Solubility of Anthracene in Sub- and Supercritical Propane

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The equilibrium solubility of anthracene (as a model of coke precursor) in sub- and supercritical propane has been measured using a static viewcell at temperatures from (298 to 405) K and pressures from (4.7 to 11.3) MPa. The values of the mole fraction of anthracene in propane were from $1.4 \cdot 10^{-4}$ to $6.6 \cdot 10^{-3}$ over the experimental conditions studied. These values are two orders of magnitude higher than those reported in the literature for anthracene in CO_2 and are indicative of the excellent solvent properties of propane for the extraction of polyaromatics, compared to supercritical CO_2. The experimental solubility data have been correlated by the Peng−Robinson equation of state using different mixing rules for the calculation of parameters a and b. The mathematical model proposed provides a good agreement between the experimental and the calculated solubility, with a standard deviation of $6 \cdot 10^{-4}$ of the model predictions.

1. Introduction

Over the last years supercritical fluid (SCF) extraction has been demonstrated to be a useful technique to develop different types of industrial processes.[1] These include applications in many fields, among them, the pharmaceutical field for the extraction of biologically active ingredients, the food processing field for decaffeination and extraction of essential oils and aroma materials from spices, and the environmental protection field for the removal of different pollutants from wastes. Within the main advantages of the use of SCF extraction compared with liquid extraction are the high-mass transfer rates, the selectivity (by the control of the pressure and temperature), and the easier separation of the solvent.

In this context, a potential application of SCF extraction is the regeneration of exhausted catalysts[2−5] used in the hydrotreating and hydrocracking reactions, during the petroleum processing to produce gasoline, kerosene, and diesel fuel among other products. In these catalytic reactions, the formation and deposition of coke on the active catalytic sites of the catalyst can cause its premature deactivation. It must be noted that some authors define coke as the carbonaceous material deposited on the catalyst after extraction with a suitable solvent.[6,7]

Since polynuclear aromatic compounds and asphaltenes are coke precursors, the formation of coke deposits on the catalysts has been attributed primarily to the presence of these type of compounds.[8,9] Therefore, the cleaning of these catalysts to recover their activity could be carried out by SCF extraction. In this case, the extraction process can be considered to involve three factors:[10] first, the coke precursor compounds must be sufficiently soluble in the supercritical solvent; second, the coke precursor compounds must be transported rapidly from the interior of the matrix in which it is contained (the catalyst); and finally, there must be diffusion of these compounds in the fluid through the pores of the catalyst.

Some works in the literature have reported solubility data of polyaromatic compounds in supercritical CO_2, ethylene, and ethane.[11−15] Generally, carbon dioxide is the most common gas used as a SCF mainly because it is easy to handle, inert, nontoxic, and nonflammable and has a convenient critical temperature.[16] However, when the extraction of organic compounds of high molecular weight is attempted, solubility in supercritical CO_2 is often too low; for this reason, other supercritical solvents, such as propane, are used.[17] However, very few works have studied the fluid phase equilibrium of systems involving polyaromatic compounds and propane as supercritical solvent,[18] despite the fact that propane can be a good supercritical solvent of these solutes if appropriate pressure and temperature conditions are selected for operation.[19,20]

In this work, the equilibrium solubility of anthracene (as a model of the coke precursor) in sub- and supercritical propane is reported for temperatures between (298 and 405) K and for pressures in the range of (4.7 to 11.3) MPa. As well, the experimental solubility has been modeled by the Peng−Robinson equation of state, using different mixing rules for the calculation of parameters a and b (including the van der Waals rule for mixtures). Apart from the environmental application mentioned above (cleaning of deactivated catalysts), it should be highlighted that these solubility data may also be used in the analysis of gas washing effects in reservoir crude oils.

2. Experimental Section

2.1. Materials. To measure the solubility of anthracene in sub- and supercritical propane, a supercritical phase monitor (SPM-20) supplied by Thar Instruments, Inc. (U.S.A.) has been used. The equipment is composed by a variable volume viewcell body with a piston, a charge-coupled device camera and illumination source (with two sapphire windows mounted 90° apart), a pressure pump (P-50, Thar Instruments), a pressure transducer, a temperature control (with embedded heaters), and a high pressure motor-driven mixer. This system allows observing phase behavior and solubility under different pressure, temperature, and concentration conditions. To liquefy the propane before its pumping, a cooling system was used.

