



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 CO₂ 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 envelopes 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 CO₂ + (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 CO₂ + (phenanthrene, anthracene and pyrene), deviations varying from 2% to 20% were found, while for CO₂ + chrysene and triphenylene, deviations vary from 2% to 10%; and for systems of CO₂ + (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 CO₂ content [2–4]. The thermodynamic modeling of asymmetric binary systems including CO₂ and heavy hydrocarbons is especially interesting, due to the wax and asphaltene precipitation phenomenon inside the reservoirs and production line [5].

Phase equilibrium CO₂ + 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 CO₂ 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 CO₂ and several hydrocarbons. Solubility data were taken from literature.

Methodology

Eight different systems were selected from literature [10–12], including CO₂ + PAH (Polycyclic aromatic hydrocarbons like phenanthrene, anthracene, pyrene, chrysene, triphenylene) and CO₂ + 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)

$$f_i^S(T, P) = f_i^F(T, P, x^F) \quad (1)$$

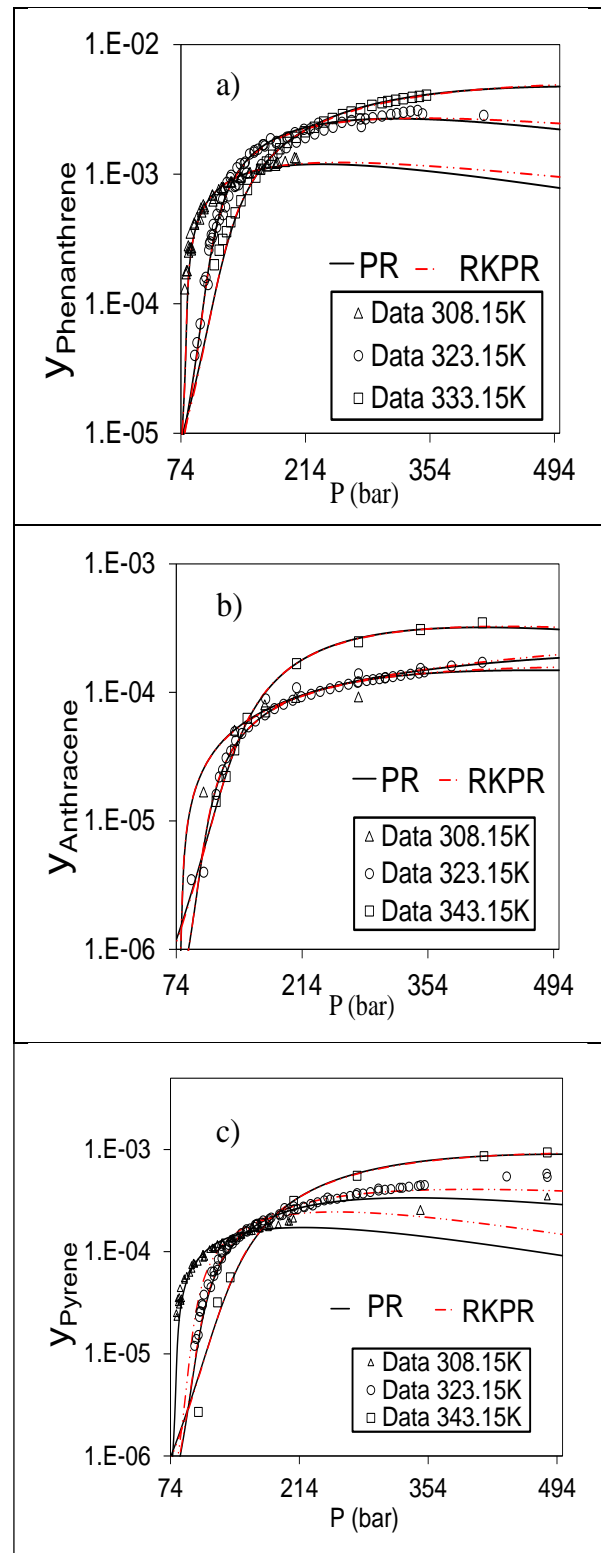
$$f_i^S(T, P) = P_i^{sat} \phi_i^s \exp \left[\frac{v_{s,i}(P - P_i^{sat})}{RT} \right] \quad (2)$$

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

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 CO₂, from the PR and RKPR EoS, compared to experimental data of. Both equation present good performance to correlate experimental data.



