PHASE DIAGRAM PREDICTIONS FOR CARBON DIOXIDE + DIFFERENT CLASSES OF ORGANIC SUBSTANCES AT HIGH PRESSURES

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The ability of a unique set of binary interaction parameters (BIPs) to predict the phase behavior of binary systems consisting of carbon dioxide (1) + organic compounds (2) from different classes is tested. The binary interaction set was determined for the carbon dioxide + 2-butanol binary mixture in a predictive way, being the intersection of the experimental temperature of the experimental upper critical endpoint (UCEP) and the experimental critical pressure maximum (CPM) traced by paths in k_{12}–l_{12} diagram. The calculations were performed with the Soave-Redlich-Kwong (SRK) cubic equation of state (EOS), coupled with classical van der Waals mixing rules (two-parameter conventional mixing rule, 2PCMR).

Keywords: carbon dioxide; *n*-butane; 1-butanol; 2-butanol; ethyl acetate; 1,2-dimethoxyethane; high pressures; phase diagrams; SRK; equation of state (EoS)

1. Introduction

Carbon dioxide (CO_2) accounts for over 80% of greenhouse gases (GHGs) emitted in atmosphere and reached a historical maximum last year [1, 2]. Many processes are responsible for the dramatic increase of carbon dioxide emissions such as burning fossil fuels (coal, natural gas, and oil) in energy production facilities and power plants, but also wood, solid waste, and other biological materials, by-product of certain chemical reactions in different industries (e.g., cement and steel factories), worldwide bushfires, land use change, etc. [3-11]. The alarming increased concentrations of CO_2 and other GHGs into atmosphere trap

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heat leading to the greenhouse effect, which results in global warming and climate change sparking extreme phenomena [8, 9].

Carbon capture and storage (CCS) or carbon capture and utilization (CCU) are favorite options among many ways of reducing the carbon dioxide [12-18]. Despite their great potential in different industries with large CO_2 emissions, the drawback is still represented by costs [13-15, 19].

In this context, our group focused on investigating the phase behavior of carbon dioxide and different classes of organic substances as a way of carbon mitigation. Phase equilibria, both experimental determinations and modelling, at high-pressures of carbon dioxide with alcohols [20-51], alkanes [52, 53], cycloalkanes [52, 54, 55], ethers [56, 57], and esters [58], were explored to illustrate the functional group effect on the solvent ability to dissolve CO_2. It is well known that the experiments are usually expensive and very time consuming [10, 59-63]. Therefore, equations of state (EoS) models are the most common approach for the correlation and/or prediction of phase equilibria and properties of the mixtures [64-67].

In the present work, we discuss the influence of binary interaction parameters (BIPs) on predicting phase diagrams using Soave–Redlich–Kwong (SRK) [68] equation of state (EoS) coupled with classical van der Waals (two-parameter conventional mixing rule, 2PCMR) for several carbon dioxide + organic substances binary systems.

2. Modelling

Since van der Waals proposed his famous equation in 1873, cubic equations have been intensively studied, and they are to date the most common approach for the correlation and prediction of phase equilibria and properties of the mixtures, being used frequently for practical applications [67].

Although cubic equations of state have their known limitations [69-73], they offer the best balance between accuracy, simplicity, reliability, and speed of computation, and remain an important and easy tool to calculate the phase behavior of many systems, even for complex mixtures like petroleum fluids [74-76].

The model chosen for studying the influence of binary interaction parameters on the prediction of phase behavior is the Soave–Redlich–Kwong (SRK) [68] equation of state (EoS) coupled with classical van der Waals (two-parameter conventional mixing rule, 2PCMR).

