

Prediction of High-Pressure Multicomponent Phase Equilibria Using a Perturbed Hard Chain Equation of State[†]

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A model based on the Perturbed Hard Chain Theory (PHCT) applicable for asymmetric mixtures where molecules differ significantly in size and shape, which are typical for supercritical extraction processes is used to predict the phase behavior at high pressure of multicomponent mixtures. The high-pressure vapor-liquid equilibrium (VLE) and phase envelope calculations for multicomponent mixtures presented in this paper are based on the predictive procedures for the pure component properties, and for the binary interaction parameters. No higher-order interaction parameters have been used. The model gives satisfactory results as far as predictivity of phase equilibrium is concerned.

Keywords: equation of state, perturbation, hydrocarbons, phase equilibria, perturbed hard chain theory

INTRODUCTION

In supercritical fluid technology there is an increasing need for prediction of phase behavior in multicomponent systems in view of their application to the extraction of natural products or petroleum fractions where, in most cases the thermophysical properties of the components and the number of the components in the mixtures are not known.

In order to judge the feasibility of a separation process using supercritical-fluid extraction, calculations must be based on the complete knowledge of the thermodynamic behavior of the mixtures involved. In many cases, experimental data on the phase behavior of components occurring in the process are not available, thus making the use of predictive models necessary. In addition, in many cases, the mixtures involved consist of many complex components. Examples are separation processes involving petroleum cuts where the mixtures are too complex to be analyzed in detail. Moreover, these mixtures contain components for which properties are not known.

Therefore, the pure component parameters should be estimated from the molecular structure of the components or from a few experimental data of the components selected as being representative of a given mixture. The binary interaction parameters, essential for a correct prediction of the multicomponent phase behavior, should be obtained directly from the chemical structure (or the functional groups) of the components present in the mixture. For simplicity, no ternary or higher-order parameters should be considered in the model.

For supercritical-fluid extraction processes, the most appropriate choice for modeling the phase behavior is an equation of state. The interaction parameters are usually estimated for each binary system present in the mixture and pure component parameters are estimated from critical properties and the acentric factor. This is an especially limiting characteristic in supercritical-fluid extraction processes where critical properties and acentric factors are often not available or are uncertain.

This paper should be considered as a necessary preliminary step towards the prediction of the solubility of natural systems (such as acids and esters) in compressed carbon dioxide. The attention here is devoted to the prediction of multicomponent hydrocarbon systems from the knowledge of pure component parameters and one single

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binary interaction parameter per class, known in advance and constant with temperature and composition.

The equation of state considered in this paper is based on the Perturbed Hard Chain Theory (PHCT).¹ Its capability has been already demonstrated in the prediction of pure component properties including volume, PVT and vapor pressure,² VLE of binary systems,³ mixture volumetric properties,^{3,4} and high pressure solubilities.⁵ The recent contribution shows the predictive power of PHCT in describing the phase behavior at high pressure of multicomponent mixtures of interest for the petroleum industry. Distribution factors, high-pressure VLE, flash calculation, mixture critical point determination, and phase envelope construction for multicomponent mixtures are presented. The calculations are based on predictions of the pure component properties and of the binary interaction parameters. No higher-order interaction parameters are present in the model.

The present investigation focuses on light gases of potential use as supercritical solvents such as carbon dioxide, ethane, propane, and long chain hydrocarbons. Besides the importance of hydrocarbon mixtures in the oil and gas industry, these systems are also of major interest in the production processes of natural products such as seeds, oils, essences, etc. Indeed, the prediction of phase equilibria of natural products requires a reliable model for nonpolar molecules to be used as a reference equation and a perturbation term that account for polar-polar and polar-nonpolar interactions. The lack of reliable experimental data for natural components currently limit the investigation of polar interactions, but the equation can potentially cope with them.

