

Phase Behavior Prediction for Binary Volatile-Nonvolatile Mixtures of *N*-Paraffins[†]

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The goal of this work is to describe the phase behavior of *n*-paraffins-supercritical fluid binary systems. The *n*-paraffins are selected in order to be representative of petroleum fractions. Calculations in the full concentration range and in the vicinity of the mixture critical point, are reported for selected binary systems, for which experimental behavior is known from literature. The calculations are performed by means of the perturbed hard chain and cubic equations-of-state. Pure component parameters of the equations are calculated either from pure component properties or via generalized correlations as a function of a characteristic parameter. The effect of binary interaction parameters and of pure component parameters on mixture properties prediction is also checked.

Keywords: theory, equation-of-state, perturbed hard-chain, critical phenomena

INTRODUCTION

High-pressure separation processes have been a very interesting and promising area of development in recent years. Supercritical-fluid extraction (SFE) is a good example of the importance of high-pressure technology applied to the separation of non-conventional materials. Petroleum industry is another active field of application of the high-pressure technology for improving the efficiency of the separation processes. Equations-of-state (EOS) have been used so far for calculating thermodynamic properties in such conditions.

Cubic EOS, namely Redlich-Kwong and Peng-Robinson, have been widely used in recent years because of their simplicity and accuracy in the high-pressure range, but unfortunately they have limitations when applied to SFE process calculation. They do not account for differences in size of components and their application to compounds whose critical properties are unknown is doubtful since one has to rely on group contribution methods for their estimation. In addition, temperature dependent binary interaction parameters are often required.¹

Non-cubic equations-of-state have been developed from statistical mechanic theories specifically to account for molecules differing in size. Among the different non-cubic EOS, the equation based on the Perturbed Hard Chain Theory (PHCT) has revealed to be promising when applied to systems containing light and heavy hydrocarbons. Previous papers¹⁻³ have reached the conclusions that models based on the PHCT are at least as good as cubic equations-of-state in correlating hydrocarbon mixtures, and they are superior as far as description of mixtures whose components are different in size is concerned. Besides, the PHCT models are recognized to be superior in extrapolation and prediction, owing to the physical meaning of the models parameters. These conclusions have been achieved with a simplified version of the PHCT model. This paper aims to verify such conclusions on a more general model based on PHCT.

The equation used in this work, based on the Perturbed Hard Chain Theory, is the one proposed by Cotterman et al. in 1986,⁴ specifically designed for describing mixtures of components very different in size. Its parameters have a well defined physical significance and the critical coordinates are not requested.

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TABLE I Values of Pure Component Parameters T^* , V^* , and c for PHCT Equation, T_c , P_c , and ω for Cubic Equation. Critical Parameters from Reid et al.⁷ and from Rogalski and Neau.⁸

T^* (K)	V^* (cc/mol)	c	T_c (K)	P_c (bar)	ω
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Parameters from Correlations

C_1	147.10	21.94	1.00	190.4	46.00
C_2	204.17	30.28	1.45	305.4	48.75
C_{16}	387.84	171.29	3.72	722.9	14.54
C_{20}	397.23	211.61	4.45	767.0	11.17
C_{22}	400.64	231.38	4.82	786.1	10.89
C_{24}	403.40	251.44	5.19	798.6	9.95

Parameters from PVT Data

C_1	149.75	21.92	0.96		
C_2	222.12	30.30	1.23		
C_{22}	400.70	239.73	4.82		

In this investigation, particular attention has been

devoted to the high-pressure petroleum industry processes.

We have considered binary systems containing a solvent

(methane, ethane) and a long chain alkane (C_{16} , C_{20} , C_{22} ,

C_{24}) for which experimental behavior is known from reli-

able literature data. The PHCT and Cubic EOS have been

compared in order to define, in terms of ranges of tempera-

ture, pressure and composition, the field of application

and the expected inaccuracy of the models. Furthermore,

the effect of the pure component parameters of the PHCT

equation-of-state in calculating properties of mixtures has

been considered.

EQUATIONS-OF-STATE AND MODELING

The models considered in this investigation are the

following:

Cubic Equations-of-State. The original

Soave-Redlich-Kwong (SRK)⁵ and the modified Peng-

Robinson (PR)⁶ equations have been considered. The

pure component parameters were taken from Reid et al.⁷

for the alkanes up to C_{20} , and estimated by a group con-

tribution method⁸ for C_{22} and C_{24} . The values of the

critical coordinates used in the calculation are reported in

Table I.

