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# Prediction of the Solubility in Asymmetric Mixtures using Peng Robinson and RKPR Equations of State

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#### Abstract

Phase equilibrium engineering involves the use of thermodynamic knowledge of phase behavior in different types of mixtures, and its quantification through mathematical models, contributing to the development of processes (e.g., chemical reactions, separation, extraction, etc.). Asymmetric mixtures, that is, mixtures containing compounds with large size difference, such as CO<sub>2</sub> and heavy hydrocarbons, are found during production and processing process of petroleum fluids, and can exhibit complex phase behavior, including liquid-liquid (LL), vapor-liquid-liquid (VLL), solid-liquid (SL) and solid-vapor-liquid (SVL) equilibria. In this context, a reliable calculation of phase envelops in a pressure - temperature plan is a fundamental tool for flow assurance concerns, especially wax deposition mitigation. In this work, the quantitative composition of the phases in equilibrium are calculated using the PR and RKPR equation of state. A suitable algorithm of predicting phase equilibria in asymmetric mixtures was developed. Binary asymmetric mixtures of CO<sub>2</sub> + (phenanthrene, anthracene, pyrene, chrysene, triphenylene, n-tetracosan, n-octacosane, n-dotricontane) were investigated, and the importance of a third parameter in the structure of an equation of state was analyzed. In general, for the equations of state, RK-PR and PR shows a good performance in correlating experimental data in this work. For phase transition in binary systems of  $CO_2$  + (phenanthrene, anthracene and pyrene), deviations varying from 2% to 20% were found, while for  $CO_2$  + chrysene and triphenylene, deviations vary from 2% to 10%; and for systems of  $CO_2$  + (n-tetracosan, n-octacosane and n-dotricontane) the deviations range between 5% and 10%.

### Keywords

Carbon Dioxide; asymmetric mixtures, solid transitions, thermodynamics modeling

### Introduction

Energy systems are the main support for global and local growth and the oil industry provide the largest contribution to these systems [1]. Challenges in the oil sector are related to the improvement in production efficiency in reservoirs containing heavy hydrocarbons and high CO<sub>2</sub> content [2–4]. The thermodynamic modeling of asymmetric binary systems including CO<sub>2</sub> and heavy hydrocarbons is especially interesting, due to the wax and asphaltene precipitation phenomenon inside the reservoirs and production line [5]. Phase equilibrium  $CO_2$  + n-alkane mixtures are of a great interest for the petroleum industry [6]. A well understanding of these systems is a fundamental step for enhanced oil recovery using  $CO_2$  as injection fluid [7,8].

The RKPR Equation of State (EoS) have shown good performance in describing the phase behavior of this type of system, in comparison with other thermodynamic models traditionally used in the oil industry such as the Peng-Robinson (PR) or the Soave-Redlich-Kwong (SRK) EoS. RKPR have been applied in last decade and have shown good performance for density correlation in such asymmetric mixtures [6,7,9,10]. The main objective of this work is to compare the PR and the RKPR Eos to correlate the onset precipitation of asymmetric binary systems of  $CO_2$  and several hydrocarbons. Solubility data were taken from literature.

#### Methodology

Eight different systems were selected from literature [10–12], including  $CO_2$  +PAH (Polycyclic aromatic hydrocarbons like phenanthrene, anthracene, pyrene, chrysene, triphenylene) and  $CO_2$  + n-alkanes (n-tetracosane, n-octacosane, n-dotriconthane). These systems were selected due to their asymmetry and their different characteristics [13,14,15].

For solid phase equilibrium the isofugacity condition is used to calculate the onset precipitations conditions (temperature, pressure e solute composition)

$$f_i^s(T, P) = f_i^F(T, P, x^F)$$
 (1)

$$f_i^s(T,P) = P_i^{sat} \varphi_i^s \exp\left[\frac{V_{s,i}(P-P_i^{sat})}{RT}\right]$$
(2)

$$f_i^F(T, P, x^F) = y_i P \varphi_i^F$$
(3)

For calculation of the fugacity coefficient of the fluid phase from RKPR equation, the algorithm proposed by Cismondi et al. [10] was used. The incipient solid phase is taken as pure solid and the equations 2 can be simplified for ideal pure solid, where the binary interaction parameters were estimated by using the Particle swarm optimization algorithm [16].

#### **Results and Discussion**

Figure 1, shows the predictions of the solubility of the PAH compound in CO<sub>2</sub>, from the PR and RK-PR EoS, compared to experimental data of. Both equation present good performance to correlate experimental data.





Figure 1. Prediction of the solubility of PAH in CO<sub>2;</sub> (a) Phenanthrene, (b) Anthracene, (c) Pyrene, (d) Chrysene, (e) Triphenylene; (–) PR-ES, (-.) RKPR-EOS.

When analyzing the  $CO_2$  + n-alkane systems (Figure 2), one can observe that in the highpressure region (higher than 170 bar, the solubility of n-alkane in  $CO_2$  is pressure independent according to the experimental data. Both models can describe this trend with the same performance, show Table 1.

Table 1. Average Relative Deviation in I  $\Delta y$  %I for PR AND RKPR model.

Solute	PR I∆y %I		RKPR I∆y %I	
	Max	Min	Max	Min
Phenantrene	12.9	2.3	12.7	1.7
Anthracene	19.4	3.6	18.8	3.2
Pyrene	21.9	6.1	20.8	6.2
Chrysene	7.9	2.3	7.3	2.1
Triphenylene	10.0	8.2	9.1	7.8
n-Tetracosane	9.7	6.1	8.0	5.9
n-Octacosane	7.9	6.7	6.4	3.5
n-Dotricontane	7.0	5.8	6.9	5.5



Figure 2. Prediction of the solubility of n-Alkanes in CO<sub>2</sub>; (a) Tetracosane, (b) n-Octacosane, (c) n-Dotriacontane; (–) PR-EOS, (-.) RKPR-EoS.

#### Conclusions

In this work, we have compared the performance of the PR and RKPR EoS, to correlate solubility data of PAH and n-alkane. Results show that both equation present good and similar performance. The solubility dependence with the pressure is limited to the low-pressure region for both compounds series. Since the RKPR have an additional structural parameter, one can conclude that in the diluted region of the investigated systems the structural parameter has no effect.

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