EQUATION OF STATE

The equation of state considered in this work is the PHCT equation derived by Cotterman et al.¹ which is based on the generalized van der Waals theory. The model has been developed in terms of the Helmholtz function and is composed by an attractive and a repulsive contribution. The repulsive contribution is based on a generalized form of the Carnahan-Starling equation. The attractive contribution is made up by two terms, one for describing the high-density and one for the low-density region (second virial term). Dispersion and polar contributions (dipole and quadrupole interactions) to the free energy are considered in each part of the attractive term. An interpolation function between the two limiting cases of dense fluid and zero density fluid is included in the model based on empirical non adjustable parameters. The main equations of the model are summarized as follows.

The residual Helmholtz free energy is given by

$$a^r(T, V) = a(T, V) - a^{IG}(T, V) = a^{ref} + a^{pert}. \quad (1)$$

The repulsive contribution is given by the Carnahan and Starling expression

$$\frac{a^{ref}}{RT} = c \frac{-(3\tau/\bar{v} - 4)(\tau/\bar{v})}{(1 - \tau/\bar{v})^2} \quad (2)$$

where c is the Prigogine parameter which accounts for flexibility and asymmetry of the molecule. The quantities necessary for the calculation of the repulsive term are

$$\tau = \frac{\pi\sqrt{2}}{6} = 0.7405$$

$$\bar{v}_{seg} = \frac{V}{n_{seg}\sigma^3\sqrt{2}} = \bar{v} = \frac{v}{v^*}. \quad (3)$$

The hard-sphere diameter is temperature dependent according to

$$\frac{d}{\sigma} = \int_0^1 \{1 - \exp[-\Gamma(r)/kT]\} dr \quad (4)$$

where Γ is the Lennard-Jones potential as a function of the molecular distance r

$$\Gamma(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (5)$$

For molecules with $c > 1$, the ratio d/σ depends on the reduced temperature defined as

$$\bar{T} = \frac{T}{T^*} = \frac{ckT}{\epsilon q}. \quad (6)$$

Integration of eq 4 in the range of reduced temperature between 0 and 15 gives

$$\frac{d}{\sigma} = \frac{1 + 0.29770\bar{T}}{1 + 0.33163\bar{T} + 0.00104777\bar{T}^3}. \quad (7)$$

A characteristic volume is defined on the basis of the temperature dependence of the hard sphere diameter

$$v^+ = v^* \left(\frac{d}{\sigma} \right)^3. \quad (8)$$

If the three quantities c , v^* , and T^* are known, the repulsive term can be calculated.

The attractive term is made up by two contributions one for the low- and one for the high-density region which are connected by an interpolation function F

$$a^{pert} = a^{SV}(1 - F) + a^{DF}F. \quad (9)$$

The dense fluid term is split in two contributions: one is due to dispersion forces and one to polar forces

$$a^{DF} = a^{DF}(disp) + a^{DF}(polar). \quad (10)$$

The dispersion term is a temperature perturbation

$$a^{DF}(disp) = \frac{a^{(1)}}{\bar{T}} + \frac{a^{(2)}}{\bar{T}^2} \quad (11)$$

where the parameters are determined from Monte Carlo computer simulations for Lennard-Jones molecules

$$\frac{a^{(1)}}{RT} = \frac{c}{\bar{v}} \left(-8.5959 - \frac{4.5424}{\bar{v}} - \frac{2.1268}{\bar{v}^2} + \frac{10.285}{\bar{v}^3} \right)$$

$$\frac{a^{(2)}}{RT} = \frac{c}{\bar{v}} \left(-1.9075 - \frac{9.9724}{\bar{v}} - \frac{22.216}{\bar{v}^2} + \frac{15.904}{\bar{v}^3} \right). \quad (12)$$

The polar term considers the contributions which arise from dipolar, quadrupolar, and dipolar-quadrupolar interactions.

