

# Fluid Phase Equilibria Modelling for Carbon Dioxide + Methanol System with Cubic Equations of State

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The purpose of this paper is to compare three cubic equations of state to model the phase behaviour of carbon dioxide + methanol system. All available literature data for carbon dioxide + methanol system were modeled with cubic equations of state (EoS) using classical van der Waals (two-parameter conventional mixing rule, 2PCMR) mixing rules. A single set of interaction parameters was used to model the global phase behaviour in the binary mixture carbon dioxide + methanol.

Keywords: vapour-liquid equilibria, carbon dioxide, methanol, equations of state (EoS)

An important role in cost-effective design and operation of chemical and biochemical plants plays the accurate knowledge of phase behaviour and of thermophysical properties of fluids [1-5]. While the thermodynamic properties determine the feasibility of a given process, the transport properties have a major impact on sizing of the equipment [1-5]. Accurate and reliable thermodynamic and transport property data, over a wide range of mixtures and conditions, are required due to the diversity of products and applications [1-5]. As the experiments are usually expensive and very time-consuming, equation of state models are the most common approach for the correlation and prediction of phase equilibria and properties of the mixtures.

In this paper we present the prediction results for the carbon dioxide + methanol binary systems by three cubic equations of state coupled with classical van der Waals mixing rules (2PCMR). The equations of state used are the general cubic equation of state (GEOS) [6-9], Peng-Robinson (PR) [10], and Soave-Redlich-Kwong (SRK) [11]. Following the same modeling procedure as in our previous papers [12-23], a single set of interaction parameters,

representing well the critical pressure maximum (CPM) and avoiding a false upper critical end point (UCEP) at high temperatures, was used to model the phase behaviour of the carbon dioxide + methanol system. The model results were compared to all available literature VLE data. The results show a satisfactory agreement between the model and the experimental data.

## Modeling

The modeling of phase behaviour of this system was made with the GEOS [6-9], PR [10], and SRK [11] EoS coupled with classical van der Waals mixing rules (2PCMR). The GEOS [6] equation of state is:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V-d)^2 + c} \quad (1)$$

with the classical van der Waals mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad b = \sum_i \sum_j x_i x_j b_{ij} \quad (2)$$

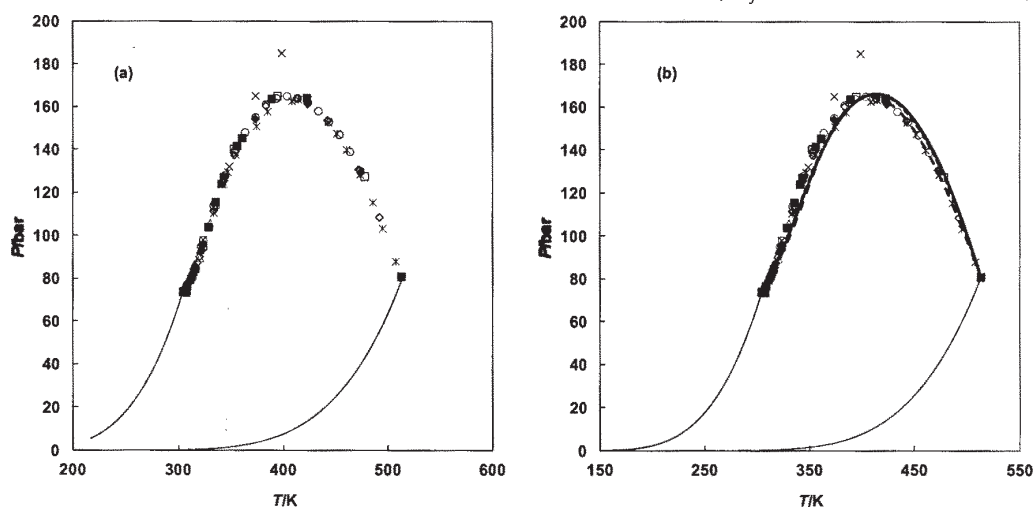


Fig. 1. *P-T* fluid phase diagram of carbon dioxide (1) + methanol (2) system: (-), Chobanov et al. [78]; (\*), Liu et al. [79]; (+), Zhu et al. [74]; (—), Zhang et al. [80]; (Δ), Joung et al. [67]; (■), Yeo et al. [81]; (o), Ziegler et al. [33]; (▲), Gurdial et al. [82]; (□), Leu et al. [75]; (◆), Brunner et al. [83]; (◇), Brunner [55]; (x), Semenova et al. [34]; (●●), critical points of pure components, [84]; □/▢ vapor pressure curves of pure components; — — —, critical line predicted by GEOS ( $k_{12} = 0.030$ ,  $l_{12} = 0.007$ ); ·····, ———, critical lines predicted by PR and SRK EOS respectively ( $k_{12} = 0.018$ ,  $l_{12} = 0.005$ )

