

## PHASE BEHAVIOR PREDICTIONS FOR CARBON DIOXIDE + ISOPROPANOL BINARY SYSTEM WITH A CUBIC EQUATION OF STATE

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### **Abstract**

*The purpose of this paper is to demonstrate the ability of a cubic equation model to predict the phase behavior of the carbon dioxide (1) + isopropanol (2) binary system. The model selected is the cubic General Equation of State – GEOS, coupled with classical van der Waals mixing rules – two-parameter conventional mixing rule, 2PCMR. One unique set of binary interaction parameters is used to predict the phase behavior of the system.*

**Key words:** Carbon dioxide, isopropanol, high pressures, VLE, GEOS, predictions

### **1. Introduction**

The carbon (as carbon dioxide, CO<sub>2</sub>) emissions produced by fossil fuel-powered plants and energy production facilities account for over 80% of greenhouse gases (GHGs) [1]. Among the many options for carbon mitigation, carbon capture and storage (CCS) is an almost essential part and could contribute approximately 20% to CO<sub>2</sub> emission reductions by 2050, as recommended by International Energy Agency (IEA) [1]. CCS holds great potential in industry and petroleum refineries given their large CO<sub>2</sub> emissions. In addition, there are many industrial processes that generate rich CO<sub>2</sub> gas streams, or in some cases pure CO<sub>2</sub>, which could reduce the costs of CCS.

At the same time, carbon dioxide is a non-hazardous and safe substance used as working fluid for many green products and processes due to its compatibility with the environment. In particular, the physical properties and

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phase behavior of complex mixtures containing CO<sub>2</sub> are nowadays associated with a wide range of applications [2-4].

Recently [5,6], we started to investigate experimentally the effect of the functional group of different classes of substances on the ability to dissolve carbon dioxide. We are equally interested in the capability of models to predict the phase behavior of these systems at high pressures.

Among the mixtures of interest, carbon dioxide + alcohol mixtures at high pressures are of particular importance in the design, simulation, and optimization of extraction processes, where alcohols are commonly used as co-solvents [7].

In this study, we focus on the carbon dioxide (1) + isopropanol (2) binary system. In a previous paper [6], we compared the prediction results by two well-known cubic equations of state (EoS), namely Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR), coupled with classical van der Waals mixing rules (2PCMR). A single set of binary interaction parameters for each EoS, determined for the carbon dioxide + 2-butanol binary system, was used to model the global phase behavior of the system.

Here, the global phase behavior of the system was modeled with a general cubic equation of state (GEOS) [8,9] coupled with classical van der Waals mixing rules (2PCMR). This cubic equation is a generalized form with four parameters for all cubic equations of state with two, three, and four parameters. One unique set of binary interaction parameters determined for the carbon dioxide + 1-propanol system was used to calculate the critical curves and vapor-liquid equilibrium diagrams.

## 2. Modeling

The modeling of phase behavior of this system was made with the GEOS equation [8,9] coupled with classical van der Waals mixing rules (2PCMR). The GEOS [8,9] 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

$$a = \sum_i \sum_j X_i X_j a_{ij} \quad b = \sum_i X_i b_i \quad (2)$$

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

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

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  $a$ ,  $b$ ,  $c$ , and  $d$  for a pure component are expressed by:

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

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

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

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

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:

$$\beta(T_r) = T_r^{-m} \quad (10)$$

The GEOS parameters  $m$  and  $\alpha_c$  were estimated by constraining the EoS to reproduce the experimental vapor pressure and liquid volume on the saturation curve between the triple point and the critical point [10].

The calculations were made using the software package *PHEQ*, developed in our laboratory [11]. The critical curves were calculated using the method proposed by Heidemann and Khalil [12], with numerical derivatives given by Stockfleth and Dohrn [13].

Instead of correlating the experimental data, we used a predictive approach. Thus, the GEOS equation was used in a semi-predictive approach to obtain a set of binary parameters yielding good results in the binary system carbon dioxide + 1-propanol (including VLE in the entire temperature range, critical points, global phase behavior) [14]. The set of binary parameters was calculated using the  $k_{12}-l_{12}$  method [15] to obtain the experimental value of the vapor-liquid critical pressure maximum (CPM) simultaneously with the temperature of the upper critical endpoint (UCEP). The binary system carbon dioxide + 1-propanol exhibits a type II phase diagram, according to the classification of van Konynenburg and Scott [16]. The parameter set ( $k_{12} = 0.042$ ;  $l_{12} = -0.021$ ) obtained for the mixture containing the position isomer was then used to model the carbon dioxide (1) + isopropanol (2) system. To our knowledge, there is no experimental evidence to support the classification into a type of phase diagram,

but it seems that the carbon dioxide + isopropanol (2-propanol) system exhibits type I or type II phase behavior, according to the classification of van Konynenburg and Scott [16] or the more recent one of Privat and Jaubert [17].