Propane (mass fraction of 0.995, Praxair) and anthracene (mass fraction of 0.990, Aldrich) were employed without further purification. The main physical properties of anthracene and

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Table 1. Molar Mass M, Normal Boiling Temperature T_{bp}, Melting Temperature T_{mp}, Critical Temperature T_c, and Critical Pressure P_c with Acentric Factor ω for Anthracene and Propane

compound	M / g·mol^{-1}	T_{bp} / K	T_{mp} / K	T_c / K	P_c / MPa	ω^a
propane	44.096	231.06	85.5[b]	369.825[c]	4.24733	0.1518[d]
anthracene	178.229	613.2[e]	489.65[f]	869.3[f]	3.124[f]	0.3531[f]

[a] ω is the acentric factor. [b] Results from ref 21. [c] Results from ref 22. [d] Results from refs 18 and 23. [e] Results from ref 24. [f] Results from ref 11.

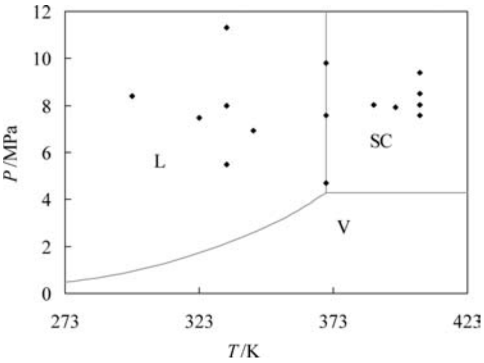

Figure 1. Experimental conditions used in the determination of anthracene's solubility in propane.

propane are shown in Table 1, although other values for anthracene's acentric factor have been reported.[1,13,25] The molar volumes of propane were obtained from the National Institute of Standards and Technology (NIST).[26]

2.2. Experimental Procedure. To obtain the static solubility data, a given amount of anthracene was placed inside the cell. After that, the cell was covered and heated up to a given temperature, by means of the temperature controller. Once the set temperature was reached, the mixer was switched on, and the propane was pumped into the cell. To determine the anthracene solubility, the pressure was increased (at isothermal conditions) in short intervals {of (0.2 to 0.4) MPa} until the point in which only one phase was observed (through the sapphire window). Between intervals the pressure was held for about 300 s before the next increase. The experiments were recorded in a PC connected to the camera. Apart from the images (of the viewcell), the videos include time, pressure, and temperature monitoring. This allows the subsequent viewing of the phase equilibrium images with their corresponding pressure and temperature real time data. The solubility was determined from the amounts of anthracene and propane loaded into the cell. To minimize the experimental error, all experiments were duplicated. Deviations of single determinations from the mean value of replicated experiments were below 2 % of the mean value.

The experimental pressure and temperature conditions used in each experiment are marked in Figure 1, where the regions for liquid, vapor, and supercritical state of propane are also indicated.

3. Results and Discussion

Table 2 shows the results obtained in the experiments carried out in this work. The solubilities reported at each condition are mean values of the duplicated experiments. It can be observed that the solubilities of anthracene in propane are in all cases below a mole fraction of 0.01 of anthracene, which is equivalent to 40.8 mg of anthracene per grams of propane. It can also be seen in such a table that the smallest values for anthracene's mole fractions were attained at the lowest values of pressure and temperature tested.

Table 2. Experimental Solubility Data of Anthracene (2) in Sub- and Supercritical Propane (1) at Temperature T and Pressure P

T / K	P / MPa	$y_2{}^a \cdot 10^3$
298	8.41	0.14
323	7.47	0.78
333	5.50	0.97
333	8.00	1.19
333	11.30	1.21
343	6.93	1.51
370	4.71	0.81
370	7.57	3.24
370	9.80	4.03
388	8.04	3.55
396	7.91	4.38
405	7.59	4.20
405	8.04	5.71
405	8.51	6.48
405	9.41	6.59

[a] y_2 is the mole fraction of anthracene.

