

Phase Equilibria of CO₂ + *n*-Alkane Binary Systems in Wide Ranges of Conditions: Development of Predictive Correlations Based on Cubic Mixing Rules

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S Supporting Information

ABSTRACT: The phase equilibria of binary CO₂ + *n*-alkane mixtures have been studied by an important number of authors, both experimentally and using different types of thermodynamic models. Modeling studies of the phase behavior of such highly nonideal systems have generally achieved only partially accurate results in the correlation of phase equilibrium data when considering wide ranges of temperature, pressure, and *n*-alkane molecular weight. In this study, a predictive correlation for the phase behavior of CO₂ + *n*-alkane systems, based on a three-parameter cubic equation of state (EOS), that is, the RK-PR EOS, coupled to cubic mixing rules (CMRs), is developed and tested. CMRs have been shown to be capable of an accurate correlation of the phase equilibria asymmetric CO₂ + *n*-alkane binary systems, in wide ranges of temperature and pressure, when using system-specific interaction parameters. For developing the predictive correlation a critical review of published experimental data for the series was carried out, covering a total of about 100 references. An important degree of inaccuracy or scatter is often found when comparing data sets from different laboratories, specially for the more asymmetric systems (CO₂ + a long chain *n*-alkane). Tables of references covering CO₂ + *n*-alkane systems from C1 to C36 are presented for different types of experimental data, including critical end points (CEPs), critical points, liquid–liquid–vapor (LLV) equilibrium, and isobaric (Txy), isothermal (Pxy), and isoplethic (PT) two-phase equilibrium data sets. Examples of disagreement between different sets of data are presented and discussed. In some cases, a decision concerning the identification of the set that should be regarded as the most reliable, can be based on the experimental method employed, on the purity of the *n*-alkane, and on the observation of other data for conditions, and/or systems in the series, which are close to those of the data set under scrutiny. Nevertheless, the availability of such information is not enough, in other cases, to assess the quality of a given data set, where we have either different data sets in disagreement or a unique set, for which we are in doubt about its accuracy. In such situation, a predictive correlation for the whole series of binary systems is helpful to make a decision on the possible level of reliability of a given phase equilibrium data set. The present study is useful both to make decisions on conflicts between contradictory phase equilibrium data sets and to predict the phase equilibria of binary systems that have no experimental information available in the literature.

1. INTRODUCTION

When considering phase equilibria in mixtures, one very important family of binary systems, both from the technological and academic points of view, is the CO₂ + *n*-alkane homologue series. The importance of this series, sometimes taken as a reference in the analysis of other nonalkane + CO₂ binary mixtures, is clear when considering, for example, CO₂ injection as a method for enhanced oil recovery, the recent approaches for CO₂ sequestration in depleted oil wells, and extractions and separations using supercritical CO₂ as solvent.^{1,2} Carbon dioxide has a large quadrupole moment³ while *n*-alkanes are nonpolar and may have a molecular weight much greater than that of CO₂. Therefore, most of the binary systems within the CO₂ + *n*-alkane homologue series are highly asymmetric with regard to both molecular size and energetic interactions. This makes the correlation/prediction of the phase equilibria of the series, over wide ranges of conditions, very difficult. This is a yet not fully solved relevant problem of physical chemistry. Most of the available previous attempts to describe the phase

equilibria of CO₂ + *n*-alkane systems in wide ranges of conditions were not completely successful (more details are provided elsewhere⁴).

Models of the equation of state (EOS) type⁵ are the proper choice for describing the fluid phase equilibria over a wide range of pressure. This is because EOSs explicitly account for the effect of density on the thermodynamic properties of pure fluids and mixtures. A standard approach is to couple to EOS type models, mixing rules quadratic with respect to mole fraction (QMRs).⁵ QMRs are double summations in mole fraction that make it possible to compute mixture parameters from pure-compound and interaction parameters. QMRs lack the flexibility required to describe highly asymmetric systems such as most of the CO₂ + *n*-alkane systems. In contrast, cubic

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mixing rules (CMRs)⁶ provide a much higher flexibility with respect to composition.⁴

In a recent work,⁴ CMRs, used for both the attractive and the repulsive mixture parameters, together with temperature-dependent interaction parameters, within the RK-PR EoS,⁷ made it possible to achieve the best simultaneous representation of critical lines and liquid–liquid–vapor (LLV) equilibria that, to our knowledge, has ever been reported for CO₂ + *n*-alkane systems showing phase behavior of type III,⁸ irrespective to the modeling approach used, in the open literature. Besides, a very good representation of two-phase equilibrium compositions in wide ranges of temperature and pressure was achieved⁴ for the system CO₂ + *n*-hexadecane. This system could be regarded as the one with more and better experimental data available.⁴ Such results⁴ were obtained by using interaction parameters specific of the particular binary system considered.

The present study is essentially a continuation of such work,⁴ in the process aiming to achieve a unique correlation of *n*-alkane carbon number-dependent interaction parameters, valid for describing the phase equilibria of the whole CO₂ + *n*-alkane homologue series.

Such a correlation would be useful to provisionally resolve conflicts between experimental data sets from different laboratories and also to predict the phase equilibria for CO₂ + *n*-alkane systems with no experimental data available.

As a piece of work required for achieving the stated general goal, we carried out a review on the experimental phase equilibrium data available for the series of CO₂ + *n*-alkane binary systems. Such a review was necessary to define our input for the parameter optimization problem. The review in the present work encompasses a range of binary systems wider than those in our previous work.⁴

It is important to note that, in view of the scatter frequently found when comparing different sets of data, and of the complexity of the high pressure phase behavior considered, it is often quite difficult to identify trends regarding the effect of temperature, pressure, or *n*-alkane carbon number on mutual solubilities.

This situation points to the need for a predictive model, which should be continuous, provide qualitatively correct patterns and trends, and have a good quantitative performance.

The requirements of continuity and proper qualitative behavior are achievable by choosing EOS-type thermodynamic models, specially EOSs of the van der Waals family, which are cubic with respect to molar volume, such as the RK-PR EOS.⁷ Achieving a good quantitative performance—not attainable with quadratic mixing rules (QMRs) according to accumulated experience—is the main objective of the present work and should be possible to fulfill based on cubic mixing rules (CMRs). For an updated discussion on the approaches that different authors have implemented for modeling the phase equilibria of the CO₂ + *n*-alkane series and on their results, the reader is referred to our previous work.⁴

2. EXPERIMENTAL DATA ON THE FLUID PHASE EQUILIBRIA OF CARBON DIOXIDE + *N*-ALKANE SYSTEMS

We performed a literature review that focused on the experimental fluid phase equilibria of binary carbon dioxide + *n*-alkane systems, where the *n*-alkane of the mixture is a linear chain molecule having 1 to 36 carbon atoms. Equilibria with the presence of solid phases have not been taken into account. The literature on the experimental phase behavior of the CO₂ + *n*-alkane

homologue series is vast. Although we have identified an important number of relevant contributions, it is unlikely that our final list in the present work is complete. Due to space limitations, the complete information about the performed literature review is available as Appendix A in the Supporting Information. There, the information on CO₂ + *n*-alkane fluid phase equilibria is arranged in Tables A1 to A6. A given table corresponds to a specific type of phase equilibrium information, according to the summary given in Table 1.

Table 1. Description of Tables with Information on Literature Contributions on the Experimental Fluid Phase Equilibria of CO₂ + *n*-Alkane Binary Mixtures

table ^a	type of experimental info.
A1	fluid–fluid critical end points (CEPs)
A2	data sets of critical points
A3	liquid–liquid–vapor (LLV) data sets
A4	isothermal fluid–fluid equilibrium data sets (Pxy sets)
A5	isobaric fluid–fluid equilibrium data sets (Txy sets)
A6	isoplethic fluid–fluid equilibrium data sets

^aTables A1 to A6 are available as Supporting Information.

According to Fall and Luks,⁹ binary systems formed by carbon dioxide and *n*-alkanes up to C6 exhibit a type I behavior, according to the classification proposed by Scott and van Konynenburg⁸ for the fluid phase behavior of binary mixtures (actually, it could be argued that the fluid phase behavior of these systems corresponds to type II but with the LLV region and the upper critical end point (UCEP) subject to the interference of the more stable solid–fluid equilibria). This means that a liquid = vapor (L = V) critical locus extends from the critical point of the pure *n*-alkane to the critical point of pure carbon dioxide, and there are no critical end points (CEPs). The binary systems containing CO₂ and *n*-alkanes from C7 to C12 display a type II phase behavior.⁸ In type II behavior, a critical locus extends between the critical points of the pure compounds, as in type I behavior, and another critical locus (liquid = liquid, L = L) appears, which finishes in an upper critical end point (UCEP). A liquid–liquid–vapor (LLV) locus goes from that UCEP to lower temperatures. The system formed by CO₂ and *n*-tridecane constitutes a “transition” from type II to type III⁸ phase behavior in this homologue series, and it presents a type IV behavior. In type IV phase behavior, the UCEP, which signals the end of the L = L critical locus, is also present, as in type II behavior. However, the critical line that stems from the critical point of the heavy compound (i.e., the *n*-alkane) ends at a lower critical end point (LCEP), and another critical locus extends from the critical point of pure CO₂ to a second UCEP (these last two types of critical lines were denoted E and D respectively, by Cismondi and Michelsen¹⁰). A LLV locus connects the last two CEPs. Finally, as already pointed out, for example, by Fall and Luks,⁹ binary mixtures made of CO₂ and *n*-alkanes, with CN (carbon number of the *n*-alkane) ≥ 14, show a type III phase behavior. In this type of behavior, a critical locus connects the critical point of pure CO₂ with an UCEP, while there exists another critical locus that originates at the critical point of the pure *n*-alkane and extends indefinitely to high pressures. This latter critical locus (denoted C by Cismondi and Michelsen¹⁰) may show local extrema in the pressure versus temperature plane. As the difference between the critical temperatures of pure carbon dioxide and the pure *n*-alkane increases, the asymmetry of the mixture rises up, and we observe

an evolution in the fluid phase behavior for this homologue series. This kind of evolution has also been observed for other homologue series.⁵

The length of Table A4 (in Supporting Information) clearly shows that isothermal two-phase equilibrium is the type of experimental data most frequently gathered and reported for the CO₂ + *n*-alkane series. Often, specially for the heavier *n*-alkanes, some important degree of scatter is observed when graphically comparing data sets at the same temperature from different literature sources. Moreover, even serious disagreements can be found, as illustrated in Figure 1 for CO₂ + *n*-hexadecane at 313.2 K.

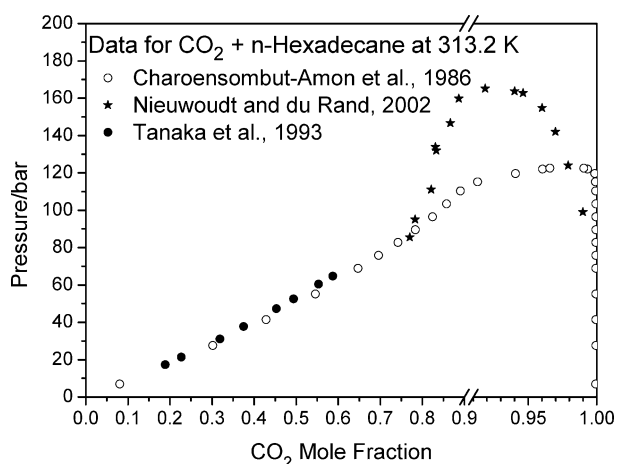


Figure 1. Experimental two-phase equilibrium data at 313.2 K for the CO₂ + *n*-hexadecane (C16) system. Markers: experimental data from a number of literature reports. This is an extreme example of disagreement between different sets of experimental data available in the literature. In this case, and considering other published data, such as some critical points, it seems that the data from Charoensombut-Amon et al. in the higher pressure range are wrong. Predictions for the same system and conditions are available in Figure 15A.

In this case, consideration of the critical line allows us to conclude that the data by Charoensombut-Amon et al.¹¹ at high pressures appear to be wrong. They suggest a false complete miscibility region, in a pressure range of about 50 bar, for mixtures that are actually globally unstable and separate into two phases. We observe that, even though the homologue series CO₂ + *n*-alkane has been widely studied, there is still some lack of important experimental information (see Table A3 in the Supporting Information).

3. MODELING APPROACH AND PARAMETERIZATION METHODOLOGY

Since this work is essentially a continuation of a previous one by Cismonti et al.,⁴ the reader is referred to that work for a more detailed background on the approach followed to describe the fluid phase equilibria of CO₂ + *n*-alkane binary systems. That previous work⁴ dealt with the procedure and results for the automated numerical optimization of the “binary system-specific” interaction parameters of CMRs + RK-PR EOS. The aim of such optimization⁴ was to accurately reproduce the fluid phase behavior for all the CO₂ + *n*-alkane binary mixtures experimentally showing type III phase behavior, that is, those with *n*-alkane carbon numbers in the range from 14 to 22. The fundamental differences here with respect to that work⁴ are two. First, now we consider not only type III phase behavior but all types of fluid phase behavior that take place in the CO₂ + *n*-alkane series, that is,

types I, II, IV, and III. Second, in addition to the individual optimization of a given system, we will consider a new and more ambitious objective function (OF). We have designed this OF to represent not the phase behavior of a specific CO₂ + *n*-alkane binary system but rather the behavior of the complete series of CO₂ + *n*-alkane binary mixtures—or an important part of it—as a whole. The reasons for considering a series-specific objective function are exposed in the following paragraphs.

Although the behavior of CO₂ + *n*-alkane binary mixtures for the lighter *n*-alkanes (type I) can generally be properly described with quadratic mixing rules (using k_{ij} and l_{ij} interaction parameters), it would, of course, be important also to consider such type I systems together with the “more difficult” asymmetric systems in the proposition and development of a more complex comprehensive approach for the series. In other words, in this work we describe all CO₂ + *n*-alkane binary mixtures using CMRs regardless the molecular weight of the *n*-alkane. On one hand, it is important that the mathematical formalism be unique for all binary systems in the series. Such unique mathematical formalism would be a requirement for dealing with multicomponent mixtures⁶ (not considered in this work). On the other hand, since QMRs are a particular case of CMRs, available two-index interaction parameters for QMRs can be easily converted into equivalent three-index interaction parameters for CMRs. This conversion can be done by applying the relationships available in ref 6.

CMRs⁴ provide eight binary interaction parameters if the repulsive ones are kept constant and the attractive ones are allowed to depend on temperature. Although CMRs provide us with great flexibility to model the phase behavior of complex systems through equations of state, we learned from our experience that it can be dangerous to free the eight CMRs interaction parameters while fitting them for a given binary system, if we do not have enough experimental information.

This can be due to the unbalanced uncertainty in the limited number of experimental data used in the objective function, and also in aiming to reproduce simultaneously two different types of phase behavior data, by using in the objective function experimental data from both the critical and classical regions.

In other words, even if we had hypothetically perfect experimental information, without error, the incompleteness or the unbalance in the set of data points used in the objective function could lead to an improper use of the CMRs flexibility, that is, to a poor prediction of regions not represented in the objective function while forcing a good reproduction of the covered ones. Our hypothesis is that, even without a crossover approach implemented, the CMRs’ flexibility can lead to a good description of both the classical and the critical regions simultaneously, provided that a careful and complete balance of data points is achieved within the objective function. When this condition is met, a proper trade-off takes place between the need for a good description of the phase equilibria in the classical region and that in the critical region, in parallel to a statistic neutralization of the uncertainty present in the data points. The latter assumes that inclusion of points with large systematic experimental errors has been prevented, and this is why a careful selection of data for the objective function is crucial. This hypothesis has been indeed confirmed in our previous work, at least for the case of CO₂ + *n*-hexadecane.⁴

However, the proper trade-off referred above is not easy to achieve, and we are limited by the availability of experimental phase equilibrium data for each particular binary CO₂ + *n*-alkane system. One alternative that we followed in some cases before,⁴

applicable to a binary system in the homologue series with some unavailable key experimental information, is to artificially generate pseudo-data points through interpolation between data for other homologue binary systems. Examples of key experimental information are some LLV equilibrium points or some critical end points. The generation of pseudo-data points is not straightforward and introduces extra sources of error in the parameter optimization process. Therefore, it may be regarded as questionable.

For all these reasons, the new alternative that we propose is to pursue the definition of a balanced objective function not for each system individually, but for the CO₂ + *n*-alkane series as a whole, and to adjust parameters that set the dependence of CMRs interaction parameters on the carbon number of the *n*-alkane rather than interaction parameters for individual binary systems. Such an approach has the added potential benefit of achieving predictive capability for those binary systems in the CO₂ + *n*-alkane series with limited or no experimental information available. This is partially the reason for our use of the words “predictive correlations” in the title of the present work. The proposed approach rests on the assumption of continuity for the phase behavior of different binary CO₂ + *n*-alkane systems along the series.

Attempts to correlate the phase equilibria of a homologue series rather than those of individual binary systems are not frequently found in the literature. An exception is some group contribution approaches, which have results of limited applicability in terms of temperature, pressure, and chain length ranges. An important and original work, in our opinion, was the one by Polishuk et al.,³ which was based on carefully designed functionalities for the l_{ij} and temperature-dependent k_{ij} parameters in terms of pure compound covolumes and critical temperatures. In that work,³ the authors managed to obtain a quite good representation of the general behavior for the series CO₂ + *n*-alkanes. This was done³ by matching only three experimental key-points, aimed to provide the appropriate balance between liquid–liquid equilibrium (LLE) and liquid–vapor equilibrium (LVE) behavior. The limitations in those results were mainly in the quantitative description of liquid phases either at LVE or, specially, at liquid–liquid–vapor equilibrium (LLVE) in the lower temperature range and in the quantitative description of the liquid–liquid critical lines toward high pressures. In the present work, given the higher flexibility of CMRs and the corresponding goal of achieving a better quantitative performance, it was necessary to consider different types of experimental data and to choose a proper objective function, as it is discussed in section 3.2

3.1. Equation of State, Mixing Rules, and Pure Compound Parameters. As in our previous work,⁴ we use here the RK-PR EOS⁷ and cubic mixing rules (CMRs).⁶ CMRs are the following:

$$a = \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N x_i x_j x_k a_{ijk} \quad (1)$$

$$a_{ijk} = (a_i a_j a_k)^{1/3} (1 - k_{ijk}) \quad (2)$$

$$b = \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N x_i x_j x_k b_{ijk} \quad (3)$$

$$b_{ijk} = \left(\frac{b_i + b_j + b_k}{3} \right) (1 - l_{ijk}) \quad (4)$$

where N is the number of components in a multicomponent mixture, a_i , b_i , and x_i are, for component i , the attractive energy parameter, the repulsive covolume parameter, and the mole fraction in the system, respectively, k_{ijk} and l_{ijk} are respectively the attractive energy interaction parameter and the covolume interaction parameter. For a binary system of components 1 and 2, the cubic mixing rules provide four independent interaction parameters: k_{112} , k_{122} , l_{112} , and l_{122} .

It is generally accepted that the properties of a dense, highly nonideal binary mixture made of two given types of molecules (e.g. molecules A and B) depend strongly on the relative amounts of components A and B, specially when comparing the extreme situations where component A is infinitely diluted in component B and, at the opposite end, where component B is infinitely diluted in component A. It can be shown for CMRs⁶ that the partial molar properties for component 1, when component 1 is infinitely diluted in component 2, depend on k_{122} and l_{122} but not on k_{112} and l_{112} . Analogously, the partial molar properties for component 2, when component 2 is infinitely diluted in component 1, depend on k_{112} and l_{112} but not on k_{122} and l_{122} .⁶ Thus, CMRs provide the means for controlling independently the properties of the fluid binary mixture at the two infinite dilution limits. This is needed, for instance, for a proper description of liquid–liquid equilibria of highly asymmetric mixtures. Notice that at any temperature and composition the mixture parameters a and b must be positive.

The attractive energy interaction parameters are made temperature-dependent as follows:⁴

$$k_{ijk} = k_{ijk}^{\infty} + k'_{ijk} e^{-T/T_{ijk}^*} \quad (5)$$

From eq 5, k_{ijk} is a monotonically decreasing or increasing function of temperature T , depending on the sign of k'_{ijk} . Parameter k_{ijk} asymptotically tends to k_{ijk}^{∞} as temperature T tends to infinity. At $T = 0$, parameter k_{ijk} has a finite value equal to $k_{ijk}^0 = (k_{ijk}^{\infty} + k'_{ijk})$. The rate at which the transition from k_{ijk}^0 to k_{ijk}^{∞} takes place is controlled by parameter T_{ijk}^* . The total number of available independent CMRs binary interaction parameters is eight: l_{112} , k_{112}^{∞} , k'_{112} , T_{112}^* , l_{122} , k_{122}^{∞} , k'_{122} , and T_{122}^* . Polishuk has used CMRs but in a form that cannot be extended to multicomponent mixtures.¹²

Regarding the pure compound parameters of the RK-PR EOS,⁷ we have made a choice different than in previous works. Based on previous observations, and with the goal of improving the prediction of densities, we decided to match the saturated liquid density of carbon dioxide at 270 K. Also, in order to get a more regular evolution of the pure *n*-alkane parameters than that obtained in our previous work,⁴ which was influenced by triple point temperatures, now the experimental saturated liquid volume is reproduced at a reduced temperature of 0.7 for all the *n*-alkanes. The resulting pure compound parameters used in this work are given in Table B1 in the Supporting Information. Notice that Table B1 also provides short acronyms for the compounds, for example, C5 for *n*-pentane.

The three-parameter RK-PR EoS⁷ is the following:

$$P = \frac{RT}{v - b} - \frac{a}{(v + \delta_1 b) \left(v + \frac{1 - \delta_1}{1 + \delta_1} b \right)} \quad (6)$$

where

$$a_i(T) = a_{c,i} \left(\frac{3}{2 + T/T_{c,i}} \right)^{k_i} \quad (7)$$

P is the absolute pressure, v the molar volume, R the universal gas constant, $a_{c,i}$ the critical attractive energy parameter for pure compound i , $T_{c,i}$ the critical temperature of pure compound i , and k_i a pure compound parameter that influences the temperature dependence of the attractive energy parameter. A linear mixing rule is set for the third parameter δ_1 . See Table B1 in the Supporting Information.

