

THE PERTURBED HARD CHAIN THEORY FOR THE PREDICTION OF SUPERCRITICAL FLUID EXTRACTION: BINARY MIXTURES

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Abstract—A perturbed hard chain theory based equation of state is investigated in view of its application to supercritical fluid extraction process calculations. This investigation is an extension of a previous paper in which attention was given to pure component properties and in which a method was proposed for estimating the pure component parameters from the molecular structure. Binary systems of supercritical fluids and nonpolar molecules are considered in this paper. A method is proposed for estimating *a priori* the binary interaction parameter from molecular structure information. A universal set of parameters is found for hydrocarbon-supercritical fluid mixtures depending only upon the supercritical fluid and the hydrocarbon family. The results obtained are fairly good and comparable with other predictive equations of state available in the literature. The advantages of using this method is its integration with the pure component parameter estimation method proposed in a previous paper. Good results were also obtained in the prediction of the volumetric properties of the liquid and the vapor phase.

INTRODUCTION

Feasibility investigations for supercritical fluid extraction processes must be based on complete knowledge of the thermodynamic behavior of the mixtures involved. The situation of lack of experimental information is very often encountered in such processes, since the mixtures involved are usually very complex, and made up of many components. Examples of similar conditions are given by the separation processes involving petroleum cuts and natural products. In both cases, the mixtures do not have a well defined number of components whose pure component properties are not known. This situation is very common and, in order to predict the phase behavior of such a mixture, a fully predictive thermodynamic model is required. 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 the given mixtures. The binary interaction parameters, essential for a correct prediction of the multicomponent phase behavior, should be calculable *a priori* by knowing the functional groups of the components present in the mixture.

For supercritical fluid extraction processes, the most obvious choice for modelling the phase behavior is an equation of state. Unfortunately, most of the equations of state are not predictive and interaction parameters need to be estimated for each binary system present in the multicomponent mixture. Furthermore, the equations of state which are usually employed contain pure component parameters which are estimated from the critical properties and the acentric factor. For the components involved in supercritical fluid extraction processes, critical properties and vapor-pressure data are very often not available or very uncertain, thus leading to weak

results in the prediction of the multicomponent phase behavior. Predictive equations of state, such as MHV2 (Dahl *et al.*, 1991) and Abdoul (Abdoul *et al.*, 1991), base their prediction capabilities on binary interaction parameters and not on pure component parameters. The problem of pure component parameters for cubic equations of state has been addressed by Carrier *et al.* (1988), among others. This method may be combined with the Abdoul method for the description of hydrocarbon mixtures.

In this paper, an equation of state based on the perturbed hard chain theory (PHCT), suitable for the prediction of pure component properties from the molecular structure, has been investigated in an attempt to determine whether or not generalized correlation for the binary interaction parameters may be established. The preliminary results obtained for mixtures of hydrocarbons and carbon dioxide, ethane and propane as supercritical fluids show the very interesting possibility of using the PHCT model in the pure prediction of the properties of multicomponent mixtures containing an undefined number of hydrocarbons.

EQUATION OF STATE

The equation of state considered in this work is the PHCT equation derived by Cotterman *et al.* (1986) based on the generalized van der Waals theory. The model has been developed in terms of the Helmholtz function by considering an attractive and a repulsive contribution. The former is made up of two terms, one for describing the high density and one for the low density region, the latter being based on a generalized form of the Carnahan-Starling equation. Dispersion and polar contributions to the free energy are considered in each part of the attractive term as well as dipole and quadrupole contributions. An interpola-

tion function between the two limiting cases of a dense fluid and zero density fluid is included in the model based on empirical nonadjustable parameters.

In a previous paper, Gregorowicz *et al.* (1991) have discussed the problem of the estimation of the pure component parameters of the equation of state. The extension to mixtures requires the definition of combining and mixing rules. Since we have used the same set of rules as in the original paper of Cotterman and Prausnitz (1986), we refer the reader to this reference for the definition of the equations.