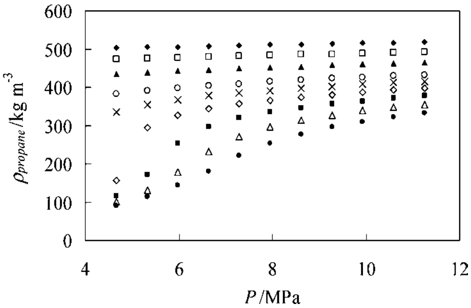

Figure 2. Variation of the density of propane ($\rho_{propane}$) as a function of the pressure and temperature in the range of experimental conditions used. Data have been obtained from NIST.[26] ◆, T = 298 K; □, T = 318 K; ▲, T = 338 K; ○, T = 358 K; ×, T = 368 K; ◇, T = 378 K; ■, T = 388 K; Δ, T = 398 K; and ●, T = 408 K.

Table 2 also shows that isobaric increases in temperature lead to increases in the amount of anthracene that propane can solubilize (in the liquid and supercritical regions). Likewise, isothermal pressure increases produce higher values of the anthracene's mole fraction, this effect being stronger at higher temperatures. However, it was observed that at 405 K increases in pressure above 8.5 MPa do not seem to cause further increases in the solubility of anthracene. As expected, the solubility variation with pressure and temperature around the critical point showed a similar trend, although more marked, as can be inferred from the experimental results presented.

These results are closely related to the propane density and therefore to the fluid solvating power, since its variation with pressure and temperature[27] (see Figure 2) follows the same trend commented for anthracene solubility. Further, at temperatures above 373 K isothermal pressure increases from about 8 MPa do not modify significantly the propane density,[27] a fact that may explain that both anthracene solvating power and anthracene solubility remain essentially constant at the highest temperatures and pressures analyzed.

Regarding the use of propane as a solvent for the removal of polyaromatics against supercritical CO_2, the results obtained in this work have been compared to those obtained by Kosal and Holder.[11] Table 3 shows the mole fractions of anthracene in CO_2 compared with those obtained in this work (anthracene in propane), for similar values of reduced temperature and pressure (T_r, P_r). Treatment of solubility data in this manner removes

Table 3. Comparison of the Solubility of Anthracene (2) in CO_2 and Propane at Reduced Temperature T_r and Reduced Pressure P_r[a]

carbon dioxide[11]			propane (this work)		
T_r	P_r	$y_2 \cdot 10^5$	T_r	P_r	$y_2 \cdot 10^5$
1.01	1.88	5.08	1.00	1.78	323.55
1.01	2.34	8.01	1.00	2.31	403.37
1.05	1.88	5.56	1.05	1.89	354.89

[a] $T_r = T/T_c$; $P_r = P/P_c$; y_2 is the mole fraction of anthracene.

the effect of proximity to the critical point. It can be observed that in all cases the mole fractions of anthracene in propane are two orders of magnitude higher than those reported for anthracene in CO_2. These results are indicative of the excellent solvent properties of propane for the extraction of polyaromatics, compared to supercritical CO_2.

3.1. Data Correlation. To calculate the solubility of a solid solute (y_2) in equilibrium with a fluid at high pressure, the following fundamental equation can be used:

$$y_2 = \frac{P_2^{\text{sat}}}{P} \cdot \frac{1}{\varphi_2^{\text{F}}} \exp\left(\frac{v_2^{\text{sat}}(P - P_2^{\text{sat}})}{RT}\right) \qquad (1)$$

where P_2^{sat} and v_2^{sat} denote the saturated vapor pressure and the solid state molar volume of the solute, P and T are the equilibrium pressure and temperature, R is the universal gas constant, and φ_2^{F} is the fugacity coefficient of the fluid phase that is indicative of the nonideal behavior of the fluid phase.

To estimate the solubility of solid anthracene, its saturation pressure (P_2^{sat}) can be calculated from the following expression:

$$\ln(P_{\text{anthracene}}^{\text{sat}}/\text{Pa}) = 31.620 - 11378\left(\frac{\text{K}}{T}\right) \qquad (2)$$

according to Bender et al.[28]

For the calculation of the fugacity coefficient (φ_2^{F}), cubic equations of state are often used, as these semiempirical equations offer simplicity and accuracy. Among the most used cubic equations of state is the one proposed by Peng and Robinson,[29] shown in eq 3, where v is the molar volume. In this equation, the first term is related to the repulsion pressure expressed by the van der Waals hard sphere equation, whereas the second term corresponds to the attraction pressure. Thus, constant b is related to the size of the hard spheres, and parameter a can be regarded as a measure of the intermolecular attraction force that depends on the temperature.