3.2. Objective Function and Experimental Data Selected. With respect to the objective function, the differences and particularities that naturally arise when aiming at the optimization of CN-dependent interaction parameters of the CO₂ + n -alkane series, instead of aiming at the optimization of “binary system-specific” interaction parameters, are the following:

- (1) It is not necessary to consider experimental phase equilibrium points for all the binary systems of the homologue series, neither it is to include binary pseudoexperimental points, obtained by interpolation between experimental points of the same nature for other binary systems. Therefore, we will consider only selected experimental points.
- (2) If we set an n -degree polynomial dependence with respect to the carbon number (CN) of the n -alkane, for each CMRs interaction parameter, then, the number of free parameters in the optimization will equal $(n + 1)$ times the number of CMRs available independent interaction parameters; that is, it will equal $[8(n + 1)]$. Notice that, when considering the whole CO₂ + n -alkane series, it is reasonable to allow the T^* parameters of eq 5 to depend on CN (instead of keeping them constant, as we did for CN from 14 to 22 in our previous work⁴). The number of polynomial functions whose parameters are to be adjusted is eight.
- (3) When selecting the phase equilibrium experimental data, we need to achieve a balance in different aspects simultaneously: between different types of data points [liquid–vapor equilibrium (LVE), liquid–liquid equilibrium (LLE), critical points, etc.], covering the range of CN from the lightest to the heavier n -alkanes, and covering also wide ranges of temperature and pressure.

We tried different polynomial dependences with respect to CN for the interaction parameters. A quartic form, for example, can be set as follows:

$$p = a_p + b_p \text{CN} + c_p \text{CN}^2 + d_p \text{CN}^3 + e_p \text{CN}^4 \quad (8)$$

where

$$p = l_{112}, l_{122}, k'_{112}, k'_{122}, k_{112}^\infty, k_{122}^\infty, T_{112}^*, \text{ or } T_{122}^* \quad (9)$$

where parameters a_p , b_p , c_p , d_p , and e_p are characteristic of the CO₂ + n -alkane homologue series, or at least of an important part of it.

See the next section for the final polynomial expression and constants for the eight parameters. The objective function used in this work is the following:

$$\text{OF} = \sum_{i=1}^{\text{NTP}} \frac{(\text{KP}_i^{\text{calc}} - \text{KP}_i^{\text{expt}})^2}{\text{KP}_i^{\text{expt}}} + \sum_{j=1}^{\text{Nz}} \left[\left| \ln \left(\frac{z_{j,1}^{\text{calc}}}{z_{j,1}^{\text{expt}}} \right) \right| + \left| \ln \left(\frac{z_{j,2}^{\text{calc}}}{z_{j,2}^{\text{expt}}} \right) \right| \right] \quad (10)$$

where KP_i is either the temperature coordinate or the pressure coordinate of a binary phase equilibrium key point. The

superscript “expt” means “experimental value” while the superscript “calc” means “calculated value”. KP_i can be, for type III CO₂ + n -alkane systems, the following (see Figure 2 of ref 4 and Table 3 of the present work): the pressure coordinate of the local minimum of the binary critical curve (CP_m), the minimum temperature in the liquid–liquid like part of the critical line (T_m), the critical temperature at the maximum critical pressure experimentally available (CT_{994}), or the critical pressure at the maximum critical temperature experimentally available ($\text{CP}_{393.3}$). KP_i can also be a critical pressure (P_c , see Table 2) of a binary system, the temperature of a critical end

Table 2. Experimental Liquid–Vapor Critical Pressures (P_c) and Critical Compositions [z_c (CO₂)] at Given Temperatures for Some CO₂ + n -Alkane Systems^a

system	temp. (K)	P_c (bar)	z_c (CO ₂)	ref
CO ₂ + methane	219.3	64.68	0.252	Mraw et al., 1978 ³⁰
	270.0	85.11	0.6468	Al-Sahhaf et al., 1983 ³¹
CO ₂ + ethane	296.82	53.52	0.2403	Horstmann et al., 2000 ³²
CO ₂ + propane	327.0	65.2	0.60	Smejkal et al., 2002 ³³
CO ₂ + n -butane	344.3	81.2	0.72	Hsu et al., 1985 ³⁴
CO ₂ + n -hexane	387.0	117.2	0.78	Liu et al., 2003 ³⁵
CO ₂ + n -octane	359.5	130.1	0.878	Choi and Yeo, 1998 ³⁶
CO ₂ + n -decane	444.26	188.36	0.843	Reamer and Sage, 1963 ³⁷
	577.04	78.6	0.40	
CO ₂ + n -tridecane	377.4	198.0	0.925	Enick et al., 1985 ³⁸

^aData selected as input for the objective function.

point or of a K point (Table 4), the saturation pressure at given temperature and composition (Table B3, Supporting Information), or the azeotropic pressure (only for the case of CO₂ + ethane). $z_{j,1}$ and $z_{j,2}$ are respectively the mole fractions of CO₂ (1) and of the n -alkane (2). These mole fractions can be the following: the critical composition (Table 2), the composition of a liquid phase under conditions of LLV equilibrium (Table 5), the composition of a phase under two-phase equilibrium conditions at given temperature and pressure (Table B2, Supporting Information), or the azeotropic composition (only for the case of CO₂ + ethane). NTP is the number of experimental pressure and temperature values used in the objective function. Analogously, Nz is the number of experimental mole fraction vectors used in the objective function.

The phase equilibrium points considered in the objective function can be classified in four main groups: critical points, critical end point temperatures, liquid–liquid–vapor equilibrium (LLVE), and two-phase equilibrium.

Critical Points. For some CO₂ + n -alkane systems with phase behavior of types I, II, and IV, we compute the pressure (P_c) and composition (z_c) of the liquid–vapor critical point at a selected temperature (Table 2), while for type III systems the same four characteristic critical coordinates previously defined⁴ (CT_{994} , T_m , CP_m , and $\text{CP}_{393.3}$) were considered (Table 3). Note in Table 2 that two critical points were considered only for the systems with methane and n -decane.

Critical End Point Temperatures. The upper critical end points (UCEPs) for the systems CO₂ + C8 and CO₂ + C10 (type II) were considered, as well as the three characteristic CEPs for the transition system CO₂ + C13 (type IV). The experimental CEP temperature values and references are given

Table 3. Characteristic Experimental Critical Coordinates for Some Type III CO₂ + *n*-Alkane Systems, Selected for the Objective Function^a

CN ^b	CT ₉₉₄ ^c (K)	T _m ^d (K)	CP _m ^e (bar)	CP _{393.3} ^f (bar)	ref
14	294.40	283.1	78	226.6	Scheidgen ³⁹
16	305.45	297.6	166	256	Scheidgen Spee and Schneider, 1991 ⁴⁰
19	321.51	317.2	269	304	Scheidgen ³⁹
22	335.97	334.2	350	357	Scheidgen ³⁹

^aThe pressures informed in the references range from 991 to 997.8 bar. The temperatures informed in the references range from 393.14 to 393.59 K ^bCN: carbon number of the *n*-alkane. ^cCT₉₉₄: critical temperature at 994 bar. ^dT_m: minimum temperature in the liquid–liquid like part of the critical line. ^eCP_m: pressure coordinate of the local minimum of the binary critical curve. ^fCT_{393.3}: critical pressure at 393.3 K.

in Table 4. K points (which are liquid–vapor UCEPs) in CO₂ + *n*-alkane systems with phase behavior of type III were

Table 4. Experimental Fluid–Fluid Critical End Point Temperatures for Some CO₂ + *n*-Alkane Systems, Considered in the Objective Function

CN	type	UCEP temp. (K)	LCEP temp. (K)	K point temp. (K)	ref
8	II	231.5			Hottovy et al., 1982 ⁴¹
10	II	248.7			Kulkarni et al., 1974 ⁴²
13	IV	279.0	310.8	314.0	Hottovy et al., 1981, ⁴³ and Fall and Luks, 1985 ⁹

not included, since their temperatures are much less sensitive to the interaction parameters, and experimentally less changing along the series, than for example the LL-UCEPs (see Figure 3).

Liquid–Liquid–Vapor Equilibrium (LLVE). The compositions of the liquid phases under conditions of LLVE, at a selected relatively low temperature, that is, away from the CEP, have been included for certain systems from CO₂ + C8 to CO₂ + C20 (Table 5).

Table 5. Experimental Liquid–Liquid–Vapor (LLV) Equilibrium Key-Points for Some CO₂ + *n*-Alkane Binary Mixtures Considered in the Objective Function

CN	T _{lowLLV} (K)	x _{lowLLV} ^a	y _{lowLLV} ^a	ref
8	216	0.444	0.978	Hottovy et al., 1982 ⁴¹
10	238.15	0.602	0.970	Kulkarni et al., 1974 ⁴²
13	258.0	0.650	0.9815	Hottovy et al., 1981 ⁴³
14	270.0	0.707	0.9815	Hottovy et al., 1981 ⁴³
16	283.2	0.716	0.9868	van der Steen et al., 1989 ⁴⁴
19	292.9	0.704	0.9958	Fall et al., 1985 ⁴⁵ (smoothed data)
20	300.4	0.704	0.998	Huie et al., 1973 ²⁶

^ax_{lowLLV} and y_{lowLLV}: compositions (CO₂ mole fraction) of the two liquid phases, under LLV conditions, at a selected low temperature T_{lowLLV}.

Two-Phase Equilibrium. Two different types of departures are computed in the objective function of eq 10 regarding two-phase equilibrium behavior: mainly composition departures for both phases at specified *T* and *P* (Table B2, Supporting

Information), but also bubble pressure departures at specified composition *x*₁ and *T* (Table B3, Supporting Information). Notice that the phase composition values in Table B2 (Supporting Information) indicate that methane (CN = 1) is lighter than CO₂ and that the system CO₂ + ethane (CN = 2) is azeotropic.

In addition, we included the azeotropic pressures and compositions for the system with ethane at 243.15 and 283.15 K, as reported by Fredenslund and Mollerup.¹³

In most cases, we selected the data either because there was good agreement between data sets from different laboratories, or because the data showed regular and smooth trends with respect to the *n*-alkane carbon number. This is, for example, the case of critical lines in type III CO₂ + *n*-alkane systems.

3.3. Optimization Strategy. As is usual in optimization processes, the problem of getting initial values for the parameters to optimize is important, and this is true especially in this case as a result of the high quantitative and qualitative sensitivity of the systems phase behavior to the parameters. Based on the arguments expressed in section 3, this is the new strategy we follow in the present work:

- Optimize the eight interaction parameters for each binary CO₂ + *n*-alkane system for which we have available relatively enough reliable information: we have considered here the binaries with C10, C13, C16, and C20. For each of these first individual optimizations (determination of 8 parameters per binary system), we used all the corresponding data in Tables 2–5 and Tables B2 and B3 in the Supporting Information, plus:
 - Artificial CT₉₉₄ values for C10 (269.2 K) and C13 (288.1 K), extrapolated from data in Table 3 (this work) or Table 2 in ref 4.
 - K point temperature and heavy phase composition values for C16 and C20 (Table 3 in ref 4), and also K point CO₂ molar fraction for C13 = 0.885 (taken from ref 9).
 - Artificial (CT₉₉₄, T_m, CP_m, CP_{393.3}) values for C20 (Table 2 in ref 4).
- Considering the values obtained for the eight interaction parameters for the first four systems (CO₂ + *n*-alkane systems with C10, C13, C16, and C20), identify the four interaction parameters whose values show the most regular behavior versus CN and perform a quadratic regression for each one.
- Optimize the CO₂ + *n*-alkane systems for which we have some important, but incomplete, experimental phase equilibrium information. In these cases, only four parameters will be free during the optimization process, while the other four (those identified in the previous point) will be fixed at predicted values from the quadratic regressions of the previous step. We considered at this stage the CO₂ + *n*-alkane binary systems with C3, C4, C6, C8, C14, C22, and C28 and also reconsidered the systems from point 1.
- From the values obtained for each interaction parameter in the previous step, make a parameter regression corresponding to a polynomial form of third order, for each interaction parameter as a function of CN.
- Taking the regression constants from steps 2 and 4 as the initial guess, optimize the third order polynomial

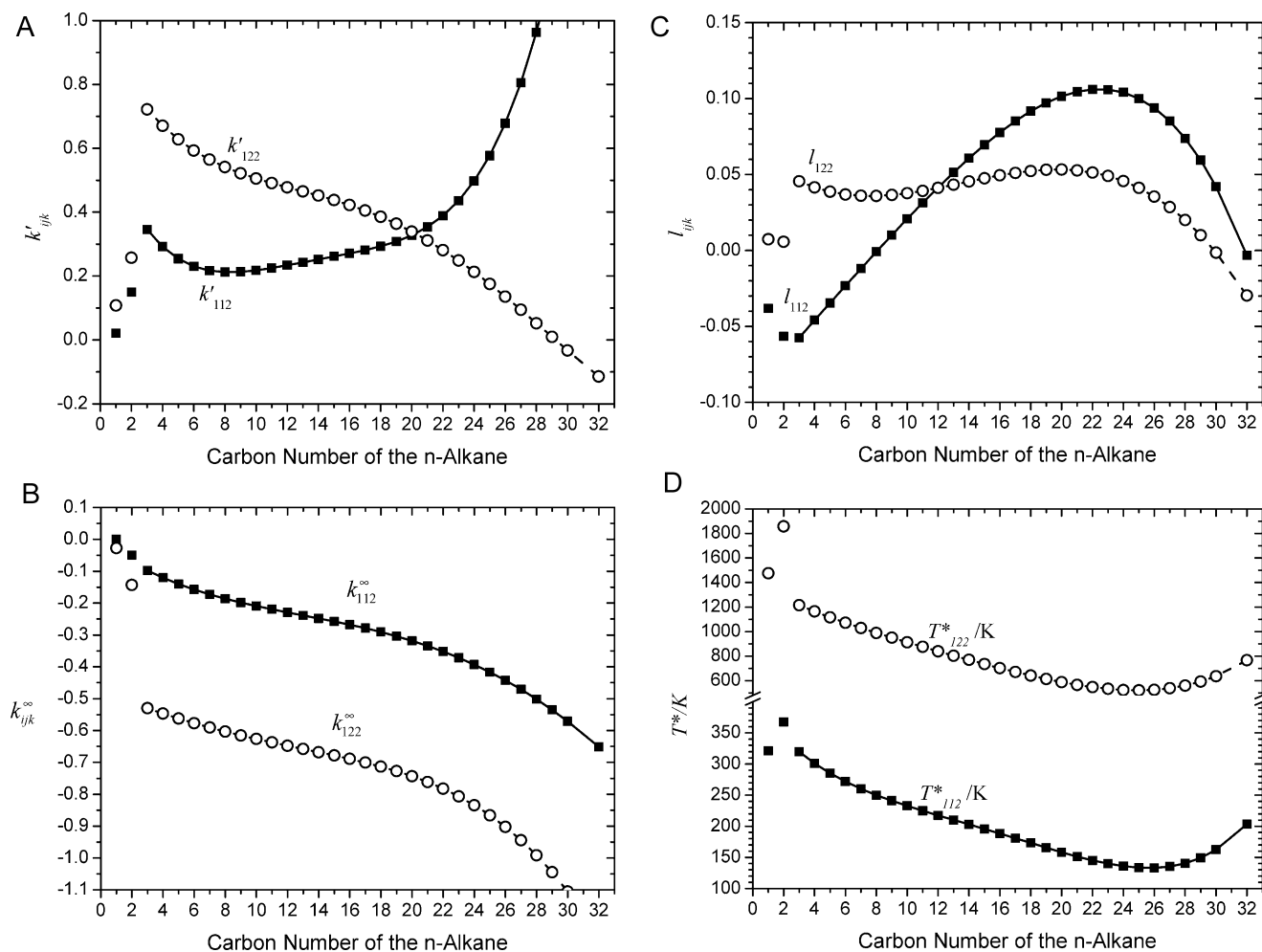


Figure 2. Evolution of the CMRs interaction parameters as functions of the *n*-alkane carbon number (CN) for the CO₂(1) + *n*-alkane (2) homologue series. From CN = 3 to CN = 32 this evolution is given by the correlation, proposed for the homologue series, represented by eq 11 used with the parameter values of Table 6. The individually obtained interaction parameters for CO₂ + C1 and CO₂ + C2 (Table B4, Supporting Information) are also included in this figure. Model: RK-PR EOS with CMRs.

constants for the eight CMRs interaction parameters (and eventually fourth order if necessary), considering all the experimental data in Tables 2–5 and Tables B2 and B3 in the Supporting Information, and no other, so that artificial data do not influence the final parameters characteristic of the CO₂ + *n*-alkane homologue series.

We stress that in eq 10 we have used KP only for key-point temperature or pressure coordinates and *z* for key-point compositional coordinates. In comparison to the terms we used before⁴ for defining the objective function, now the KP terms for temperature or pressure values are more weighted (note that these terms are not dimensionless anymore and that the values should be in K and bar, respectively). Also, in the key-point composition terms [*j*-summation in eq 10], the $z_{jl}^{\text{calc}}/z_{jl}^{\text{expt}}$ ratios different from unity are now penalized rather than the differences ($z_{jl}^{\text{calc}} - z_{jl}^{\text{expt}}$). This will assign enough importance to the experimental points in diluted regions, for example, to mixtures of compound 1 diluted in 2, whose equilibria are governed, when using CMRs, by the binary parameters with indices 1, 2, and 2, that is, l_{122} , k_{122}^{∞} , k'_{122} and T_{122}^* .

For minimizing our objective functions with different numbers of systems and points, we used the FORTRAN

function Praxis, for unconstrained optimization. Praxis is based on the principal axis method by Richard Brent.^{14,15}

We have evaluated (a) the results of a unique correlation for the whole series, that is, for the binary systems from CO₂ + C1 to CO₂ + C32 considered all together, and (b) the results of complementary runs carried out after removing from the objective function the terms corresponding to one or more specific binary systems. Such results showed that the partial objective functions for some binary systems could be further decreased but at the expense of increasing the partial objective function of other systems. By partial objective function, we mean the contribution by a specific binary CO₂ + *n*-alkane system to the objective function of the CO₂ + *n*-alkane homologue series. The removal of one or two of the heavier alkane CO₂ + *n*-alkane systems did not lead to a significant improvement for the rest of the series, but the result was different after eliminating the binary systems with the lightest *n*-alkanes, that is, the systems CO₂ + C1 and CO₂ + C2. Therefore, we finally decided to generate a correlation valid from C3 on, and to adjust the first two systems (CO₂ + C1 and CO₂ + C2) individually.

Although the correlation could be expressed exactly in the form of eq 8, we present the polynomial functions, and corresponding values for the coefficients, based on the independent variable

Table 6. Correlation Constants for the CMRs Interaction Parameters of the CO₂(1) + *n*-Alkane (2) Homologue Series for *n*-Alkane Carbon Numbers from 3 to 32 (eq 11)^a

interaction param.	param.					
		a_p	$10b_p$	$100c_p$	$1000d_p$	$10000e_p$
k'_{112}		0.24280	0.09265	0.00300	-0.04749	0.14508
k'_{122}		0.46507	-0.12826	-0.01555	-0.10831	0.03556
k^{∞}_{112}		-0.23865	-0.09383	-0.00099	-0.04289	0.00487
k^{∞}_{122}		-0.65776	-0.10049	0.00026	-0.03794	-0.01094
l_{112}		0.05138	0.09621	-0.02287	-0.01446	-0.00428
l_{122}		0.04326	0.02134	0.00336	-0.01963	0.00069
$T^*_{112}/1000$ (K)		0.21033	-0.07266	0.00047	-0.01727	0.01903
$T^*_{122}/1000$ (K)		0.80392	-0.35007	0.03694	0.00913	0.03312

^aModel: RKPR-EOS.

(CN-13) in accordance with the actual optimization procedure we followed:

$$p = a_p + b_p(\text{CN}-13) + c_p(\text{CN}-13)^2 + d_p(\text{CN}-13)^3 + e_p(\text{CN}-13)^4 \quad (11)$$

where $p = l_{112}, l_{122}, k'_{112}, k'_{122}, k^{\infty}_{112}, k^{\infty}_{122}, T^*_{112}, T^*_{122}$. Note that for a given interaction parameter p the constant a_p is the parameter value for the binary system CO₂ + *n*-tridecane. The interaction parameters obtained from these correlations are shown in Figure 2 as functions of CN. Figure 2 also shows the interaction parameters for the systems CO₂ + methane and CO₂ + ethane, which were optimized individually. The numerical values for the coefficients in eq 11 are given in Table 6 for each type of interaction parameter.

4. RESULTS AND DISCUSSION

In the following sections we analyze the performance of the obtained correlation of parameters, both for representing the phase behavior of CO₂ + *n*-alkane systems considered in the optimization and for predicting the phase behavior for those CO₂ + *n*-alkane systems not included in the objective function. The prediction of densities for different types of equilibrium and systems is also analyzed. For most of the figures prepared, we selected systems and conditions for which experimental data sets from different laboratories were available and could be compared. The results for a few CO₂ + *n*-alkane systems adjusted individually, including the CO₂ + methane and CO₂ + ethane cases, will also be presented and discussed as an alternative when the correlation predictions are not accurate enough.