It is important, though, to summarize the adjustable parameters of the model used in this investigation and their physical significance. The reference term does not include any adjustable parameter. A binary parameter k_{ij} is included in the geometric combining rule of the pure component property ϵ (the potential energy per unit area). 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 to be different from the k_{ji} parameter, thus showing that the cases of the two infinite dilution zones are different. No other adjustable parameters are included in the dense fluid term. The second virial term also has an energy binary interaction parameter that accounts for the non-randomness that may occur in the low density region.

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

The pure component PHCT parameters T^* , v^* and c have been predicted, on the basis of the molecular structure, by means of the generalized correlations given by Gregorowicz *et al.* (1991). The linear correlations are of the following form:

$$P_{cp} = mV_B + q \quad (1)$$

where P_{cp} is the desired pure component parameter, V_B is the Bondi volume and m and q are numerical values reported in Table 1. A fine tuning of the T^* parameter may be performed if at least a single vapor pressure datum is available.

CALCULATIONS

A parameter estimation program has been developed, with particular attention being given to reducing the CPU time and improving the reliability of the search procedure. The density calculation routine is based on the algorithm proposed by Topliss *et al.* (1988). The objective function, minimized to obtain the binary interaction parameters, has been written in terms of pressure only, and the Fletcher implementation of the Levenberg-Marquardt method has been

Table 1. Value of the linear regression constants m and q for the generalized correlations of the pure component parameters of the PHCT model

	V^*	c	cT^*
m	0.955	0.0157	10.01
q	4.380	0.7920	30.19

used for optimization:

$$OF = \sum_i \frac{(P_i^{EXP} - P_i^{CALC})^2}{(P_i^{EXP})^2} \quad (2)$$

The results reported in the tables are written in terms of per cent average deviations in pressure and mole fractions. Relative pressure deviations are defined as

$$\Delta P = \frac{100}{n} \sum_i \frac{|P_i^{EXP} - P_i^{CALC}|}{P_i^{EXP}} \quad (3)$$

In a similar way, the deviation for equilibrium factors K are defined. To avoid unrealistic weighting of the results in the dilute regions, the mole fraction deviations have been defined in absolute terms as follows:

$$\Delta x = \frac{1}{n} \sum_i |x_i^{EXP} - x_i^{CALC}| \quad (4)$$

The calculation procedure was as follows. For each supercritical solvent considered (carbon dioxide, ethane and propane), several binary systems of solvents and hydrocarbons were selected from different classes (paraffines, aromatics, naphthenes) with increasing molecular weight. Each binary system was regressed and the optimum binary interaction parameter obtained.

Data regression with other objective functions (unreported results, but available upon request from the authors) was also performed on selected binary systems, but no substantial difference was observed in the parameters and statistical results. This is not surprising, since high pressure equilibrium is more sensitive to pressure than to mole fraction variations even if appropriate weights are assigned to the terms of the objective function. The effect of the binary interaction parameter on the second virial term is negligible, and considering k_{ij} to be different from k_{ji} also makes no substantial improvement in the regression. The former result is obvious since the experimental data are for high pressure; the latter reflects the symmetric situation of the two infinite dilution regions which are typical for nonpolar systems. The binary systems considered in this work are reported in Table 2.

RESULTS

For each binary system, the optimum interaction parameter has been determined from the experimental data reported in Table 2. Since the binary interaction parameters (k_{ij}) are defined as segment-segment interactions, their values should be considered constant

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Table 2. List of systems investigated with temperature range and reference