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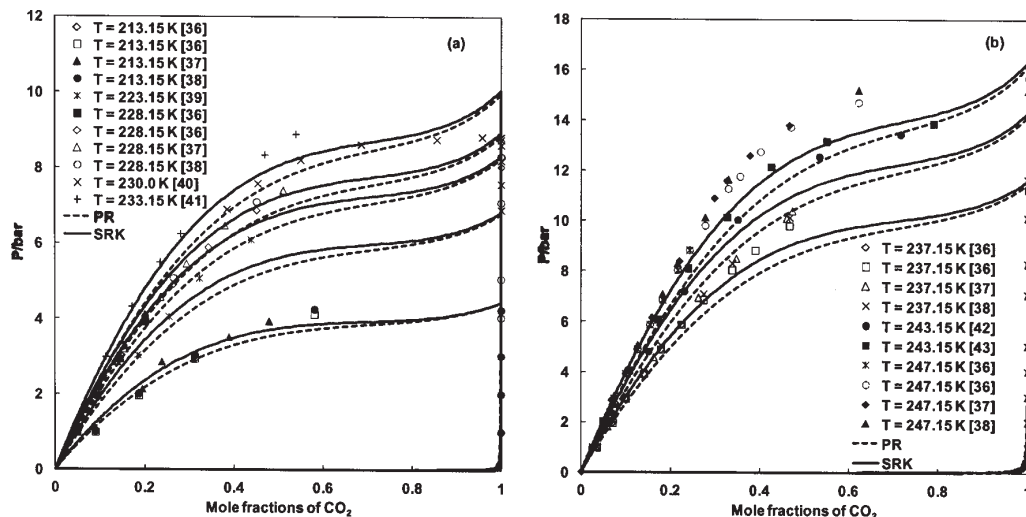


Fig. 2. Comparison of literature VLE data and calculations by thermodynamic models for carbon dioxide + methanol at different temperatures: symbols, experimental data; lines, predictions by PR and SRK ( $k_{12} = 0.018, l_{12} = 0.005$ ) respectively

$$c = \sum_i \sum_j x_i x_j c_{ij} \quad d = \sum_i x_i d_i \quad (3)$$

$$a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij}); b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}); c_{ij} = \pm (c_i c_j)^{1/2} \quad (4)$$

with "+" for  $c_i c_j > 0$  and "-" for  $c_i c_j < 0$ . Generally, negative values are common for the  $c$  parameter of pure components.

The four parameters  $a, b, c, d$  for a pure component are expressed by:

$$a = \frac{R^2 T_c^2}{P_c} \beta(T_r) \Omega_a \quad b = \frac{R T_c}{P_c} \Omega_b \quad (5)$$

$$c = \frac{R^2 T_c^2}{P_c^2} \Omega_c \quad d = \frac{R T_c}{P_c} \Omega_d \quad (6)$$

Setting four critical conditions, with  $\alpha_c$  as the Riedel's criterion:

$$P_r = 1; \left( \frac{\partial P_r}{\partial V_r} \right)_{T_r} = 0; \left( \frac{\partial^2 P_r}{\partial V_r^2} \right)_{T_r} = 0; \alpha_c = \left( \frac{\partial P_r}{\partial T_r} \right)_{V_r} \quad (7)$$

at  $T_r = 1$  and  $V_r = 1$ , the expressions of the parameters  $\Omega_a, \Omega_b, \Omega_c, \Omega_d$  are obtained:

$$\Omega_a = (1-B)^3; \quad \Omega_b = Z_c - B; \quad \Omega_c = (1-B)^2 (B-0.25) \quad (8)$$

$$\Omega_d = Z_c - \frac{(1-B)}{2} \quad B = \frac{1+m}{\alpha_c + m} \quad (9)$$

where  $P_r, T_r, V_r$  are the reduced variables and  $Z_c$  is the critical compressibility factor.

The temperature function used is:

$$a(T) = a \cdot \beta(T_r); \quad \beta(T_r) = T_r^{-m} \quad (10)$$

The GEOS parameters  $m$  and  $\alpha_c$  were estimated by constraining the EoS to reproduce the experimental vapour pressure and liquid volume on the saturation curve between the triple point and the critical point [6].

The SRK [11] and PR [10] EoS respectively are:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V \cdot (V+b)} \quad (11)$$

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \quad (12)$$

As pointed out previously [8], the relations (8) and (9) are general forms for all the cubic equations of state with two, three, and four parameters. The parameters of the SRK EoS can be obtained from the eqs. (8) and (9) by setting [6-9] the following restrictions:  $\Omega_c = -(\Omega_b/2)^2$  and  $\Omega_d = -\Omega_b/2$ .