4.1. Evolution of Phase Behavior Along the CO₂ + *n*-Alkane Homologue Series, as Predicted from the Correlation. The type of phase behavior predicted for CO₂ + *n*-tridecane is, naturally, quite sensitive to interaction parameters, whatever equation of state and mixing rules used, and frequently, either type II or type III is predicted for this system (see refs 16 and 17). During our optimization process, we found that something similar applies to the CO₂ + methane system, since, surprisingly, the phase behavior for this system (sometimes assumed as a typical case of type I) is not far from being of type III. Nevertheless, the correlation summarized in eq 11 and Table 6 [complemented with parameters for the first two (CO₂ + C1 and CO₂ + C2) systems in Table B4 in the Supporting Information] correctly predicts the type of fluid phase behavior for all the binary systems in the CO₂ + *n*-alkane series, that is, type II up to C12, type IV for C13, and type III from C14 on. This can be seen in Figure 3 which shows the evolution of the CO₂ + *n*-alkane phase behavior with the

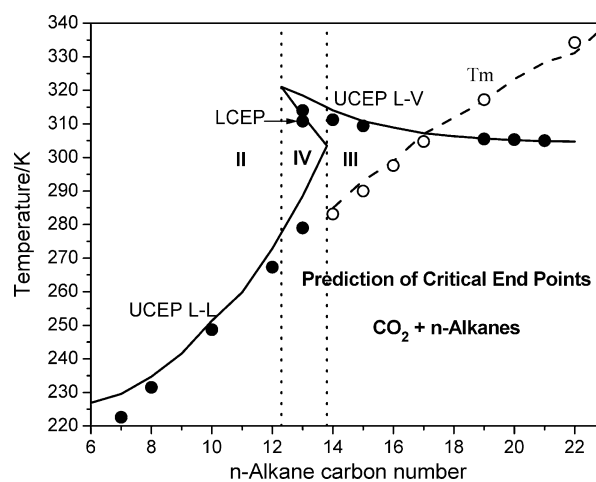


Figure 3. Experimental critical end points (CEPs, Table A1 in the Supporting Information, full circles) and CEPs predicted from the parameters correlation in eq 11 and Table 6 (solid line) for the CO₂ + *n*-alkane homologue series. The boundaries (vertical dotted lines) between types II–IV and IV–III are approximately sketched in the figure, only for illustrative purposes. Predicted T_m values are also shown (dashed line) and compared to experimental values (empty circles, Table 2 of ref 4). Model: RK-PR EOS with CMRs.

n-alkane CN, through calculated and experimental critical end point temperatures. Figure 3 also shows the experimental and predicted T_m values for type III systems, while Figures 4 and 5 present the evolution of liquid–vapor critical lines, both in the P – T and x – T spaces, for CO₂ + *n*-alkane systems containing from C1 to C5 and from C6 to C10, respectively. We remark that, within the CN range of Figures 4 and 5, only critical points for CO₂ + C1 and CO₂ + C2 (optimized individually) and for CO₂ + C3, CO₂ + C4, CO₂ + C6, CO₂ + C8, and CO₂ + C10 (part of the series optimization) were considered in the objective function (Table 2) through a single system-point by default and through two critical points for CO₂ + C1 and two critical points for CO₂ + C10 (Table 2). Still, the evolution of the calculated critical lines appears to be correct for all the systems from C1 to C10 when compared to experimental data. Moreover, although not shown in the figures, our parameters predict a virtual UCEP for CO₂ + C1 at 178.3 K, which is in agreement with the deep study on this system published by Rainwater.¹⁸ Such UCEP is virtual because of the interference of solid–fluid transitions; that is, the UCEP is metastable. Rainwater¹⁸ points out that “If the UCEP locus in Figure 3 of Miller and Luks¹⁹ is extrapolated to a carbon number of one, a temperature of about 180 K is obtained”, and using a

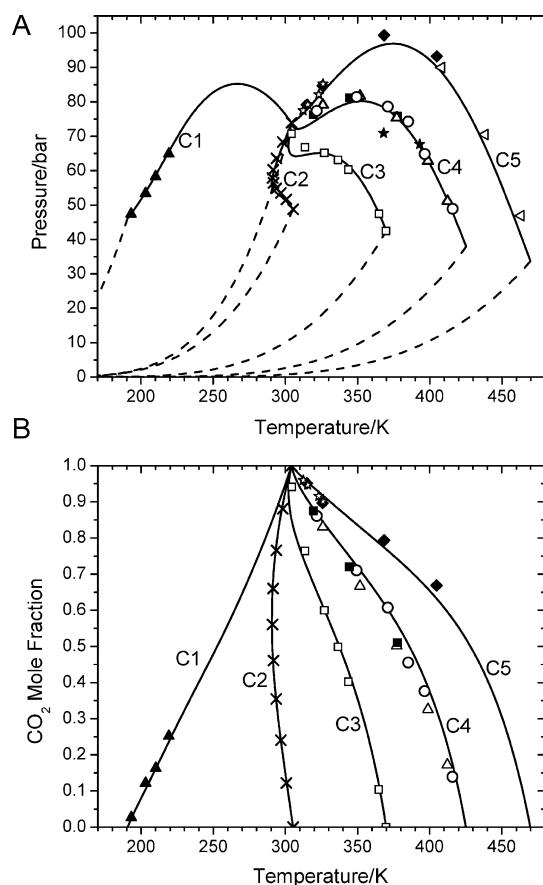


Figure 4. Calculated critical lines for $\text{CO}_2 + n$ -alkane binary systems from $\text{CO}_2 + \text{methane}$ to $\text{CO}_2 + n$ -pentane. From $\text{CN} = 3$ to $\text{CN} = 5$, the calculations were performed using the parameters correlation in eq 11 and Table 6. For $\text{CN} = 1$ and $\text{CN} = 2$, the interaction parameters were taken from Table B4 (Supporting Information). The dashed lines are calculated pure compound saturation curves. Markers: experimental critical points taken from references in Table A2 (Supporting Information). Model: RK-PR EOS with CMRs. Table B1 (Supporting Information) defines the labels of the n -alkanes.

nonclassical model, Rainwater¹⁸ predicts a UCEP temperature of 181.9 K. This value is in good agreement with our value (i.e., 178.3 K) in spite of the fact that, opposite to Rainwater's model,¹⁸ the present model does not explicitly account for nonclassical effects.

The evolution is also correct for the calculated critical lines shown in Figure 6 for carbon numbers from 13 to 22, considering the behavior of both the liquid–vapor and liquid–liquid parts of such critical lines, including the higher pressure region (the maximum pressure in Figure 6 is 1000 bar). Note that no ad hoc weight factors have been used in this work in the objective function that eq 10 defines. Besides, only four experimental high-pressure critical points were considered for each one of four selected type III systems (see Table 3).

The compositions of the phases in liquid–liquid–vapor equilibrium are presented in Figure 7 for the $\text{CO}_2 + n$ -alkane systems. The experimental data (markers) correspond only to the liquid phases at LLVE. The predictions from eq 11 and Table 6 achieve a significantly better quantitative agreement with experimental data than that found in previous studies based on quadratic mixing rules, particularly for the alkane-rich phases (see refs 3 and 20). Note also the smooth and qualitatively correct evolution predicted when going from one

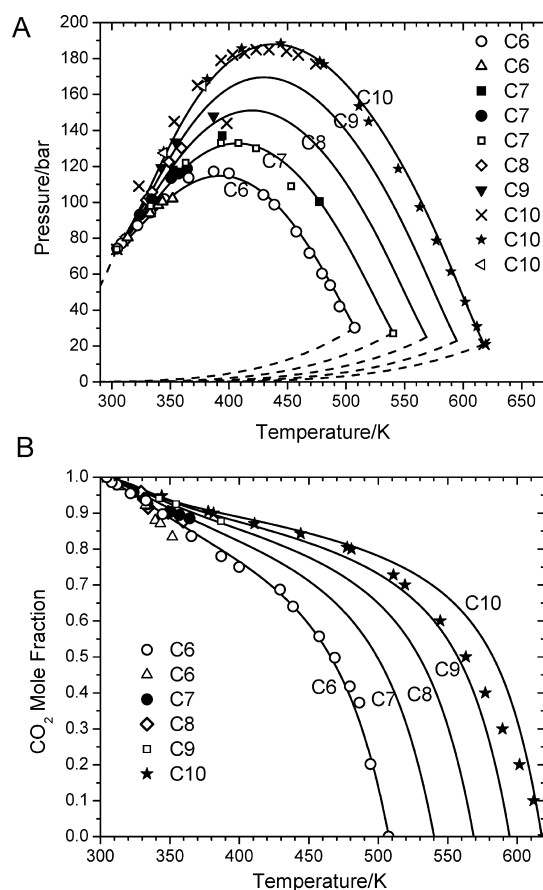


Figure 5. Critical lines for the binary systems of CO_2 with n -hexane (C6) to n -decane (C10), calculated from the parameters correlation in eq 11 and Table 6. Dashed lines are calculated pure compound saturation curves. Markers: experimental critical points taken from references in Table A2 (Supporting Information). Model: RK-PR EOS with CMRs. Table B1 (Supporting Information) defines the labels of the n -alkanes.

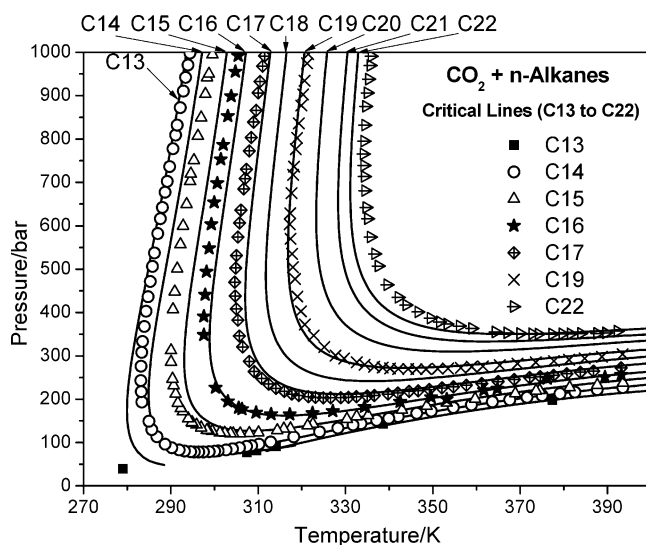


Figure 6. Critical lines for the binary systems of CO_2 with n -tridecane (C13) to n -docosane (C22), calculated from the parameter correlation in eq 11 and Table 6. Markers: experimental critical points taken from references in Table A2 (Supporting Information). Model: RK-PR EOS with CMRs. Table B1 (Supporting Information) defines the labels of the n -alkanes.

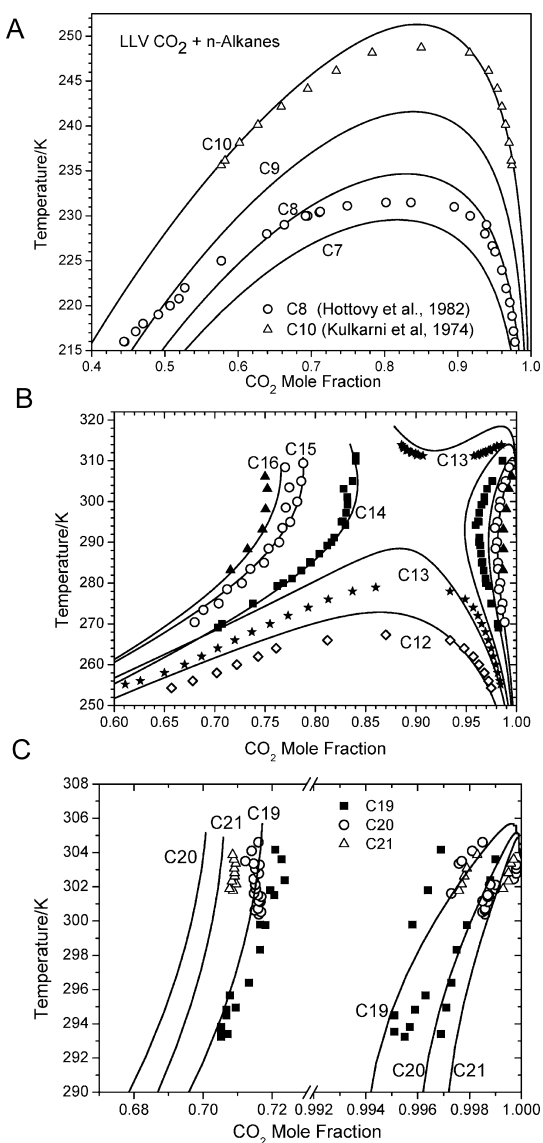


Figure 7. Liquid–liquid–vapor (LLV) equilibrium in the temperature–composition space, for $\text{CO}_2 + n$ -alkane binary systems from $\text{CO}_2 + \text{C7}$ to $\text{CO}_2 + \text{C21}$. Markers: Experimental data taken from Hottovy et al. 1982 (C8), Kulkarni et al. (C10), van der Steen et al. (C14–C15–C16), Fall and Luks (C13), Hottovy et al. 1981 (C12–C13–C14–C15,) and Fall et al., (C19–C20–C21). Lines were calculated from the parameter correlations in eq 11 and Table 6. Model: RK-PR EOS with CMRs. Table B1 (Supporting Information) defines the labels of the n -alkanes.

binary system to the next one, and that only one intersection point is observed. This, which is quite likely to be an artificial outcome of the model, happens between the C13 and C14 curves in the low temperature region for lines describing the composition of the alkane-rich liquid phase at LLVE. This type of experimentally not confirmed intersection points is usually more frequent when using QMRs (these intersections were explicitly shown by Cismondi²⁰ and seem to occur also in results by Polishuk et al.³). We also found multiple intersection points in our early attempts to correlate the phase equilibria of the $\text{CO}_2 + n$ -alkane homologue series with CMRs.

The only qualitatively surprising effect found in the predictions, which is opposed to the behavior of the experimental data, is the position of the heavy liquid branch for the system

$\text{CO}_2 + \text{C20}$ (Figure 7), showing the lowest (instead of intermediate) CO_2 content, with respect to those for the systems $\text{CO}_2 + \text{C19}$ and $\text{CO}_2 + \text{C21}$. As discussed in the next section, this result could be related to the inclusion of two “bad” data points for the system with n -eicosane (C20). The unwanted behavior found for the predicted CO_2 content of the n -alkane rich liquid phase at LLV equilibrium, could have been avoided by introducing proper inequality restrictions when optimizing the description of the phase equilibria of the $\text{CO}_2 + n$ -alkane series.

At a quantitative level, it can be observed from Figure 7 that there would still be room for further improvement of the LLV description for some systems, specially for the $\text{CO}_2 + \text{C8}$ and $\text{CO}_2 + \text{C13}$ mixtures. Figure 8 shows the predictions from

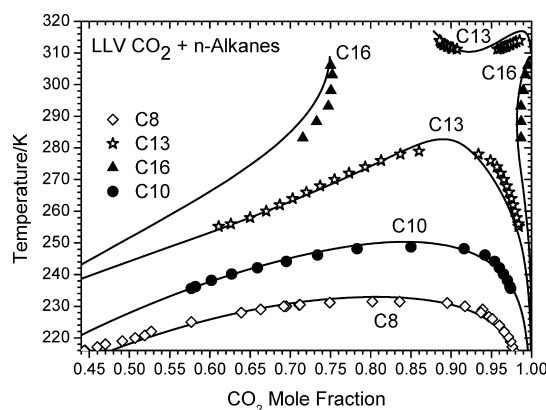


Figure 8. Liquid–liquid–vapor (LLV) equilibrium in the temperature–composition space, for some $\text{CO}_2 + n$ -alkane binary systems, predicted from parameters in Table B4 (Supporting Information). Markers: Experimental data points taken from the same references indicated for Figure 7. Model: RK-PR EOS with CMRs. Table B1 (Supporting Information) defines the labels of the n -alkanes.

the individually obtained sets of parameters in Table B4 (Supporting Information), for the systems $\text{CO}_2 + \text{C8}$, $\text{CO}_2 + \text{C10}$, $\text{CO}_2 + \text{C13}$, and $\text{CO}_2 + \text{C16}$. We must remark that these parameters are not the result of correlating a large number of “binary system-specific” experimental data of only a LLV nature but rather the result of minimizing the objective function for each binary system, considering all corresponding experimental data in Tables 2–5, and Tables B2 and B3 in the Supporting Information, where the critical end point temperatures and liquid compositions at LLV equilibrium for only one temperature per system are complemented with other type of data for different conditions. To fix ideas, the curve labeled “C8” in Figure 8 is a prediction from binary parameters specific of the $\text{CO}_2 + \text{C8}$ system (Table B4, Supporting Information) that were fitted from the following experimental information of the $\text{CO}_2 + \text{C8}$ system: one critical point (Table 2), the UCEP temperature (Table 4), and one LLV point (Table 5).

4.2. Description of Two-Phase Equilibria for Systems Considered in the Optimization. Figures 9–15 show different Pxy diagrams for the binary mixtures of CO_2 with methane, ethane, propane, n -butane, n -hexane, n -decane, and n -hexadecane, all of them having contributed with data considered in the objective functions (Tables 2–5 and Tables B2 and B3 in the Supporting Information). The description of vapor–liquid equilibria appears to be very accurate in comparison to experimental data for the systems of CO_2 with methane (Figure 9) and ethane (Figure 10), which were optimized (each of them individually, Table B4, Supporting

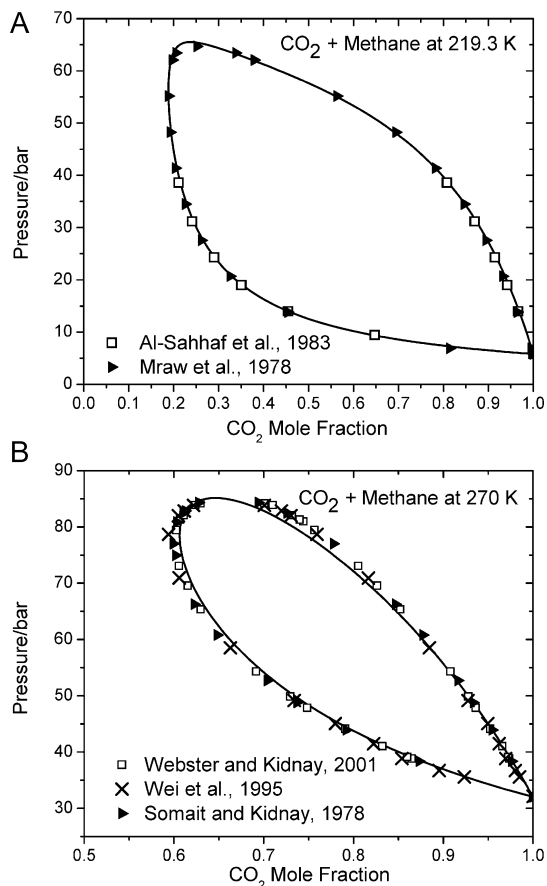


Figure 9. Isothermal two-phase equilibrium (Pxy) diagrams for CO₂ + methane (C1), calculated from parameters in Table B4 in the Supporting Information (solid lines). Markers: experimental data taken from references in Table A4 (Supporting Information). Model: RK-PR EOS with CMRs.

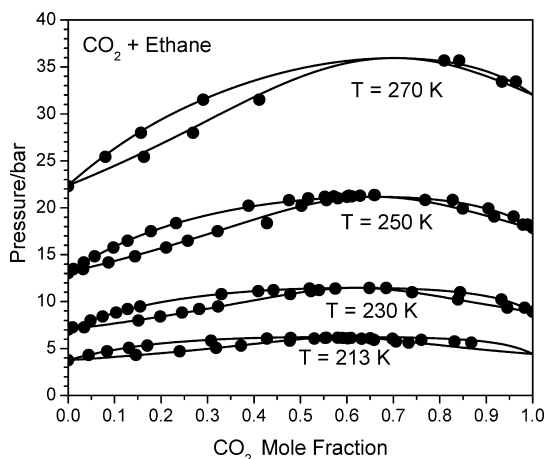


Figure 10. Predicted isothermal two-phase equilibrium (Pxy) diagrams for CO₂ + ethane (C2), calculated from parameters in Table B4, Supporting Information, (solid lines). Markers: Experimental points taken from references in Table A4 (Supporting Information). Model: RK-PR EOS with CMRs.

Information) separately from the rest of the series. Predictions for the other systems (Figures 11–15) are also quite successful, with some exceptions regarding bubble pressures. In particular, a systematic shift of the liquid branches to higher CO₂ mole

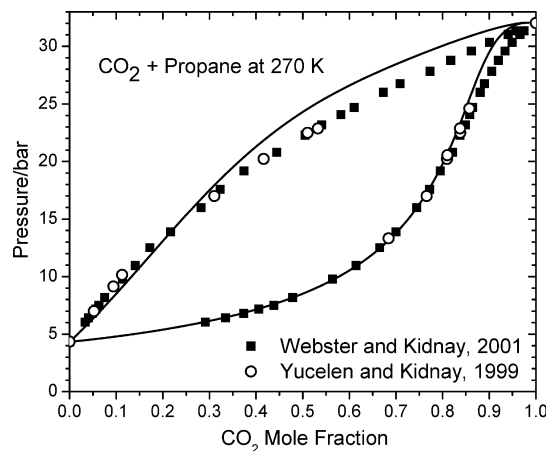


Figure 11. Isothermal two-phase equilibrium (Pxy) diagram for CO₂ + propane (C3) at 270 K, calculated (solid lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (Supporting Information). Model: RK-PR EOS with CMRs.

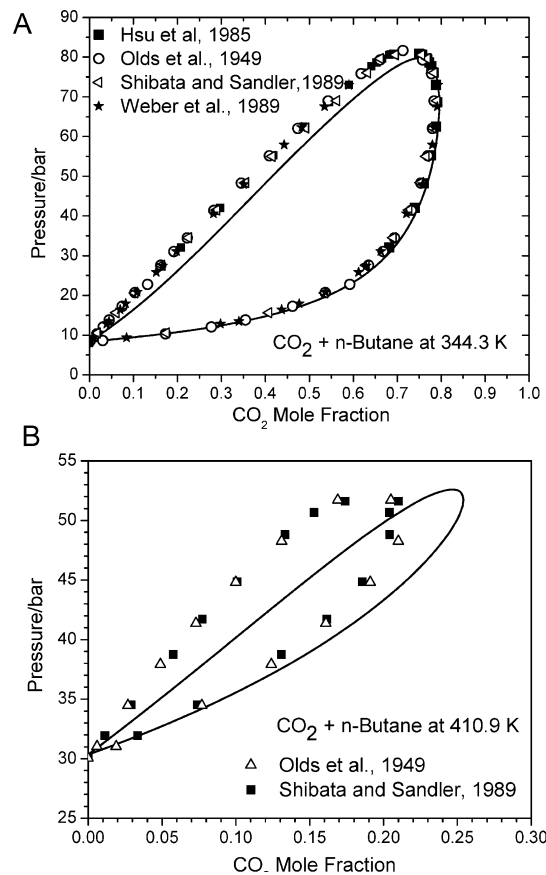


Figure 12. Isothermal two-phase equilibrium (Pxy) diagrams for CO₂ + *n*-butane (C4), calculated (solid lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (Supporting Information). Model: RK-PR EOS with CMRs.

fractions is observed for the mixtures CO₂ + C4 (Figure 12) and CO₂ + C6 (Figure 13) and, to a lesser extent, also for the system CO₂ + C10 (Figure 14). This effect is more evident in the diagram with *n*-butane at 410.9 K (Figure 12). It is important to note that, in predictions or correlations from

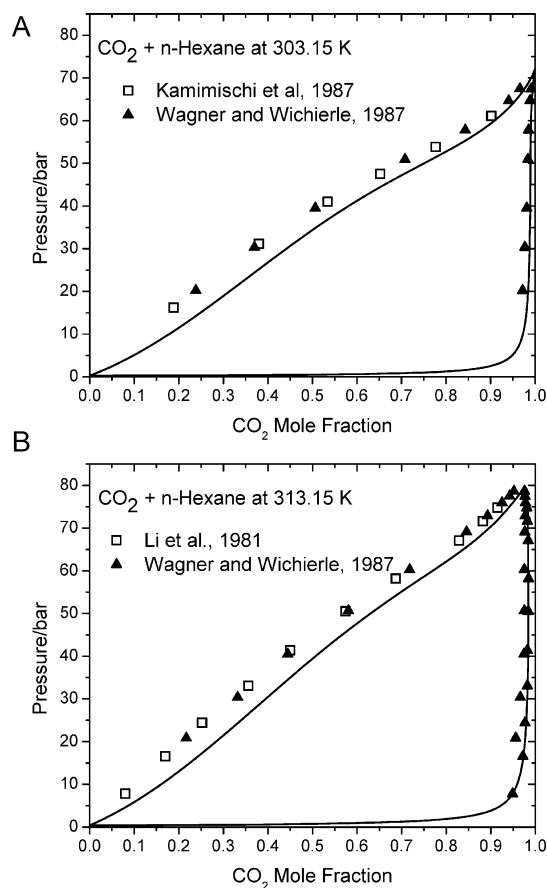


Figure 13. Isothermal two-phase equilibrium (Pxy) diagrams for CO_2 + *n*-hexane (C6), calculated (solid lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (Supporting Information). Model: RK-PR EOS with CMRs.

other authors,^{17,21,22} relatively larger errors are also found at high temperatures close to the *n*-butane critical point, when comparing to lower temperatures for CO_2 + *n*-butane. Notice in Figure 12 that the size of the vapor–liquid equilibrium region is much smaller at 410.9 K than at 344.3 K.