$$a^{DF}(polar) = a^{\mu\mu} + a^{\mu Q} + a^{QQ} \quad (13)$$

where

$$a^{\mu\mu} = a_{\mu\mu}^{(2)} \left[1 - \frac{a_{\mu\mu}^{(3)}}{a_{\mu\mu}^{(2)}} \right]^{-1} = f(c, \bar{T}, v^*, \bar{\mu})$$

$$a^{QQ} = a_{QQ}^{(2)} \left[1 - \frac{a_{QQ}^{(3)}}{a_{QQ}^{(2)}} \right]^{-1} = f(c, \bar{T}, v^*, \bar{Q})$$

$$a^{\mu Q} = f(c, \bar{T}, v^*, \bar{\mu}, \bar{Q}). \quad (14)$$

The second virial term is expressed by

$$a^{SV} = \frac{RT}{v} (B^{disp} - B^{\mu\mu} - B^{QQ}) \quad (15)$$

where

$$B^{disp} = -cv^+ \left(12.541 + \frac{\Omega(c)}{\bar{T}^6} \right)$$

$$\times \left[\exp\left(\frac{0.67372}{\bar{T}}\right) - 0.98071 \right],$$

$$B^{\mu\mu} = f(c, v^*, \bar{T}, \bar{\mu}),$$

and

$$B^{QQ} = f(c, v^*, \bar{T}, \bar{Q}). \quad (16)$$

The attractive term is then obtained if one knows the same parameters c , v^* , and T^* that are needed in the repulsive term.

The interpolation function is defined as

$$F = 1 - \exp\left[-\left(\frac{6}{\bar{T}}\right) \frac{(\epsilon q / k)^{tot}}{T\bar{v}}\right]. \quad (17)$$

To summarize, the parameters that are necessary for the calculation of the thermodynamic properties are the following:

$$v^* = \frac{r\sigma}{\sqrt{2}}$$

$$T^* = \frac{\epsilon q}{ck} \quad (18)$$

$c = 1/3$ external degree of freedom where r is the number of segments for a given molecule, σ is the soft-core Lennard-Jones diameter, ϵ is the potential energy per unit area of the given molecule, q is the surface area of the molecule and k is the Boltzman constant.

The extension to mixtures of the PHCT model requires the definition of combining and mixing rules. We have used the same set of rules as in the original paper of Cotterman and Prausnitz⁶ and we refer the reader to this reference for computational details. Only a brief description of the mixing rules and the relevant binary interaction parameters are reported. The mixing rules in the repulsive term involve only the c and v parameters and are the following:

$$\langle c \rangle = \sum_i c_i x_i$$

$$\langle v^+ \rangle = \sum_i x_i v_i^+. \quad (19)$$

The attractive term has different mixing rules in the high-density and the low-density regions. The second virial term (low-density) mixing rule is defined as

$$a^{SV} = \frac{RT}{v} \sum_i \sum_j x_i x_j (B_{ij}^{disp} - B_{ij}^{\mu\mu} - B_{ij}^{QQ}). \quad (20)$$

The relevant combining rules are defined as

$$c_{ij} = \frac{1}{2}(c_i + c_j)$$

$$(cv^+)_{ij} = \frac{1}{2}(c_i v_j^+ + c_j v_i^+) \\ T_{ij}^* = \frac{(c_i T_i^*)^{1/2} (c_j T_j^*)^{1/2}}{c_{ij}} (1 - k_{ij}^B). \quad (21)$$

In the dense fluid term the expansion is similar to the case of the pure component

$$a^{(1)} = a^{(1)}(\langle cT^* v^+ \rangle, \langle v^+ \rangle) \\ a^{(2)} = a^{(2)}(\langle cT^{*2} v^+ \rangle, \langle v^+ \rangle). \quad (22)$$

The combining rule for the volumetric term is the same as defined in the repulsive term, while the energetic term is given by

$$\langle cT^{*m} v^+ \rangle = \sum_i \sum_j x_i x_j c_i \left(\frac{\epsilon_{ij} / q}{c_i k} \right)^m \frac{r_j d_{ij}^s N_{av}}{\sqrt{2}} \quad (23)$$

where

$$d_{ij} = \frac{1}{2}(d_i + d_j) \\ \epsilon_{ij} = (\epsilon_{ii} \epsilon_{jj}) \times (1 - k_{ij}). \quad (24)$$

No binary interaction parameters are used in the interpolation function. It is only necessary to define the following expression:

$$\langle T^* (\epsilon q / k)^{\text{tot}} v^+ \rangle = \sum_i \sum_j x_i x_j \left(\frac{T_i^* + T_j^*}{2} \right) \\ \times \left\{ \frac{[(\epsilon q / k)_i^{\text{tot}} v_i^+ + (\epsilon q / k)_j^{\text{tot}} v_j^+]}{2} \right\}. \quad (25)$$

It is important, to summarize all the adjustable parameters of the model used in this investigation and their physical significance.