System	Temperature range (K)	Reference
CO ₂ -propane	274-344	Knapp <i>et al.</i> (1982)
CO ₂ -heptane	310-394	Knapp <i>et al.</i> (1982)
CO ₂ -octane	313-383	King <i>et al.</i> (1983)
CO ₂ -decane	344-377	Nagarajan and Robinson (1986)
CO ₂ -hexadecane	463-663	Sebastian <i>et al.</i> (1980)
CO ₂ -methylcyclohexane	311-477	Ng and Robinson (1979)
CO ₂ -toluene	311-477	Knapp <i>et al.</i> (1982)
CO ₂ -ethylbenzene	308-328	Tan <i>et al.</i> (1991)
CO ₂ -styrene	308-328	Tan <i>et al.</i> (1991)
Ethane-heptane	234-500	Knapp <i>et al.</i> (1982)
Ethane-octane	273-373	Knapp <i>et al.</i> (1982)
Ethane-decane	277-477	Knapp <i>et al.</i> (1982)
Ethane-methylcyclohexane	313-473	Richon <i>et al.</i> (1991)
Ethane-propylcyclohexane	313-473	Richon <i>et al.</i> (1991)
Ethane-benzene	293-533	Knapp <i>et al.</i> (1982)
Ethane-toluene	313-473	Richon <i>et al.</i> (1991)
Ethane-propylbenzene	313-473	Richon <i>et al.</i> (1991)
Ethane-metaxylene	313-473	Richon <i>et al.</i> (1991)
Ethane-mesitylene	313-473	Richon <i>et al.</i> (1991)
Propane-butane	353-413	Knapp <i>et al.</i> (1982)
Propane-hexane	333-473	Knapp <i>et al.</i> (1982)
Propane-decane	277-510	Knapp <i>et al.</i> (1982)
Propane-methylcyclohexane	313-472	Richon <i>et al.</i> (1991)
Propane-propylcyclohexane	313-473	Richon <i>et al.</i> (1991)
Propane-benzene	310-477	Knapp <i>et al.</i> (1982)
Propane-toluene	394-473	Richon <i>et al.</i> (1991)
Propane-propylbenzene	393-473	Richon <i>et al.</i> (1991)
Propane-metaxylene	313-473	Richon <i>et al.</i> (1991)
Propane-mesitylene	313-473	Richon <i>et al.</i> (1991)

within a given family of supercritical fluids and hydrocarbons. This statement may be explained by assuming that the supercritical fluid represents one of the segments in the interaction model, while the other is the hydrocarbon segment. If the supercritical fluid is not changed, 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 a hydrocarbon family, only one single value of the interaction parameter should be required, independently of the molecular weight of the hydrocarbon.

After the selection of this constant value of k_{ij} , calculations were done to check the deviation between experimental and calculated data isotherm by isotherm and for all the isotherms together. Calculations without binary interaction parameters have been performed for the sake of completeness, even though one would expect that in a model written in terms of segment-segment interactions the results obtained without interaction parameters would not be satisfactory even for hydrocarbons (Gasem and Robinson, 1990).

Table 3 reports, as an example, the results obtained in the individual fitting for the CO₂-toluene system.

For this system, a constant value of 0.04 for the binary interaction parameter can be assumed and no particular trend with temperature is detected. In the table, the results predicted without binary interaction parameters are also reported.

Similar conclusions can be obtained for other systems containing CO₂. Table 4 reports the results for all the binary systems investigated. Deviations between calculated and experimental data at different temperatures (see Table 2 for the temperature range of the binary system considered) with a constant value of the binary interaction parameter are given and compared with those obtained without a binary interaction parameter (detailed results are available from the authors upon request). Figure 1 shows the dispersion of the binary interaction parameters for some systems containing CO₂. It can be seen that the suggested general value (0.04) for the binary interaction parameter gives quite satisfactory results.

For systems with ethane and propane as supercritical components, the same approach has been used. First, an individual fitting of different sets of isothermal data was performed, thus obtaining the optimum parameter for each isotherm. Second, a global (constant) value of the interaction parameter for the binary system considered was obtained. Third, a general value for the binary interaction parameter to be used within each family of hydrocarbons was determined.

Table 3. Deviations between calculated and experimental data for the system carbon dioxide-toluene at different temperatures: comparison among calculations with the optimum parameter, no binary parameter and a suggested constant value of the parameter

T (K)	N^\dagger	Parameter	ΔP	ΔY	$\Delta K1$	$\Delta K2$
311	8	0.000	11.97	0.003	0.38	41.0
		0.027 (opt)	2.64	0.001	0.15	29.0
		0.040	7.03	0.007	0.10	27.0
352.6	10	0.000	15.12	0.015	2.10	36.0
		0.037 (opt)	3.07	0.008	1.30	20.0
		0.040	3.50	0.007	1.20	19.0
393	8	0.000	13.53	0.018	2.80	21.0
		0.027 (opt)	6.40	0.014	3.10	14.0
		0.040	6.40	0.015	3.70	14.0
477	8	0.000	10.72	0.021	4.40	9.8
		0.049 (opt)	0.64	0.008	2.80	3.8
		0.040	2.29	0.008	2.20	4.3

N is the number of data points.