In view of the excellent results when correlating individual systems, which were illustrated in Figures 8–10, the deviations observed for liquid phases in Figures 11–14 could be possibly ascribed to a deficiency of the specific polynomial series correlation (eq 11 and Table 6) in the CN range from 3 to 10 rather than to the CMRs.

Note that the results, for example in Figure 9 for CO_2 + methane, show the same or higher level of accuracy, than correlations using a more theoretical and complex model like PCP-SAFT (Figure 15 in Tang et al.²³).

Figure 16 shows the Pxy diagram for CO_2 + *n*-hexadecane at 333.2 K, for which three sets of experimental data from different authors are available. Note that no experimental data points at this temperature were considered in the objective function for obtaining the constants of Table 6 for the CO_2 + *n*-alkane homologue series correlation. Then, the predictions shown in Figure 16 can be regarded as an interpolation between data for CO_2 + *n*-hexadecane (and other systems) at different temperatures. The data from D'Souza et al.²⁴ and Holscher et al.²⁵ agree quite well among themselves and also with the predictions. Instead, the data from Charoensombut-Amon et al.,¹¹ are shifted to higher CO_2 molar fractions, specially in the critical region. In

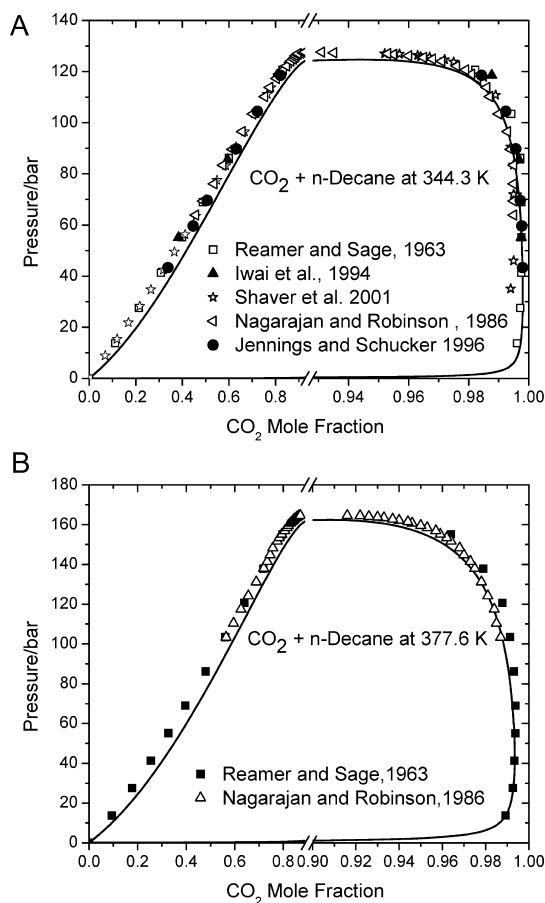


Figure 14. Isothermal two-phase equilibrium (Pxy) diagrams for CO_2 + *n*-decane (C10), calculated (solid lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (Supporting Information). Model: RK-PR EOS with CMRs.

spite of such shift, this time the observed critical pressure (but not the critical composition) reasonably agrees with other experimental studies (this was not the case at 313.2 K in Figure 1).

Predictions for CO_2 + *n*-eicosane are in excellent agreement with data from Huie et al.²⁶ and from Sato et al.²⁷ as shown in Figure 17. At the same time, the figure suggests that data reported by Kordikowski and Schneider²⁸ for 353.2 and 393.2 K might suffer from a systematic underestimation of CO_2 content in the liquid phase. It is remarkable that, even when the equilibrium points for both temperatures at 250 bar were taken from this source (Kordikowski and Schneider²⁸) and included in the objective function (Table B2, Supporting Information), the optimization results lead to predictions at 353.2 and 393.2 K that reasonably agree in the light phase but clearly disagree with those data points at 250 bar in the liquid phase [note, the high values of OF and OF_{corr} for CO_2 + C20 in the last column of Table B4 (Supporting Information), even when other systems have contributed more terms to the series objective function]. Instead, predictions reproduce well other data for CO_2 + C20 and neighbor CO_2 + *n*-alkane systems, which show a smooth and coherent evolution of the series. Still, these conflictive points at 250 bar may have influenced the results to some extent, bringing the liquid branches to lower CO_2 content, and this could be related to the unexpected position of the predicted heavy liquid phase branch for CO_2 + C20 in Figure 7, previously pointed out. It is usually difficult to establish whether different experimental data sets for different

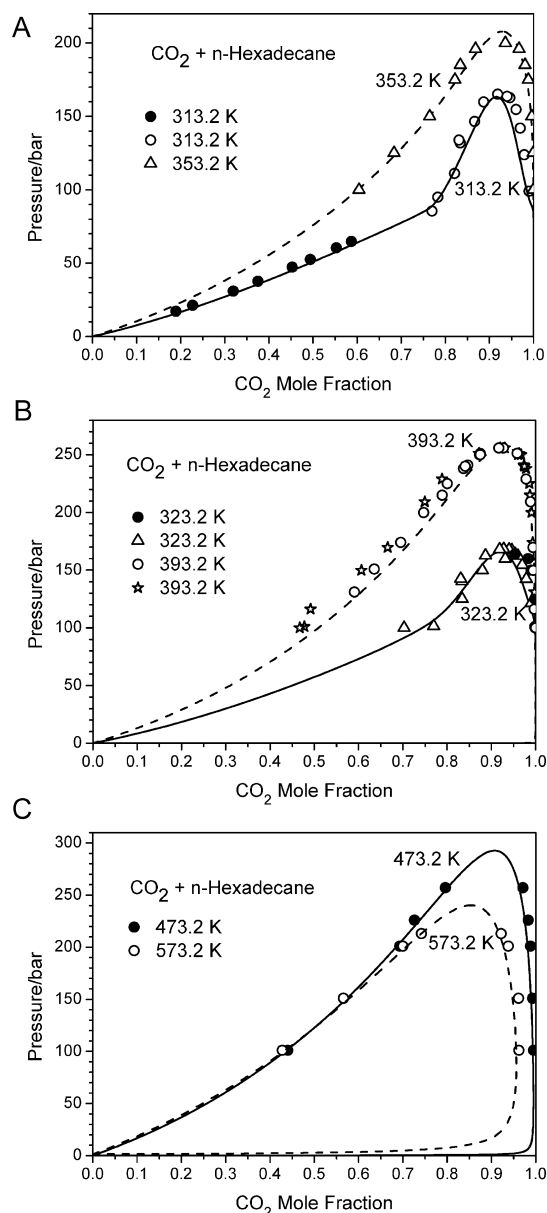


Figure 15. Isothermal two-phase equilibrium (P_{xy}) diagrams for $\text{CO}_2 + n$ -hexadecane (C16), calculated (lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (Supporting Information): Tanaka et al. (313.2 K), Nieuwoudt and du Rand (313.2 and 323.2 K), Pöhler (323.2 K), Kordikowski and Schneider (353.2 K), Spee and Schneider (393.2 K), Holscher et al. (393.2 K) and Brunner et al. (473.2 and 573.2 K). Only points for two pressures at 393.2 K and two pressures at 573.2 K were considered in the correlation (Table B2, Supporting Information). Model: RK-PR EOS with CMRs.

conditions, or even for different binary systems in the same homologue series, are in agreement, that is, whether they are consistent with a reasonable evolution of the phase behavior in the series. The case of Figure 17 illustrates how a good correlation of the series, at least within a certain carbon number range, can help; that is, this is a case where a correlation of phase equilibria of a homologue series as a whole can be used to identify sets of experimental data which may have a high level of error. More specifically, Figure 17 and the accompanying analysis suggest that the phase equilibrium data for $\text{CO}_2 + \text{C}_{20}$ by Kordikowski and Schneider²⁸ are, to some

extent, inaccurate. This should be taken as a provisional conclusion that should be confirmed or rejected through carefully carried out new experiments, at the conditions of Figure 17, if possible, by different laboratories.

We want to point out that the correct prediction of bubble pressures in the low CO_2 content region for the systems $\text{CO}_2 + \text{C}_{16}$ and $\text{CO}_2 + \text{C}_{20}$ (Figures 15–17) was not such in our first

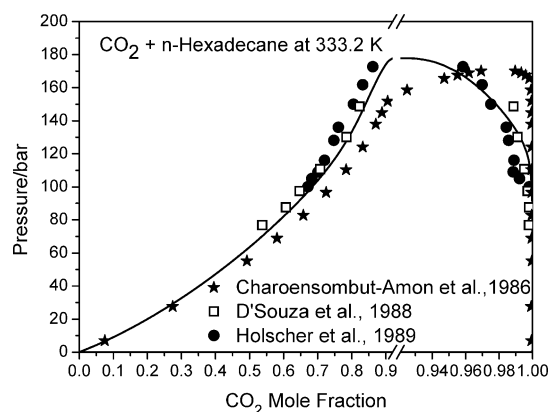


Figure 16. Isothermal two-phase equilibrium (P_{xy}) diagram for $\text{CO}_2 + n$ -hexadecane (C16) at 333.2 K, calculated (solid lines) from the parameter correlation in eq 11 and Table 6, and comparison to three different sets of experimental data (markers) in mutual disagreement. References included in Table A4 (Supporting Information). Model: RK-PR EOS with CMRs.

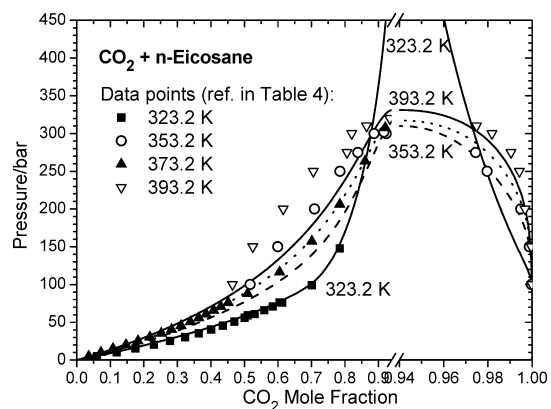


Figure 17. Isothermal two-phase equilibrium (P_{xy}) diagrams for $\text{CO}_2 + n$ -eicosane (C20), calculated (lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (Supporting Information). Within the temperature range of the present figure only points for 250 bar at 353.2 and 393.2 K (Table B2, Supporting Information) and one bubble pressure at 373.2 K (Table B3, Supporting Information) were considered in the correlation. Model: RK-PR EOS with CMRs.

attempts to correlate the $\text{CO}_2 + n$ -alkane series. That was surprising at first, since experience with QMRs told us that this should be an easy test, and usually only the critical or high pressure region is difficult to predict or even correlate. However, the flexibility of CMRs and the bifurcation that takes place for example for a symmetric QMRs k_{12} interaction parameter into the CMRs k_{112} and k_{122} parameters, that govern the two binary infinite dilution ends, led us to identify the need of introducing bubble pressure experimental data of lower pressure in the objective function (see data at around 20 bar in Table B3 in the Supporting Information).

Figures 18–20 present the isothermal Pxy diagrams for the mixtures of different heavy *n*-alkanes with CO₂ at 373.2, 393.2,

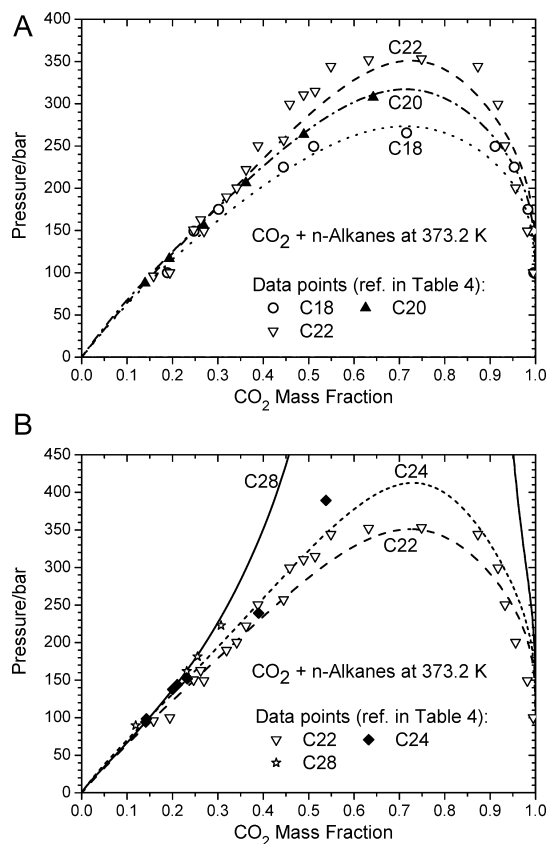


Figure 18. Isothermal two-phase equilibrium (Pxy) diagrams for binary mixtures of CO₂ with different heavy *n*-alkanes at 373.2 K, calculated (lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (Supporting Information). Model: RK-PR EOS with CMRs. Table B1 (Supporting Information) defines the labels of the *n*-alkanes.

and 423.2 K, respectively. Notice that, in all three figures, we have plotted the pressure as a function of the CO₂ mass fraction rather than as a function of the CO₂ mole fraction. This choice for the CO₂ concentration scale facilitates the interpretation of the figures. In general, and considering some level of uncertainty in the experimental data which is evident, the calculated curves agree well with the experimental points. A clear exception is the case of the system CO₂ + C32 (Figure 19 B) where we see a good agreement between the model and the experimental data only for the liquid phase below 310 bar. At 393.2 K, the system CO₂ + C32 presents, experimentally, a critical point with a critical pressure in the order of 640 bar (Figure 19 B), while the model (solid line) shows a higher degree of immiscibility. Evidently, the model predicts a T_m value greater than the actual one. Notice that only three experimental points for the system CO₂ + C32, with a maximum pressure less than 51 bar, were used in CO₂ + *n*-alkane series objective function (Tables B2 and B3 in the Supporting Information).

The phase equilibrium experimental data for CO₂ + C20 at 373.2 K (Figure 18) and 423.2 K (Figure 20) are well reproduced by the model. This is not the case for CO₂ + C20 at 393.2 K in Figure 19, where the CO₂ + C20 experimental data,

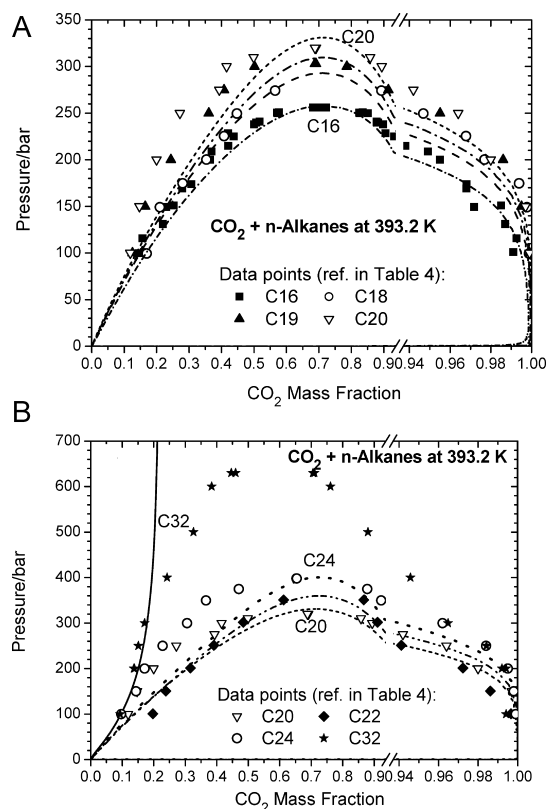


Figure 19. Isothermal two-phase equilibrium (Pxy) diagrams for binary mixtures of CO₂ with different heavy *n*-alkanes at 393.2 K, calculated (lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (Supporting Information). Only two pressures for *n*-hexadecane at this temperature and one for *n*-eicosane were considered in the correlation (Table B2, Supporting Information). Model: RK-PR EOS with CMRs. Table B1 (Supporting Information) defines the labels of the *n*-alkanes.

previously detected as probably wrong, are from Kordikowski and Schneider.²⁸

Again, a careful examination of the evolution of data sets in Figure 19 suggests that there would be important errors in the experimental liquid phase composition, for one or more data sets in Figure 19, since the data sets do not follow a clear trend with respect to the *n*-alkane CN.

4.3. Prediction of Two-Phase Equilibria for Systems Not Considered in the Optimization. This study is a first implementation of our approach for the parametrization of CMRs for a complete homologue series of binary systems. To analyze the possibilities and limitations of such an approach and to detect possible improvements, instead of intending to obtain the ultimate correlation for the CO₂ + *n*-alkane series, we deliberately left some CO₂ + *n*-alkane systems out of the objective function, even when there are important experimental phase equilibrium data available for them. The reason for that was to explore the predictive potential of the approach. Figures 21–23 show, respectively, the prediction of isothermal Pxy diagrams for the binary mixtures CO₂ + *n*-heptane (C7), CO₂ + *n*-dodecane (C12), and CO₂ + *n*-pentadecane (C15). For the system CO₂ + C7 (Figure 21) the deviations in the liquid phase are similar to those previously noticed for CO₂ + C4 (Figure 12), CO₂ + C6 (Figure 13), and CO₂ + C10 (Figure 14). Figures 22 and 23 show, in general, a good

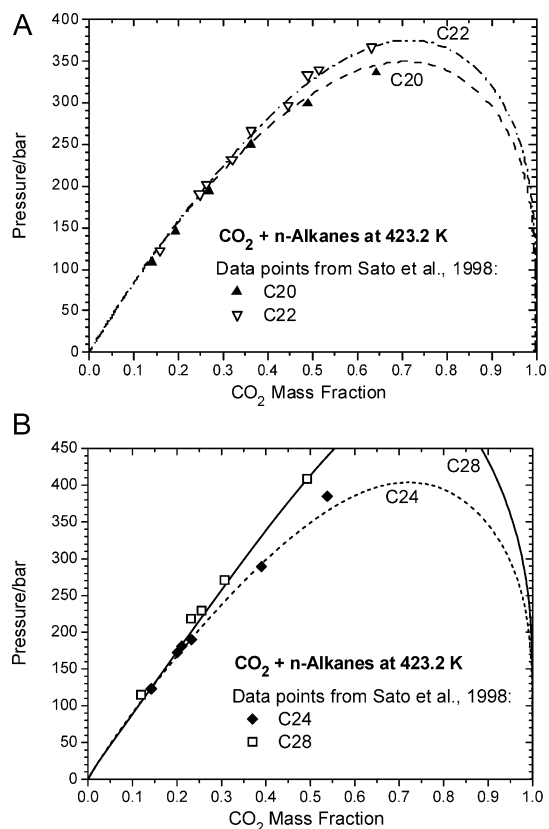


Figure 20. Isothermal two-phase equilibrium (Pxy) diagrams for binary mixtures of CO₂ with different heavy *n*-alkanes at 423.2 K, calculated (lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (Supporting Information). Only one point at this temperature and for C28 (Table B3, Supporting Information) was considered in the correlation. Model: RK-PR EOS with CMRs. Table B1 (Supporting Information) defines the labels of the *n*-alkanes.

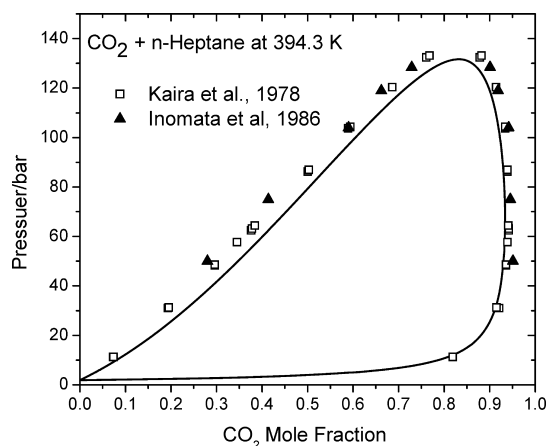


Figure 21. Predicted isothermal two-phase equilibrium (Pxy) diagram for CO₂ + *n*-heptane (C7), calculated (solid lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (Supporting Information). Model: RK-PR EOS with CMRs. No experimental data for the system CO₂ + *n*-heptane were used in the objective function whose minimization led to the parameter values of Table 6.

agreement with experimental data, considering that they correspond to pure predictions.

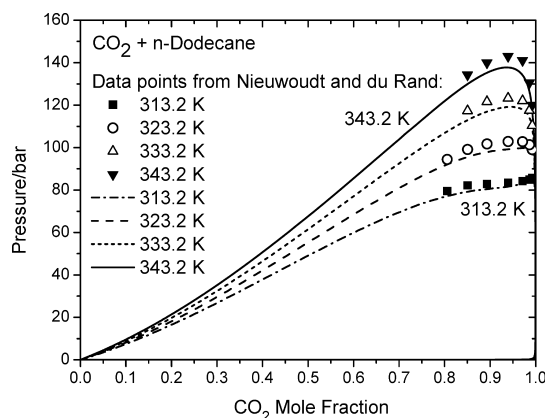


Figure 22. Predicted isothermal two-phase equilibrium (Pxy) diagrams for CO₂ + *n*-dodecane (C12), calculated (lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (Supporting Information). Model: RK-PR EOS with CMRs. No experimental data for the system CO₂ + *n*-dodecane were used in the objective function whose minimization led to the parameter values of Table 6.