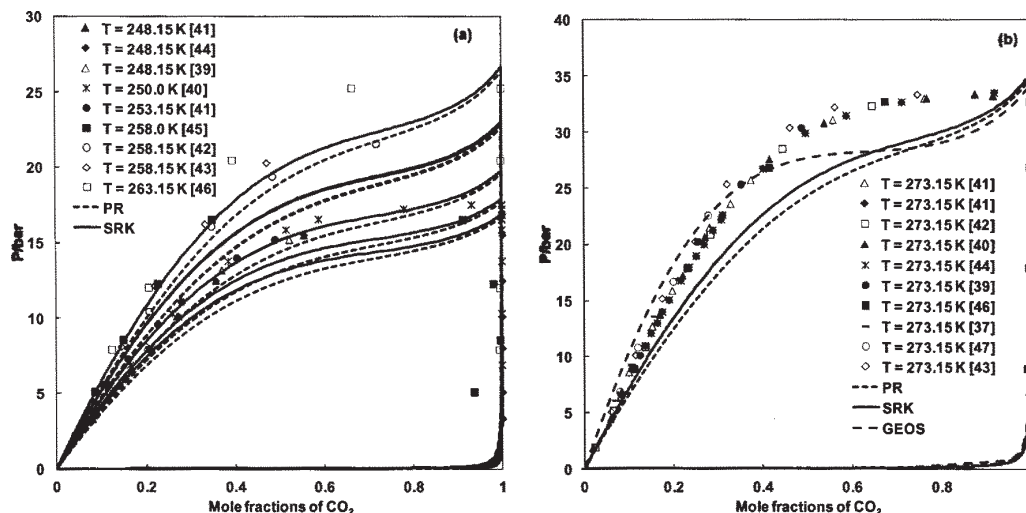


Fig. 3. Comparison of literature VLE data and calculations by thermodynamic models for carbon dioxide + methanol at different temperatures: symbols, experimental data; lines, predictions by GEOS ( $k_{12} = 0.030, l_{12} = 0.007$ ), PR, and SRK ( $k_{12} = 0.018, l_{12} = 0.005$ ) respectively

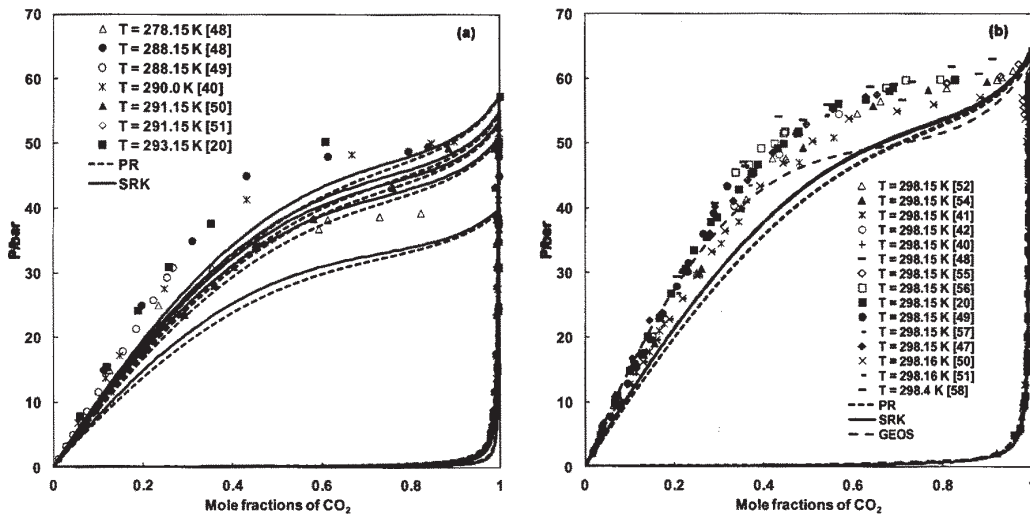


Fig. 4. Comparison of literature VLE data and calculations by thermodynamic models for carbon dioxide + methanol at different temperatures: symbols, experimental data; lines, predictions by GEOS ( $k_{12} = 0.030, l_{12} = 0.007$ ), PR, and SRK ( $k_{12} = 0.018, l_{12} = 0.005$ ) respectively