The binary interaction parameters were set to zero

for the SRK, in accordance with the normal use of such

equation, while they were calculated by the Abdoul

method⁹ for the PR equation. The binary interaction pa-

rameters obtained by the Abdoul's method are very small

for the ethane-alkane systems, while somewhat high for

the methane-alkane systems. The numerical values are

reported in the tables.

Perturbed Hard Chain Theory Equation.

The PHCT equation herein considered is based on the

low-high density split,⁴ especially useful for describing

systems of interest in high pressure processes.

Peters et al.¹⁰ have already stressed the importance

of the pure component parameters for mixture calcula-

tions. Consequently, we have considered in this investi-

gation different possibilities for evaluating parameters of

the PHCT equation and grouped the calculations as fol-

lows:

- pure component parameters and mixture parameters

- given by Cotterman et al.⁴ (PHCT1);

- pure component parameters for both hydrocarbons

- estimated from generalized correlation as a function

- of Bondi volume obtained from PVT data¹¹ and

- mixture parameters set to zero (PHCT2);

- pure component parameters for both hydrocarbons

- estimated from generalized correlation as a function

- of Bondi volume obtained from PVT data¹¹ and

- mixture parameters reported by Cotterman et al.,

- 1986 (PHCT3).

A further case has been investigated, namely the ap-

plication of experimental PVT data for the heavy compo-

nent parameter estimation. It yielded results very much

like the previous cases (PHCT2 and PHCT3) since the pa-

rameters obtained from fitting of PVT data resulted to be

numerically very similar to those given by the general

correlations.

CALCULATION PROCEDURE AND RESULTS

A flash program has been used for the calculation.¹²

The results, reported in terms of relative per cent deviation

in pressure, are grouped according to the systems

investigated.

Ethane-Docosane System. An extensive ex-

perimental study on this system is available in the litera-

ture.

TABLE II
Relative Percent Bubble Pressure Deviations ($\Delta P/P$ %) for the System Ethane(1)–Docosane(2) at 320 K; Experimental Data from Peters et al.¹³ The Vapor Phase Composition is always $y_2 \cong 0$. ($k_{12} = 0.001$ for PR Equation.)

Exp. Data		% Pressure Deviation				
x_2	P (bar)	PHCT1	PHCT2	PHCT3	SRK	PR
0.1079	69.21	(-)*	-64.3	-111.8	15.1	13.0
0.1471	60.76	(-)*	-10.3	-36.6	11.8	9.6
0.2100	51.56	-128.7	3.8	-2.9	6.5	7.2
0.2978	41.08	-46.3	9.4	3.0	6.0	3.5
0.3962	31.35	-35.3	12.7	6.0	0.8	1.6
0.5023	23.10	-30.4	15.4	8.6	-4.3	-6.8
0.6580	13.48	-28.6	16.0	9.7	-13.9	-16.3
0.7965	7.25	-24.7	19.7	12.7	-18.8	-21.1
Average:		>50.0	20.9	23.9	10.0	9.9

TABLE III
Relative Percent Bubble Pressure Deviations ($\Delta P/P$ %) for the System Ethane(1)–Docosane(2) at Different Temperatures; Experimental Data from Peters et al.,¹³ ($k_{12} = 0.001$ for PR Equation); N is the Number of Experimental Data Points.

Exp. Data			% Pressure Deviation				
N	T (K)	x_2	PHCT1	PHCT2	PHCT3	SRK	PR
8	320	<0.2	<50	37.31	74.21	12.44	11.26
		>0.2	>50	15.47	7.14	8.54	9.43
8	340	<0.2	>50	20.27	39.62	14.90	11.83
		>0.2	>50	11.32	7.57	11.88	12.90
7	360	>0.2	>45	9.52	61.29	12.94	14.31

ture¹³ over a wide range of temperature and pressure, thus allowing us to consider this system as representative of the short–long chain alkane mixtures. The experimental data considered are bubble point values given by authors. The values are not directly measured, but obtained by them after fitting measured temperature data for different compositions. From the detailed results of the calculations reported in Tables II and III several conclusions may be drawn.

Among the cubic equations-of-state, the SRK and PR give the same average deviation in pressure (around 10%) independent of temperature or the range of pressure. For the sake of simplicity, the PR model will be considered in the rest of the tables as representative of the cubic equations-of-state.