The GEOS parameters, critical data, the acentric factors of the pure substances used in the calculations are presented in Table 1 [18].

Table 1.  
Critical data, acentric factor [18], and GEOS parameters for pure compounds

Compound	$T_c/K$	$P_c/\text{bar}$	$V_c/\text{cm}^3\cdot\text{mol}^{-1}$	$\Omega$	$a_c$	$M$
carbon dioxide	304.21	73.83	93.90	0.2236	7.0517	0.3146
2-propanol (isopropanol)	508.30	47.64	220.0	0.6669	9.3838	0.6695

### 3. Results and discussions

In Fig. 1, the critical phase behavior of the carbon dioxide + isopropanol system by GEOS/2PCMR is presented. All available critical data in the literature are compared with GEOS predictions. As can be seen, the model predicts type I phase behavior, meaning that there is only vapor-liquid continuous critical curve stretching between the critical points of the pure components.

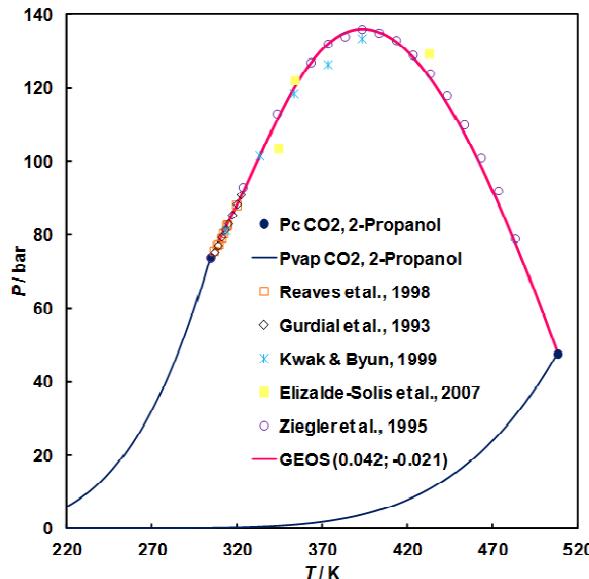
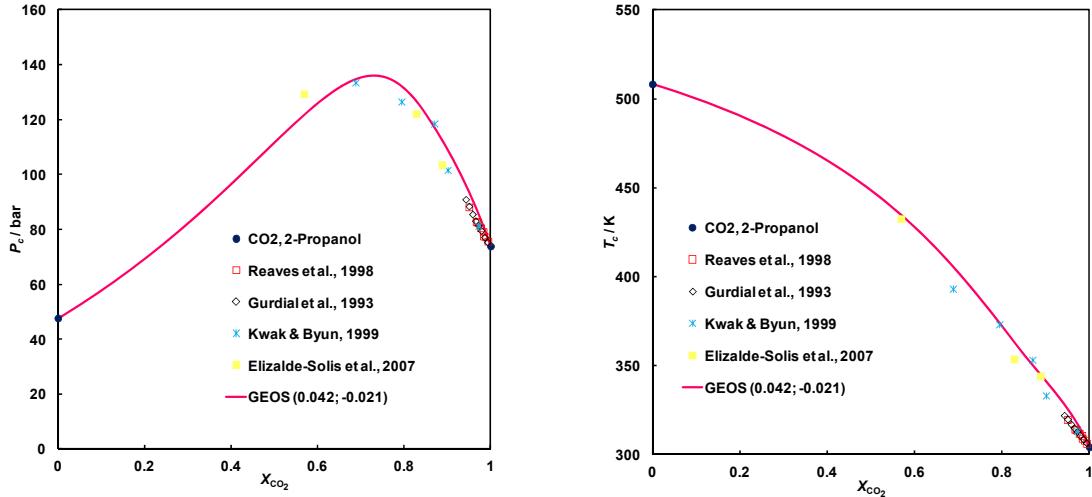
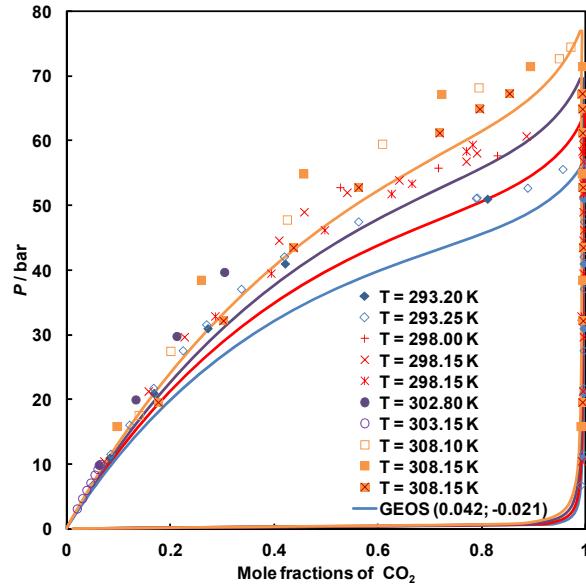


