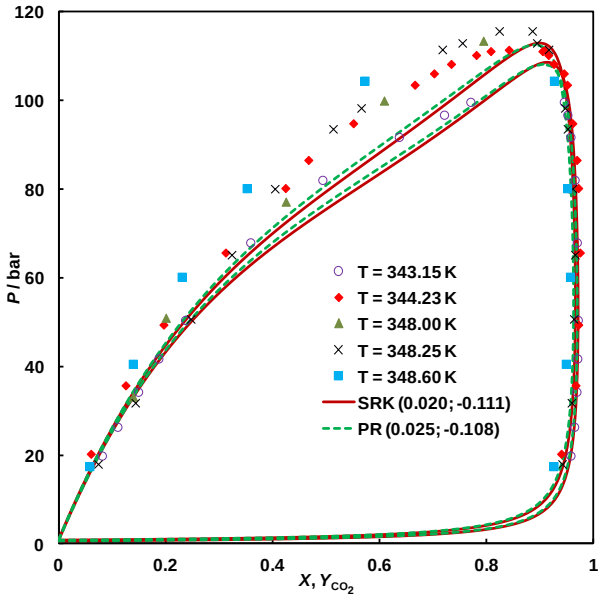

Fig. 7. Comparison of literature VLE data [48,37,50,51,45] and predictions by SRK (solid tick lines) and PR (dashed tick lines) EOSs for carbon dioxide (1) + 2-propanol (2) system.

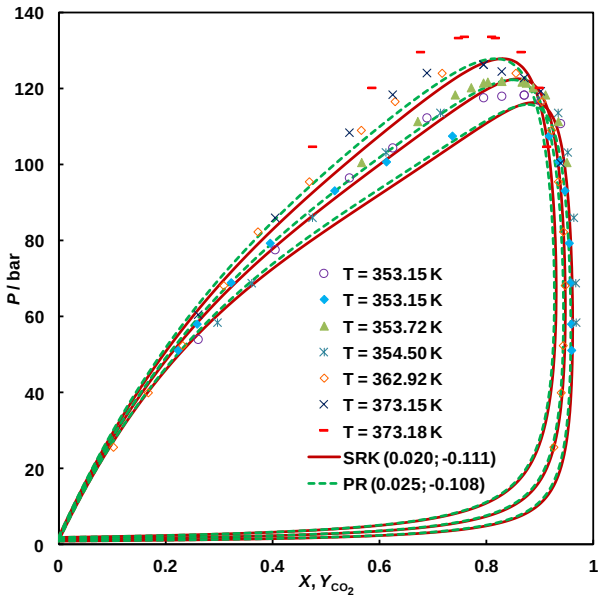

Fig. 8. Comparison of literature VLE data [36,48,37,39,51,36,37] and predictions by SRK (solid tick lines) and PR (dashed tick lines) EOSs for carbon dioxide (1) + 2-propanol (2) system.

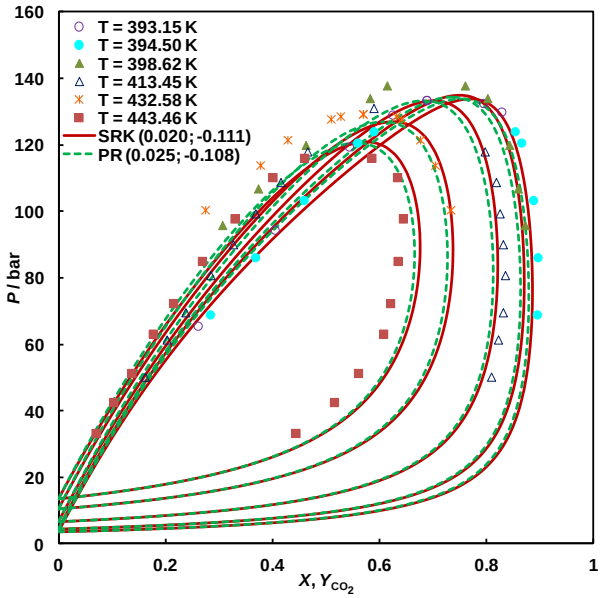

Fig. 9. Comparison of literature VLE data [36,39,37,37,37,37] and predictions by SRK (solid tick lines) and PR (dashed tick lines) EOSs for carbon dioxide (1) + 2-propanol (2) system.