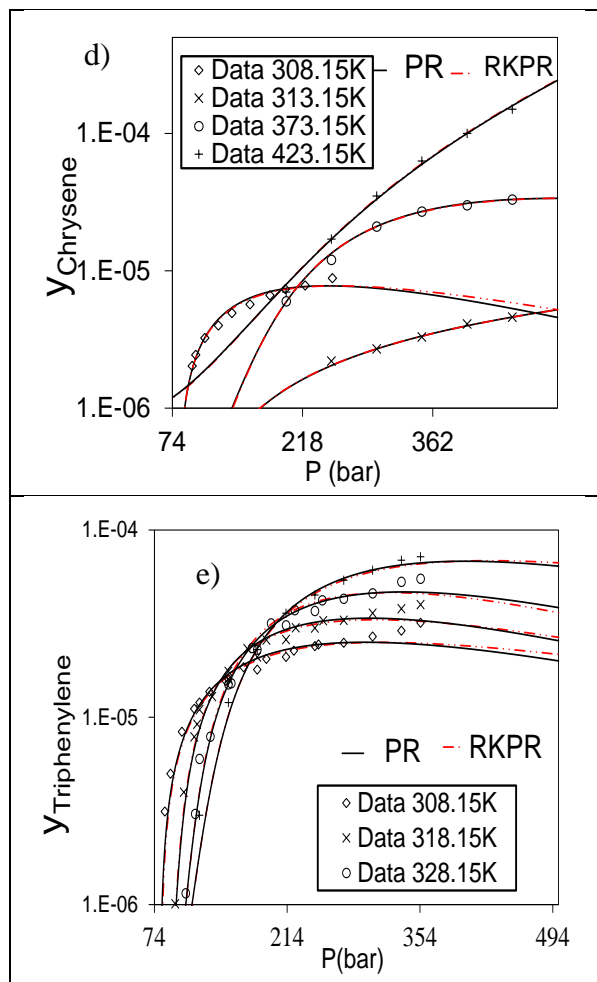


Figure 1. Prediction of the solubility of PAH in CO₂: (a) Phenanthrene, (b) Anthracene, (c) Pyrene, (d) Chrysene, (e) Triphenylene; (—) PR-ES, (---) RKPR-EoS.

When analyzing the CO₂ + n-alkane systems (Figure 2), one can observe that in the high-pressure region (higher than 170 bar, the solubility of n-alkane in CO₂ 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 |Δy %| for PR AND RKPR model.

Solute	PR Δy %		RKPR Δy %	
	Max	Min	Max	Min
Phenanthrene	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

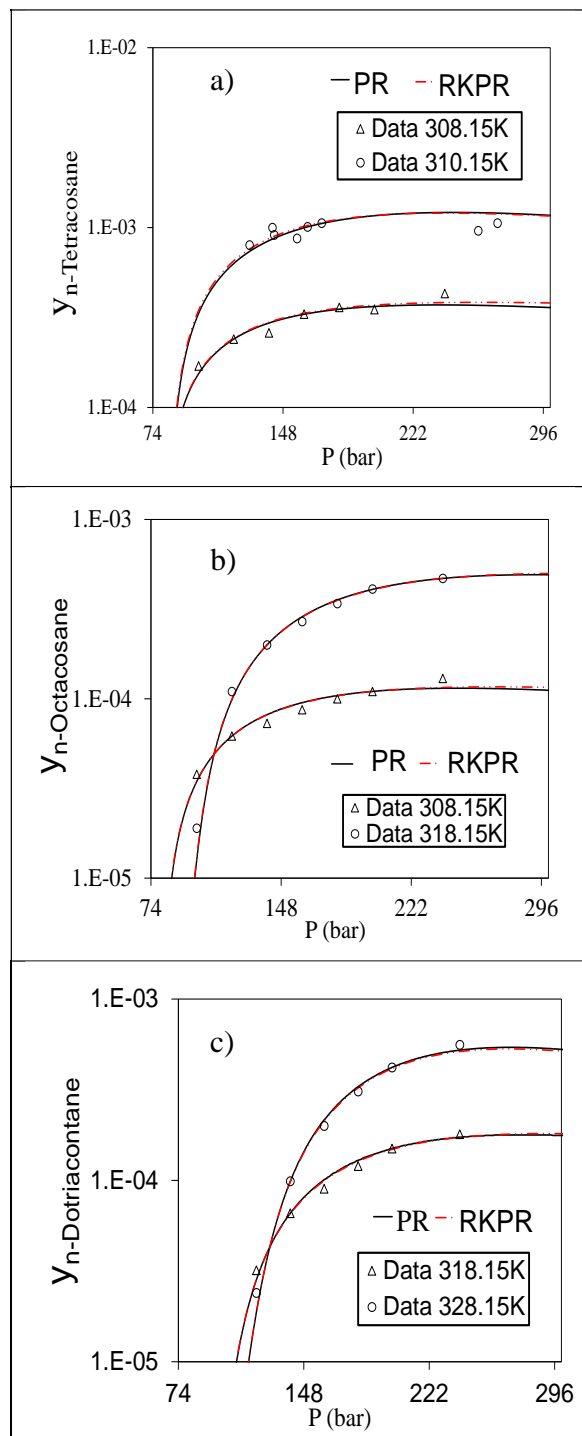


Figure 2. Prediction of the solubility of n-Alkanes in CO₂: (a) Tetracosane, (b) n-Octacosane, (c) n-Dotriacontane; (—) PR-EoS, (---) RKPR-EoS.