The Soave–Redlich–Kwong equation of state is:

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

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

$$a = 0.45748 \frac{R^2 T_c^2}{P_c} \alpha(T) \tag{2}$$

$$b = 0.08664 \frac{RT_c}{P_c} \tag{3}$$

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

$$m_{SRK} = 0.480 - 1.574\omega - 0.176\omega^2 \tag{5}$$

The two parameter conventional mixing rules are given by:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{6}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{7}$$

where

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right) \tag{8}$$

$$b_{ij} = \frac{b_i + b_j}{2}\left(1 - l_{ij}\right) \tag{9}$$

The calculations were made using the software package *PHEQ* (Phase Equilibria Database and Applications), developed in our laboratory [77], and GPEC (Global Phase Equilibrium Calculations) [78, 79]. In our in-house software, the module for calculating the critical curves is called CRIMIX and uses the method proposed by Heidemann and Khalil [80] with the numerical derivatives given by Stockfleth and Dohrn [81].

3. Results and discussion

Phase diagrams display the domains occupied by the different phases of a system, the boundaries that separate these regions, and the special points of the system, as a function of two independent variables. They are calculated using equations of state and the best known classification of phase diagrams for binary systems was proposed by van Konynenburg and Scott [82].

In a previous paper [40], we predicted the phase diagram for the carbon dioxide + 2-butanol binary system using the k_{12}–l_{12} method [43, 45, 83], meaning that we determined a unique set of interaction parameters in a wide range of

temperatures, representing exactly the experimental critical pressure maximum (CPM) and the experimental temperature of the upper critical endpoint (UCEP). This single set determined for the SRK EoS is k_{12} = 0.020 and l_{12} = -0.111. Stevens et al. [84] have provided experimental evidence that the binary system carbon dioxide + 2-butanol exhibits liquid–liquid immiscibility and therefore the system is a type II phase diagram, according to the classification of van Konynenburg and Scott [82] or the recent one of Privat and Jaubert [85]. Type II phase behavior is characterized by a continuous liquid–vapor critical curve stretching between the critical points of the pure components as in type I phase behavior, but additionally presents a liquid–liquid critical curve which intersects the three-phase liquid–liquid–vapor equilibrium line in an upper critical endpoint, as sketched in Fig. 1.

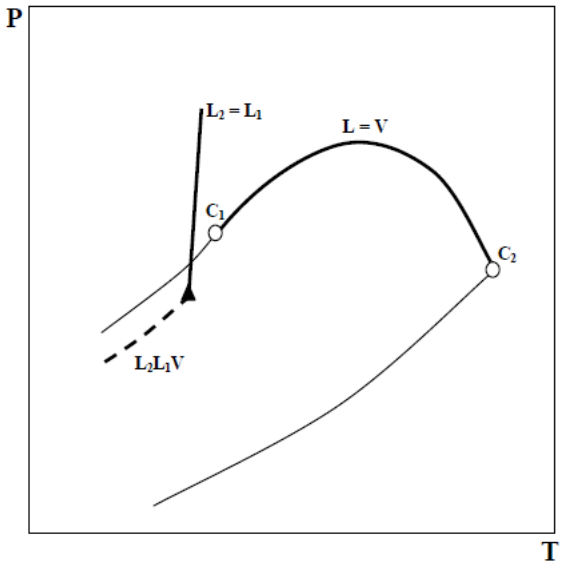


Fig.1. *P–T* fluid phase diagram for type II phase behavior

Table 1

Critical data (T_c, P_c) and acentric factor (ω) for pure components [86]

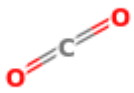
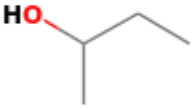
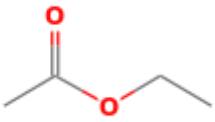
Compounds	Formula	Molecular weight	CAS number	T_c/K	p_c/MPa	ω
Carbon dioxide	CO_2	44.0095	124-38-9	304.21	7.383	0.22362
n-Butane	*n*-C_4H_{10}	58.1222	106-97-8	425.12	3.796	0.200164
1-Butanol	1-$C_4H_{10}O$	74.1216	71-36-3	563.0	4.414	0.589462
2-Butanol	2-$C_4H_{10}O$	74.1216	78-92-2	536.2	4.202	0.576776
1,2-Dimethoxyethane	$C_4H_{10}O_2$	90.1210	110-71-4	536.15	3.87061	0.347486
Ethyl acetate	$C_4H_8O_2$	88.1051	141-78-6	523.3	3.88	0.366409

We also showed that this set of parameters can accurately predict the phase behavior for carbon dioxide + 2-propanol system [30], which has a type I or type II phase diagram. It can be noticed that 2-propanol belongs to the same class of organic compounds as 2-butanol (secondary alcohols), but with three C atoms.