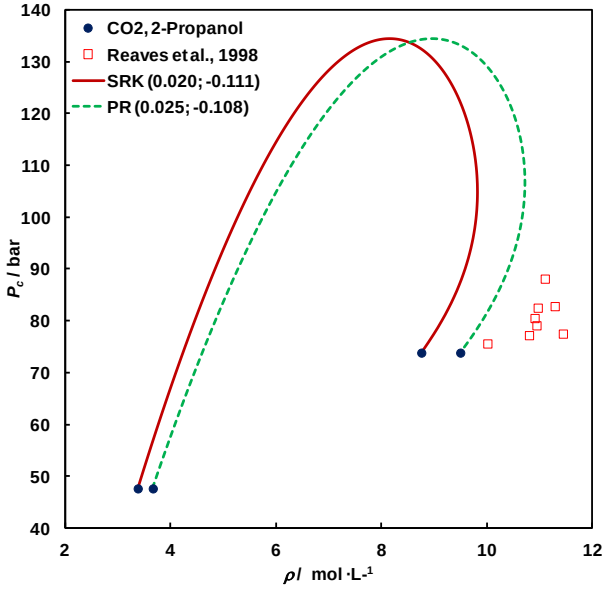

Fig. 10. *P*–ρ projection of the phase diagram for carbon dioxide (1) + 2-propanol (2) system: symbols, literature data [34]; lines, prediction by SRK (solid tick lines) and PR (dashed tick lines) EOSs.

It can be also noticed that at higher temperatures the vapor phase compositions are better predicted by SRK.
Finally we show the prediction results by SRK and PR for the pressure-density curves. In Fig. 10 we compare the scarce literature data with the model predictions.

The calculations were made using our in-house [59] software package ***PHEQ*** (**Ph**ase **Eq**uilibria Database and Applications), and GPEC [60-63] (Global Phase Equilibrium Calculations). The module calculating the critical curve, called CRITHK in our software, is using the method proposed by Heidemann and Khalil [64] with the numerical derivatives given by Stockfleth and Dohrn [65].

4. Conclusions

The SRK and PR EOSs coupled with classical quadratic van der Waals mixing rules were used to predict the phase behavior of the carbon dioxide (1) + 2-propanol (2) binary system. The predictions were done with one set of binary interaction parameters for each model that was obtained for carbon dioxide (1) + 2-butanol (2) system, being the intersection of the experimental temperature of UCEP and critical pressure maximum (CPM) traced by paths in k_{12}–l_{12} diagram.

The predictions (VLE data and critical curves) are remarkable good for both models.

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R E F E R E N C E S

[1]. *R. Dohrn*, Fluid Phase Equilib. **106**, 1995, 213–282.
[2]. *M. Christov, R. Dohrn*, Fluid Phase Equilib. **202**, 2002, 153–218.
[3]. *R. Dohrn, S. Peper, J.M.S. Fonseca*, Fluid Phase Equilib. **288**, 2010, 1–54.
[4]. *J.M.S. Fonseca, R. Dohrn, S. Peper*, Fluid Phase Equilib. **300**, 2011, 1–69.
[5]. *S. Peper, R. Dohrn*, J. Supercrit. Fluids **66**, 2012, 2–15.
[6]. *B. Díaz-Reinoso, A. Moure, H. Domínguez, J.C. Parajó*, J. Agric. Food Chem. **54**, 2006, 2441–2469.
[7]. *C. Secuianu, V. Feroiu, D. Geană*, J. Chem. Eng. Data **48**, 2003, 1384–1386.
[8]. *C. Secuianu, V. Feroiu, D. Geană*, Rev. Chim. (Bucharest) **54**, 2003, 874–879.
[9]. *C. Secuianu, V. Feroiu, D. Geană*, Sci. Technol. Environ. Prot. J. **10**, 2003, 62–70.
[10]. *C. Secuianu, V. Feroiu, D. Geană*, J. Chem. Eng. Data **49**, 2004, 1635–1638.
[11]. *C. Secuianu, V. Feroiu, D. Geană*, Univ. Politeh. Buchar. Sci. Bull.-Ser. B-Chem. Mat. Sci. **66**, 2004, 9–18.
[12]. *C. Secuianu, V. Feroiu, D. Geană*, Sci. Technol. Environ. Prot. J. **11**, 2004, 48–60.