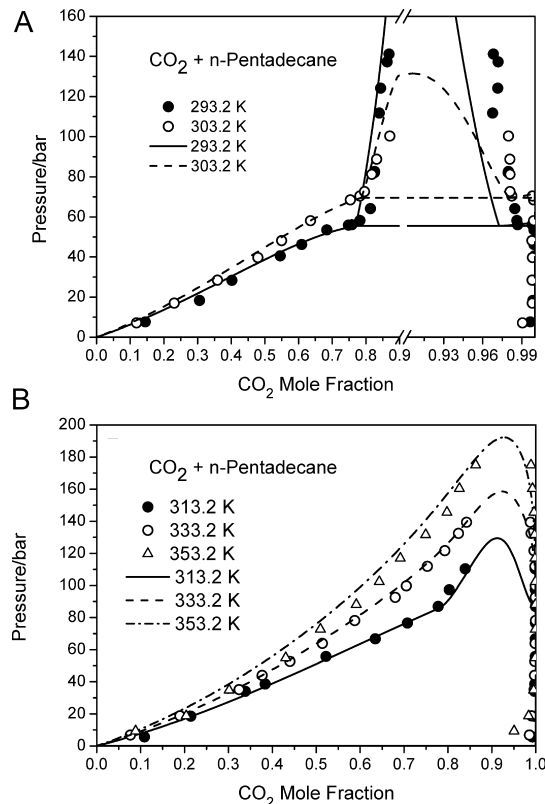


Figure 23. Predicted isothermal two-phase equilibrium (Pxy) diagrams for CO₂ + *n*-pentadecane (C15), calculated (lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (available in the Supporting Information). Model: RK-PR EOS with CMRs. No experimental data for the system CO₂ + *n*-pentadecane, were used in the objective function whose minimization led to the parameter values of Table 6.

4.4. Prediction of Densities. As it can be concluded from Tables A2–A6 (in the Supporting Information), there is a limited amount of published density data available, in comparison to compositional data, for the series of CO₂ + *n*-alkane binary mixtures. Still, there are some sets of density data

reported for different types of equilibrium, which are important for testing the predictions of density when correlating phase equilibrium in the P - T - x space. Figure 24 shows good

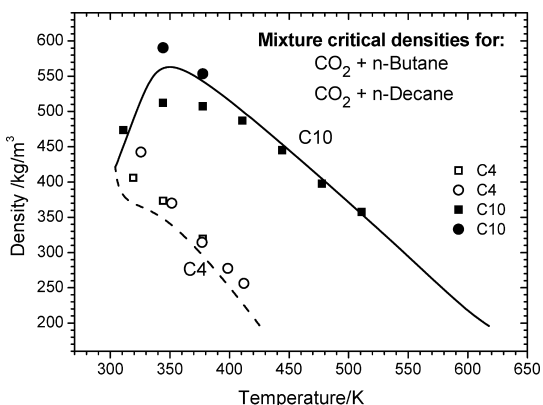


Figure 24. Critical lines, in the density–temperature space, for the binary systems of CO_2 with n -butane (C4) and n -decane (C10). Lines predicted from the parameter correlation in eq 11 and Table 6. Markers: Experimental critical points taken from references in Table A2 (Supporting Information). No binary experimental density data were used while fitting the parameters reported in Table 6. Model: RK-PR EOS with CMRs.

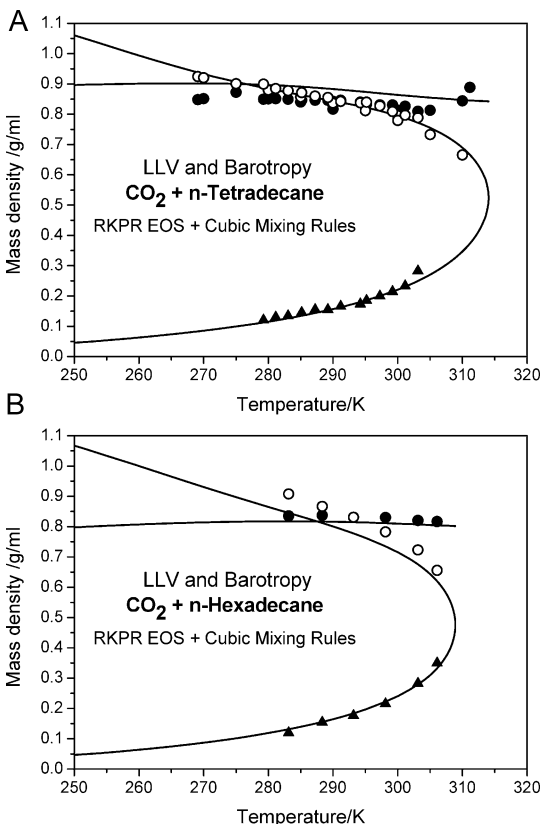


Figure 25. Prediction of density and barotropy along the liquid–liquid–vapor (LLV) equilibrium region, for the binary systems of CO_2 with n -tetradecane (C14) and n -hexadecane (C16). Lines predicted from the parameters correlation in eq 11 and Table 6. Markers: Experimental densities at LLV equilibrium taken from references in Table A3 (Supporting Information). No binary experimental density data were used while fitting the parameters reported in Table 6. Model: RK-PR EOS with CMRs.

agreement in the critical lines for CO_2 + C4 and CO_2 + C10. This applies also to the barotropy phenomenon along the LLV line, as can be seen in Figure 25 for CO_2 + C14 and CO_2 + C16. The error in the predicted barotropic temperatures is around 10 and 5 K, respectively. A comparison to Figure 12 of our previous work¹ confirms that it was appropriate to change the pure compound RK-PR parameters, as already discussed in section 3.1, where the pure compound volumetric information used to obtain the pure compound RK-PR parameters is indicated.

Figures 26 and 27 show isothermal liquid–vapor equilibrium density curves for the systems CO_2 + C4 and CO_2 + C10

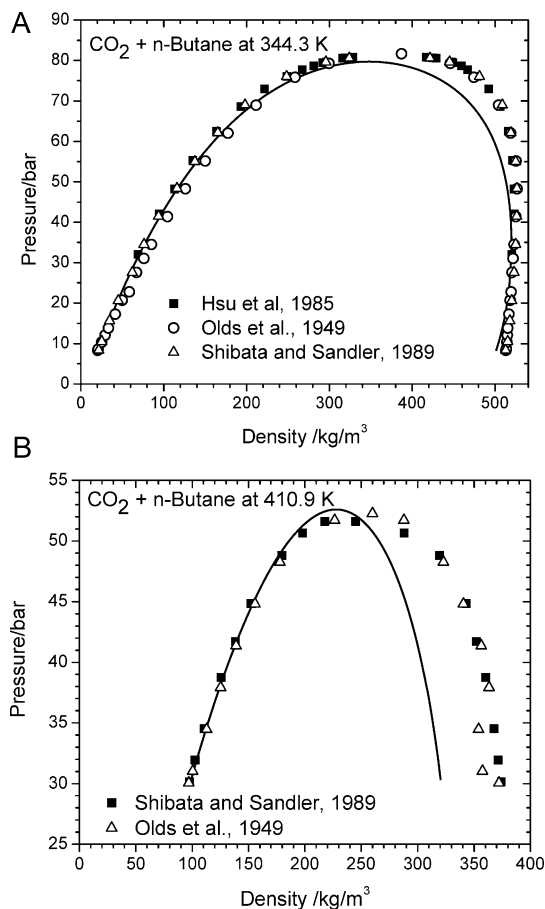


Figure 26. Isothermal two-phase equilibrium pressure–density diagrams for CO_2 + n -butane (C4), calculated (solid lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (available in the Supporting Information). No binary experimental density data were used while fitting the parameters reported in Table 6. Model: RK-PR EOS with CMRs. The corresponding Pxy diagrams are shown in Figure 12.

at the same temperatures considered in Figures 12 and 14. The only important discrepancy observed between data and predictions, that is, the underestimation of saturated liquid densities by 10–15% in Figure 26 at 410.9 K, is clearly related both to the corresponding liquid branch composition shift in Figure 12, previously pointed out, and to the underestimation of saturated liquid densities for pure compounds (n -butane in this case) as the critical pure compound temperature is approached. On the other hand, the degree of

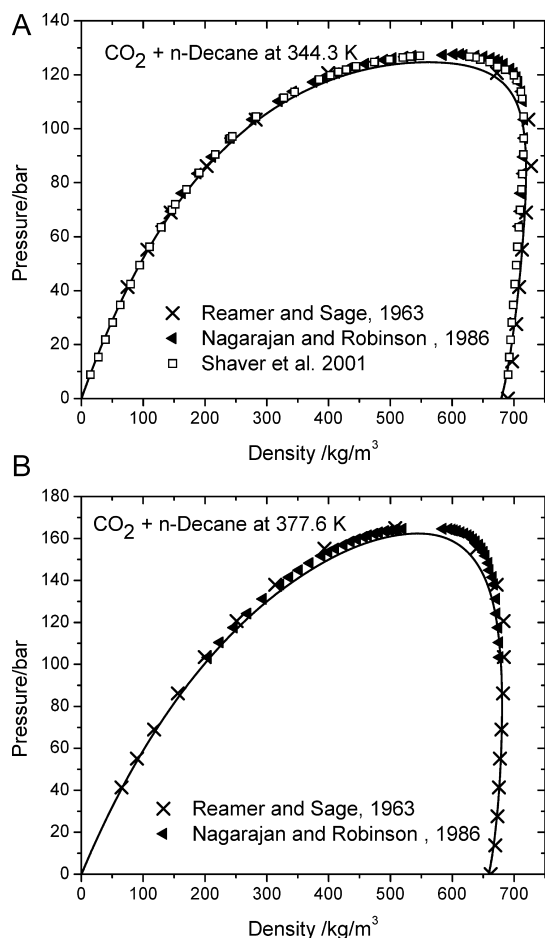


Figure 27. Isothermal two-phase equilibrium pressure–density diagrams for $\text{CO}_2 + n$ -decane (C10), calculated (solid lines) from the parameter correlation in eq 11 and Table 6. Markers: experimental data taken from references in Table A4 (available in the Supporting Information). No binary experimental density data were used while fitting the parameters reported in Table 6. Model: RK-PR EOS with CMRs. The corresponding Pxy diagrams are shown in Figure 14.

agreement between experimental and predicted densities is remarkably good for $\text{CO}_2 + \text{C}_{10}$ in Figure 27.

4.5. Final Remarks. The description of the fluid phase equilibria of the $\text{CO}_2 + n$ -alkane homologue series, obtained from the (series-specific) correlation defined by eq 11 and Table 6, and illustrated in the previous sections, for vapor–liquid and liquid–liquid regions and for the supercritical region of CO_2 , is, to our knowledge, the most accurate series-specific description presented so far in the literature for $\text{CO}_2 + n$ -alkane binary systems, at least for n -alkane carbon numbers from 10 on.

Although the eq 11/Table 6 correlation could be recommended for predicting $\text{CO}_2 + n$ -alkane binary phase equilibria, particularly in the CN range from intermediate molecular weight to heavier n -alkanes, we need to remark that it was not our intention to develop, at this stage, something such as the best possible series-specific correlation using CMRs.

The goal of further improving such correlation, with a model like the one used here (RK-PR + CMRs), which offers high flexibility but simultaneously sets an important challenge for its parametrization, requires the availability of a first study for the whole $\text{CO}_2 + n$ -alkane series, such as the present one. The development of this work led us to become aware of the relative importance and limitations of different aspects related

to the process of building a series-specific correlation. For instance, important issues related to the objective function are the definition of the terms, which was improved with respect to our previous work, the balance between different types of experimental data and the effect of not including certain experimental points.

Especially, the systematic deviations observed for carbon numbers up to 10 in the alkane-rich liquid composition (Figures 11 to 14) could be partially attributed to some limitations of the polynomial form. This functional form does not set reasonable limits for CN tending either to zero or to infinity. Besides, it would be interesting to explore in the future the use of the interval-Newton approach (INA) for minimizing the objective function of the series. According to Gau and Stadtherr,²⁹ the INA is a general-purpose technique, applicable to parameter estimation problems of considerable size, that offers mathematical and computational guarantees that the global optimum has been found. This is, however, achieved at the expense of higher computation times in comparison to local methods, which do not provide the mentioned guarantees. Exploring the use of the INA could be carried out through a constrained formulation or through an unconstrained formulation established by incorporating the model equations into the objective function.

It is therefore clear that there would be room for improving the predictive correlation obtained here for describing the phase equilibria of the $\text{CO}_2 + n$ -alkane homologue series of binary systems.

In other words, and in view of the complexity of the problem of parametrizing a complete series, that is, of the diversity of aspects affecting the objective function and of the high flexibility of CMRs which can be hard to manage, we consider that it is important to report suboptimal results like the ones presented here, discussing limitations of procedures or approaches that we have already overcome and also the problems that still need to be fixed or the aspects that would require further study and improvement.

5. CONCLUSIONS

As a part of the required work for developing a predictive correlation for the fluid phase equilibria of the $\text{CO}_2 + n$ -alkane homologue series, nearly 100 references containing phase equilibrium data for the series of $\text{CO}_2 + n$ -alkane binary systems have been identified and classified in six tables. A strategy for the development of a correlation of cubic mixing rules (CMRs) interaction parameters for the whole series of $\text{CO}_2 + n$ -alkane binary systems was discussed and implemented. A correlation, defined by a set of fourth order polynomials, valid for the binary systems from $\text{CO}_2 + \text{C}_3$ to $\text{CO}_2 + \text{C}_{32}$, was obtained from the minimization of an objective function (OF). This OF considered a relatively small number of selected experimental fluid phase equilibrium data points of some $\text{CO}_2 + n$ -alkane binary systems. The correlative and predictive capacities of the correlation are very good in general for the different types of fluid phase equilibria. However, some limitations were observed in the description of the liquid phase composition for carbon numbers up to C10, that is, an overestimation of the CO_2 content of such phase.

A variety of recommendations have been provided, in order to get a good description of the phase behavior from flexible models like CMRs, based on our experience and on the issues we identified when designing an objective function for a series

with a complex phase behavior such as the CO₂ + *n*-alkane series.

The correlation of specific experimental data or the optimization of a single binary CO₂ + *n*-alkane system can be preferable when accuracy is required for particular applications and good and enough data are available. It has been shown that, when that is not the case, the correlation of a series of binary systems as a continuum entity can compensate for the partial lack of experimental data for some systems and even provide good predictions for those systems with no data available at all. The flexibility of CMRs allowed us to obtain a good description of the complex phase behavior of the series of asymmetric CO₂ + *n*-alkane binary systems. The availability of this type of predictive correlation can also be important in applications like CO₂-enhanced oil recovery (EOR), where a mixture of an important number of compounds of the same family, differing in molecular weight, are put in contact with one solvent.

Although we have focused in this work on the phase behavior of the highly non ideal CO₂ + *n*-alkane series, the CMRs and the methodology here proposed for generating a series-specific correlation could be applied to other series with a complex phase behavior. Examples of them are the water + hydrocarbon series or the series of binary systems made of a light solvent, for example, CO₂, ethane, or propane and an alkyl-ester, a primary alcohol, or a long tailed organic acid. For binary systems with association effects, for example, with hydrogen bonding, we expect the CMRs interaction parameters to account for them, even when such effects are not explicitly considered by the CMRs.

The present approach could be used to identify existing experimental binary phase equilibrium data sets potentially having high systematic errors. It would also be applicable to the identification of convenient conditions to carry out phase equilibrium measurements for binary systems with no experimental information available in the literature.

■ ASSOCIATED CONTENT

📄 Supporting Information

Appendix A: literature review. Appendix B: additional tables. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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Supporting Information for the IEC Res Manuscript:

Phase Equilibria Of CO₂ + n-Alkane Binary Systems In Wide Ranges of Conditions: Development of Predictive Correlations Based on Cubic Mixing Rules

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Description:

This document contains Appendix A, which presents a literature review on the experimental fluid phase equilibria of binary carbon dioxide + n-alkane systems; and Appendix B, which presents a number of tables referred to in the main text of the article.

APPENDIX A: Experimental Data on the fluid phase equilibria of Carbon Dioxide + n-Alkane systems

We performed a literature review that focused on the experimental fluid phase equilibria of binary carbon dioxide + n-alkane systems, where the n-alkane of the mixture is a linear chain molecule having 1 to 36 carbon atoms. Equilibria with presence of solid phases have not been taken into account. The literature on the experimental phase behavior of the CO₂ + n-alkane homologue series is vast. Although we have identified an important number of relevant contributions, it is unlikely for our final list in the present work to be complete.

The information on CO₂ + n-alkane fluid phase equilibria is arranged in tables A1 to A6. A given table corresponds to a specific type of phase equilibrium information. The least familiar type is probably the “critical end point” (CEP). A CEP is a point where a line of binary critical points

(critical line) terminates. At a CEP a critical phase is at equilibrium with a non critical phase (see reference¹ for more details) . At a so-called “K” CEP the critical phase corresponds to a vapor-liquid critical point.

The tables have as main entry the carbon number (CN) of the n-alkane of the studied CO₂ + n-alkane mixture. All tables report the method employed to obtain the experimental data, according to Deiters and Schneider², who classify the methods, considering their underlying principles, into synthetic and analytic. In the synthetic methods, a mixture of known composition is prepared, and then its phase behavior is observed as a function of temperature and/or pressure. In the analytic methods, the phase separation is promoted through changes in temperature and/or pressure (as in the synthetic methods); then samples of the phases are withdrawn and analyzed through appropriate methods. Furthermore, we consider an additional criterion for the classification of the experimental methods; we assort them as static or dynamic methods. In the former case, none of the phases of the system flows through the equilibrium cell during the measurements. In the latter case, one or more phases are allowed to flow during the measurement to promote the equilibrium condition inside the equilibrium cell. For more details, see reference³. Other possible classifications have been proposed^{3, 4, 5, 6, 7}.

Tables A1 to A6 also report the purity of the compounds in the mixture together with the corresponding units. Notice that the last column in each table identifies the reference from which the data were taken.

Table A1 presents information on literature contributions reporting experimental critical end points (CEPs) for CO₂ + n-alkane binary mixtures, and it also reports the temperature and pressure coordinates of such CEPs. According to Fall and Luks⁸, binary systems formed by carbon dioxide and n-alkanes up to C6 exhibit a type I behavior according to the classification proposed by Scott

and van Konynenburg⁹ for the fluid phase behavior of binary mixtures⁽¹⁾. This means that a liquid=vapor (L=V) critical locus extends from the critical point of the pure n-alkane to the critical point of pure carbon dioxide, and there are no CEPs. The binary systems containing CO₂ and n-alkanes from C7 to C12 display a type II phase behavior⁹. In type II behavior, a critical locus extends between the critical points of the pure compounds, as in type I behavior, and another critical locus (liquid=liquid, L=L) appears, which finishes in an upper critical end point (UCEP). A liquid-liquid-vapor (LLV) locus goes from that UCEP to lower temperatures. The system formed by CO₂ and n-Tridecane constitutes a “transition” from type II to type III⁹ phase behavior in this homologue series, and it presents a type IV behavior. In type IV phase behavior, the UCEP which signals the end of the L=L critical locus is also present, as in type II behavior. However, the critical line that stems from the critical point of the heavy compound, i.e., the n-alkane, ends at a lower critical end point (LCEP); and another critical locus extends from the critical point of pure CO₂ to a second UCEP (these last two types of critical lines were denoted E and D respectively, by Cismondi and Michelsen¹⁰). A LLV locus connects the last two CEPs. Finally, as already pointed out, for example, by Fall and Luks⁸, binary mixtures made of CO₂ and n-alkanes, with CN greater than or equal to 14, show a type III phase behavior. In this type of behavior a critical locus connects the critical point of pure CO₂ with an UCEP, while there exists another critical locus that originates at the critical point of the pure n-alkane and extends indefinitely to high pressures. This latter critical locus (denoted C by Cismondi and Michelsen¹⁰) may show local extrema in the pressure vs. temperature plane. As the difference between the critical temperatures of pure carbon dioxide and the pure n-alkane increases, the asymmetry of the mixture rises up, and we observe an evolution in the fluid phase behavior for this homologue series. This kind of evolution has also been observed for other homologue series¹.

⁽¹⁾ Actually, it could be argued that the fluid phase behavior of these systems corresponds to type II, but with the LLV region and the Upper CEP (UCEP) subject to the interference of the more stable solid-fluid equilibria.

Table A2 summarizes information on critical point experimental data sets reported in the literature for CO₂ + n-alkane binary mixtures. Table A2 gives, for each record, the temperature and pressure ranges for the measured critical loci, together with the temperature and pressure uncertainty estimates. It also indicates whether the experimental critical composition, density, and composition uncertainty, are available. “N/A” or “NO” in Tables A1 to A6 means a lack of information for the corresponding field in the quoted reference (see last column in Tables A1 to A6). “YES” means availability of some information for the corresponding field.

Table A3 reports the literature sources of liquid-liquid-vapor (LLV) experimental data for CO₂ + n-alkane binary mixtures. For each record in Table A3, we provide information similar in nature to that given in Table A2. Table A3 includes an additional field (“Phases informed”) that identifies the phases for which the authors have reported the experimental composition and/or density. “L1” is the liquid phase richer in the n-alkane, “L2” is the liquid phase richer in CO₂, and “V” is the vapor phase, being the phases “L1”, “L2” and “V” in equilibrium.

From the data depicted in Table A3, we observe that there is a lack of LLV experimental information for some binary systems in this homologue series, as the ones corresponding to C7, C9, C11, C17 and C18. For some of the systems here classified as type III (CN>13), corresponding to n-Docosane and heavier n-alkanes, the LLV locus is interrupted by the appearance of a quadruple point (Q point)^{11, 12} where three fluid phases are at equilibrium with a solid phase. Since the pure n-alkane melting point increases with the n-alkane molecular weight, the Q point temperature of the binary CO₂ + n-alkane system also increases with it.