In the present work, we used the same set, tailored for the carbon dioxide + 2-butanol (2B) system, to predict the phase behavior of carbon dioxide + *n*-butane (nB), + 1-butanol (1B), + 1,2-dimetoxyethane (DME), and + ethyl acetate (EA) binary systems and study the influence of BIP on the mixtures with organic compounds from different classes. The critical data and the acentric factors of the pure substances [86] used in the calculations are presented in Table 1, while their chemical structures [87] are shown in Table 2.

Table 2

Chemical structures of pure components [87]

Compounds	Chemical structure
Carbon dioxide	
n-Butane	
1-Butanol	
2-Butanol	
1,2-Dimethoxyethane	
Ethyl acetate	

The organic substances selected as the second component in the binary systems all have four carbon atoms and zero, one, or two oxygen atoms, respectively. We compare one *n*-alkane (*n*-butane), two alcohols (the position isomers, 1- and 2-butanol), one ester (ethyl acetate), and one di-ether (1,2-dimethoxyethane). The critical pressures of 1-butanol and 2-butanol are very

similar, as are those of *n*-butane, ethyl acetate, and 1,2-dimethoxyethane, while the critical temperatures are increasing from *n*-butane, to ethyl acetate, 1,2-dimethoxyethane and 2-butanol, for which they are almost identical, and up to the highest value of 1-butanol.

Table 3

Available literature critical data for CO_2 (1) +n-Butane (2), + 1-Butanol (2), + 2-Butanol (2), +Ethyl Actetate (2), + 1,2-Dimethoxyethane (2) binary systems

Binary System	T_{range}/K	P_{range}/MPa	NEXP*	Observations	References
CO_2 + nB	368.15÷418.15	4.702÷7.901	3	VLE critical curve	Leu and Robinson [88]
	304.16÷424.92	3.790÷7.395	15	VLE critical curve	Horstmann et al. [89]
CO_2 + 1B	305.50÷329.20	7.580÷10.810	8	VLE critical curve	Gurdial et al. [90]
	315.26÷427.24	8.710÷17.373	6	VLE critical curve	Yeo et al. [91]
	304.25÷562.95	4.400÷7.390	19	VLE critical curve	Ziegler et al. [92]
CO_2 + 2B	304.10÷532.03	4.226÷8.290	17	VLE critical curve	Stevens et al. [84]
	249.34÷251.39	1.674÷1.787	6	LLV equilibrium line and UCEP	Stevens et al. [84]
	335.14÷431.73	10.473÷14.023	5	VLE critical curve	Silva-Oliver and Galicia-Luna [93]
CO_2 + EA	313.20÷393.20	8.160÷11.530	5	VLE critical curve	Byun et al. [94]
	304.25÷523.45	3.880÷7.638	16	VLE critical curve	Chester & Haynes [95]
CO_2 + 1,2-DME	333.15÷420.05	9.900÷12.870	15	VLE critical curve	Sima et al. [57]

*Number of experimental points

Table 4

Predicted UCEPs by SRK/2PCMR model (k_{12} = 0.020 and l_{12} = -0.111)

Binary System	T_{UCEP}/K	P_{UCEP}/MPa
CO_2 + nB	188.3122	0.11687
CO_2 + 1B	275.6178	2.93557
CO_2 + 2B	252.9606	1.54910
CO_2 + EA	215.0685	0.41040

CO_2 + 1,2-DME	217.3275	0.45158

We carefully reviewed the literature for the selected binary systems and the available critical data are presented in Table 3.