The pure component PHCT parameters are T^* , v^* , and c . It has been found^{1,2} that the three pure component parameters have a well defined physical meaning. The v^* parameter is related to a characteristic volume and accounts for size effects. It can be estimated directly from the hard sphere diameter and can be considered very similar to the van der Waals b -parameter in cubic equations of state. The c parameter is related to the symmetry of the molecule and accounts for the external degrees of freedom. The T^* parameter is an energetic parameter related to the

intermolecular potential and influenced, for example, by the vapor pressure curve. A nice feature of the model is that the three parameters are directly related to the chemical structure of the components. The pure component parameters have been calculated on this basis by means of the generalized correlations given in ref. 2. The linear correlations are expressed as a function of the Bondi volume. A fine tuning of the T^* parameter may be performed if at least a single vapor-pressure data point is available.

The binary interaction parameters are included in the mixing and combining rules to account for the nonideality of the mixing process. The interactions are defined as segment-segment interactions and their values should be considered constant at least within a given family of supercritical-fluid hydrocarbons. In the case of the interaction between a supercritical fluid it is taken as one segment in the interaction model, while the other is the hydrocarbon segment. The segment-segment interaction does not change with increasing length of the hydrocarbon. The total interaction between the molecules changes as the chain length of the hydrocarbon increases, but the PHCT model accounts for this effect by considering the number of segments in the molecules. Consequently, to calculate phase equilibria for all the binary mixtures of a supercritical solvent with an hydrocarbon family, only one single value of the interaction parameter should be required, independent of the molecular weight of the hydrocarbon. The reference term does not include any adjustable binary parameter. A binary parameter k_{ij} is included in the geometric combining rule of the property ϵ (the potential energy per unit area which is used in the definition of T^* — eq 24). This parameter, accounts for the nonapplicability of the random mixing in terms of segments making up the mixture. The k_{ij} parameter can be considered different from the k_{ji} , thus differentiating between the case of the two infinite dilution zones. No other adjustable parameters are included in the dense fluid term. The second virial term has also an energy binary interaction parameter (eq 21) that accounts for the nonrandomness that may occur in the low-density region.

The model includes at most three binary interaction parameters, one of them (in the second virial term) becomes relevant only at very low pressure, and will therefore be neglected in this investigation. The use of two unlike k_{ij} is not justified by the behavior in the limiting regions for the systems investigated in this work. In conclusion, only one binary interaction parameter will be used.

In a previous paper, Gregorowicz et al.² have discussed the estimation of the pure component parameters of the equation of state. The application of the PHCT equation to binary mixtures³ has shown that, for some classes of components, it was possible to estimate a binary interaction parameter which was constant with temperature and composition within the given class. This interesting behavior of the model has been further investi-

TABLE I
Binary Interaction Parameters k_{ij} Used in the Calculations

Interaction	k_{ij}
CO ₂ — all hydrocarbons	0.040
Paraffinic hydrocarbons—paraffinic hydrocarbons	0.012
Paraffinic hydrocarbons—cycloparaffinic hydrocarbons	0.015
Paraffinic hydrocarbons—aromatic hydrocarbons	0.030
Paraffinic hydrocarbons—alkyl aromatic	0.025
Methane—all hydrocarbons	0.030

gated in this paper extending the classes considered in ref. 3 and applying the binary interaction parameters to multicomponent mixtures.

RESULTS AND DISCUSSION

All the relevant pure component and binary interaction parameters necessary for the multicomponent calculation reported in this work have been calculated by using the methods reported in refs. 2, 3, and 7 and summarized as follows.