Table 4. Deviations between calculated and experimental data for systems containing carbon dioxide: comparison between calculations with a suggested constant value of the parameter and without a binary parameter

Second component	N^\dagger	Parameter	ΔP	ΔY	$\Delta K1$	$\Delta K2$
Propane	45	0.000	9.20	0.020	3.12	15.0
		0.040	1.10	0.007	0.92	12.0
<i>n</i> -Heptane	24	0.000	12.12	0.010	1.22	28.0
		0.040	1.82	0.003	0.42	24.0
<i>n</i> -Octane	23	0.000	7.04	0.008	1.97	12.8
		0.040	5.06	0.002	0.21	10.0
<i>n</i> -Decane	25	0.000	15.03	0.015	3.11	32.0
		0.040	2.04	0.006	0.97	19.0
<i>n</i> -Hexadecane	44	0.000	12.01	0.030	4.31	28.0
		0.040	1.08	0.007	0.36	21.0
Methylcyclohexane	31	0.000	14.34	0.018	4.00	29.0
		0.040	5.09	0.018	3.40	31.0
Toluene	34	0.000	12.98	0.014	2.80	30.0
		0.040	4.73	0.008	2.40	25.0
Ethylbenzene	18	0.000	19.59	0.001	0.14	34.0
		0.040	5.52	0.001	0.08	21.0
Butylbenzene	14	0.000	24.74			
		0.040	21.23			
Styrene	18	0.000	18.90	0.001	0.11	35.0
		0.040	9.66	0.001	0.08	30.0
Decaline	33	0.000	42.26			
		0.040	19.69			

N is the number of data points.

From an analysis of the results of the fittings at each temperature, again no trend in the change of the values of binary interaction parameters with temperature (in the temperature range considered) was detected, thus allowing us to determine a common value for the k_{ij} of each supercritical solvent-hydrocarbon family. Comparison of the values obtained showed that it is not possible to assume, as in the case for the CO₂ systems, a constant k_{ij} for all the systems investigated. In fact, the k_{ij} are different for the systems

containing paraffin, cycloparaffin or aromatic hydrocarbons as the second component. Figure 2 shows the variation of the relative deviation in pressure for paraffin systems as a function of the optimum value of the binary interaction parameter: a value between 0.010 and 0.015 is satisfactory for describing systems belonging to this group. Figures 3 and 4 show results for cycloparaffin and aromatics; also in this case an optimal value (between 0.010 and 0.020 for cycloparaffin and around 0.025 for the aromatics) can be

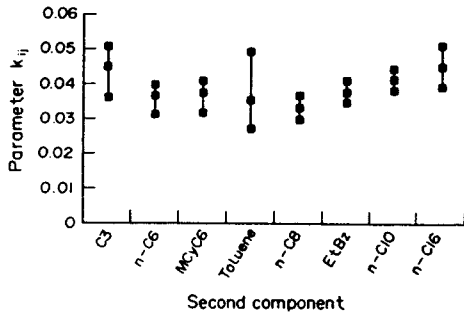


Fig. 1. Minimum, maximum and average value of the binary interaction parameters for some system containing carbon dioxide.

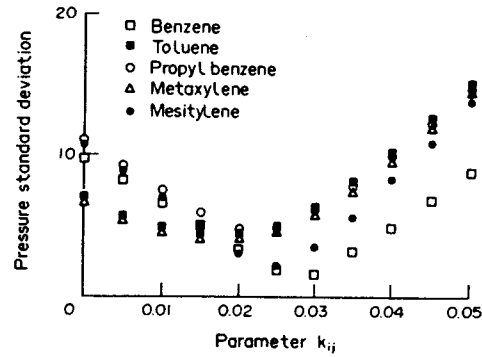


Fig. 4. Relative pressure deviation as a function of the binary interaction parameter for mixtures containing ethane and aromatics.