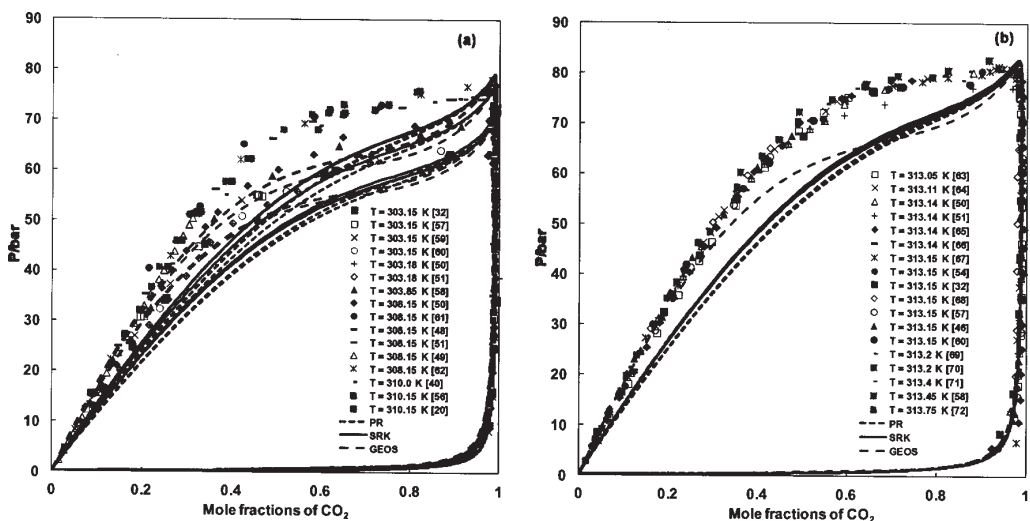


Fig. 5. Comparison of literature VLE data and calculations by thermodynamic models for carbon dioxide + methanol at different temperatures: symbols, experimental data; lines, predictions by GEOS ( $k_{12} = 0.030, l_{12} = 0.007$ ), PR, and SRK ( $k_{12} = 0.018, l_{12} = 0.005$ ) respectively

It follows

$$\Omega_c = (1-B)^2 (B-0.25) = -\frac{(Z_c - B)^2}{4} \quad (13)$$

$$\Omega_d = Z_c - 0.5(1-B) = -\frac{(Z_c - B)}{2} \quad (14)$$

It results:  $Z_c$  (SRK) = 1/3, and the relation for  $B$  (SRK)

$$B = 0.25 - \frac{1}{36} \left( \frac{1-3B}{1-B} \right)^2 \quad (15)$$

Solving iteratively this equation gives  $B$ (SRK) = 0.2467, and correspondingly

$$\Omega_a(\text{SRK}) = (1-B)^3 = 0.42748 \text{ and } \Omega_b(\text{SRK}) = Z_c - B = 0.08664$$

For PR EoS we set the restrictions [6-9]:  $\Omega_c = -2(\Omega_b)^2$  and  $\Omega_d = \Omega_b$ . It results

$$B = 0.25 - \frac{1}{8} \left( \frac{1-3B}{1-B} \right)^2 \quad (16)$$

$$Z_c = \frac{1+B}{4} \quad (17)$$

giving  $B$ (PR) = 0.2296 and  $Z_c$ (PR) = 0.3074.

The calculations were made using the software packages PHEQ, developed in our laboratory [24], and GPEC [25]. The calculation of the critical curves implemented in PHEQ is based on the method proposed

by Heidemann and Khalil [26], with numerical derivatives given by Stockfleth and Dohrn [27].

## Results and discussions

The carbon dioxide + methanol binary system can be attributed to type I phase diagram, according to the classification of van Konynenburg and Scott [28]. In the  $P$ - $T$  diagram [29], this type is characterized by one critical curve which runs continuously from the critical point of more volatile component (carbon dioxide) to the critical point of the less volatile component (methanol). In this study, the GEOS, PR, and SRK equations are used in a semi predictive approach to obtain a set of binary parameters yielding good results in the binary system carbon dioxide + methanol (including VLE in the entire temperature range and critical points).

Previously [30], it was shown that many thermodynamic models fail to predict correctly the behavior of this system. While experimental data suggest that this system behaves like type I, the models falsely predict liquid-liquid splitting at low temperatures, which is a different type of phase behaviour. The three models considered in this study also predict type II phase diagram, meaning that another liquid = liquid ( $L = L$ ) critical curve appears, which intersects in an upper critical endpoint (UCEP) with a three phase liquid-liquid-vapor (LLV) equilibrium line, which goes to lower temperatures. Therefore, the GEOS, PR, and SRK parameters were calculated to obtain the experimental value of the vapour-liquid critical pressure maximum (CPM) simultaneously with decreasing the temperature of the UCEP at lower temperature. The choice of this temperature for the false UCEP is justified by the existence