A large number of pure components of different molecular structure has been selected and the related thermophysical properties have been stored in a relational database. The pure component properties considered have been vapor pressure, saturated liquid, and vapor volumes and single-phase PVT data. This database has been used to estimate the pure component parameters v^* , c , and T^* by minimizing an objective function written in terms of all the data available. These parameters have been regressed with Bondi volume as independent variable. A linear relationships resulting from this regression, is used

TABLE II
Comparison Between Correlated and Predicted Results for Some Selected Binary Systems Not Used for the Determination of the Class Characteristic Binary Parameters Reported in Table I. Experimental Data from Ref. 8. $\Delta P\%$ = Percent Relative Deviation in Pressure; Δy = absolute deviation in Vapor Phase Mole Fraction.

System		Regression		Prediction	
		$\Delta P\%$	Δy	$\Delta P\%$	Δy
Carbon dioxide	<i>n</i> -butane	4.165	0.018	4.411	0.019
	<i>n</i> -decane	6.718	0.019	7.752	0.020
	toluene	4.093	0.015	4.802	0.015
Ethane	ethylene	2.112	0.310	3.122	0.035
	propane	1.369	0.024	1.354	0.023
	<i>i</i> -butane	1.991	0.027	3.248	0.024
	<i>n</i> -pentane	1.781	0.028	2.544	0.026
	cyclohexane	2.685	0.024	4.484	0.026
Propane	propylene	1.377	0.008	1.379	0.008
	<i>i</i> -pentane	2.506	0.024	2.259	0.024
	<i>n</i> -heptane	2.106	0.030	1.965	0.030
Methane	ethane	1.020	0.007	5.519	0.021
	propane	3.140	0.018	5.538	0.019
	<i>n</i> -pentane	2.990	0.026	5.171	0.282
	<i>n</i> -heptane	3.277	0.046	3.544	0.046
	<i>n</i> -octane	3.640	0.003	7.145	0.024
	benzene	5.047	0.040	5.047	0.036
	toluene	4.322	0.025	4.294	0.024
	<i>m</i> -xylene	4.078	0.019	5.446	0.017
<i>n</i> -Butane	<i>n</i> -octane	1.023	—	1.081	—
	<i>n</i> -decane	1.623	0.016	2.039	0.015
<i>n</i> -Pentane	<i>n</i> -octane	0.670	0.001	3.917	0.010
Carbon dioxide	<i>n</i> -tetradecane	10.09	—	13.19	—
	<i>n</i> -docosane	4.197	—	5.789	—
	<i>n</i> -tetracosane	3.302	—	4.505	—
Ethane	<i>n</i> -eicosane	4.672	0.098	10.37	0.128
	<i>n</i> -tetratetracontane	17.50	—	17.57	—
Propane	<i>n</i> -eicosane	3.300	—	3.746	—

TABLE III
 Prediction of Multicomponent Mixtures by Means of PHCT Equation with the Parameters Reported in Table I. Experimental Data from Ref. 8.