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \qquad (3)$$

For pure components, $a(T)$ and b can be written as shown in eqs 4 to 6.

$$a_i(T) = 0.45724\frac{R^2 T_{C,i}^2}{P_{C,i}}\alpha(T) \qquad (4)$$

$$b_i = 0.07780\frac{RT_{C,i}}{P_{C,i}} \qquad (5)$$

$$\alpha_i(T) = \left(1 + (0.37464 + 1.54226\omega_i - 0.26992\omega_i^2) \times \left(1 - \sqrt{\frac{T}{T_{C,i}}}\right)\right)^2 \qquad (6)$$

However, for mixtures of components, the mixture parameters (a_M and b_M) can be calculated from eqs 7 and 8, that involve the pure component parameters (a_i and b_i) and the mole fractions of the each component (y_i) in the mixture. For the calculation of a_{ij} and b_{ij}, different mixing rules are used.

$$a_M = \sum_i \sum_j y_i y_j a_{ij} \qquad (7)$$

$$b_M = \sum_i \sum_j y_i y_j b_{ij} \qquad (8)$$

In this work, several mixing rules have been tested (for the estimation of a_{ij} and b_{ij}) to improve the correlation of the experimental solubility. They are summarized in Table 4. The most commonly used mixing rules are the one-fluid rules of van der Waals which are called mixing rules 1 (MR1) in this work. MR1 uses one parameter (k_{12}) to correct the value of a_M. For the remaining mixing rules studied in this work (MR2, MR3, MR4, MR5, and MR6), two parameters are used. For rules MR2, MR3, MR4, and MR5, two parameters are used in different combinations: k_{12} to correct the value of a_M and δ_{12} to correct the value of b_M. In case of MR6, the two parameters, k_{12} and k_{21}, are used to correct a_M.

The Peng–Robinson equation can be expressed on its cubic form as shown by eq 9, where Z is the compressibility factor, given by eq 10, and A and B are defined by eqs 11 and 12.

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \qquad (9)$$

$$Z = \frac{Pv}{RT} \qquad (10)$$

$$A = \frac{a_M P}{R^2 T^2} \qquad (11)$$

$$B = \frac{b_M P}{RT} \qquad (12)$$

Applying the thermodynamic relationship:

$$\ln\frac{\text{f}}{P} = \int_0^P \left(\frac{v}{RT} - \frac{1}{P}\right)\text{d}P \qquad (13)$$

the following expression for the fugacity coefficient of component i in a fluid mixture (φ_i^{F}) can be calculated by eq 14, and consequently, the molar fraction of component i can be estimated by eq 1.[30]

$$\ln(\varphi_i^{\text{F}}) = \frac{2\sum_j y_j b_{ij} - b_M}{b_M}(Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \times \left(\frac{2\sum_k y_k a_{ik}}{a_M} - \frac{2\sum_j y_j b_{ij} - b_M}{b_M}\right)\ln\left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B}\right) \qquad (14)$$

In this work, the Peng–Robinson equation of state has been used to calculate the compressibility factor (Z) and the fugacity coefficient (φ_2^{F}) by solving eqs 9 and 14, for the different mixing rules proposed in Table 4, and then, the values of the mole fractions of anthracene have been estimated by eq 1. To obtain optimal values of the adjustable parameters (k_{12}, δ_{12}, and k_{21}) for the different mixing rules, the values of the mole fractions calculated (y_2^{cal}) have been compared to the experimental ones, by minimizing the objective function OBF given by eq 15.

$$\text{OBF} = \sum_n (y_2 - y_2^{\text{cal}})^2 \qquad (15)$$

As well, the standard deviation (σ) between the calculated and the experimental results was determined for each mixing rule