The PHCT1 model gives very high deviations (>50%), but as soon as a generalized correlation based on PVT data for ethane is used for calculating pure component parameters (PHCT2 and PHCT3), the description be-

comes satisfactory. The use of a binary interaction parameter (PHCT3) does not influence the average deviation (around 20% in both cases), but the deviation distribution is modified; Figure 1 shows that, with the same value of interaction parameters, it is impossible to represent both the high pressure (which is solvent rich) and low pressure (which is heavy component rich) regions of the isotherm considered.

In the dilute region and at pressures close to the mixture critical point (see Figure 1), the PR equation is superior to any version of the PHCT equation considered for this system. The PHCT equation given reasonable results only with an adjusted (negative) value of the interaction parameter valid only in this region. This conclusion is in agreement with literature results¹⁰ and it is due to the fact that the calculated critical point of ethane by PHCT is shifted to a higher temperature (10 K) and higher pressure (8 bar).¹¹

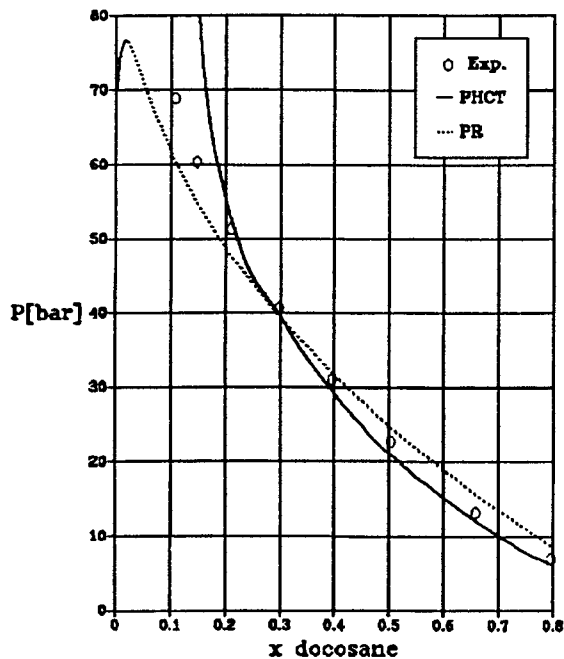


Figure 1. Comparison of the PHCT3 and PR models for the prediction of ethane-docosane system at 320 K; values of the binary interaction parameters are reported in Table II for PR EOS.

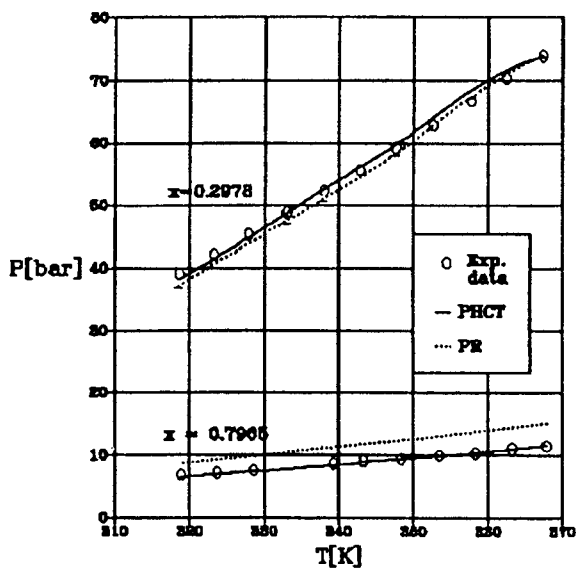


Figure 2. Comparison of the PHCT3 and PR models for the prediction of ethane-docosane system as a function of temperature at fixed composition; values of the binary interaction parameters are reported in Table II for PR EOS.

At heavy component concentrations larger than 20%, the results are different (Table III and Figure 2) and the PHCT3 equation is superior to the other models. The PHCT2 model gives results comparable to the PR equation (even though at high temperature PHCT2 is superior) and PHCT1 remains not applicable because of the poor

TABLE IV
Relative Percent Bubble Pressure Deviations ($\Delta P/P$ %) for the System Ethane(1)-Hexadecane(2) at Different Temperatures; Experimental Data from Goede et al.¹⁴ ($k_{12} = 0.01$ for PR Equation); N is the number of Experimental Data Points.