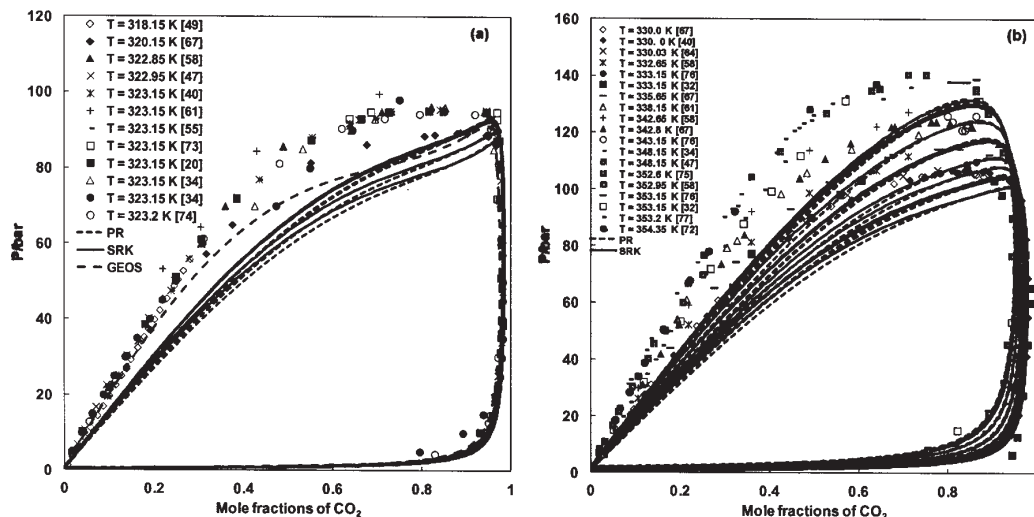


Fig. 6. Comparison of literature VLE data and calculations by thermodynamic models for carbon dioxide + methanol at different temperatures: symbols, experimental data; lines, predictions by GEOS ( $k_{12} = 0.030$ ,  $l_{12} = 0.007$ ), PR, and SRK ( $k_{12} = 0.018$ ,  $l_{12} = 0.005$ ) respectively

in the literature of an experimental isotherm at 213.15 K. The region of the type I (II) phase behaviour can be obtained by tracing the tricritical boundary curve in the  $k_{12}$ - $l_{12}$  diagram [31]. These types of phase behaviour are located on the left side of the tricritical boundary [31]. Our procedure leads to parameters located in this area. In a recent paper [32], we calculated a set of binary parameters using the  $k_{12}$ - $l_{12}$  method [22,31] to obtain simultaneously the experimental value of the vapour-liquid critical pressure maximum (CPM) and the temperature of UCEP with the GEOS equation. The UCEP temperature ( $\sim 200$  K) and CPM (165.0 bar [33]) have been traced by paths in  $k_{12}$ - $l_{12}$  diagram, and their intersection has given the values of the interaction parameters. The values of the interaction binary parameters ( $k_{12}$  and  $l_{12}$ ) fulfilling these requirements are  $k_{12} = 0.030$  and  $l_{12} = 0.007$  [32]. This set of interaction parameters was then used to predict the topology of phase behaviour and the critical and the bubble- and dew-point lines.

In this paper, using a similar procedure as described above, a unique set of binary interaction parameters was determined for both the SRK and PR equations. Thus, the set of binary interaction parameters is  $k_{12} = 0.018$ ,  $l_{12} = 0.005$  ( $T_{UCEP} \sim 180$  K,  $P_{CPM} \sim 166$  bar for PR;  $T_{UCEP} \sim 195$  K,  $P_{CPM} \sim 166.1$  bar for SRK respectively). Figure 1 presents the comparison of the three models with all available critical data (12 data sets) for the binary system studied. It can be seen that the critical experimental data are scattered (fig. 1. (a)). The highest deviation in pressure is about 20 bars [34]. While the difference in the critical pressure maximum is about two bars among the different sets, the difference in the experimental critical temperature is about 11 K. The best prediction of the critical curve is achieved by GEOS, followed by PR and SRK EoS, which show a similar behaviour (fig. 1. (b)). GEOS predicts also better the critical points of isotherms located at higher temperatures, while PR and SRK predict better the critical points of isotherms located at lower temperatures. It can be also seen that both PR and SRK predict the CPM at a higher temperature than the experimental one.

Nr. Crt.	T/K	$P_{range}$ /bar	NEXP <sup>a</sup>	Reference
1	213.15	1.0-2.9	3	Shenderei et al. [36]
2	213.15	0.98-4.12	4	Shenderei et al. [36]
3	213.15	1.12-3.94	5	Schneider [37]
4	213.15	1.01-4.26	4	Katayama and Nitta [38]
5	223.15	3.04-6.08	4	Takeuchi et al. [39]
6	228.15	1.0-3.9	4	Shenderei et al. [36]
7	228.15	0.98-8.04	8	Shenderei et al. [36]
8	228.15	1.08-7.40	12	Schneider [37]
9	228.15	1.01-8.31	7	Katayama and Nitta [38]
10	230.00	6.9-8.83	6	Hong and Kobayashi [40]
11	233.15	3.0-8.9	6	Weber et al. [41]
12	237.15	1.0-5.9	6	Shenderei et al. [36]
13	237.15	0.98-11.28	11	Shenderei et al. [36]
14	237.15	1.82-10.43	6	Schneider [37]
15	237.15	1.01-11.65	9	Katayama and Nitta [38]
16	243.15	2.1-13.5	6	Chang and Rousseau [39]
17	243.15	2.03-13.88	8	Yorizane et al. [40]
18	247.15	1.0-8.8	9	Shenderei et al. [36]
19	247.15	0.98-15.69	16	Shenderei et al. [36]
20	247.15	0.01-13.78	8	Schneider [37]
21	247.15	1.01-15.20	10	Katayama and Nitta [38]
22	248.15	3.3-16.9	7	Weber et al. [41]
23	248.15	3.3-16.9	7	Zeck [44]
24	248.15	5.07-15.20	5	Takeuchi et al. [39]
25	250.00	6.9-17.51	7	Hong and Kobayashi [40]
26	253.15	5.6-15.2	6	Weber et al. [41]
27	258.00	5.10-16.52	4	Ferrell et al. [45]
28	258.15	2.2-21.6	6	Chang and Rousseau [42]
29	258.15	4.05-20.27	5	Yorizane et al. [43]
30	263.15	7.92-25.27	4	Naidoo et al. [46]
31	273.15	4.5-33.0	9	Weber et al. [41]
32	273.15	6.6-34.9	20	Weber et al. [41]
33	273.15	1.94-32.3	6	Chang and Rousseau [42]