Table A4 presents information on literature contributions reporting fluid phase equilibrium data measured at constant temperature for CO₂ + n-alkane mixtures. In this table we inform the

temperature of the isothermal set, the pressure range of the measured data, the availability or not of the compositions and composition uncertainties of the phases at equilibrium (n-alkane richer and CO₂ richer phases), and the uncertainties in temperature and pressure, if available. Besides, we include an additional field stating whether the experimental density of the mixture has been reported in the corresponding reference.

The length of Table A4 clearly shows that isothermal two-phase equilibrium is the type of experimental data most frequently gathered and reported for the CO₂ + n-alkane series. Often, specially for the heavier n-alkanes, some important degree of scatter is observed when graphically comparing data sets at the same temperature from different literature sources.

Moreover, even serious disagreements can be found, as illustrated in Fig. 1 for CO₂ + n-Hexadecane at 313.2 K (see the main body of this work).

Table A5 gives information on experimental data sets at constant system pressure (T_{xy} sets) available in the literature for two-phase fluid-fluid equilibria of CO₂ + n-Alkane binary mixtures.

Table A6 presents information on experimental fluid-fluid equilibria isoplethic data sets available in the literature for CO₂ + n-alkane binary mixtures. For a given data set, Table A6 reports the isopleth composition, and the temperature and pressure ranges of the experimental data. Table A6 also informs the composition, temperature and pressure uncertainties. It also indicates whether the density of the mixture has been reported in the corresponding reference.

We stress that the most often reported experimental phase equilibrium data sets, in the present collection, are of the isothermal type (see Tables A4 to A6). We observe that, even though the

homologue series CO₂ + n-alkane has been widely studied, there is still some lack of important experimental information (see, e.g., Table A3).

Table A1. Experimental data on fluid-fluid critical end points for CO₂ + n-Alkane binary mixtures

CN	Method	Purity		Units for Purity		UCEP				LCEP				UCEP				Reference
		CO ₂	Alk.	CO ₂	Alk.	T (K)	Absolute T uncertainty (K)	P (bar)	Absolute P uncertainty (bar)	T (K)	Absolute T uncertainty (K)	P (Bar)	Absolute P Uncertainty (bar)	T (K)	Absolute T Uncertainty (K)	P (Bar)	Absolute P Uncertainty (bar)	
7	Analytic static	99.9	99.9	Mole %	Mole %	222.6	0.2	6.5	0.03									Im and Kurata, 1971 ¹³
8	Analytic static	99.99	99.0	Mole %	Mole %	231.5	0.03	9.2	0.07									Hottovy et al., 1982 ¹⁴
10	Static synthetic	> 99.99	>99.0	%	%	248.7	0.15	16.4	0.07									Kulkarni et al., 1974 ¹⁵
12	Analytic static	99.99	99	Mole %	Mole %	267.3	0.02	28.8	0.07									Hottovy et al., 1981 ¹⁶
13	Analytic static	99.99	99	Mole %	Mole %	279.0	0.02	39.3	0.07									Hottovy et al., 1981 ¹⁶
13	Analytic static	99.99	99	Mole %	Mole %					310.8	0.02	81.1	0.07	314.0		87.2		Fall and Luks, 1985 ⁸
14	Analytic static	99.99	99	Mole %	Mole %									311.2	0.02	82.6	0.07	Hottovy et al., 1981 ¹⁶
15	Analytic static	99.99	99	Mole %	Mole %									309.4	0.02	80.2	0.07	Hottovy et al., 1981 ¹⁶
19	Analytic static	99.99	99	Mole %	Mole %									305.5		75.8		Fall et al. 1985 ¹⁷
20	Analytic static	99.99	99	Mole %	Mole %									305.3	0.02	75.5	0.07	Hottovy et al., 1981 ¹⁶
20	Analytic static	99.99	99	Mole %	Mole %									305.2		75.4		Fall et al. 1985 ¹⁷
21	Analytic static	99.99	99	Mole %	Mole %									305.0		75		Fall et al. 1985 ¹⁷

Table A2. Data sets of experimental critical points available for CO ₂ + n-Alkane binary mixtures													
CN	Method	Purity		Units for Purity		T range (K)	Absolute T uncertainty (K)	P range (bar)	Absolute P Uncertainty (bar)	Composition informed	Composition uncertainty	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk								
1	DA	99.99	99.99	%	%	193.1-219.3	0.01	47.4-64.9	0.7	YES	YES	NO	Mraw et al, 1978 ¹⁸
2	DS	0.99995	0.9995	Mass fr.	Mass fr.	291-305.4	0.5	57.11-48.17	0.5	YES	YES	NO	Horstmann et al, 2000 ¹⁹
3	SA	99.5	99.9	%	%	304.4-366.2	0.3	54.5-70.5	0.3	YES	YES	NO	Poettmann and Katz, 1945 ²⁰
3	SA	99.95	98	% vol.	% vol.	304.3-364.8	N/A	47.4-70.7	N/A	YES	NO	NO	Smejkal et al, 2002 ²¹
3	SA	99.95	98	% vol.	% vol.	327-369.7	N/A	42.5-65.2	N/A	YES	NO	NO	Smejkal et al, 2002 ²¹
4	SA	99.5	99.0	%	%	321.8-415.8	0.3	48.9-81.4	0.3	YES	YES	NO	Poettmann and Katz, 1945 ²⁰
4	SA	0.999	0.999	Mole fr.	Mole fr.	325.9-412.3	0.06	51.1-81.7	0.01	YES	YES	YES	Olds et al., 1949 ²²
4	DA	99.99	99.98	%	%	319.3-377.6	N/A	75.7-81.2	N/A	YES	NO	YES	Hsu et al, 1985 ²³
4	SA	99.9	99.9	%	%	368.15-418.15	0.1	46.4-77.98	0.1	NO	YES	NO	Leu and Robinson, 1987 ²⁴
5	SA	99.5	99.0	%	%	314.8-404.8	0.3	79.2-99.4	0.3	YES	YES	NO	Poettmann and Katz, 1945 ²⁰
5	SS	99.995	>99.8	%	%	312.35- 326.15	0.05	77.5- 85.2	0.25	Yes		Yes	Chen et al, 2003 ²⁵
5	SA	99.9	99.4	%	%	408.1-463.1	0.1	45.2-81.8	0.1	NO	YES	NO	Leu and Robinson, 1987 ²⁶
6	SS	99.9	99.9	%	%	313.6-351.8	0.1	80.4-102.0	0.6	YES	YES	NO	Choi and Yeo, 1998 ²⁷
6	SS	> 99.5	> 99.5	Mole %	Mole %	304.5-507.4	0.3	30.2-117.2	0.3	YES	YES	NO	Liu et al., 2003 ²⁸
7	SA	> 99.9	> 99.9	Mole %	Mole %	310.6-477.2	0.18	77.9-137.1	0.21	NO	YES	NO	Kalra et al., 1978 ²⁹
7	SS	99.9	99.9	%	%	324.0-364.3	0.1	93.0-118.8	0.6	YES	YES	NO	Choi and Yeo, 1998 ²⁷
7	DS	N/A	N/A	N/A	N/A	304.2-620.1	N/A	27.0-133.0	0.5	NO	NO-	NO	Chester and Haynes, 1997 ³⁰
8	SS	99.9	99.9	%	%	329.4-359.5	0.1	101.2-130.3	0.6	YES	YES	NO	Choi and Yeo, 1998 ²⁷
9	SS	99.9	99.9	%	%	342.3-386.8	0.1	119.2-148.0	0.6	YES	YES	NO	Choi and Yeo, 1998 ²⁷
10	SA	0.9995	0.9934	Mole fr.	Mole fr.	304.1-619.3	0.09	21.0-176.8	0.01	YES	YES	YES	Reamer and Sage, 1963 ³¹
10	DS	Reagent grade	SFC/S FE grade	N/A	N/A	304.2-620.1	N/A	21.1-185	0.5	NO	NO	NO	Chester and Haynes, 1997 ³⁰
10	DA	99.99	99.0	%	%	344.3-377.6	N/A	127.2-164.9	N/A	YES	NO	YES	Nagarajan and Robinson, 1986 ³²
13	SS	99.99	99.0	%	%	300.8-377.4	0.25	67.5-198.0	0.12	YES	NO	NO	Enick et al., 1985 ³³
13	SS	99.99	99.0	%	%	310.8-313.0	0.25	82.77-86.32	0.12	YES	NO	NO	Enick et al., 1985 ³³
14	SS	N/A	N/A	N/A	N/A	283.1-393.5	N/A	78.2- 997.8	N/A	NO	NO	NO	Scheidgen, 1997 ³⁴
14	SA	N/A	N/A	N/A	N/A	283.0-353.0	N/A	80.0-215.0	N/A	NO	NO	NO	Scheidgen and Schneider, 2000 ³⁵
15	SA	N/A	N/A	N/A	N/A	290.0-353.0	N/A	120.0-210.0	N/A	NO	NO	NO	Scheidgen and Schneider, 2000 ³⁵
15	SA	N/A	N/A	N/A	N/A	283-393	0.1	100-1000	1	NO	NO	NO	Pöhler et al. 1996 ³⁶
15	SS	N/A	N/A	N/A	N/A	290.0-387.66	N/A	120.9-995	N/A	NO	NO	NO	Scheidgen, 1994 ³⁷
16	SS	N/A	N/A	N/A	N/A	297.6-389.5	N/A	165.2-991.7	N/A	NO	NO	NO	Scheidgen, 1994 ³⁷
16	DA	N/A	N/A	N/A	N/A	308.1-343.1	N/A	122.9-258.7	N/A	YES	NO	NO	Charoensombut-Amon et al, 1986 ³⁸
16	SA	N/A	N/A	N/A	N/A	293-393	0.1	100-1000	1	NO	NO	NO	Pöhler et al. 1996 ³⁶

Table A2. Data sets of experimental critical points available for CO₂ + n-Alkane binary mixtures													
CN	Method	Purity		Units for Purity		T range (K)	Absolute T uncertainty (K)	P range (bar)	Absolute P Uncertainty (bar)	Composition informed	Composition uncertainty	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk								
16	SA	N/A	N/A	N/A	N/A	295.0-393.0	N/A	150.0-100.0	N/A	NO	NO	NO	Scheidgen and Schneider, 2000 ³⁵
16	SA	N/A	>99.5	N/A	%	393.2	0.2	256	2.0	YES	YES	NO	Spee and Schneider, 1991 ³⁹
17	SS	N/A	N/A	N/A	N/A	304.7-393.1	N/A	203.3-991.1	N/A	NO	NO	NO	Scheidgen, 1997 ³⁴
17	SS	N/A	N/A	N/A	N/A	323.2-393.2	N/A	213-273	N/A	NO	NO	NO	Pöhler, 1994 ⁴⁰
18	SS	N/A	N/A	N/A	N/A	333.2-393.2	N/A	240-287	N/A	NO	NO	NO	Pöhler, 1994 ⁴⁰
18	SA	N/A	N/A	N/A	N/A	323-393	0.1	235-290	1	YES	NO	NO	Pöhler et al. 1996 ³⁶
19	SS	N/A	N/A	N/A	N/A	317.2-393.5	N/A	269.2-995.4	N/A	NO	NO	NO	Scheidgen, 1997 ³⁴
19	SS	N/A	N/A	N/A	N/A	318.2-348.2	N/A	275-455	N/A	NO	NO	NO	Pöhler, 1994 ⁴⁰
19	SA	N/A	>99.0	N/A	%	353.2-393.2	0.1	275.0-303.0	1.0	YES	NO	NO	Kordikowski and Schneider 1993 ⁴¹
20	SA	N/A	>99.0	N/A	%	353.2-393.2	0.1	302.0-320.0	1.0	YES	NO	NO	Kordikowski and Schneider 1993 ⁴¹
22	SS	N/A	N/A	N/A	N/A	334.2-392.3	N/A	350.3-991.0	N/A	NO	NO	NO	Scheidgen, 1997 ³⁴
22	SS	N/A	N/A	N/A	N/A	393.2	N/A	357	N/A	NO	NO	NO	Pöhler, 1994 ⁴⁰
22	SA	N/A	99	N/A	N/A	343.2-393.2	0.1	370-430	1	YES	NO	NO	Pöhler and Schneider 1995 ⁴²
24	SA	N/A	>99.0	N/A	%	393.2	0.1	398.0	1.0	YES	NO	NO	Kordikowski and Schneider 1993 ⁴¹

SA: Static analytic. SS: Static synthetic. DA: Dynamic Analytic. DS: Dynamic synthetic. Mole fr.: Mole fraction. Mass fr.: Mass fraction

Table A3. Data Sets of Experimental Liquid-Liquid-Vapor equilibrium (LLV) points available for CO ₂ + n-Alkane binary mixtures.													
CN	Method	Purity		Units for Purity		T range (K)	Absolute T uncertainty (K)	P range (bar)	Absolute P uncertainty (bar)	Phases informed	Composition uncertainty informed	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk								
8	SA	99.99	99.0	Mole %	Mole %	216.0-231.1	0.03	5.1-9.1	0.071	L1	YES	YES	Hottovy et al., 1982 ¹⁴
8	SA	99.99	99.0	Mole %	Mole %	217.2-231.0	0.03	5.3-9	0.071	L2	YES	YES	Hottovy et al., 1982 ¹⁴
10	SS	> 99.99	>99.0	%	%	235.6-248.7	0.15	10.6-16.4	0.07	L1-L2	NO	YES	Kulkarni et al., 1974 ¹⁵
12	SA	99.99	99	Mole %	Mole %	254.3-267.3	0.02	20.1-28.8	0.07	L1-L2	NO	YES	Hottovy et al. 1981 ¹⁶
13	SS	99.99	99.0	%	%	310.8-313.0	0.25	82-85.5	0.12	L1-L2	NO	YES	Enick et al., 1985 ³³
13	SA	99.99	99	Mole %	Mole %	255.2-279.0	0.02	20.8-39.3	0.07	L1-L2	NO	YES	Hottovy et al. 1981 ¹⁶
13	SA	99.99	99	Mole %	Mole %	310.7-314.0	0.02	81.1-87.2	0.07	L1-L2	YES	YES	Fall and Luks 1985 ⁸
14	SA	99.99	99	Mole %	Mole %	269.1-311.1	0.02	30.8-82.6	0.07	L1-L2	NO	YES	Hottovy et al. 1981 ¹⁶
14	SA	99.99	99	%	%	279.3-303.1	0.03	39.8-69.2	0.1	L1-L2-V	YES	YES	Van der Steen et al. 1989 ⁴³
14	ISA	99.995	N/A	Volume %	N/A	290-300	0.1	51.9-54.9	0.2	L1-L1	NO	YES	Laugier et al., 1990 ⁴⁴
15	SA	99.99	99	Mole %	Mole %	270.4-309.4	0.02	31.9-80.2	0.07	L1-L2	NO	YES	Hottovy et al. 1981 ¹⁶
15	SA	99.99	99	%	%	273.4-308.4	0.03	34.5-78.4	0.1	L1-L2-V	YES	YES	Van der Steen et al. 1989 ⁴³
15	SA	0.997	0.99	Mass fraction	Mass fraction	298.15	0.1	62.8	1.25	L1-L2-V	YES	NO	Secuianu et al., 2007 ⁴⁵
15	SA	0.997	0.99	Mass fraction	Mass fraction	292.8-309.1	0.1	55.3-80.2	0.1	N/A	YES	NO	Secuianu et al., 2010 ⁴⁶
16	SA	99.99	98	%	%	283.2-306.1	0.03	44.4-75.5	0.1	L1-L2-V	YES	YES	Van der Steen et al. 1989 ⁴³
19	SA	99.99	99	%	%	292.9-305.5	0.02	56.7-75.7	0.07	L1-L2	YES	YES	Fall et al. 1985 ¹⁷
20	SA	99.99	99	Mole %	Mole %	300.4-305.2	0.05	67.5-75.5	0.07	L1-L2	YES	YES	Huie et al. 1973 ⁴⁷
20	SA	99.99	99	%	%	300.3-305.2	0.02	67.3-75.4	0.07	L1-L2	YES	YES	Fall et al. 1985 ¹⁷
21	SA	99.99	99	%	%	301.5-305	0.02	69.2-75.1	0.07	L1-L2	YES	YES	Fall et al. 1985 ¹⁷

SA: Static analytic. ISA: Indirect static analytic. SS: Static synthetic.

Table A4. Isothermal Data Sets of Experimental Fluid-Fluid Equilibria (Pxy) available for CO ₂ + n-Alkane binary mixtures														
CN	Method	Purity		Units for Purity		T (K)	Absolute T Uncertainty (K)	P range (bar)	Absolute P uncertainty (bar)	Alk. richer phase	CO ₂ richer phase	Composition uncertainty informed	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk									
1	SA	99.99	99.99	%	%	153.1	0.01	11.5-11.6	0.07	YES	YES	YES	NO	Mraw et al, 1978 ¹⁸
1	SA	99.99	99.99	%	%	173.1	0.01	24.7-26.0	0.07	YES	YES	YES	NO	Mraw et al, 1978 ¹⁸
1	SA	99.99	99.99	%	%	183.1	0.01	33.6-36.4	0.07	YES	YES	YES	NO	Mraw et al, 1978 ¹⁸
1	SA	99.99	99.99	%	%	193.1	0.01	42.9-47.4	0.07	YES	YES	YES	NO	Mraw et al, 1978 ¹⁸
1	SA	99.99	99.99	%	%	203.1	0.01	47.6-52.7	0.07	YES	YES	YES	NO	Mraw et al, 1978 ¹⁸
1	SA	99.99	99.99	%	%	210.1	0.01	41.6-57.5	0.07	YES	YES	YES	NO	Mraw et al, 1978 ¹⁸
1	SA	99.99	99.99	%	%	219.3	0.01	5.7-63.8	0.07	YES	YES	YES	NO	Mraw et al, 1978 ¹⁸
1	SA	99.995	99.99	%	%	230	0.01	8.9-71.4	0.1	YES	YES	YES	NO	Webster and Kidnay, 2001 ⁴⁸
1	SA	99.995	99.99	%	%	270	0.01	32-84.2	0.1	YES	YES	YES	NO	Webster and Kidnay, 2001 ⁴⁸
1	DA	N/A	N/A	N/A	N/A	270	0.02	31.6-83.2	0.0015	YES	YES	YES	NO	Somait and Kidnay, 1978 ⁴⁹
1	SA	99.97	99.95	%	%	288.5	0.01	50.5-80.4	0.2	YES	YES	YES	NO	Xu et al, 1992 ⁵⁰
1	SA	99.97	99.95	%	%	293.4	0.01	56.5-78.8	0.2	YES	YES	YES	NO	Xu et al, 1992 ⁵⁰
1	DA	99.99	99.97	%	%	230	0.02	8.9-69.9	0.35	YES	YES	YES	NO	Wei et al, 1995 ⁵¹
1	DA	99.99	99.97	%	%	250	0.02	17.8-80.5	0.35	YES	YES	YES	NO	Wei et al, 1995 ⁵¹
1	DA	99.99	99.97	%	%	270	0.02	32.1-83.8	0.35	YES	YES	YES	NO	Wei et al, 1995 ⁵¹
1	DA	99.991	99.97	%	%	219.3	0.02	5.81- 38.61	0.14	YES	YES	YES	No	Al-Sahhaf et al, 1983 ⁵²
1	DA	99.991	99.97	%	%	240	0.02	12.87- 77.72	0.14	YES	YES	YES	No	Al-Sahhaf et al, 1983 ⁵²
1	DA	99.991	99.97	%	%	270	0.02	32.03- 85.11	0.14	YES	YES	YES	No	Al-Sahhaf et al, 1983 ⁵²
1	DA	N/A	99.97	N/A	%	230	0.01	8.9-71.75	0.05	YES	YES	YES	NO	Davalos et al., 1976 ⁵³
1	DA	N/A	99.97	N/A	%	250	0.01	17.95-81.77	0.05	YES	YES	YES	NO	Davalos et al., 1976 ⁵³
1	DA	N/A	99.97	N/A	%	270	0.01	31.94-85.93	0.05	YES	YES	YES	NO	Davalos et al., 1976 ⁵³
2	DA	99.99	99	%	%	207	0.02	2.9-4.7	0.35	YES	YES	YES	NO	Wei et al, 1995 ⁵¹
2	DA	99.99	99	%	%	210	0.02	3.3-5.5	0.35	YES	YES	YES	NO	Wei et al, 1995 ⁵¹
2	DA	99.99	99	%	%	213	0.02	3.8-6.2	0.35	YES	YES	YES	NO	Wei et al, 1995 ⁵¹
2	DA	99.99	99	%	%	230	0.02	7.0-11.5	0.35	YES	YES	YES	NO	Wei et al, 1995 ⁵¹
2	DA	99.99	99	%	%	250	0.02	13.3-21.3	0.35	YES	YES	YES	NO	Wei et al, 1995 ⁵¹
2	DA	99.99	99	%	%	270	0.02	22.1 -35.7	0.35	YES	YES	YES	NO	Wei et al, 1995 ⁵¹
3	SS	> 99.9	> 99.8	%	%	294.3	0.01	22.1-47.1	0.001	YES	NO	YES	NO	Kaminishi et al, 1987 ⁵⁴
3	SA	99.995	99.5	%	%	230	0.01	0.97-7.8	0.1	YES	YES	YES	NO	Webster and Kidnay, 2001 ⁴⁸
3	SA	99.995	99.5	%	%	270	0.01	4.3-92.9	0.1	YES	YES	YES	NO	Webster and Kidnay, 2001 ⁴⁸
3	DA	99.99	99.95	%	%	240	0.01	1.5-12.7	0.1	YES	YES	YES	NO	Yucelen and Kidnay, 1999 ⁵⁵
3	DA	99.99	99.95	%	%	270	0.01	4.28-31.6	0.1	YES	YES	YES	NO	Yucelen and Kidnay, 1999 ⁵⁵
3	DA	99.99	99.95	%	%	330	0.01	19.5-57.7	0.1	YES	YES	YES	NO	Yucelen and Kidnay, 1999 ⁵⁵
4	DA	99.99	99.98	%	%	319.3	N/A	21.8-76.3	N/A	YES	YES	YES	YES	Hsu et al, 1985 ²³