Exp. Data			% Pressure Deviation		
N	T (K)	x_2	PHCT2	PHCT3	PR
2	320	<0.2	(-)*	(-)*	2.40
5		>0.2	10.79	10.05	7.12
2	340	<0.2	(-)*	(-)*	2.34
4		>0.2	6.35	4.75	6.89
2	360	<0.2	(-)*	(-)*	8.00
5		>0.2	5.52	4.55	8.89

* Calculation not possible or reliable.

TABLE V
Relative Percent Bubble Pressure Deviations ($\Delta P/P$ %) for the System Ethane(1)-Eicosane(2) at Different Temperatures; Experimental Data from Peters et al.¹⁵ ($k_{12} = 0.002$ for PR Equation); N is the Number of Experimental Data Points.

Exp. Data			% Pressure Deviation		
N	T (K)	x_2	PHCT2	PHCT3	PR
6	320	<0.2	(-)*	(-)*	5.99
9		>0.2	10.58	4.28	10.88
6	340	<0.2	(-)*	(-)*	7.79
9		>0.2	8.81	5.04	10.99
4	360	<0.2	(-)*	(-)*	8.00
6		>0.2	6.48	6.22	8.52
2	400	<0.2	(-)*	(-)*	22.48
5		>0.2	3.26	5.98	8.79

* Calculation not possible or reliable.

values of the parameters for ethane. In general, the PHCT2 and PHCT3 models give better results for higher temperatures.

Ethane-Hexadecane, -Eicosane, -Tetracosane Systems. The results obtained with the ethane-C22 system are confirmed by those reported in Tables IV, V, and VI, for other long chain alkanes. Moreover, the results on these systems allows us to make some conclusions on the performance of the models for increasing molecular weight of the long-chain alkane.

The deviations from experimental data obtained with the PR equation increase as the number of carbon atoms of the long chain alkane is increasing. This is not sur

TABLE VI
Relative Percent Bubble Pressure Deviations ($\Delta P/P$ %) for the System Ethane(1)-Tetracosane(2) at Different Temperatures; Experimental Data from Peters et al.¹⁶ ($k_{12} = 0.001$ for PR Equation); N is the Number of Experimental Data Points.

Exp. Data			% Pressure Deviation		
N	T (K)	x_2	PHCT2	PHCT3	PR
3	320	<0.2	(-)*	(-)*	19.92
2		>0.2	8.59	1.07	9.61
2	340	<0.2	(-)*	(-)*	17.06
5		>0.2	11.72	7.80	18.08

* Calculation not possible or reliable.

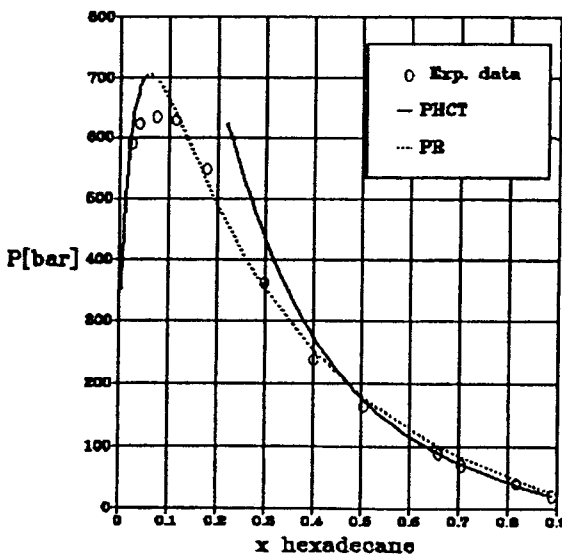


Figure 3. Comparison of the PHCT3 and PR models for the prediction of methane-hexadecane system at 320 K; values of the binary interaction parameters are reported in Table VII.

TABLE VII
Relative Percent Bubble Pressure Deviations ($\Delta P/P$ %) for the System Methane(1)-Hexadecane(2) at Different Temperatures; Experimental Data from Glaser et al.¹⁷ ($k_{12} = 0.05$ for PR Equation); N is the Number of Experimental Data Points.

Exp. Data			% Pressure Deviation	
N	T (K)	x_2	PHCT3	PR
3	320	<0.2	(-)*	6.21
2		>0.2	9.86	7.87
2	340	<0.2	(-)*	>20.0
5		>0.2	13.21	8.52

* Calculation not possible or reliable.