Fig. 1.  $P-T$  fluid phase diagram for carbon dioxide (1) + isopropanol (2) system: symbols, literature data [19-23]; thick line, predictions by GEOS.

Although the parameters were obtained for mixture with the position isomer, namely the carbon dioxide + 1-propanol binary system, it can be noticed that the critical curve is remarkably well predicted. In Fig. 2, the critical pressures and temperatures are plotted against carbon dioxide compositions. GEOS predictions are in good agreement with the available experimental data.

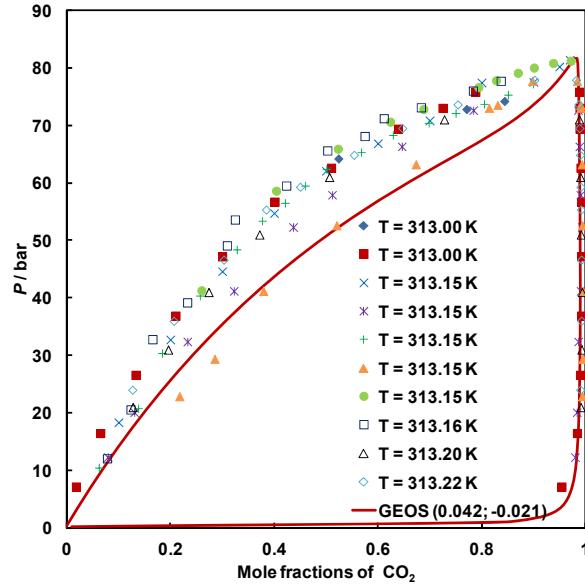


**Fig. 2.**  $P$ - $x$  and  $T$ - $x$  projections of the phase diagram for carbon dioxide (1) + isopropanol (2) system: symbols, literature data [19-22]; lines, predictions by GEOS.

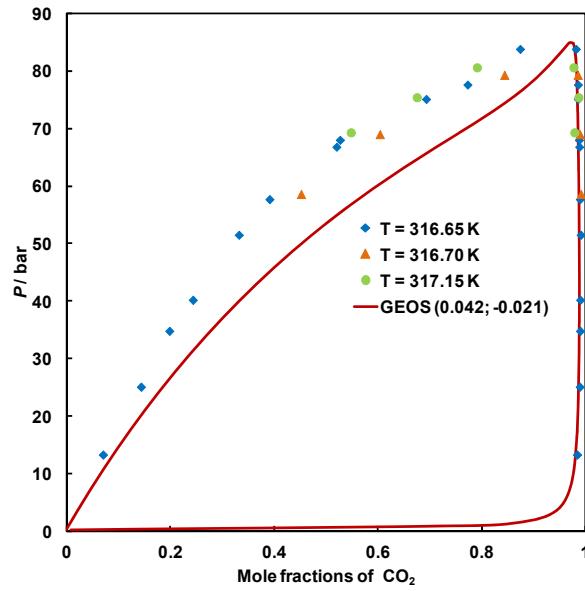


**Fig. 3.** Comparison of literature VLE data [24,27-31,24] and predictions by GEOS for carbon dioxide (1) + isopropanol (2) system.