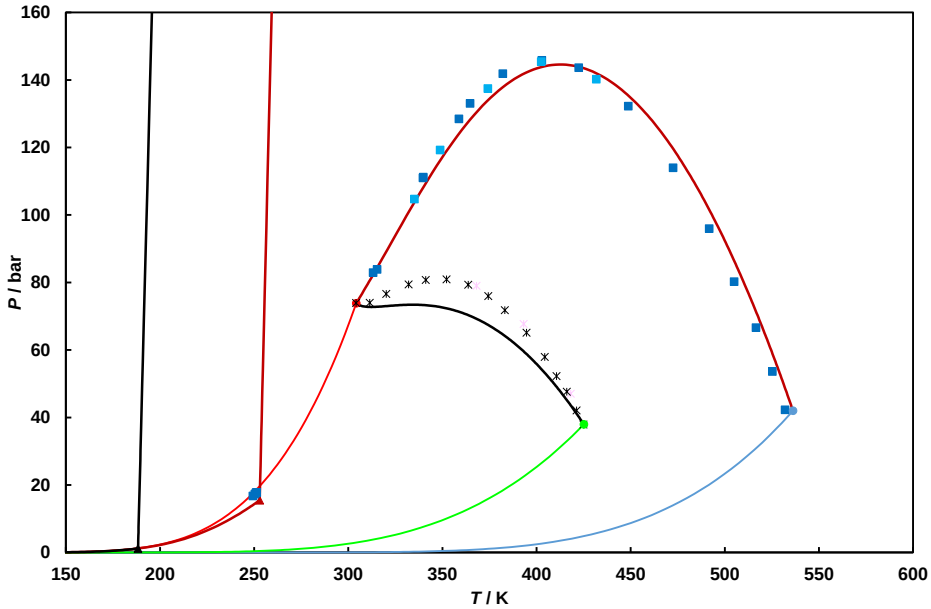


Fig. 2. Comparison of *P*–*T* fluid phase diagrams for carbon dioxide (1) + 2-butanol (2) and carbon dioxide (1) + *n*-butane (2) systems. Square symbols, literature data [84, 93] and red dark tick lines, predictions by SRK model for CO_2 + 2B. Star symbols, literature data [88, 89] and black tick lines, predictions by SRK model for CO_2 + nB.

The available experimental data from literature were compared with the SRK model predictions using the same BIPs for each system. We also compared the predicted phase behavior of each system with the reference system, carbon dioxide + 2-butanol. The model predicts type II phase behavior for all systems.

Thus, the predicted phase diagram of carbon dioxide (1) + *n*-butane (2) binary mixture is compared with that of carbon dioxide (1) + 2-butanol system in Fig. 2. The model predicts the liquid–liquid–vapor line at very low temperatures and underestimates the CPM by about 8 bar for the carbon dioxide + *n*-butane system. The carbon dioxide + *n*-butane predicted UCEP is situated at a very low temperature, much lower than that of carbon dioxide + 2-butanol system. The coordinates of the predicted UCEPs are given in Table 4 for all studied mixtures.

The SRK predictions for the carbon dioxide + 1-butanol system are compared with the carbon dioxide + 2-butanol system in Fig. 3. The model predicts type II phase behavior for the system containing the position isomer, 1-

butanol, as well. The liquid–vapor predicted critical curve for the carbon dioxide + 1-butanol binary system is shifted at higher temperatures compared with the experimental data, as can be seen in Fig. 3.