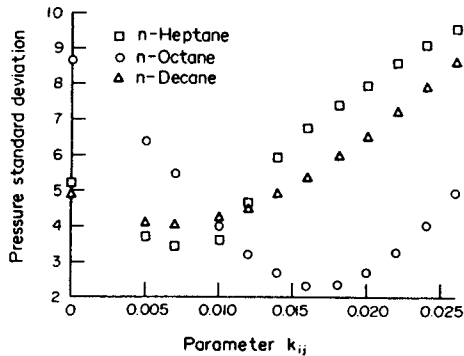


Fig. 2. Relative pressure deviation as a function of the binary interaction parameter for mixtures containing ethane and paraffins.

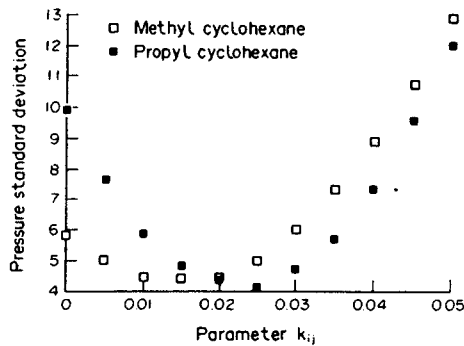


Fig. 3. Relative pressure deviation as a function of the binary interaction parameter for mixtures containing ethane and cycloparaffins.

determined. Benzene is the only case that shows a slightly higher value (0.030). This can be explained; since benzene is the only completely aromatic molecule; the other components in the aromatic family contain some methyl or ethyl substitutes that provide a given grade of paraffinic character to the molecule.

Consequently, a binary interaction parameter value of 0.012 for paraffin, 0.015 for cycloparaffin and 0.030 for benzene-containing systems is suggested. For the case of alkyl aromatic compounds, a value of 0.025 may be used as a first approximation, but the value of the binary interaction parameter can be calculated on

the basis of those of paraffin and benzene systems taking into account the percentage of C atoms that are paraffinic or aromatic.

Table 5 summarizes the results for the systems containing ethane. Results are presented for the entire temperature range considered, and comparisons are given for the calculation obtained without binary interaction parameters and with the values suggested in the preceding paragraphs.

Binary systems containing propane as the supercritical compound have also been investigated following the procedure described above; the results obtained are reported in Table 6, along with the predictions obtained with no binary interaction parameter. The results of the fittings confirm the conclusions reported in the preceding paragraph. Since the binary interaction parameter considers interactions between segments, the same value has been found for systems containing ethane and propane.

CONCLUSIONS

The aim of this work was to develop a general method for estimating interaction parameters for binary systems containing hydrocarbons and a supercritical fluid. From the results obtained, it is possible to predict the behavior of binary mixtures consisting of hydrocarbons and CO₂, ethane and propane using the values of the parameters reported in Table 7, which are constant for a given class of hydrocarbons. These results, together with those already obtained for the prediction of pure component parameters (Gregorowicz *et al.*, 1991), suggest the use of the PHCT equation as a completely predictive tool for the description of binary mixtures containing hydrocarbons and a supercritical component.

A comparison was made between the method proposed in this work and other predictive models for the description of the behavior of binary mixtures. Table 8 compares the PHCT predictive method used here with the Peng-Robinson EOS in which the interactions were calculated using the group contribution method of Abdoul (Abdoul *et al.*, 1991). The method based on the PHCT gives lower deviations, especially for systems whose components are very different in

Table 5. Deviations between calculated and experimental data for systems containing ethane: comparison between calculations with a suggested constant value of the parameter and without a binary parameter