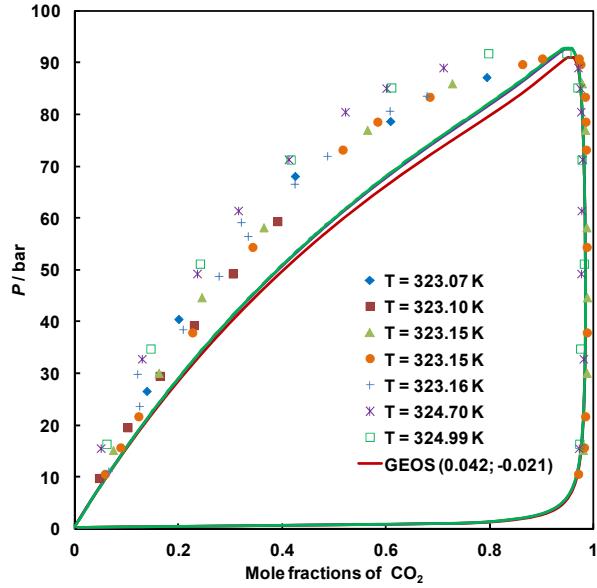
The set of binary interaction parameters was also used to predict all available vapor-liquid equilibrium (VLE) data in a wide range of temperatures and pressures. The literature experimental data and GEOS predictions are compared in Figs. 3-10.



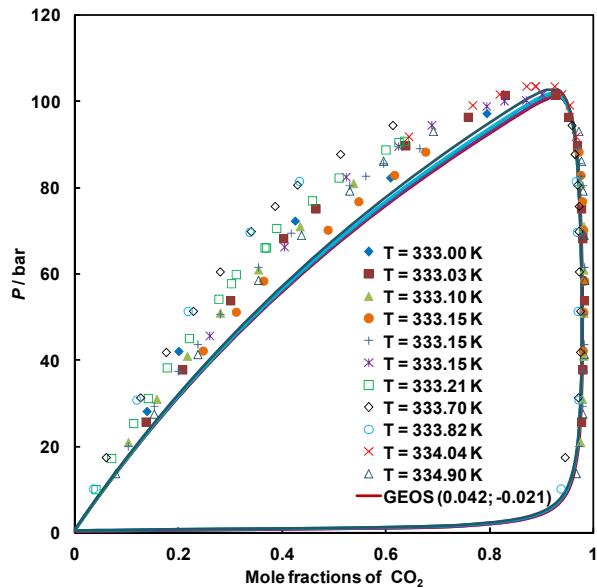
**Fig. 4.** Comparison of literature VLE data [36,26,30,33,31,21,35,39,35,25,38,32] and predictions by GEOS for carbon dioxide (1) + isopropanol (2) system.



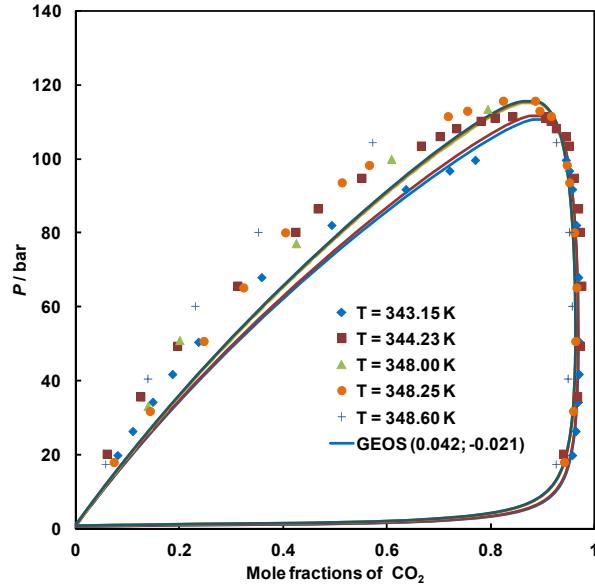
**Fig. 5.** Comparison of literature VLE data [24,40-41] and predictions by GEOS for carbon dioxide (1) + isopropanol (2) system.