Table 1  
LITERATURE EXPERIMENTAL DATA FOR  
THE CARBON DIOXIDE + METHANOL  
BINARY SYSTEM

34	273.15	6.9-34.47	10	Hong and Kobayashi [40]
35	273.15	6.6-34.9	20	Zeck [44]
36	273.15	10.13-30.40	4	Takeuchi et al. [39]
37	273.15	8.91-32.73	4	Naidoo et al. [46]
38	273.15	0.04-16.93	6	Schneider [37]
39	273.15	6.89-22.6	4	Krichevskii and Lebedeva [47]
40	273.15	5.07-33.34	8	Yorizane et al. [43]
41	278.15	15.0-39.3	8	Bezanehtak et al. [48]
42	288.15	15.0-49.5	7	Bezanehtak et al. [48]
43	288.15	1.3-30.9	10	Gui et al. [49]
44	290.00	6.9-51.64	9	Hong and Kobayashi [40]
45	291.15	5.6-43.3	11	Chang et al. [50]
46	291.15	5.6-49.3	12	Chang et al. [51]
47	293.15	7.9-57.29	7	Secuianu et al. [20]
48	298.15	9.5-47.6	3	Rousseau et al. [52]
49	298.15	2.2-61.3	13	Katayama et al. [53]
50	298.15	7.9-59.5	8	Ohgaki and Katayama [54]
51	298.15	7.8-50.8	11	Weber et al. [41]
52	298.15	2.6-54.5	8	Chang and Rousseau [42]
53	298.15	17.3-57.5	13	Hong and Kobayashi [40]
54	298.15	15.0-60.8	9	Bezanehtak et al. [48]
55	298.15	17.3-62.3	17	Brunner et al. [55]
56	298.15	5.0-59.9	20	Secuianu et al. [56]
57	298.15	5.0-64.34	31	Secuianu et al. [20]
58	298.15	2.2-43.4	14	Gui et al. [49]
59	298.15	13.0-54.2	6	Laursen et al. [57]
60	298.15	6.89-40.23	6	Krichevskii and Lebedeva [47]
61	298.16	9.2-57.1	17	Chang et al. [50]
62	298.16	9.2-57.1	17	Chang et al. [51]
63	298.40	15.4-63.1	8	Reighard et al. [58]
64	303.15	9.6-63.3	10	Secuianu et al. [32]
65	303.15	12.40-55.10	7	Laursen et al. [57]
66	303.15	8.40-54.0	6	Schwinghammer et al. [59]
67	303.15	32.40-64.10		Pinto et al. [60]
68	303.18	8.9-63.2	16	Chang et al. [50]
69	303.18	5.6-43.3	16	Chang et al. [51]
70	303.85	16.6-69.0	8	Reighard et al. [58]
71	308.15	13.2-70.1	16	Chang et al. [50]
72	308.15	40.5-73.1	6	Roskar et al. [61]
73	308.15	15.4-74.3	9	Bezanehtak et al. [48]
74	308.15	13.2-70.1	16	Chang et al. [51]
75	308.15	2.4-50.4	21	Gui et al. [49]
76	308.15	22.29-78.22	7	Snedeker [62]
77	310.00	6.9-77.43	19	Hong and Kobayashi [40]
78	310.15	21.5-76.0	17	Secuianu et al. [56]
79	310.15	4.8-76.0	19	Secuianu et al. [20]
80	313.05	11.39-75.34	11	Elbaccouch et al. [63]
81	313.11	36.20-79.10	13	Sato et al. [64]
82	313.14	13.2-80.3	17	Chang et al. [50]
83	313.14	13.2-77.2	17	Chang et al. [51]
84	313.14	5.73-78.73	16	Raessi et al. [65]
85	313.14	5.73-78.73	16	Tochigi et al. [66]
86	313.15	6.9-81.5	12	Joung et al. [67]
87	313.15	5.8-80.6	9	Ohgaki and Katayama [54]
88	313.15	8.6-77.4	8	Secuianu et al. [32]
89	313.15	20.11-75.06	8	Kodama et al. [68]
90	313.15	15.90-63.40	5	Laursen et al. [57]
91	313.15	12.91-67.58	8	Naidoo et al. [46]
92	313.15	42.0-78.2	5	Pinto et al. [60]
93	313.20	7.0-82.1	13	Yoon et al. [69]
94	313.20	9.3-79.30	7	Xie et al. [70]
95	313.40	6.8-77.1	8	Suzuki et al. [71]
96	313.45	19.8-82.8	8	Reighard et al. [58]
97	313.75	2.96-78.85	13	Xia et al. [72]
98	318.15	1.2-55.8	22	Gui et al. [49]
99	320.15	6.0-89.5	11	Joung et al. [67]
100	322.85	23.0-96.3	7	Reighard et al. [58]
101	322.95	6.89-55.93	8	Krichevskii and Lebedeva [47]
102	323.15	9.9-95.5	14	Hong and Kobayashi [40]
103	323.15	53.3-99.6	4	Roskar et al. [61]
104	323.15	9.9-95.5	14	Brunner et al. [55]
105	323.15	61.1-94.8	4	Secuianu et al. [73]
106	323.15	10.3-95.1	10	Secuianu et al. [20]
107	323.15	5.0-98.0	15	Semenova et al. [34]
108	323.15	60.0-96.0	7	Zhu et al. [74]
109	323.20	4.4-95.0	10	Leu et al. [75]
110	330.00	7.8-105.9	12	Joung et al. [67]