Table 4. Mixing Rules for the Calculation of the Mixture Parameters a_M and b_M of the Peng−Robinson Equation

	mixing rules 1	mixing rules 2	mixing rules 3
a_{ij}	$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij})$	$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij})$	$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij})$
b_{ij}	$b_{ij} = (b_i + b_j)/2$	$b_{ij} = ((b_i + b_j)/2)(1 - \delta_{ij})$	$b_{ij} = ((b_i^{1/3} + b_j^{1/3})^3/8)(1 - \delta_{ij})$
observations	$k_{ij} = k_{ji}, k_{ii} = 0$	$k_{ij} = k_{ji}, k_{ii} = 0, \delta_{ij} = \delta_{ji}, \delta_{ii} = 0$	$k_{ij} = k_{ji}, k_{ii} = 0, \delta_{ij} = \delta_{ji}, \delta_{ii} = 0$
reference	29	15, 31	14

	mixing rules 4	mixing rules 5	mixing rules 6
a_{ij}	$a_{ij} = ((a_i + a_j)/2)(1 - k_{ij})$	$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij})$	$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij} + (k_{ij} - k_{ji})y_i)$
b_{ij}	$b_{ij} = ((b_i + b_j)/2)(1 - \delta_{ij})$	$b_{ij} = (b_i b_j)^{1/2}(1 - \delta_{ij})$	$b_{ij} = (b_i + b_j)/2$
observations	$k_{ij} = k_{ji}, k_{ii} = 0, \delta_{ij} = \delta_{ji}, \delta_{ii} = 0$	$k_{ij} = k_{ji}, k_{ii} = 0, \delta_{ij} = \delta_{ji}, \delta_{ii} = 0$	$k_{ij} \neq k_{ji}, k_{ii} = 0$
reference	this work	this work	31, 32

Table 5. Results Obtained in the Correlation of the Solubility of Anthracene in Propane Using the Peng−Robinson Equation of State

	number of parameters	k_{12}	δ_{12}	k_{21}	σ
mixing rules 1	1	−0.01811			$1.38 \cdot 10^{-03}$
mixing rules 2	2	−0.31891	−0.74601		$6.90 \cdot 10^{-04}$
mixing rules 3	2	−0.31280	−0.92003		$6.90 \cdot 10^{-04}$
mixing rules 4	2	0.34599	−0.60970		$6.00 \cdot 10^{-04}$
mixing rules 5	2	−0.31879	−1.04904		$6.90 \cdot 10^{-04}$
mixing rules 6	2	−16.00086		0.03868	$7.64 \cdot 10^{-04}$

(eq 16), to evaluate which of the mixing rules allow better correlation of the experimental solubility of anthracene in propane, in the range of temperature and pressure studied.

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}(y_2 - y_2^{cal})^2}{N - 1}} \qquad (16)$$

Table 5 summarizes the results obtained in the correlation of the experimental data, showing the optimized parameters and the standard deviation obtained using the different mixing rules. It can be observed that the mixing rules using only one parameter (MR1) yield higher value for the standard deviation than those using two (the double), as should be expected. Within the mixing rules using two parameters (MR2, MR3, MR4, MR5, and MR6), it can be observed that their standard deviations are of the same order of magnitude. Thus, MR6 yields worse adjustment results, and it can be explained by the fact that the two parameters (k_{12} and k_{21}) are correcting the value of a_M, but no parameter is used for the correction of b_M. On the other hand, MR2, MR3, MR4, and MR5 use one parameter for correcting a_M and the other one for correcting b_M. Attending to the equations proposed for these mixing rules (in Table 4), it can be observed that they are combinations of very similar equations, and that is why they yield practically the same value for the standard deviation. The best adjustment of the experimental results was obtained with MR4. In general, it can be affirmed that with the mixing rules MR2, MR3, MR4, and MR5 very good values of the standard deviation are obtained, so all of these equations can be used to estimate a_M and b_M for the Peng−Robinson equation of state, in the prediction of the solubility of anthracene in sub- and supercritical propane.