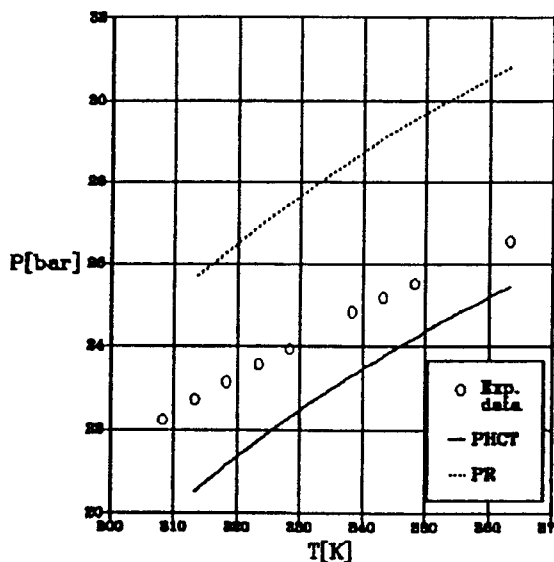


Figure 4. Comparison of the PHCT3 and PR models for the prediction of methane-hexadecane system as a function of temperature at fixed composition; values of the binary interaction parameters are reported in Table VII.

prising since cubic equations do not take into account chainlike molecules; moreover, the critical properties calculation methods introduce an uncertainty in the model. For PHCT, on the other hand, deviations remain constant independently on the length of the second component.

Methane-Hexadecane System. For all the systems with ethane considered above, no experimental binary data in the vicinity of the critical point were reported. On the other hand, this system is interesting because the critical point of the mixture is evidenced by the experimental measurements (maximum in the P/x curve).

In this case the use of generalized correlations for PHCT parameters (PHCT1) leads to similar results to those obtained by PHCT3 (see Table VII), but the use of a binary interaction parameter equal to zero (PHCT2) is not acceptable (deviations > 50%).

Figure 3 shows that very large deviations in the critical zone are observed for the PR equation, while the PHCT model is not applicable in this region. As in the case of systems containing ethane, this is essentially due to the poor description of the pure component critical point exhibited by the PHCT equation.

In Figure 4, the PR and the PHCT3 (or PHCT1) prove to be equivalent (even though PHCT is superior at high temperatures) for high hexadecane concentration.

CONCLUSIONS

The investigation of binary systems representative of petroleum mixtures at high pressure and in the vicinity of the critical point allows us to draw some conclusions on the applicability of the PHCT equation.

The pure component properties of the solute must be described in a very accurate way in order to achieve a reasonable description of the mixture properties. In this work, the generalized correlations for the pure component parameters developed by Gregorowicz et al.¹¹ have been applied with success for predicting the pure component parameters for all the component in the mixtures.

The deviations between calculated and experimental mixture data are independent on the chain length of the second hydrocarbon. The binary interaction parameters describing the interaction between a solvent (ethane for example) and a series of hydrocarbons whose chain length is increasing, remain constant. This fact is very important in order to judge upon the prediction capabilities of the PHCT model. As a matter of fact, the constancy of the binary parameters means first that the generalized correlations for the pure heavy component properties are reliable and, second, that the physical meaning attributed to the binary parameters, namely a segment-segment interaction, is correct. From a practical point of view this means that simple generalized correlations and a single binary parameter produces useful predictions for the complete ethane/*n*-paraffin series, including the heaviest members of the series.

The capability of the PHCT equation to predict mixture behavior with the binary interaction parameter set to zero, is very poor, showing that this common practice is not applicable when parameters account for segment-segment interactions.

The PHCT equation is not applicable in all the concentration-pressure range, unless ad hoc binary interaction parameters are estimated for the critical region.

The PR (or SRK) equation allows calculation in the whole range, but the deviations in the critical zone are rather high. The variation of the root mean squared deviations with temperature given by the PR model shows that a temperature dependent interaction parameters should be used.

The PHCT model proved to be superior to the PR at high temperature and in the heavy component rich composition range.

These calculations, and the good volumetric predictions that the PHCT can achieve, indicate the separation of oils as a possible area of application of the PHCT

models since, in these processes, the concentration of the heavy components is larger than 20%. Furthermore, the possibility of using generalized correlation of the pure component parameters as function of the Bondi volume reveals to be extremely useful since the oil industry normally deals with pseudocomponents whose critical coordinates are not known.

On the other hand the retrograde condensation of natural gas seems to be hard to describe since the models investigated are either inapplicable (PHCT) or give large deviations (cubic EOS) in the region of interest.

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