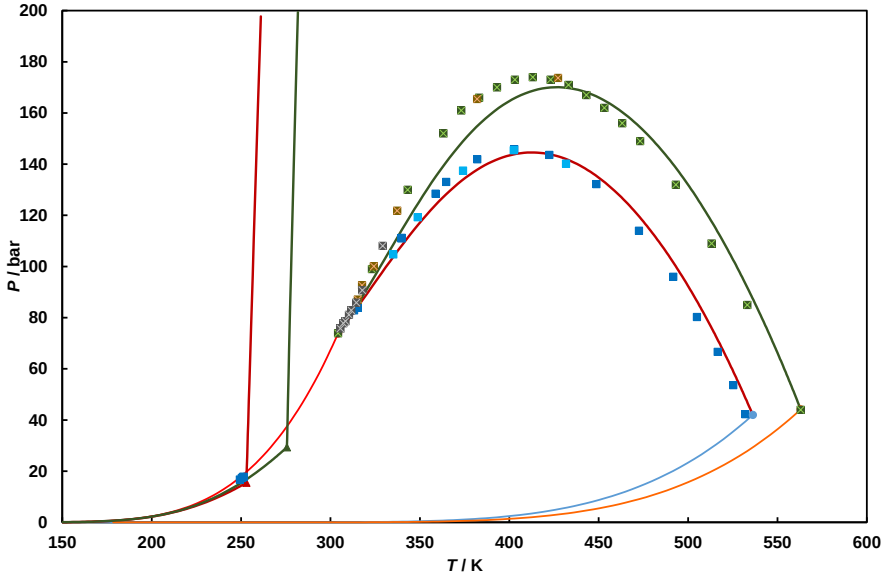


Fig. 3. Comparison of *P*–*T* fluid phase diagrams for carbon dioxide (1) + 2-butanol (2) and carbon dioxide (1) + 1-butanol (2) systems. Square symbols, literature data [84, 93] and red dark tick lines, predictions by SRK model for CO_2 + 2B. Crossed square symbols, literature data [90-92] and dark green tick lines, predictions by SRK model for CO_2 + 1B.

The CPM is slightly underestimated, but the corresponding temperature is ~ 14 degrees higher than the experimental one. The predicted UCEP for the carbon dioxide + 1-butanol system is located at a higher temperature than that of carbon dioxide + 2-butanol system.

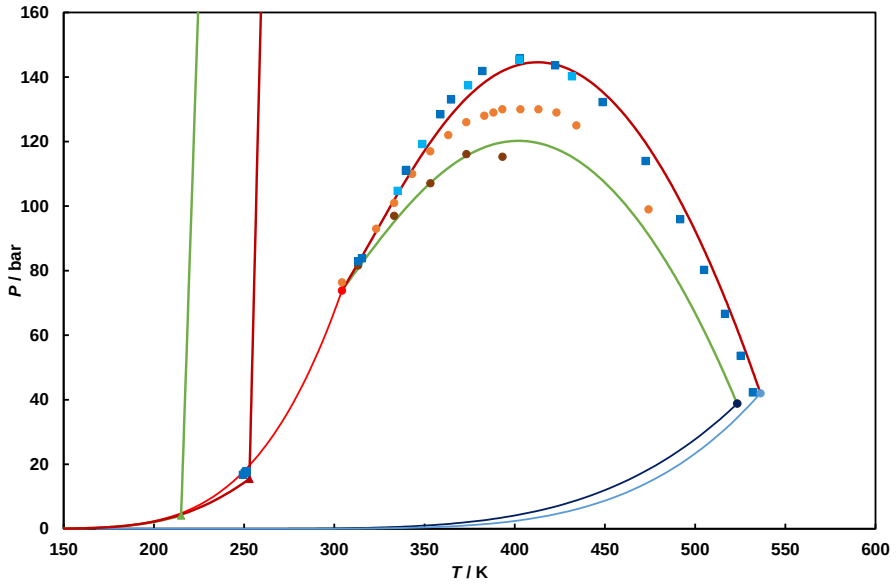


Fig. 4. Comparison of *P*–*T* fluid phase diagrams for carbon dioxide (1) + 2-butanol (2) and carbon dioxide (1) + ethyl acetate (2) systems. Square symbols, literature data [84, 93] and red dark tick lines, predictions by SRK model for CO_2 + 2B. Circle symbols, literature data [94, 95] and light green tick lines, predictions by SRK model for CO_2 + EA.