[13]. *C. Secuianu, V. Feroiu, D. Geană*, Sci. Technol. Environ. Prot. J. **12**, 2005, 77–86.
[14]. *C. Secuianu, V. Feroiu, D. Geană*, Fluid Phase Equilib. **261**, 2007, 337–342.
[15]. *C. Secuianu, V. Feroiu, D. Geană*, Fluid Phase Equilib. **270**, 2008, 109–115.
[16]. *C. Secuianu, V. Feroiu, D. Geană*, J. Chem. Eng. Data **53**, 2008, 2444–2448.
[17]. *C. Secuianu, V. Feroiu, D. Geană*, J. Supercrit. Fluids **47**, 2008, 109–116.
[18]. *C. Secuianu, V. Feroiu, D. Geană*, Cent. Eur. J. Chem. **7**, 2009, 1–7.
[19]. *C. Secuianu, V. Feroiu, D. Geană*, J. Chem. Eng. Data **54**, 2009, 1493–1499.
[20]. *C. Secuianu, V. Feroiu, D. Geană*, Rev. Chim. (Bucharest) **60**, 2009, 472–475.
[21]. *C. Secuianu, V. Feroiu, D. Geană*, J. Chem. Thermodyn. **42**, 2010, 1286–1291.
[22]. *C. Secuianu, V. Feroiu, D. Geană*, J. Supercrit. Fluids **55**, 2010, 653–661.
[23]. *C. Secuianu, V. Feroiu, D. Geană*, Int. J. Liq. State Sci. **2**, 2010, 1–14.
[24]. *C. Secuianu, V. Feroiu, D. Geană*, J. Chem. Eng. Data **56**, 2011, 5000–5007.
[25]. *C. Secuianu, J. Qian, R. Privat, J.-N. Jaubert*, Ind. Eng. Chem. Res. **51**, 2012, 11284–11293.
[26]. *S. Sima, S. Ioniţă, C. Secuianu, V. Feroiu, D. Geană*, Rev. Chim.-Bucharest **65** (3), 2014, 272–279.
[27]. *S. Sima, C. Secuianu, V. Feroiu, D. Geană*, Cent. Eur. J. Chem. **12** (9), 2014, 893–900.
[28]. *S. Sima, C. Secuianu, V. Feroiu, D. Geană*, Cent. Eur. J. Chem. **12** (9), 2014, 953–961.
[29]. *S. Ioniţă, S., C. Secuianu, V. Feroiu, D. Geană*, Univ. Politeh. Buchar. Sci. Bull.-Ser. B-Chem. Mat. Sci. **77** (1), 2015, 31–40.
[30]. *C. Secuianu, V. Feroiu, D. Geană*, Fluid Phase Equilib. **428**, 2016, 62–75.
[31]. *C. Secuianu, S. Ioniţă, V. Feroiu, D. Geană*, J. Chem. Thermodyn. **93**, 2016, 360–373.
[32]. *P.H. van Konynenburg, R.L. Scott*, Philos. Trans. Royal Soc. London, Series A **298**, 1980, 495–540.
[33]. *Th.W. de Loos*, Understanding phase diagrams, in: E. Kiran, J.M.H. Levelt Sengers (Eds.), Supercritical Fluids. Fundamentals for Application, Kluwer, Dordrecht, 72–75, 1994.
[34]. *J.T. Reaves, A.T. Griffith, C.B. Roberts*, J. Chem. Eng. Data **43** (4), 1998, 683–686.
[35]. *G.S. Gurdial, N.R. Foster, S.L.J. Yun, K.D. Tilly*, in ACS Symp. Ser. **514**, 1993, 34–45.
[36]. *C. Kwak, H.S. Byun*, Kongop Hwahak **10** (2), 1999, 324–329.
[37]. *O. Elizalde-Solis, L.A. Galicia-Luna, L. E. Camacho-Camacho*, Fluid Phase Equilib. **259** (1), 2007, 23–32.
[38]. *J.W. Ziegler, T.L. Chester, D.P. Innis, S.H. Page, J.G. Dorsey*, in ACS Symp. Ser. **608**, 1995, 93–110.
[39]. *M. Radosz*, J. Chem. Eng. Data **31** (1), 1986, 43–45.
[40]. *S. Yao, F. Liu, Z. Han, Z. Zhu*, Gaoxiao Huaxue Gongcheng Xuebao **3** (3), 1989, 9–15.
[41]. *Z. Luo, Y. Wei, Y. Hu*, Huagong Xuebao **41** (4), 1990, 395–402.
[42]. *T. Suzuki, N. Tsuge, K. Nagahama*, Fluid Phase Equilib. **67**, 1991, 213–226.
[43]. *R. Yaginuma, T. Nakajima, H. Tanaka, M. Kato*, J. Chem. Eng. Data **42** (4), 1997, 814–816.
[44]. *A. Bamberger, G. Maurer*, J. Chem. Thermodyn. **32**, 2000, 685–700.
[45]. *L.A. Galicia-Luna, A. Ortega-Rodriguez, D. Richon*, J. Chem. Eng. Data **45** (2), 2000, 265–271.
[46]. *A. Stratmann*, In-situ Raman-spectroscopy of evaporation equilibria. Measurement of two-component systems under elevated pressure and elevated temperature, Ph.D. Thesis 2 Ruhr University Bochum, Germany, 2003.
[47]. *M.J. Lazzaroni, D. Bush, J.S. Brown, C.A. Eckert*, J. Chem. Eng. Data **50** (1), 2005, 60–65.
[48]. *J.S. Lim, Y.G. Jung, K.P. Yoo*, J. Chem. Eng. Data **52** (6), 2007, 2405–2408.
[49]. *L. Zevnik, J. Levec*, J. Supercrit. Fluids **41** (3), 2007, 335–342.
[50]. *W. Khalil, C. Coquelet, D.Richon*, J. Chem. Eng. Data **52** (5), 2007, 2032–2040.
[51]. *L.A. Galicia-Luna, O. Elizalde-Solis*, Fluid Phase Equilib. **296** (1), 2010, 46–52.
[52]. *T. Aida,T. Aizawa, M. Kanakubo, H. Nanjo*, J. Phys. Chem. B **114** (43), 2010, 13628–13636.
[53]. *T.Z. Li, Z.G. Tang, H. Hu, D. Guo*, Gaoxiao Huaxue Gongcheng Xuebao **26** (1), 2012, 1–6.