Table A4. Isothermal Data Sets of Experimental Fluid-Fluid Equilibria (Pxy) available for CO ₂ + n-Alkane binary mixtures														
CN	Method	Purity		Units for Purity		T (K)	Absolute T Uncertainty (K)	P range (bar)	Absolute P uncertainty (bar)	Alk. richer phase	CO ₂ richer phase	Composition uncertainty informed	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk									
4	DA	99.99	99.98	%	%	344.3	N/A	32.1-81.2	N/A	YES	YES	YES	YES	Hsu et al, 1985 ²³
4	DA	99.99	99.98	%	%	377.6	N/A	28.8-75.8	N/A	YES	YES	YES	YES	Hsu et al, 1985 ²³
4	SA	99.9	99.9	%	%	368.1	0.1	13.7-78	0.1	YES	YES	YES	NO	Leu and Robinson, 1987 ²⁴
4	SA	99.9	99.9	%	%	393.1	0.1	21.8-66.8	0.1	YES	YES	YES	NO	Leu and Robinson, 1987 ²⁴
4	SA	99.9	99.9	%	%	418.1	0.1	32.7-46.4	0.1	YES	YES	YES	NO	Leu and Robinson, 1987 ²⁴
4	DA	N/A	N/A	N/A	N/A	310.9	0.05	3.6-74	0.07	YES	YES	NO	YES	Shibata and Sandler, 1989 ⁵⁶
4	DA	N/A	N/A	N/A	N/A	344.3	0.05	8.3-80.6	0.07	YES	YES	NO	YES	Shibata and Sandler, 1989 ⁵⁶
4	DA	N/A	N/A	N/A	N/A	410.9	0.05	30.1-51.6	0.07	YES	YES	NO	YES	Shibata and Sandler, 1989 ⁵⁶
4	DA	99.99	99.94	%	%	309.1	0.01	3.4-24.6	0.03	YES	YES	YES	NO	Weber et al., 1989 ⁵⁷
4	DA	99.99	99.94	%	%	344.3	0.01	8.3-72.9	0.03	YES	YES	YES	NO	Weber et al., 1989 ⁵⁷
4	DA	99.99	99.94	%	%	369.3	0.01	14.2-78.5	0.03	YES	YES	YES	NO	Weber et al., 1989 ⁵⁷
4	DA	99.99	99.94	%	%	394.3	0.01	22.5-65.6	0.03	YES	YES	YES	NO	Weber et al., 1989 ⁵⁷
4	SA	> 99.99	> 99.95	%	%	310.9	0.1	11-70.8	0.3	YES	YES	YES	NO	Traub and Stephan, 1990 ⁵⁸
4	SA	0.999	0.999	Mole fr.	Mole fr.	310.9	0.06	4.4-65.5	0.01	YES	YES	YES	YES	Olds et al., 1949 ²²
4	SA	0.999	0.999	Mole fr.	Mole fr.	344.3	0.06	10.3-79.7	0.01	YES	YES	YES	YES	Olds et al., 1949 ²²
4	SA	0.999	0.999	Mole fr.	Mole fr.	377.6	0.06	21.4-75.2	0.01	YES	YES	YES	YES	Olds et al., 1949 ²²
4	SA	0.999	0.999	Mole fr.	Mole fr.	410.9	0.06	42.6-51.9	0.01	YES	YES	YES	YES	Olds et al., 1949 ²²
4	DA	99.9	99.9	%	%	250	0.02	0.39-16.3	0.0035	YES	YES	YES	YES	Brown et al, 1989 ⁵⁹
4	DA	99.9	99.9	%	%	270	0.02	0.9-27.7	0.0035	YES	YES	YES	YES	Brown et al, 1989 ⁵⁹
5	SA	99.9	99.4	%	%	408.1	0.1	11.8-88.8	0.1	YES	YES	YES	NO	Leu and Robinson, 1987 ²⁶
5	SA	99.9	99.4	%	%	438.1	0.1	20.2-69.5	0.1	YES	YES	YES	NO	Leu and Robinson, 1987 ²⁶
5	SA	99.9	99.4	%	%	463.1	0.1	29.5-46.3	0.1	YES	YES	YES	NO	Leu and Robinson, 1987 ²⁶
5	DA	99.99	> 99	%	%	252.7	0.01	1.6-17.7	0.07	YES	YES	YES	NO	Cheng et al, 1989 ⁶⁰
5	DA	99.99	> 99	%	%	273.4	0.01	2.6-32.	0.07	YES	YES	YES	NO	Cheng et al, 1989 ⁶⁰
5	DA	99.99	> 99	%	%	294.1	0.01	1.7-51.7	0.07	YES	YES	YES	NO	Cheng et al, 1989 ⁶⁰
5	DA	99.99	> 99	%	%	311.6	0.01	4.1-70.4	0.07	YES	YES	YES	NO	Cheng et al, 1989 ⁶⁰
5	DA	99.99	> 99	%	%	344.3	0.01	4.6-89.8	0.07	YES	YES	YES	NO	Cheng et al, 1989 ⁶⁰
5	DA	99.99	> 99	%	%	377.7	0.01	7.8-94.9	0.07	YES	YES	YES	NO	Cheng et al, 1989 ⁶⁰
5	DA	99.99	> 99	%	%	394.3	0.01	9.7-90.2	0.07	YES	YES	YES	NO	Cheng et al, 1989 ⁶⁰
5	DA	99.99	> 99	%	%	423.5	0.01	19.7-76.3	0.07	YES	YES	YES	NO	Cheng et al, 1989 ⁶⁰

Table A4. Isothermal Data Sets of Experimental Fluid-Fluid Equilibria (Pxy) available for CO₂ + n-Alkane binary mixtures

CN	Method	Purity		Units for Purity		T (K)	Absolute T Uncertainty (K)	P range (bar)	Absolute P uncertainty (bar)	Alk. richer phase	CO ₂ richer phase	Composition uncertainty informed	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk									
5	DA	99.99	> 99	%	%	442.5	0.01	26.2-60.6	0.07	YES	YES	YES	NO	Cheng et al, 1989 ⁶⁰
5	DA	99.99	> 99	%	%	458.5	0.01	31.2-43.5	0.07	YES	YES	YES	NO	Cheng et al, 1989 ⁶⁰
5	SA	99.99	99.6	%	%	310.1	0.03	5.6-72.1	0.3	YES	YES	YES	NO	Tochigi et al, 1998 ⁶¹
5	SA	99.99	99.6	%	%	333.1	0.03	5.9-86.4	0.3	YES	YES	YES	NO	Tochigi et al, 1998 ⁶¹
5	SA	99.99	99.6	%	%	363.1	0.03	9.3-95.4	0.3	YES	YES	YES	NO	Tochigi et al, 1998 ⁶¹
6	SA	99.99	> 99.99	%	%	298.1	N/A	4.4-51.4	0.01	YES	YES	NO	NO	Ohgaki and Katayama, 1976 ⁶²
6	SA	99.99	> 99.99	%	%	313.1	N/A	6.2-75.6	0.01	YES	YES	NO	NO	Ohgaki and Katayama, 1976 ⁶²
6	SS	> 99.9	> 99.8	%	%	273.1	0.01	10.7-31.5	0.001	YES	NO	YES	NO	Kaminishi et al, 1987 ⁵⁴
6	SS	> 99.9	> 99.8	%	%	283.1	0.01	12.4-40.1	0.001	YES	NO	YES	NO	Kaminishi et al, 1987 ⁵⁴
6	SS	> 99.9	> 99.8	%	%	298.1	0.01	15.3-55.4	0.001	YES	NO	YES	NO	Kaminishi et al, 1987 ⁵⁴
6	SS	> 99.9	> 99.8	%	%	303.1	0.01	16.2-61.1	0.001	YES	NO	YES	NO	Kaminishi et al, 1987 ⁵⁴
6	SA	99.68	> 99.9	%	%	303.1	0.002	20.2-67.5	0.02	YES	YES	YES	NO	Wagner and Wichtierle, 1987 ⁶³
6	SA	99.68	> 99.9	%	%	313.1	0.002	20.8-78.7	0.02	YES	YES	YES	NO	Wagner and Wichtierle, 1987 ⁶³
6	SA	99.68	> 99.9	%	%	323.1	0.002	18.6-84.9	0.02	YES	YES	YES	NO	Wagner and Wichtierle, 1987 ⁶³
6	SA	99.99	99.0	Mole %	Mole %	313.1	0.05	7.8-74.8	0.14	YES	YES	N/A	NO	Li et al, 1981 ⁶⁴
6	SA	99.99	99.0	Mole %	Mole %	353.1	0.05	8.6-106.6	0.14	YES	YES	N/A	NO	Li et al, 1981 ⁶⁴
6	SA	99.99	99.0	Mole %	Mole %	393.1	0.05	9.0-116.0	0.14	YES	YES	N/A	NO	Li et al, 1981 ⁶⁴
7	SA	> 99.9	> 99.9	Mole %	Mole %	310.6	0.18	1.9-75.6	0.21	YES	YES	YES	YES	Kalra et al., 1978 ²⁹
7	SA	> 99.9	> 99.9	Mole %	Mole %	352.6	0.18	4.2-116.1	0.21	YES	YES	YES	YES	Kalra et al., 1978 ²⁹
7	SA	> 99.9	> 99.9	Mole %	Mole %	394.3	0.18	11.3-133.1	0.21	YES	YES	YES	YES	Kalra et al., 1978 ²⁹
7	SA	> 99.9	> 99.9	Mole %	Mole %	477.2	0.18	17.5-99.2	0.21	YES	YES	YES	YES	Kalra et al., 1978 ²⁹
7	DA	99.9	>99.0	Vol %	Vol%	394.0	0.1	50-130	0.2	YES	YES	YES	NO	Inomata et al, 1986 ⁶⁵
8	DA	99.99	99	%	%	313.2	0.04	15-75	0.4	YES	YES	YES	NO	Weng and Lee 1992 ⁶⁶
8	DA	99.99	99	%	%	328.2	0.04	20-95	0.4	YES	YES	YES	NO	Weng and Lee 1992 ⁶⁶
8	DA	99.99	99	%	%	348.2	0.04	20-113.5	0.4	YES	YES	YES	NO	Weng and Lee 1992 ⁶⁶
8	SA	99.995	99	%	Mole %	322.4	0.03	20.1-85.3	0.08	YES	YES	NO	NO	Jiménez-Gallegos 2006 ⁶⁷
8	SA	99.995	99	%	Mole %	348.3	0.03	20.7-114.6	0.08	YES	YES	NO	NO	Jiménez-Gallegos 2006 ⁶⁷
8	SA	99.995	99	%	Mole %	372.5	0.03	31.5-137.7	0.08	YES	YES	NO	NO	Jiménez-Gallegos 2006 ⁶⁷
8	SA	99.995	> 99	Mole %	%	322.4	0.03	20.1-85.3	0.06	YES	YES	YES	NO	Jiménez-Gallegos et al., 2006 ⁶⁷
8	SA	99.995	> 99	Mole %	%	348.2	0.03	20.7-114.6	0.06	YES	YES	YES	NO	Jiménez-Gallegos et al., 2006 ⁶⁷
8	SA	99.995	> 99	Mole %	%	372.5	0.03	31.5-137.7	0.06	YES	YES	YES	NO	Jiménez-Gallegos et al., 2006 ⁶⁷
9	DA	99.999	99.99	%	%	343.2	0.1	37.3-118.0	0.07	YES	YES	YES	NO	Jennings and Schucker, 1996 ⁶⁸
9	DA	99.999	99	%	%	343.2	0.3	37.3-118	0.2	YES	YES	NO	NO	Jennings and Schucker 1996 ⁶⁸
10	DA	99.999	99.99	%	%	344.2	0.1	43.3-118.5	0.07	YES	YES	YES	NO	Jennings and Schucker, 1996 ⁶⁸
10	SA	0.9995	0.9934	Mole fr.	Mole fr.	277.6	2	3.45-39.1	0.01	YES	YES	YES	YES*	Reamer and Sage, 1963 ³¹
10	SA	0.9995	0.9934	Mole fr.	Mole fr.	310.9	0.09	6.9-80.0	0.01	YES	YES	YES	YES*	Reamer and Sage, 1963 ³¹

Table A4. Isothermal Data Sets of Experimental Fluid-Fluid Equilibria (Pxy) available for CO₂ + n-Alkane binary mixtures

CN	Method	Purity		Units for Purity		T (K)	Absolute T Uncertainty (K)	P range (bar)	Absolute P uncertainty (bar)	Alk. richer phase	CO ₂ richer phase	Composition uncertainty informed	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk									
10	SA	0.9995	0.9934	Mole fr.	Mole fr.	344.3	0.09	13.8-128.2	0.01	YES	YES	YES	YES*	Reamer and Sage, 1963 ³¹
10	SA	0.9995	0.9934	Mole fr.	Mole fr.	377.6	0.09	13.8-164.9	0.01	YES	YES	YES	YES*	Reamer and Sage, 1963 ³¹
10	SA	0.9995	0.9934	Mole fr.	Mole fr.	410.9	0.09	13.8-185.6	0.01	YES	YES	YES	YES*	Reamer and Sage, 1963 ³¹
10	SA	0.9995	0.9934	Mole fr.	Mole fr.	444.3	0.09	13.8-188.4	0.01	YES	YES	YES	YES*	Reamer and Sage, 1963 ³¹
10	SA	0.9995	0.9934	Mole fr.	Mole fr.	477.6	0.09	13.8-178.4	0.01	YES	YES	YES	YES*	Reamer and Sage, 1963 ³¹
10	SA	0.9995	0.9934	Mole fr.	Mole fr.	510.9	0.09	13.8-153.3	0.01	YES	YES	YES	YES*	Reamer and Sage, 1963 ³¹
10	DA	99.9	99.9	%	%	313.0	0.02	10.0-77.9	0.1	NO	YES	YES	NO	Chylinski and Gregorowicz 1998 ⁶⁹
10	DA	> 99.9	> 99	Volume %	%	311.0	0.1	45.5-68.6	0.18	YES	YES	NO	NO	Iwai et al., 1994 ⁷⁰
10	DA	> 99.9	> 99	Volume %	%	344.3	0.1	55.1-118.5	0.18	YES	YES	NO	NO	Iwai et al., 1994 ⁷⁰
10	DA	99.9	> 99.0	Volume %	Volume %	411.2	0.1	50-180	0.2	YES	YES	YES	NO	Inomata et al, 1986 ⁶⁵
10	DA	99.99	99.0	%	%	344.3	N/A	63.85-127.4	0.14	YES	YES	NO	YES	Nagarajan and Robinson , 1986 ³²
10	DA	99.99	99.0	%	%	377.6	N/A	103.4-164.9	0.14	YES	YES	NO	YES	Nagarajan and Robinson , 1986 ³²
10	DA	> 99.99	> 99.0	%	%	462.5	0.11	19.6-51.3	0.03	YES	YES	NO	NO	Sebastian et al, 1980 ⁷¹
10	DA	> 99.99	> 99.0	%	%	476.9	0.11	14.4-50.7	0.03	YES	YES	NO	NO	Sebastian et al, 1980 ⁷¹
10	DA	> 99.99	> 99.0	%	%	542.9	0.11	19.6-51.7	0.03	YES	YES	NO	NO	Sebastian et al, 1980 ⁷¹
10	DA	> 99.99	> 99.0	%	%	583.6	0.25	20.0-51.0	0.03	YES	YES	NO	NO	Sebastian et al, 1980 ⁷¹
10	DA	99.99	99.8	%	%	310.9	0.02	27.8-80.4	0.08	YES	NO	NO	YES	Han et al, 1992 ⁷²
10	DA	99.98	99.0	%	%	313.1	0.01	14.3-78.3	0.16	YES	YES	YES	YES	Adams et al, 1988 ⁷³
10	DA	99.9	99.9	%	%	313	0.02	10-77.9	0.1	NO	YES	YES	NO	Chylinski and Gregorowicz 1998 ⁶⁹
10	DA	99.999	99	%	%	343.2	0.3	43.3-118.5	0.2	YES	YES	NO	NO	Jennings and Schucker 1996 ⁶⁸
10	DA	99.5	99	%	%	344.3	0.06	8.9-127	0.14	YES	YES	YES	YES	Shaver et al. 2001 ⁷⁴
10	SA	99.99	99	%	%	344.8	0.1	2.6-11	0.05	YES	NO	YES	YES	Tsuji et al. 2004 ⁷⁵
10	SA	99.995	> 99	Mole %	%	319.1	0.03	34.8-89	0.06	YES	YES	YES	NO	Jiménez-Gallegos et al., 2006 ⁶⁷
10	SA	99.995	> 99	Mole %	%	344.7	0.03	45.8-126.6	0.06	YES	YES	YES	NO	Jiménez-Gallegos et al., 2006 ⁶⁷
10	SA	99.995	> 99	Mole %	%	372.9	0.03	32.4-160.6	0.06	YES	YES	YES	NO	Jiménez-Gallegos et al., 2006 ⁶⁷
12	SS	N/A	> 99	-	%	313.2	N/A	79.5-85.7	< 1	YES	YES	NO	NO	Nieuwoudt and du Rand 2002 ⁷⁶
12	SS	N/A	> 99	-	%	323.2	N/A	94.4-102.9	< 1	YES	YES	NO	NO	Nieuwoudt and du Rand 2002 ⁷⁶
12	SS	N/A	> 99	-	%	333.2	N/A	110.4-123.3	< 1	YES	YES	NO	NO	Nieuwoudt and du Rand 2002 ⁷⁶
12	SS	N/A	> 99	-	%	343.2	N/A	120.0-143	< 1	YES	YES	NO	NO	Nieuwoudt and du Rand 2002 ⁷⁶
12	SA	99.995	99.9	%	%	318.1	0.5	9.5-45.28	0.007	YES	YES	YES	NO	Gardeler et al, 2002 ⁷⁷
14	DA	99.99	99	%	%	344.3	N/A	69-163.8	N/A	YES	YES	NO	YES	Gasem et al. 1989 ⁷⁸
15	SA	99.999	99	%	%	313.2	N/A	17.0-64.1	N/A	YES	NO	YES	YES	Tanaka and Yamaki, 1993 ⁷⁹
15	SA	0.997	0.99	Mass fr.	Mass fr.	298.1	0.1	5.9-127.8	1.25	YES	YES	YES	NO	Secuianu et al., 2007 ⁴⁵
15	SA	0.997	0.99	Mass fr.	Mass fr.	316.1	0.1	5.1-105.3	1.25	YES	YES	YES	NO	Secuianu et al., 2007 ⁴⁵
15	SA	0.997	0.99	Mass fr.	Mass fr.	293.1	0.1	7.6-141.2	0.1	YES	YES	YES	NO	Secuianu et al., 2010 ⁴⁶
15	SA	0.997	0.99	Mass fr.	Mass fr.	303.1	0.1	7.2-100.3	0.1	YES	YES	YES	NO	Secuianu et al., 2010 ⁴⁶

Table A4. Isothermal Data Sets of Experimental Fluid-Fluid Equilibria (Pxy) available for CO₂ + n-Alkane binary mixtures

CN	Method	Purity		Units for Purity		T (K)	Absolute T Uncertainty (K)	P range (bar)	Absolute P uncertainty (bar)	Alk. richer phase	CO ₂ richer phase	Composition uncertainty informed	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk									
15	SA	0.997	0.99	Mass fr.	Mass fr.	313.1	0.1	5.6-110.3	0.1	YES	YES	YES	NO	Secuianu et al., 2010 ⁴⁶
15	SA	0.997	0.99	Mass fr.	Mass fr.	333.1	0.1	6.8-139.4	0.1	YES	YES	YES	NO	Secuianu et al., 2010 ⁴⁶
15	SA	0.997	0.99	Mass fr.	Mass fr.	353.1	0.1	9.3-175	0.1	YES	YES	YES	NO	Secuianu et al., 2010 ⁴⁶
16	SS	N/A	99	-	%	313.2	N/A	85.5-165.1	< 1	YES	YES	NO	NO	Nieuwoudt and du Rand 2002 ⁷⁶
16	SS	N/A	99	-	%	323.2	N/A	101.5-168.4	< 1	YES	YES	NO	NO	Nieuwoudt and du Rand 2002 ⁷⁶
16	DA	N/A	N/A	N/A	N/A	343.1	N/A	6.9-258.7	N/A	YES	YES	NO	YES	Charoensombut-Amon et al, 1986 ³⁸
16	DA	N/A	N/A	N/A	N/A	333.1	N/A	6.9-218.6	N/A	YES	YES	NO	YES	Charoensombut-Amon et al, 1986 ³⁸
16	DA	N/A	N/A	N/A	N/A	323.1	N/A	6.9-144.3	N/A	YES	YES	NO	YES	Charoensombut-Amon et al, 1986 ³⁸
16	DA	N/A	N/A	N/A	N/A	313.1	N/A	6.9-122.9	N/A	YES	YES	NO	YES	Charoensombut-Amon et al, 1986 ³⁸
16	DA	N/A	N/A	N/A	N/A	308.1	N/A	6.9-144.3	N/A	YES	YES	NO	NO	Charoensombut-Amon et al, 1986 ³⁸
16	SA	N/A	> 99.5	N/A	%	393.2	0.2	101.0-256.0	1.0	YES	YES	YES	NO	Spee and Schneider, 1991 ³⁹
16	SA	N/A	> 99.0	N/A	%	353.2	0.1	100.0-200.0	1.0	YES	YES	NO	NO	Kordikowski and Schneider, 1993 ⁴¹
16	DA	> 99.99	> 99.0	%	%	463.0	0.11	20.1-51.7	0.03	YES	YES	NO	NO	Sebastian et al, 1980 ⁷¹
16	DA	> 99.99	> 99.0	%	%	542.8	0.11	20.1-50.8	0.03	YES	YES	NO	NO	Sebastian et al, 1980 ⁷¹
16	DA	> 99.99	> 99.0	%	%	623.5	0.11	20.2-50.6	0.03	YES	YES	NO	NO	Sebastian et al, 1980 ⁷¹
16	DA	> 99.99	> 99.0	%	%	663.7	0.11	20.9-50.6	0.03	YES	YES	NO	NO	Sebastian et al, 1980 ⁷¹
16	SA	99.5	> 99.0	%	%	473.1	1.0	101.0-257.0	0.5	YES	YES	YES	NO	Brunner et al, 1994 ⁸⁰
16	SA	99.5	> 99.0	%	%	573.1	1.0	101.0-213.0	0.5	YES	YES	YES	NO	Brunner et al, 1994 ⁸⁰
16	SA	N/A	99	N/A	%	333.2	0.2	5-290	0.1	YES	YES	YES	NO	Holscher et al 1989 ⁸¹
16	SA	N/A	99	N/A	%	393.2	0.2	5-290	0.1	YES	YES	YES	NO	Holscher et al 1989 ⁸¹
16	DA	99.5	99	%	%	305.2	0.45	100-130	0.04	NO	YES	YES	NO	Rose et al. 2000 ⁸²
16	DA	99.5	99	%	%	311.2	0.45	70-180	0.04	NO	YES	YES	NO	Rose et al. 2000 ⁸²
16	SA	99.999	98	%	%	313.2	N/A	17.2-64.7	N/A	YES	NO	YES	YES	Tanaka et al. 1993 ⁷⁹
16	DA	99.9	99	Mole %	Mole %	314.2	0.01	80.6-136.1	0.07	YES	YES	NO	NO	D'Souza et al. 1988 ⁸³
16	DA	99.9	99	Mole %	Mole %	333.2	0.01	76.9-148.7	0.07	YES	YES	NO	NO	D'Souza et al. 1988 ⁸³
16	DA	99.9	99	Mole %	Mole %	353.2	0.01	112.1-161.2	0.07	YES	YES	NO	NO	D'Souza et al. 1988 ⁸³
18	DA	99.998	98	Mole %	Mole %	310	0.05	100-200	0.002	NO	YES	YES	NO	Eustaquio-Rincón, Trejo 2001 ⁸⁴
18	DA	99.998	98	Mole %	Mole %	313	0.05	100-200	0.002	NO	YES	YES	NO	Eustaquio-Rincón, Trejo 2001 ⁸⁴
18	DA	99.998	98	Mole %	Mole %	333	0.05	100-200	0.002	NO	YES	YES	NO	Eustaquio-Rincón, Trejo 2001 ⁸⁴
18	DA	99.998	98	Mole %	Mole %	353	0.05	100-200	0.002	NO	YES	YES	NO	Eustaquio-Rincón, Trejo 2001 ⁸⁴
18	SA	N/A	N/A	N/A	N/A	353.2	0.1	90-260	1	YES	YES	NO	NO	Pöhler et al. 1996 ³⁶
18	SA	N/A	N/A	N/A	N/A	373.2	0.1	90-270	1	YES	YES	NO	NO	Pöhler et al. 1996 ³⁶
18	SA	N/A	N/A	N/A	N/A	393.2	0.1	90-270	1	YES	YES	NO	NO	Pöhler et al. 1996 ³⁶
19	SAV	N/A	> 99.0	N/A	%	353.2	0.1	100.0-275.0	1.0	YES	YES	NO	NO	Kordikowski and Schneider, 1993 ⁴¹
19	SAV	N/A	> 99.0	N/A	%	393.2	0.1	100.0-303.0	1.0	YES	YES	NO	NO	Kordikowski and Schneider, 1993 ⁴¹
19	SA	99.99	99.9	%	%	313	0.1	2.9-86.4	0.07	YES	NO	YES	YES	Elbaccouch et al. 2003 ⁸⁵