System	T (K)	P (bar)		RMSD	AvD	MaxD	% D
Methane-propane-n-decane	410.93	68.95	ΔP	2.65	2.38	4.66	3.4
			$\Delta YC1$	0.020	0.012	0.030	
			$\Delta YC3$	0.020	0.010	0.031	
			$\Delta YC10$	0.004	0.002	0.009	
Methane-propane-n-decane	410.93	137.9	ΔP	8.34	5.12	16.9	5.1
			$\Delta YC1$	0.030	0.003	0.070	
			$\Delta YC3$	0.017	0.001	0.043	
			$\Delta YC10$	0.013	0.002	0.028	
Methane-n-butane-n-decane	344.26	68.95	ΔP	2.78	2.33	4.57	3.4
			$\Delta YC1$	0.052	0.003	0.008	
			$\Delta YC4$	0.005	0.003	0.008	
			$\Delta YC10$	0.001	0.001	0.001	
Methane-n-butane-n-decane	344.26	86-103	ΔP	3.97	3.12	7.03	3.3
			$\Delta YC1$	0.007	0.001	0.019	
			$\Delta YC4$	0.006	0.001	0.012	
			$\Delta YC10$	0.003	0.002	0.007	
Methane-n-butane-n-decane	344.16	68.95	ΔP	1.08	1.00	1.55	1.4
			$\Delta YC1$	0.007	0.001	0.017	
			$\Delta YC4$	0.007	0.001	0.006	
			$\Delta YC10$	0.001	0.001	0.006	
Methane-n-butane-n-decane	344.26	55.16	ΔP	1.67	1.45	2.21	2.6
			$\Delta YC1$	0.009	0.002	0.012	
			$\Delta YC4$	0.008	0.006	0.011	
			$\Delta YC10$	0.005	0.003	0.012	
Methane-n-butane-n-decane	344.26	86.19	ΔP	1.69	1.50	2.29	1.7
			$\Delta YC1$	0.007	0.002	0.017	
			$\Delta YC4$	0.005	0.001	0.004	
			$\Delta YC10$	0.003	0.002	0.008	
Methane-n-butane-n-decane	344.26	103.42	ΔP	2.07	1.87	2.63	1.8
			$\Delta YC1$	0.009	0.003	0.020	
			$\Delta YC4$	0.006	0.001	0.012	
			$\Delta YC10$	0.003	0.001	0.008	
Methane-n-pentane-i-pentane	344-410	34-140	ΔP	3.48	1.02	11.0	2.0
			$\Delta YC1$	0.041	0.021	0.141	
			$\Delta YC5$	0.012	0.008	0.036	
			$\Delta YX15$	0.029	0.013	0.102	
CO ₂ -n-butane-n-decane	344	95-97	ΔP	18.5	14.4	25.9	16.0
CO ₂ -n-butane-butylbenzene	344	92-107	ΔP	21.1	15.8	37.1	17.0
Ethane-n-butane-n-pentane	338.71	34-60	ΔP	0.730	0.140	1.39	1.3
			$\Delta YC2$	0.121	0.019	0.552	
			$\Delta YC4$	0.056	0.010	0.251	
			$\Delta YC5$	0.066	0.009	0.303	
Ethane-n-butane-n-pentane	366.48	36-62	ΔP	0.961	0.702	2.24	1.6
			$\Delta YC2$	0.045	0.003	0.174	
			$\Delta YC4$	0.014	0.001	0.053	
			$\Delta YC5$	0.035	0.002	0.150	

for the prediction of pure component parameters not included in the original database. For two of the parameters, v^* and c , the linear relationships have been retained, while the equation of state T^* parameter has been fine tuned to an experimental vapor pressure data, if available.

The binary interaction parameters have been estimated with a similar procedure. A data base of binary phase equilibrium data has been established and the binary interaction parameters of the model have been fitted to the

data to give the minimum deviation. These values, along with their error bars, have been grouped by component classes and an unique value of the parameter for each combination of classes has been selected. The binary classes of components considered in ref. 3 have been extended and checked by considering systems not included in the data base originally used in ref. 3. The binary parameters obtained in ref. 3 and used in this investigation are reported in Table I. Table II shows some prediction re-

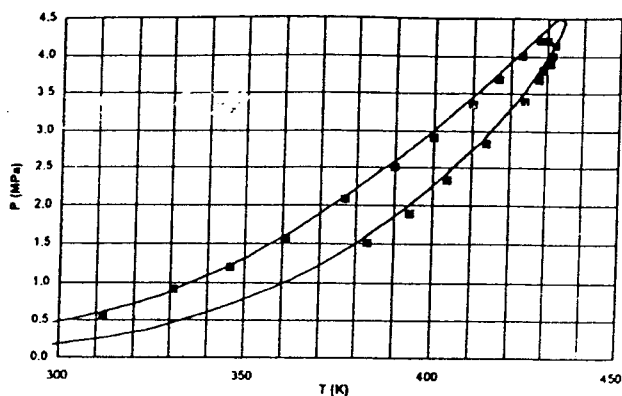


Figure 1. Calculated (—) and experimental (■) phase envelope for a hydrocarbon mixture of propane ($z = 0.3376$), *n*-butane ($z = 0.3398$), and *n*-pentane ($z = 0.3326$). Experimental data from ref. 9.