Fig. 4 shows the comparison of carbon dioxide + 2-butanol and carbon dioxide + ethyl acetate binary systems. It can be noticed that the available experimental data are not in agreement for the carbon dioxide + ethyl acetate binary system, the difference in CPM being about 15 bar for the two literature sets [94, 95]. The SRK model prediction for the liquid–vapor curve is in agreement with the experimental critical pressure reported by Byun et al. [94] and with the critical temperatures measured by Chester et al. [95]. The temperature corresponding to the CPM for the carbon dioxide + ethyl acetate system is very well predicted and in agreement with the experimental data from Chester et al. [95]. The predicted UCEP for the carbon dioxide + ethyl acetate is located at a lower temperature than that of carbon dioxide + 2-butanol system.

Finally, the predictions by SRK/2PCMR for the carbon dioxide + 1,2-dimethoxyethane and carbon dioxide + 2-butanol binary mixtures are shown in Fig. 5. The liquid–vapor critical curve is remarkably well predicted for the carbon dioxide + 1,2-dimethoxyethane system. The predicted UCEP for carbon dioxide + 1,2-dimethoxyethane system is at a lower temperature than that of carbon dioxide + 2-butanol system.

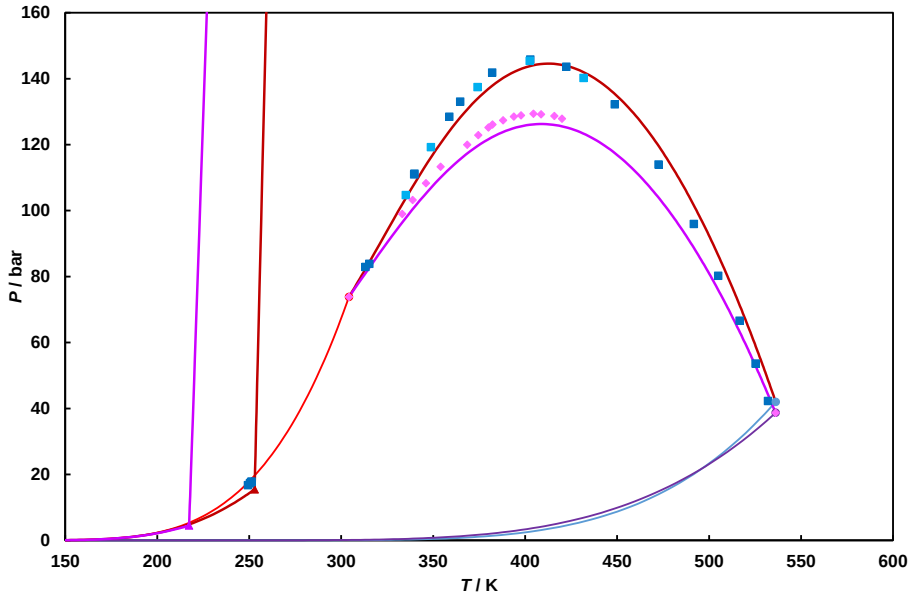


Fig. 5. Comparison of *P*–*T* fluid phase diagrams for carbon dioxide (1) + 2-butanol (2) and carbon dioxide (1) + 1,2-dimethoxyethane (2) systems. Square symbols, literature data [84, 93] and red dark tick lines, predictions by SRK model for CO_2 + 2B. Diamond symbols, literature data [57] and pink tick lines, predictions by SRK model for CO_2 + DME.

It can be noticed that the liquid–vapor critical curves are ranging increasingly from ~70 bar to ~175 bar in the order carbon dioxide + *n*-butane, + ethyl acetate, + 1,2-dimethoxyethane, + 2-butanol, and + 1-butanol, respectively.

4. Conclusions

The phase behavior of several binary systems containing carbon dioxide and an organic compound belonging to various classes (*n*-alkane, primary and secondary alcohols, di-ether, ester) was predicted using the SRK/2PCMR with a single set of binary interaction parameters (k_{12} = 0.020 and l_{12} = -0.111). The unique set of BIPs was determined for the carbon dioxide + 2-butanol system using the k_{12}-l_{12} method and further used to successfully model the carbon dioxide + *n*-butane, + 1-butanol, + ethyl acetate, and + 1,2-dimethoxyethane binary systems.

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