Finally, to give a visual idea of the adjustment of each mixing rule used with the Peng−Robinson equation, Figures 3, 4, and 5 summarize the predicted mole fractions of anthracene (y_2^{cal}) against the experimental values (y_2), for the different mixing rules studied. It can be observed that using MR1 leads to an important dispersion of the estimated and the experimental values, which results in a negative regression coefficient (R^2). Likewise, in Figures 3 to 5 it can be seen that the slopes of y_2^{cal}

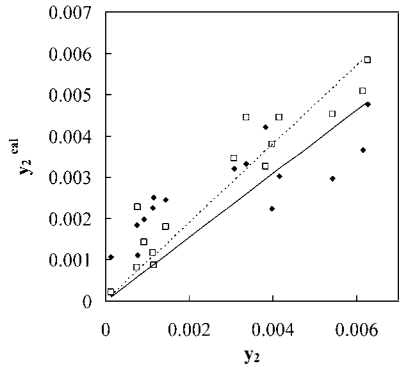

Figure 3. Comparison of the experimental and calculated solubility of anthracene in propane using the Peng−Robinson equation of state with mixing rules 1 and 2 (MR1 and MR2). ◆, MR1; □, MR2; solid line, lineal correlation MR1 ($y_2^{cal} = 0.7712y_2$; $R^2 = -0.1055$); dashed line, lineal correlation MR2 ($y_2^{cal} = 0.9490y_2$; $R^2 = 0.8610$).

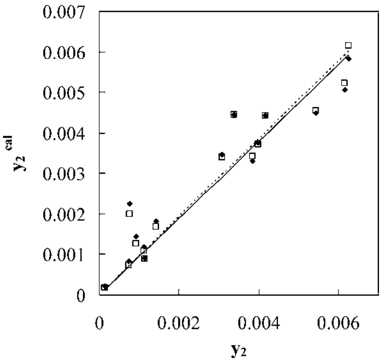

Figure 4. Comparison of the experimental and calculated solubility of anthracene in propane using the Peng−Robinson equation of state with mixing rules 3 and 4 (MR3 and MR4). ◆, MR3; □, MR4; solid line, lineal correlation MR3 ($y_2^{cal} = 0.9479y_2$; $R^2 = 0.8595$); dashed line, lineal correlation MR4 ($y_2^{cal} = 0.9616y_2$; $R^2 = 0.9024$).

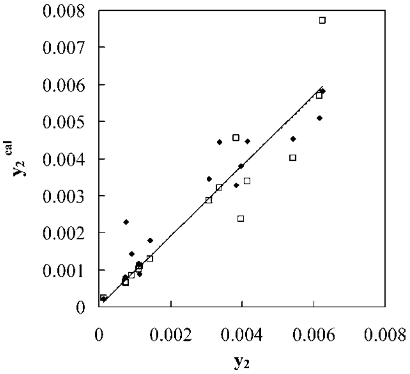

Figure 5. Comparison of the experimental and calculated solubility of anthracene in propane using the Peng−Robinson equation of state with mixing rules 5 and 6 (MR5 and MR6). ◆, MR5; □, MR6; solid line, lineal correlation MR5 ($y_2^{cal} = 0.9490y_2$; $R^2 = 0.8610$); dashed line, lineal correlation MR6 ($y_2^{cal} = 0.9441y_2$; $R^2 = 0.8834$).

against y_2 are near 1 in the remaining cases (MR2, MR3, MR4, MR5, and MR6). In addition, it can be noted that the regression coefficients (R^2) obtained when comparing the estimated and experimental solubility values are related to the fitting of the different mixing rules used. Thus, the highest regression coefficient corresponds to MR4, the mixing rules leading to the lowest standard deviation and so to the best adjustment of the experimental results.

Conclusions

The solubility of anthracene in sub- and supercritical propane was measured using a static method at temperatures from (298 to 405) K and pressures from (4.5 to 11.3) MPa. The mole fractions of anthracene in propane vary from $1.4 \cdot 10^{-4}$ to $6.6 \cdot 10^{-3}$ over the range of experimental conditions analyzed. These mole fraction values are two orders of magnitude higher than those obtained for anthracene in supercritical CO_2 at similar conditions of reduced temperature and pressure and highlight the excellent solvent properties of propane for the extraction of polyaromatics, compared to supercritical CO_2. The experimental solubility has been modeled by the Peng−Robinson equation of state using different mixing rules for the calculation of parameters *a* and *b*, and good fits were obtained (standard deviation of $6.0 \cdot 10^{-4}$ for the best fitting).

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