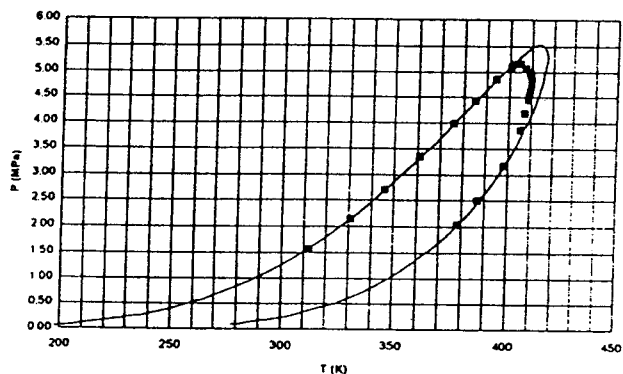


Figure 2. Calculated (—) and experimental (■) phase envelope for a hydrocarbon mixture of ethane ($z = 0.2542$), propane ($z = 0.2554$), *n*-butane ($z = 0.2554$), and *n*-pentane ($z = 0.2537$). Experimental data from ref. 9.

sults on binary systems not included in the original data base reported in terms of per cent relative deviation in pressure ($\Delta P\%$) and absolute deviation in vapor phase mole fraction (Δy). Relative deviations are used for pressure and, to avoid unrealistic weighing of the results in the dilute regions, absolute deviations are used for mole fractions. The predictions are rather satisfactory, especially for the binary systems of hydrocarbon–hydrocarbon and CO_2 –hydrocarbon.

The PHCT equation has been implemented into the process simulator ASPEN PLUSTM (versions 8 and 9) thus taking the advantage of its reliable and powerful numerical methods necessary for calculating the phase envelopes, multicomponent flash, and VLE at high pressure. Details on the interfacing techniques are reported in ref. 7.

Table III shows results for multicomponent VLE calculations obtained by using PHCT interfaced to ASPEN PLUSTM with the binary parameters listed in Table I. The results are written in terms of deviations in pressure (ΔP) and deviations in vapor mole fractions (Δy) for the three components indicated by the number of carbon atoms. The deviations reported in Table III are re-

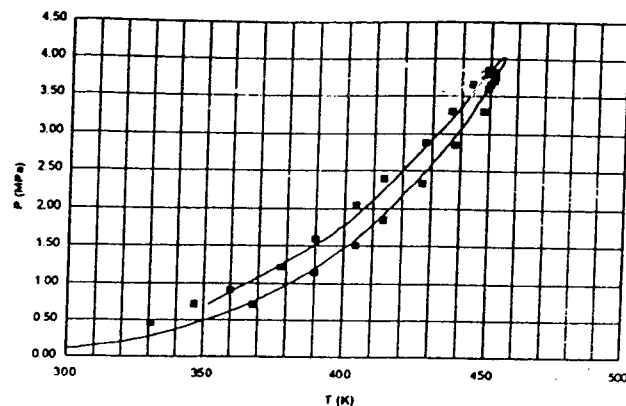


Figure 3. Calculated (—) and experimental (■) phase envelope for a hydrocarbon mixture of *n*-butane ($z = 0.6449$), *n*-pentane ($z = 0.2359$), and *n*-hexane ($z = 0.1192$). Experimental data from ref. 9.

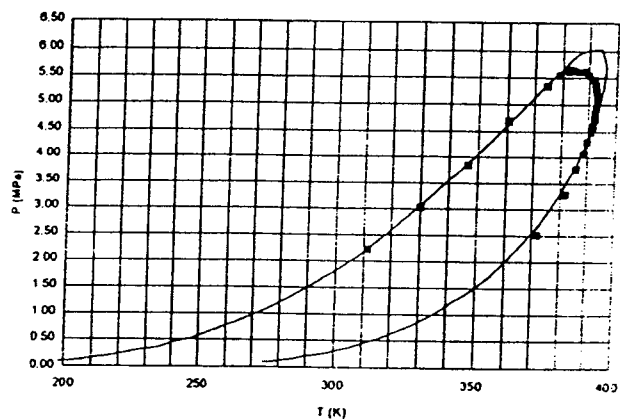


Figure 4. Calculated (—) and experimental (■) phase envelope for a hydrocarbon mixture of ethane ($z = 0.3977$), propane ($z = 0.2926$), *n*-butane ($z = 0.1997$), *n*-pentane ($z = 0.0713$), and *n*-hexane ($z = 0.1369$). Experimental data from ref. 9.