Second component	N^{\dagger}	Parameter	ΔP	ΔY	$\Delta K1$	$\Delta K2$
<i>n</i> -Heptane	48	0.000	5.20	0.012	3.30	79.0
		0.012	4.64	0.015	4.80	94.0
<i>n</i> -Octane	64	0.000	8.69	0.006	1.00	150.0
		0.012	3.19	0.006	1.00	160.0
<i>n</i> -Decane	95	0.000	4.92	0.007	1.80	48.0
		0.012	4.51	0.006	1.20	51.0
Methylcyclohexane	26	0.000	5.82	0.012	2.50	140.0
		0.015	4.43	0.011	2.10	145.0
Propylcyclohexane	25	0.000	9.36	0.012	2.50	26.0
		0.015	4.92	0.009	2.00	22.0
Benzene	79	0.000	9.69	0.009	5.80	7.1
		0.030	1.66	0.009	5.50	11.0
Toluene	20	0.000	7.03	0.019	5.30	17.0
		0.025	4.94	0.012	3.50	9.0
Propylbenzene	25	0.000	11.07	0.011	2.10	29.0
		0.025	4.60	0.007	1.40	18.0
Metaxylene	27	0.000	6.72	0.018	3.10	30.0
		0.025	4.83	0.011	2.30	19.0
Mesitylene	25	0.000	10.79	0.016	3.20	37.0
		0.025	2.16	0.013	2.50	26.0

$^{\dagger}N$ is the number of data points.

Table 6. Deviations between calculated and experimental data for systems containing propane: comparison between calculations with a suggested constant value of the parameter and without a binary parameter

Second component	N^{\dagger}	Parameter	ΔP	ΔY	$\Delta K1$	$\Delta K2$
<i>n</i> -Butane	30	0.000	2.03	0.103	3.30	3.6
		0.012	1.68	0.010	3.30	3.4
<i>n</i> -Hexane	34	0.000	1.60	0.011	3.00	8.3
		0.012	1.96	0.008	2.00	6.0
<i>n</i> -Decane	55	0.000	3.55	0.010	2.70	28.0
		0.012	4.75	0.011	2.50	26.0
Methylcyclohexane	25	0.000	6.38	0.012	3.00	14.0
		0.015	4.57	0.008	2.00	12.0
Propylcyclohexane	24	0.000	5.87	0.011	1.80	24.0
		0.015	3.24	0.009	1.50	22.0
Benzene	73	0.000	9.60	0.022	6.50	16.0
		0.030	2.48	0.011	3.00	18.0
Toluene	16	0.000	7.53	0.019	3.90	19.0
		0.025	1.83	0.021	3.90	14.0
Propylbenzene	18	0.000	6.62	0.021	3.60	33.0
		0.025	3.35	0.018	2.90	27.0
Metaxylene	21	0.000	8.43	0.018	4.20	23.0
		0.025	2.35	0.017	4.20	18.0
Mesitylene	21	0.000	11.22	0.021	4.10	32.0
		0.025	2.49	0.016	2.90	22.0

$^{\dagger}N$ is the number of data points.

size. Comparisons were also made with the MHV2 model for some systems containing CO₂ (Table 9), and the pressure deviations obtained by using the PHCT are of the same order of magnitude or slightly lower. An advantage of using the PHCT method is the

fact that the pure-component parameters are also completely predicted.

A further advantage of the use of the PHCT equation is given by the very good prediction of the volumetric properties of both the liquid and the va-

pour phase, as can be seen in Table 10 for the volumetric properties of mixtures and in Table 11 for the infinite dilution partial molar volumes of organic compounds in carbon dioxide (Cortesi *et al.*, 1993). None of the existing predictive methods can compete with this precision in volume calculations. The PHCT equation, as can be seen from Table 8, gives good results for systems whose molecules are very different in size, thus indicating good possibilities for the prediction of the phase behavior of high molecular weight systems such as petroleum cuts and natural products.

The only disadvantage in the use of the PHCT is that the critical region is not described accurately, as has already been pointed out by Gregorowicz *et al.* (1991); the model cannot be used with confidence in the critical region. This statement, which may appear to undermine the advantages of using the PHCT equation to model supercritical fluid extraction processes, does not have dramatic consequences as far as the applicability to real calculations is concerned.

Supercritical fluid extraction processes are normally carried out at temperatures above the critical isotherm of the solvent ($T_c = 1.2-2$) and at a pressure well above the critical pressure of the solvent. In these conditions, it is necessary to calculate the solubility of a given molecule in the dense gas (usually well above the critical point) during the extraction step, and, even more important, to perform flash calculations at sub-critical conditions (well below the critical pressure) during the separation step. The model is perfectly applicable in such conditions.