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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Responsibility Notice

The authors are the only responsible for the paper content.

References

- [1] B. Hunt, D. Muir, M. Sommer, The Potential Macroeconomic Impact of the Unconventional Oil and Gas Boom in the United States, *IMF Work. Pap.* 15 (2015) 1. doi:10.5089/9781484353189.001.
- [2] M. Zirrahi, H. Hassanzadeh, J. Abedi, M. Moshfeghian, Prediction of solubility of CH₄, C₂H₆, CO₂, N₂ and CO in bitumen, *Can. J. Chem. Eng.* 92 (2014) 563–572. doi:10.1002/cjce.21877.
- [3] N.P. Freitag, B.J. Kristoff, Comparison of Carbon Dioxide and Methane as Additives at Steamflood Conditions, *SPE J.* 3 (1998) 14–18. doi:10.2118/30297-PA.
- [4] S.L. Kokal, S.G. Sayegh, Phase behavior and physical properties of CO₂-saturated heavy oil and its constitutive fractions: Experimental data and correlations, *J. Pet. Sci. Eng.* 9 (1993) 289–302. doi:10.1016/0920-4105(93)90060-R.
- [5] O.C. Mullins, E.Y. Sheu, A. Hammami, A.G. Marshall, *Asphaltenes, Heavy Oils, and Petroleomics*, in: *Asph. Heavy Oils, Pet.*, Springer New York, New York, NY, 2007: p. 669.
- [6] M. Cismondi, J. Mollerup, E.A. Brignole, M.S. Zabaloy, Modeling the high-pressure phase equilibria of carbon dioxide–triglyceride systems: A parameterization strategy, *Fluid Phase Equilib.* 281 (2009) 40–48. doi:10.1016/j.fluid.2009.03.019.
- [7] M. Cismondi, S.B. Rodríguez-Reartes, J.M. Milanésio, M.S. Zabaloy, Phase Equilibria of CO₂ + n-Alkane Binary Systems in Wide Ranges of Conditions: Development of Predictive Correlations Based on Cubic Mixing Rules, *Ind. Eng. Chem. Res.* 51 (2012) 6232–6250. doi:10.1021/ie2018806.
- [8] P.E. Hegel, M.S. Zabaloy, G.D.B. Mabe, S. Pereda, E.A. Brignole, Phase equilibrium engineering of the extraction of oils from seeds using carbon dioxide+propane solvent mixtures, *J. Supercrit. Fluids.* 42 (2007) 318–324. doi:10.1016/j.supflu.2006.12.023.
- [9] M. Cismondi, J. Mollerup, Development and application of a three-parameter RK–PR equation of state, *Fluid Phase Equilib.* 232 (2005) 74–89. doi:10.1016/j.fluid.2005.03.020.
- [10] M. Cismondi Duarte, M.V. Galdo, M.J. Gomez, N.G. Tassin, M. Yanes, High pressure phase behavior modeling of asymmetric alkane+alkane binary systems with the RKPR EOS, *Fluid Phase Equilib.* 362 (2014) 125–135. doi:10.1016/j.fluid.2013.09.039.
- [11] T. Jindrová, J. Mikyška, A. Firoozabadi, Phase Behavior Modeling of Bitumen and Light Normal Alkanes and CO₂ by PR-EOS and CPA-EOS, *Energy & Fuels.* 30 (2016) 515–525. doi:10.1021/acs.energyfuels.5b02322.
- [12] J.O. Valderrama, N.A. González, V.H. Alvarez, Gas-solid equilibrium in mixtures containing supercritical CO₂ using a modified regular solution model, *Ind. Eng. Chem. Res.* 42 (2003) 3857–3864. doi:10.1021/ie020797y.
- [13] M. Ashtari, L. Carbognani Ortega, F. Lopez-Linares, A. Eldood, P. Pereira-Almao, New Pathways for Asphaltenes Upgrading Using the Oxy-Cracking Process, *Energy & Fuels.* 30 (2016) 4596–4608. doi:10.1021/acs.energyfuels.6b00385.
- [14] O.P. Strausz, T.W. Mojelsky, E.M. Lown, The molecular structure of asphaltene: an unfolding story, *Fuel.* 71 (1992) 1355–1363. doi:10.1016/0016-2361(92)90206-4.
- [15] S. Zendejboudi, A. Shafiei, A. Bahadori, L.A. James, A. Elkamel, A. Lohi, Asphaltene precipitation and deposition in oil reservoirs - Technical aspects, experimental and hybrid neural network predictive tools, *Chem. Eng. Res. Des.* 92 (2014) 857–875. doi:10.1016/j.cherd.2013.08.001.
- [16] G. Kundu, A. Kumar, Optimized critical parameters for n-alkanes up to C₁₀₀ for reliable multiphase behavior of hydrocarbon mixture using SRK EOS, *Fluid Phase Equilib.* 541 (2021) 133-037. doi.org/10.1016/j.fluid.2021.113037.