[54]. *H. Nourozieh, M. Kariznovi, J. Abedi*, J. Chem. Thermodyn. **65**, 2013, 191–197.
[55]. *D.Y. Peng, D.B. Robinson*, Ind. Eng. Chem. Fundam. **15**, 1976, 59–64.
[56]. *G. Soave*, Chem. Eng. Sci. **27**, 1972, 1197–1203.
[57]. *I. Polishuk, J. Wisniak, H. Segura*, Chem. Eng. Sci. **56**, 2001, 6485–6510.
[58]. Evaluated Standard Thermophysical Property Values, DIPPR Project 801 full version, Brigham Young University, Provo Utah, 2005.
[59]. *D. Geană, L. Rus*, in Proc. Romanian Int. Conf. Chem. Chem. Eng. (RICCCE XIV), Bucharest, Romania, 2, 170–178, 2005.
[60]. *M. Cismondi, M. Michelsen, J. Supercrit. Fluids* **39**, *2007, 287–295.*
[61]. *M. Cismondi, M. Michelsen*, Fluid Phase Equilib. **259**, 2007, 228–234.
[62]. *M. Cismondi, M.L. Michelsen, M.S. Zabaloy*, Ind. Eng.Chem. Res. **47** (23), 2008, 9728–9743.
[63]. http://gpec.phasety.com
[64]. *R.A. Heidemann, A.M. Khalil*, A. M. AIChE J. **26**, 1980, 769–779.
[65]. *R. Stockfleth, R. Dohrn*, Fluid Phase Equilib. **145**, 1998, 43–52.