However, in order to improve the description of the thermodynamic behavior in the close vicinity of the critical point (if the process requires it), the pure component properties and the binary interaction parameters may be recalculated based on data in the critical region.

Finally, the good results obtained for mixtures and the stability of the binary interaction parameters with temperature and with the molecular weight of the second component is further proof that the general

Table 7. Binary interaction parameters suggested

Interaction	k_{ij}
CO ₂ -hydrocarbons	0.040
C ₂ H ₆ -paraffinic hydrocarbons	0.012
C ₂ H ₆ -cycloparaffinic hydrocarbons	0.015
C ₂ H ₆ -aromatic hydrocarbons	0.030
C ₂ H ₆ -alkyl aromatic hydrocarbons	0.025
C ₃ H ₈ -paraffinic hydrocarbons	0.012
C ₃ H ₈ -cycloparaffinic hydrocarbons	0.015
C ₃ H ₈ -aromatic hydrocarbons	0.030
C ₃ H ₈ -alkyl aromatic hydrocarbons	0.025

Table 8. Comparison between the PHCT model considered and the Abdoul predictive method for some systems containing ethane

Second component	T (K)	ΔP	
		PHCT	PR
<i>n</i> -Hexadecane	320-360	6.83	7.05
<i>n</i> -Eicosane	320-400	5.11	10.00
<i>n</i> -Dotriacontane	320-360	7.04	12.10
<i>n</i> -Tetracosane	320-340	4.23	13.20

Table 9. Comparison between PHCT and MHV2 methods for some systems containing CO₂

Second component	T (K)	ΔP		ΔY	
		PHCT	MHV2	PHCT	MHV2
Methylcyclohexane	311-477	5.09	6.3	0.018	0.014
Ethylbenzene	313-366	5.52	6.2	0.001	0.002

Table 10. Prediction of the total liquid and vapor volumes (per cent deviations) for some systems containing CO₂[†]

Second component	N	Parameter	ΔV^L	ΔV^V
Propane	45	0.000	2.6	14.0
		0.040	1.8	3.1
<i>n</i> -Heptane	24	0.000	3.0	34.0
		0.040	3.0	5.4
<i>n</i> -Octane	23	0.000	22.0	25.0
		0.040	4.0	10.0
<i>n</i> -Decane	25	0.000	1.5	41.0
		0.040	1.2	9.1

[†]The calculations have been done with the PHCT model with the binary parameters given in Table 7.

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Table 11. Partial molar volumes of organic compounds in carbon dioxide at 323.15 K and 0.355 g/cm³; this density value corresponds to the minimum in the partial molar volume along the isotherm

Second component	Partial molar volumes (cm ³ /mol)	
	Experimental [†]	Calculated PHCT
<i>n</i> -Hexane	- 711.97	- 727.20
<i>n</i> -Octane	- 897.77	- 1030.52
<i>n</i> -Decane	- 1177.33	- 1204.03
<i>n</i> -Dodecane	- 1526.69	- 1752.59
Benzene	- 649.85	- 687.82
Toluene	- 747.51	- 1192.86
Ethylbenzene	- 864.61	- 1370.76

[†]Experimental data from Cortesi *et al.* (1993).

correlations for the pure component parameters as a function of temperature and molecular structure are correct.

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NOTATION

<i>c</i>	number of external degrees of freedom (pure component parameter)
<i>K</i>	distribution factor ($= y/x$)
k_{ij}	binary interaction parameter
<i>m</i>	see Table 1 and eq. (1)
<i>P</i>	pressure
P_{cp}	pure component parameter ($= T^*$, v^* or c)
<i>q</i>	see Table 1 and eq. (1)
T^*	characteristic temperature (energetic pure component parameter)
v^*	characteristic volume (volumetric pure component parameter)
V_B	Bondi's volume
<i>x</i>	mole fraction of the high density phase
<i>y</i>	mole fraction of the low density phase

Greek letter

ϵ	potential energy per unit area
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