11	330.00	6.9-106.46	13	Hong and Kobayashi [40]
12	330.03	86.20-107.10	4	Sato et al. [64]
13	332.65	26.3-111.9	6	Reighard et al. [58]
14	333.15	105.78-109.94	6	Page et al. [76]
15	333.15	6.6-103.4	10	Secuianu et al. [32]
16	335.65	8.4-114.6	12	Joung et al. [67]
17	338.15	54.1-119.4	8	Roskar et al. [61]
18	342.65	30.1-127.4	6	Reighard et al. [58]
19	342.80	6.7-124.0	14	Joung et al. [67]
20	343.15	125.85-125.85	7	Page et al. [76]
21	348.15	5.0-132.0	17	Semenova et al. [34]
22	348.15	6.89-69.71	9	Krichevskii and Lebedeva [47]
23	352.60	8.3-140.3	9	Leu et al. [75]
24	352.95	34.1-140.4	6	Reighard et al. [58]
25	353.15	137.70-138.92	5	Page et al. [76]
26	353.15	15.2-131.2	8	Secuianu et al. [32]
27	353.20	5.73-78.73	16	Tsuji and Hongo [77]
28	354.35	7.99-92.59	8	Xia et al. [72]
29	362.55	38.1-154.0	6	Reighard et al. [58]
30	363.15	145.40-147.83	5	Page et al. [76]
31	363.15	9.67-85.64	8	Naidoo et al. [46]
32	372.75	42.2-154.7	5	Reighard et al. [58]
33	373.15	38.1-154.2	11	Hong and Kobayashi [40]
34	373.15	152.80-152.80	3	Page et al. [76]
35	373.15	20.1-154.2	12	Brunner et al. [55]
36	373.15	5.0-165.0	17	Semenova et al. [34]
37	373.15	85.0-155.0	6	Zhu et al. [74]
38	373.15	21.57-120.68	9	Naidoo et al. [46]
39	383.15	155.33-155.64	3	Page et al. [76]
40	393.15	144.39-145.60	3	Page et al. [76]
41	394.20	10.3-165.0	9	Leu et al. [75]
42	395.00	16.64-97.35	8	Xia et al. [72]
43	398.15	10.0-185.0	18	Semenova et al. [34]
44	423.15	36.7-161.3	11	Hong and Kobayashi [40]
45	423.15	36.7-161.3	11	Brunner et al. [55]
46	423.15	70.0-162.0	7	Zhu et al. [74]
47	473.15	75.2-129.3	4	Hong and Kobayashi [40]
48	473.15	75.2-129.3	4	Brunner et al. [55]
49	473.15	70.0-130.0	5	Zhu et al. [74]
150	477.60	52.9-127.5	8	Leu et al. [75]