spectively the root-mean-square deviation (RMSD), the average absolute deviation (AvD), the maximum deviation (MaxD), and the relative per cent deviation (%D) for pressure only. The results obtained in Table III shows the prediction performance of the equation. For hydrocarbon mixtures the predictions are comparable to the experimental uncertainty, while for systems containing carbon dioxide the predictions are not as accurate, but this behavior should be checked on a higher number of systems.

One of the most severe tests for an equation of state is the calculation of phase envelopes. For this reason, some phase envelopes for hydrocarbon mixtures have been calculated with the PHCT equation. Some results are shown in Figures 1–4. The results are good far from the critical point and are reasonable even if not accurate in the vicinity of the critical point. This results should be considered positively as far as process simulation is concerned. Indeed, to be of any use in process simulation, the predicted phase behavior must show the same trend as

TABLE IV
Comparison Between Different Predictive Models on Selected Systems. PHCT is the Model Used in this Work, Abdoul¹⁰ is a Predictive Method for the Estimation of Binary Interaction Parameters of Peng-Robinson Equation, MHV2¹¹ is a Predictive Equation of State Based on Group Contribution Methods and SRK is the Soave-Redlich-Kwong¹² Equation with Zero Binary Interaction Parameters. Experimental Data from Ref. 8.

System	T (K)	Pressure RMSD			
		PHCT	Abdoul	MHV2	SRK
Ethane + <i>n</i> -hexadecane	320-360	6.83	7.05		12.10
Ethane + <i>n</i> -eicosane	320-400	5.11	10.00		11.41
Ethane + <i>n</i> -tetracosane	320-240	4.23	13.20		10.15
Carbon dioxide + methylcyclohexane	311-477	5.09		6.30	7.55
Carbon dioxide + ethylbenzene	313-366	5.52		6.20	6.97
Carbon dioxide + <i>n</i> -tetracosane	320-340	4.50			11.22
Methane + <i>n</i> -butane + <i>n</i> -decane	344.26	1.83	3.77		4.01

the real behavior. Undesirable would be, for example, nonexisting liquid-liquid split at high pressure.

For sake of completeness a comparison among predictive equations of state on some selected representative systems has been reported in Table IV. The systems have been chosen among those presenting large differences in size and shape of the components and the better performance of the PHCT equation is outstanding. For systems with similar size and shapes, the difference in the deviations obtained by the models is not so marked.

CONCLUSIONS

The calculation reported in this paper demonstrates the predictive capabilities of the PHCT equation of state considered for mixtures of light gases and hydrocarbons. The results reported have been obtained by using a prediction method for the three pure component parameters in which only a single vapor-pressure data point was used. The binary interaction parameters used are constant for each combination of classes, no higher-order interaction parameters have been used and no binary parameters have been regressed or fine tuned on multicomponent experimental data. Therefore the calculations shown are pure predictions and in this respect the results are to be considered good. The results obtained for hydrocarbons-supercritical solvents show that the model can be confidently used in the petroleum industry particularly for its good performance in phase envelope calculations. Furthermore, the model could be extended to treat natural and biosubstances, provided the specific interaction coefficients involved in the model will be quantified. Unfortunately, the lack of experimental data for these systems limits, at present, the establishment of a data base and the consequent calculations.

If we couple the results reported in this investigation on the prediction of multicomponent hydrocarbon systems with other previously reported results^{4,5,7} showing the good mixture volumetric property predictions, we can conclude that the PHCT equation can be considered a useful tool for the prediction of physical properties for supercritical extraction processes. Further investigations are needed to extend these conclusions to multicomponent natural products such as systems containing acids, esters, and similar compounds.

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