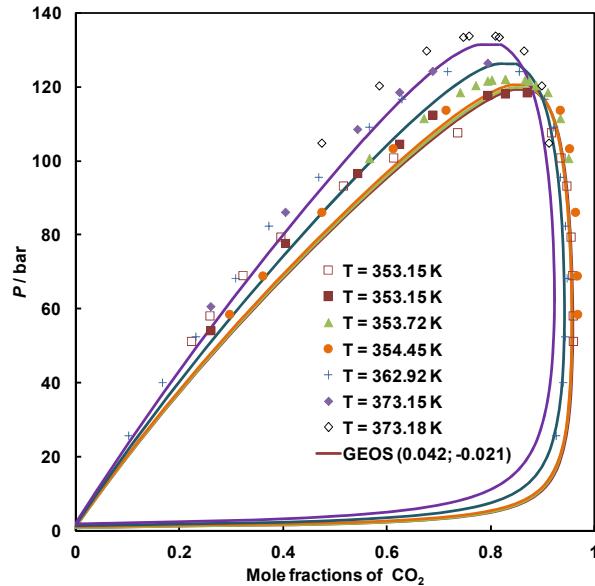
**Fig. 6.** Comparison of literature VLE data [30,28,24,37,35,34,34] and predictions by GEOS for carbon dioxide (1) + isopropanol (2) system.



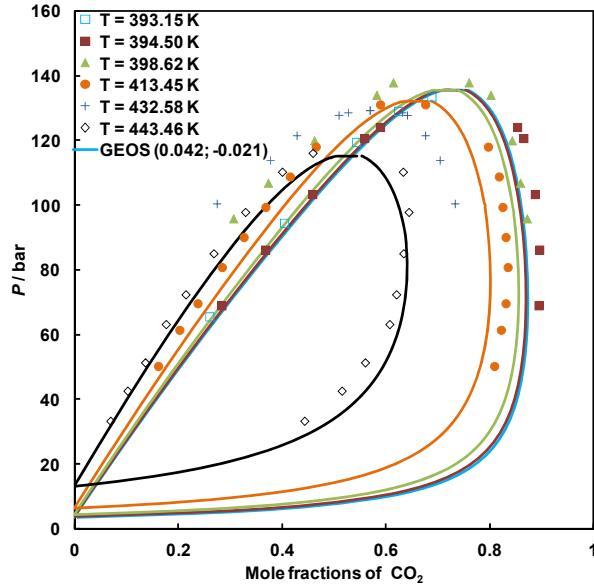
**Fig. 7.** Comparison of literature VLE data [30,38,21,37,27,35,25,35,32,34,34,22,40] and predictions by GEOS for carbon dioxide (1) + isopropanol (2) system.



**Fig. 8.** Comparison of literature VLE data [37,22,30,38,34] and predictions by GEOS for carbon dioxide (1) + isopropanol (2) system.



**Fig. 9.** Comparison of literature VLE data [21,37,22,40,38,21,22] and predictions by GEOS for carbon dioxide (1) + isopropanol (2) system.



**Fig. 10.** Comparison of literature VLE data [21,40,22,22,22,22] and predictions by GEOS for carbon dioxide (1) + isopropanol (2) system.

Although more than 500 equilibrium experimental points were collected for the carbon dioxide + isopropanol system in the PHEQ database, it can be easily noticed that there is a high degree of scatter among them. Figs. 4, 6, and 7 are very good examples of scattered experimental data, as several data sets are available at these temperatures (313.15, 323.15, and 333.15 K), from different research groups all over the world.

In all figures it can be observed that GEOS predictions are reasonably good. As expected, the critical points are very well predicted at each temperature. The general trend is that the liquid curve is underestimated, but as temperature increases, the predictions improve. The vapor phase is very well predicted over the entire range, except at very high temperatures (Fig. 10).

## 6. Conclusions

The cubic GEOS was used to predict the phase behavior of the carbon dioxide + isopropanol system. One unique set of binary interaction parameters obtained using the  $k_{12}-l_{12}$  method for the carbon dioxide + 1-propanol system was applied to model the carbon dioxide + isopropanol mixture in a wide range of temperatures and pressures. The predicted results were compared with the available literature data for carbon dioxide + isopropanol binary system. The topology of phase behavior is very well predicted, taking into account the relatively simple model and the modeling procedure used.

### Acknowledgements

„This work was supported by a grant of Ministry of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P4-ID-PCE-2016-0629, within PNCDI III”.

Dr. Sima acknowledges the partial financial support of the Romanian Chemical Engineering Society for presenting this work at the 20<sup>th</sup> Romanian International Conference on Chemistry and Chemical Engineering – RICCCE 20, September 6-9, 2017, Poiana Brasov, Romania.

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