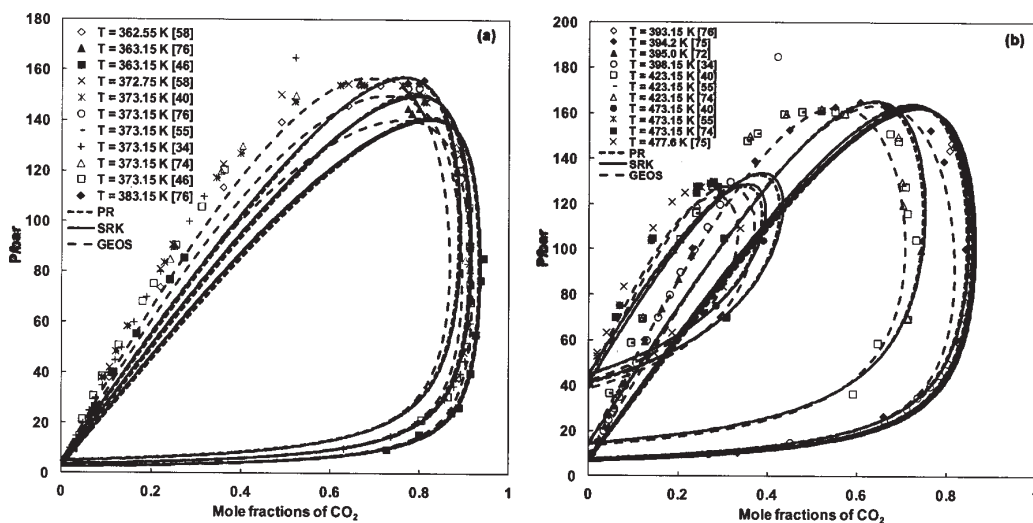


Fig. 7. Comparison of literature VLE data and calculations by thermodynamic models for carbon dioxide + methanol at different temperatures: symbols, experimental data; lines, predictions by GEOS ( $k_{12} = 0.030$ ,  $l_{12} = 0.007$ ), PR, and SRK ( $k_{12} = 0.018$ ,  $l_{12} = 0.005$ ) respectively.

In a previous paper [32], GEOS calculations with the set of parameters ( $k_{12} = 0.030$ ,  $l_{12} = 0.007$ ) were done for 75 data sets from the literature and new measured experimental data reported in that work, at temperatures between 230 and 477.6 K. In the present paper, 150 data sets (except data sets were only the vapour phase was reported) with 1400 experimental points were considered, as new measurements were reported in the literature since our previous paper and, additionally, the DETHERM database [35] was accessed. The experimental conditions of the available information for the carbon dioxide + methanol binary system are summarized in table 1. PR and SRK EoS with an unique set of parameters ( $k_{12} = 0.018$ ,  $l_{12} = 0.005$ ) were used to calculate all available data (table 1). The average absolute deviations in bubble point pressure (AADP, %) and vapor phase compositions (AADY, %) for the

carbon dioxide + methanol systems were also calculated for the three thermodynamic models used by the following equations:

$$AADP(\%) = \frac{1}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} \left| \frac{P_i^{\text{exp}} - P_i^{\text{calc}}}{P_i^{\text{exp}}} \right| \cdot 100 \quad (18)$$

$$AADY(\%) = \frac{1}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} |Y_i^{\text{exp}} - Y_i^{\text{calc}}| \cdot 100 \quad (19)$$

The best predictions are obtained by GEOS, the overall AADP being for this model 16.4%, followed by SRK (17.0 %), and PR (19.4 %). The prediction results by SRK and PR and the experimental data are plotted in figures 2-7. As in our previous paper [32] we shown the GEOS predictions,

the results by this model are illustrated only in the figures (3 (b), 4 (b), 5, 6 (a), 7) which are not very busy. It can be also remarked that the experimental data are very scatter at all temperatures (figs. 2-7), though the system received much attention.

Taking into account the semi predictive approach used in this work, the single sets of interaction parameters leads to satisfactory prediction of VLE for the carbon dioxide + methanol system. Compared to a correlation method, the deviations between experimental data and modeling results are rather high. A temperature-dependent  $k_{12}$  in a semi predictive approach was used in an earlier paper [31]. As shown in that work, obtaining the temperature dependence of  $k_{12}$  is difficult and does not lead to better results. However, even the errors are significantly smaller when correlating the experimental data, at lower temperatures, the calculation leads also to a false liquid-liquid splitting (as a maximum and a minimum in the bubble-point curves). This behaviour can be observed with other models too (different equation of state coupled with classical and  $G^E$  mixing rules). This is a known problem in correlating such systems. Therefore, the proposed approach in this work is justified to avoid the false liquid-liquid splitting and to represent correctly the phase behaviour.

### Conclusions

Three thermodynamic models with classical van der Waals (two-parameter conventional mixing rule, 2PCMR) mixing rules were used to compare the phase behaviour of the carbon dioxide + methanol binary system. One set of interaction parameters was used to predict the critical and sub-critical phase behaviour in the binary mixture carbon dioxide + methanol in a wide range of temperatures. The predicted results were compared with all the available literature data for carbon dioxide + methanol binary systems. The phase behaviour was satisfactory reproduced, taking into account the semi predictive procedure used.

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### List of symbols

a, b, c, d	- Equation of state parameters
CPM	- Critical Pressure Maximum
EoS	- Equation of State
GEOS	- General cubic equation of state
$k_{12}, l_{12}$	- Binary interaction parameters
L	- Liquid
Lit.	- Literature
m, $\alpha_c$	- GEOS parameters
NEXP	- Number of experimental points
P	- Pressure
2 PCMR	- Two-parameters conventional mixing rule
PR	- Peng-Robinson equation of state
SRK	- Soave-Redlich-Kwong equation of state
T	- Temperature
UCEP	- Upper critical endpoint
V	- Volume
VLE	- Vapor-Liquid Equilibria
x, y	- Mole fractions

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