Table A4. Isothermal Data Sets of Experimental Fluid-Fluid Equilibria (Pxy) available for CO₂ + n-Alkane binary mixtures

CN	Method	Purity		Units for Purity		T (K)	Absolute T Uncertainty (K)	P range (bar)	Absolute P uncertainty (bar)	Alk. richer phase	CO ₂ richer phase	Composition uncertainty informed	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk									
19	SA	99.99	99	%	%	313.1	0.02	11.2-79.1	0.07	YES	NO	YES	YES	Fall et al. 1985 ¹⁷
19	SA	99.99	99	%	%	333.1	0.02	9.4-79.6	0.07	YES	NO	YES	YES	Fall et al. 1985 ¹⁷
20	SS	N/A	99	N/A	%	315.9	N/A	77.4-249.6	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
20	SS	N/A	99	N/A	%	320.6	N/A	86.4-223.1	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
20	SS	N/A	99	N/A	%	329.6	N/A	104.3-258.9	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
20	SS	N/A	99	N/A	%	339.1	N/A	104.3-303.5	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
20	SS	N/A	99	N/A	%	348.3	N/A	115.0-293.2	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
20	SA	N/A	> 99.0	N/A	%	353.2	0.1	100.0-302.0	1.0	YES	YES	NO	NO	Kordikowski and Schneider, 1993 ⁴¹
20	SA	N/A	> 99.0	N/A	%	393.5	0.1	100.0-320.0	1.0	YES	YES	NO	NO	Kordikowski and Schneider, 1993 ⁴¹
20	SS	99.5	99.0	%	%	323.2	0.05	59.1-147.8	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
20	SS	99.5	99.0	%	%	373.2	0.05	87.9-307.8	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
20	SS	99.5	99.0	%	%	423.2	0.05	109.2-335.7	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
20	SS	99.5	99.0	%	%	473.2	0.05	122.1-344.1	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
20	SA	99.99	99	Mole %	Mole %	310.2	0.05	5.1-76.0	0.07	YES	NO	YES	YES	Huie et al. 1973 ⁴⁷
20	SA	99.99	99	Mole %	Mole %	323.2	0.05	5.1-76.0	0.07	YES	NO	YES	YES	Huie et al. 1973 ⁴⁷
20	SA	99.99	99	Mole %	Mole %	348.2	0.05	5.1-76.0	0.07	YES	NO	YES	YES	Huie et al. 1973 ⁴⁷
20	SA	99.99	99	Mole %	Mole %	373.2	0.05	5.1-76.0	0.07	YES	NO	YES	YES	Huie et al. 1973 ⁴⁷
20	DA	99.5	99	%	%	322.9	N/A	5.4-24.8	N/A	YES	NO	YES	NO	Feng and Mather 1992 ⁸⁷
21	SA	99.99	99	%	%	318.1	0.02	11.5-77.6	0.07	YES	NO	YES	YES	Fall et al. 1985 ¹⁷
21	SA	99.99	99	%	%	338.1	0.02	9.3-78.2	0.07	YES	NO	YES	YES	Fall et al. 1985 ¹⁷
22	SS	99.5	98.0	%	%	323.2	0.05	63.7-123.8	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
22	SS	99.5	98.0	%	%	373.2	0.05	96.1-352.1	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
22	SS	99.5	98.0	%	%	423.2	0.05	121.7-366.4	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
22	SS	99.5	98.0	%	%	473.2	0.05	135.8-373.0	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
22	SA	99.99	99	%	%	323.2	0.01	11.1-71.8	0.07	YES	NO	YES	YES	Fall and Luks 1984 ⁸⁸
22	SA	99.99	99	%	%	348.2	0.01	11.1-71.6	0.07	YES	NO	YES	YES	Fall and Luks 1984 ⁸⁸
22	SA	99.99	99	%	%	373.2	0.01	9.6-65.6	0.07	YES	NO	YES	YES	Fall and Luks 1984 ⁸⁸
22	SA	N/A	99	N/A	%	343.2	0.1	100-430	1	YES	YES	NO	NO	Pöhler and Schneider 1995 ⁴²
22	SA	N/A	99	N/A	%	353.2	0.1	100-390	1	YES	YES	NO	NO	Pöhler and Schneider 1995 ⁴²
22	SA	N/A	99	N/A	%	373.2	0.1	100-370	1	YES	YES	NO	NO	Pöhler and Schneider 1995 ⁴²
22	SA	N/A	99	N/A	N/A	393.2	0.1	100-370	1	YES	YES	NO	NO	Pöhler and Schneider 1995 ⁴²
24	SS	N/A	99	N/A	%	329.7	N/A	154.8-281.4	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
24	SS	N/A	99	N/A	%	339.2	N/A	166.0-283.7	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
24	SS	N/A	99	N/A	%	348.1	N/A	172.4-279.8	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
24	SS	N/A	99	N/A	%	357.1	N/A	185.0-301.6	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
24	SA	N/A	> 99.0	N/A	%	353.2	0.1	100.0-475.0	1.0	YES	YES	NO	NO	Kordikowski and Schneider, 1993 ⁴¹

Table A4. Isothermal Data Sets of Experimental Fluid-Fluid Equilibria (Pxy) available for CO ₂ + n-Alkane binary mixtures														
CN	Method	Purity		Units for Purity		T (K)	Absolute T Uncertainty (K)	P range (bar)	Absolute P uncertainty (bar)	Alk. richer phase	CO ₂ richer phase	Composition uncertainty informed	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk									
24	SA	N/A	> 99.0	N/A	%	393.2	0.1	98.0-300.0	1.0	YES	YES	NO	NO	Kordikowski and Schneider, 1993 ⁴¹
24	SS	99.5	99.0	%	%	373.2	0.05	94.3-389.4	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
24	SS	99.5	99.0	%	%	423.2	0.05	122.8-348.8	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
24	SS	99.5	99.0	%	%	473.2	0.05	140.9-311.3	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
24	DA	99	99	%	%	373.1	0.2	10.1-50.6	0.002	YES	YES	NO	NO	Tsai and Yau 1990 ⁸⁹
24	DA	99	99	%	%	473.1	0.2	10.1-50.6	0.002	YES	YES	NO	NO	Tsai and Yau 1990 ⁸⁹
24	DA	99	99	%	%	573.1	0.2	10.1-50.6	0.002	YES	YES	NO	NO	Tsai and Yau 1990 ⁸⁹
28	SS	99.5	98.0	%	%	373.2	0.05	89.7-222.8	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
28	SS	99.5	98.0	%	%	423.2	0.05	115.0-408.5	0.8	YES	NO	YES	NO	Sato et al, 1998 ⁸⁶
28	SS	N/A	≥ 98	N/A	%	338.5	N/A	140.1-278.7	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
28	SS	N/A	≥ 98	N/A	%	348.0	N/A	148.4-289.9	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
28	SS	N/A	≥ 98	N/A	%	357.0	N/A	162.3-284.4	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
28	SS	N/A	≥ 98	N/A	%	366.4	N/A	172.3-289.5	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
28	DA	99.99	99	%	%	308	0.1	80-220	0.5	NO	YES	YES	YES	Reverchon et al. 1993 ⁹⁰
28	DA	99.99	99	%	%	313	0.1	90-275	0.5	NO	YES	YES	YES	Reverchon et al. 1993 ⁹⁰
28	DA	99.99	99	%	%	318	0.1	105-250	0.5	NO	YES	YES	YES	Reverchon et al. 1993 ⁹⁰
28	DA	99.8	99	%	%	373.4	0.1	10.6-50.5	0.05	YES	NO	NO	NO	Huang et al. 1988 ⁹¹
28	DA	99.8	99	%	%	473.5	0.1	10-50.6	0.05	YES	NO	NO	NO	Huang et al. 1988 ⁹¹
28	DA	99.8	99	%	%	573.4	0.1	9.9-50.5	0.05	YES	YES	NO	NO	Huang et al. 1988 ⁹¹
30	DA	99.99	99	%	%	308	0.1	90-250	0.5	NO	YES	YES	YES	Reverchon et al. 1993 ⁹⁰
30	DA	99.99	99	%	%	318	0.1	105-250	0.5	NO	YES	YES	YES	Reverchon et al. 1993 ⁹⁰
32	SAV	N/A	> 97.0	N/A	%	393.2	0.2	100-630	1.0	YES	YES	YES	NO	Spee and Schneider, 1991 ³⁹
32	SA	99.99	99	%	%	348	0.01	9.5-72.1	0.07	YES	NO	YES	YES	Fall and Luks 1984 ⁸⁸
32	SA	99.99	99	%	%	373	0.01	11.6-72.2	0.07	YES	NO	YES	YES	Fall and Luks 1984 ⁸⁸
32	SA	99.99	99	%	%	398	0.01	9.5-72.3	0.07	YES	NO	YES	YES	Fall and Luks 1984 ⁸⁸
32	DA	99	99	%	%	373.1	0.2	10.1-50.6	0.11	YES	YES	NO	NO	Tsai and Yau 1990 ⁸⁹
32	DA	99	99	%	%	473.1	0.2	10.1-50.6	0.1	YES	YES	NO	NO	Tsai and Yau 1990 ⁸⁹
32	DA	99	99	%	%	573.1	0.2	10.1-50.6	0.1	YES	YES	NO	NO	Tsai and Yau 1990 ⁸⁹
36	SS	N/A	98	N/A	%	344.0	N/A	201.0-289.6	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
36	SS	N/A	98	N/A	%	348.5	N/A	201.4-297.5	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
36	SS	N/A	98	N/A	%	357.0	N/A	205.3-291.3	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶
36	SS	N/A	98	N/A	%	366.9	N/A	211.5-289.7	< 1	YES	YES	NO	YES	Nieuwoudt and du Rand 2002 ⁷⁶

* Density informed for some points. SA: Static analytic. SAV: Static analytic visual. SS: Static synthetic. DA: Dynamic Analytic. DS: Dynamic synthetic.
Mole fr.: Mole fraction. Mass fr.: Mass fraction

Table A5. Isobaric Data Sets of Experimental Fluid-Fluid Equilibria (Txy) available for CO₂ + n-Alkane binary mixtures														
CN	Method	Units for Purity		Purity		P (bar)	Absolute P uncertainty (bar)	T range (K)	Absolute T uncertainty (K)	Alk. richer phase	CO ₂ richer phase	Composition uncertainty informed	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk									
16	Static analytic	N/A	> 99.5	N/A	%	250.0	1.0	294.4-413.3	0.2	YES	YES	YES	NO	Spee and Schneider, 1991 ³⁹
19	Static analytic	N/A	> 99.0	N/A	%	250	1.0	303.1-383.1	0.1	YES	YES	N/A	NO	Kordikowski and Schneider, 1993 ⁴¹
22	Analytic static	N/A	99	N/A	%	34.5	1	330-400	0.1	YES	YES	NO	NO	Pöhler and Schneider 1995 ⁴²

Table A6. Isoplethic Data Sets of Experimental Fluid-Fluid Equilibria available for CO ₂ + n-Alkane binary mixtures													
CN	Method	Purity		Units for Purity		Composition* (z _{CO2})	Absolute composition uncertainty (mole fraction)	T range (K)	Absolute T uncertainty (K)	P range (bar)	Absolute P uncertainty (bar)	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk								
2	SS	0.99995	0.9996	Mole fr.	Mole fr.	0.7397	N/A	292.7-285.1	0.11	61.59-51.56	0.11	YES	Goodwin and Moldover, 1997 ⁹²
2	SS	0.99995	0.9996	Mole fr.	Mole fr.	0.4924	N/A	291.1-285.0	0.06	55.99-49.54	0.07	YES	Goodwin and Moldover, 1997 ⁹²
2	SS	0.99995	0.9996	Mole fr.	Mole fr.	0.4924	N/A	287.3-283.7	0.13	52.03-46.7	0.15	YES	Goodwin and Moldover, 1997 ⁹²
2	SS	0.99995	0.9996	Mole fr.	Mole fr.	0.2516	N/A	295.4-292.4	0.25	52.32-46.84	0.28	YES	Goodwin and Moldover, 1997 ⁹²
3	SA	99.5	99.9	%	%	0.7873	0.003	290.4-311.7	0.3	33.7-69.1	0.3	NO	Poettmann and Katz, 1945 ²⁰
3	SA	99.5	99.9	%	%	0.3599	0.001	295.6-347.6	0.3	12.5-66.7	0.3	NO	Poettmann and Katz, 1945 ²⁰
3	SA	99.5	99.9	%	%	0.5065	0.002	299.9-337.0	0.3	19.0-68.0	0.3	NO	Poettmann and Katz, 1945 ²⁰
3	SA	99.5	99.9	%	%	0.1519	0.0005	303.7-366.1	0.3	11.0-54.5	0.3	NO	Poettmann and Katz, 1945 ²⁰
3	SA	99.5	99.9	%	%	0.9601	0.004	298.9-303.9	0.3	62.9-71.1	0.3	NO	Poettmann and Katz, 1945 ²⁰
3	SA	99.5	99.9	%	%	0.9393	0.004	291.4-304.4	0.3	51.0-70.5	0.3	NO	Poettmann and Katz, 1945 ²⁰
3	DA	99.995	99.99	%	%	0.076	0.001	213.2- 349.8	0.05	0.59-35.74	0.1 %	No	Acosta et al, 1984 ⁹³
3	DA	99.995	99.99	%	%	0.181	0.001	210.9- 349.8	0.05	0.62-46.08	0.1 %	No	Acosta et al, 1984 ⁹³
3	DA	99.995	99.99	%	%	0.244	0.001	216.5- 333.2	0.05	0.83-38.46	0.1 %	No	Acosta et al, 1984 ⁹³
3	DA	99.995	99.99	%	%	0.349	0.001	216.5-333.2	0.05	0.76-51.21	0.1 %	No	Acosta et al, 1984 ⁹³
3	DA	99.995	99.99	%	%	0.442	0.001	216.5- 327.6	0.05	0.76-58.59	0.1 %	No	Acosta et al, 1984 ⁹³
4	SA	99.5	99.0	%	%	0.4551	0.002	305.5-388.8	0.3	6.6-74.6	0.3	NO	Poettmann and Katz, 1945 ²⁰
4	SA	99.5	99.0	%	%	0.7102	0.003	306.1-355.1	0.3	9.6-81.6	0.3	NO	Poettmann and Katz, 1945 ²⁰
4	SA	99.5	99.0	%	%	0.8609	0.003	306.8-324.8	0.3	30.7-77.5	0.3	NO	Poettmann and Katz, 1945 ²⁰
4	SA	99.5	99.0	%	%	0.6073	0.003	299.9-374.8	0.3	6.1-78.8	0.3	NO	Poettmann and Katz, 1945 ²⁰
4	SA	99.5	99.0	%	%	0.3761	0.002	300.8-397.1	0.3	4.5-66.1	0.3	NO	Poettmann and Katz, 1945 ²⁰
4	SA	99.5	99.0	%	%	0.1393	0.005	301.7-416.4	0.3	2.9-50.0	0.3	NO	Poettmann and Katz, 1945 ²⁰
5	SA	99.5	99.0	%	%	0.9511	0.004	295.3-315.1	0.3	31.0-79.8	0.3	NO	Poettmann and Katz, 1945 ²⁰
5	SA	99.5	99.0	%	%	0.8967	0.004	299.8-338.9	0.3	19.0-88.5	0.3	NO	Poettmann and Katz, 1945 ²⁰
5	SA	99.5	99.0	%	%	0.7938	0.003	299.8-383.1	0.3	5.2-99.4	0.3	NO	Poettmann and Katz, 1945 ²⁰
5	SA	99.5	99.0	%	%	0.6687	0.003	299.7-411.4	0.3	1.6-95.3	0.3	NO	Poettmann and Katz, 1945 ²⁰
5	SA	99.5	99.0	%	%	0.4553	0.002	299.9-399.9	0.3	1.4-64.4	0.3	NO	Poettmann and Katz, 1945 ²⁰
6	SS	99.9	99.9	%	%	0.974	0.01461	310.7-314.4	0.1	77.8-81.0	0.6	NO	Choi and Yeo, 1998 ²⁷
6	SS	99.9	99.9	%	%	0.922	0.01383	313.1-343.5	0.1	77.5-97.7	0.6	NO	Choi and Yeo, 1998 ²⁷
6	SS	99.9	99.9	%	%	0.880	0.0132	314.3-358.2	0.1	71.8-106.7	0.6	NO	Choi and Yeo, 1998 ²⁷
6	SS	99.9	99.9	%	%	0.871	0.013065	313.8-346.0	0.1	75.6-101.3	0.6	NO	Choi and Yeo, 1998 ²⁷

Table A6. Isolethic Data Sets of Experimental Fluid-Fluid Equilibria available for CO ₂ + n-Alkane binary mixtures													
CN	Method	Purity		Units for Purity		Composition* (z _{CO2})	Absolute composition uncertainty (mole fraction)	T range (K)	Absolute T uncertainty (K)	P range (bar)	Absolute P uncertainty (bar)	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk								
6	SS	99.9	99.9	%	%	0.834	0.01251	313.7-358.1	0.1	75.3-103.7	0.6	NO	Choi and Yeo, 1998 ²⁷
7	SS	99.9	99.9	%	%	0.958	0.01437	313.2-327.9	0.1	82.1-96.0	0.6	NO	Choi and Yeo, 1998 ²⁷
7	SS	99.9	99.9	%	%	0.925	0.013875	328.7-338.3	0.1	96.0-104.3	0.6	NO	Choi and Yeo, 1998 ²⁷
7	SS	99.9	99.9	%	%	0.904	0.01356	313.1-363.3	0.1	75.5-119.1	0.6	NO	Choi and Yeo, 1998 ²⁷
7	SS	99.9	99.9	%	%	0.895	0.013425	322.9-368.1	0.1	83.6-121.5	0.6	NO	Choi and Yeo, 1998 ²⁷
7	SS	99.9	99.9	%	%	0.885	0.013275	323.6-370.1	0.1	85.5-119.5	0.6	NO	Choi and Yeo, 1998 ²⁷
7	SS	0.99995	0.99	Mole fr.	Mole fr.	0.2918	N/A	362.9-459.4	0.01	43.8-500.2	0.5	YES	Fenghour et al, 2001 ⁹⁴
7	SS	0.99995	0.99	Mole fr.	Mole fr.	0.3888	N/A	321.1-404.7	0.01	40.4-554.8	0.5	YES	Fenghour et al, 2001 ⁹⁴
7	SS	0.99995	0.99	Mole fr.	Mole fr.	0.4270	N/A	301.8-368.0	0.01	34.6-500.2	0.5	YES	Fenghour et al, 2001 ⁹⁴
8	SS	99.9	99.9	%	%	0.958	0.01437	313.1-342.9	0.1	81.9-112.9	0.6	NO	Choi and Yeo, 1998 ²⁷
8	SS	99.9	99.9	%	%	0.939	0.014085	313.1-338.4	0.1	76.9-106.8	0.6	NO	Choi and Yeo, 1998 ²⁷
8	SS	99.9	99.9	%	%	0.916	0.01374	313.1-348.1	0.1	76.9-119.1	0.6	NO	Choi and Yeo, 1998 ²⁷
8	SS	99.9	99.9	%	%	0.902	0.01353	313.1-363.3	0.1	77.8-133.7	0.6	NO	Choi and Yeo, 1998 ²⁷
8	SS	99.9	99.9	%	%	0.878	0.01317	313.1-368.1	0.1	76.5-135.5	0.6	NO	Choi and Yeo, 1998 ²⁷
8	SS	99.8	N/A	%	N/A	0.437	0.02	298.15-437.85	0.2	34.5-82.5	2	NO	Schneider et al., 1967 ⁹⁵
8	SS	99.8	N/A	%	N/A	0.508	0.02	287.25-531.35	0.2	35-105	2	NO	Schneider et al., 1967 ⁹⁵
8	SS	99.8	N/A	%	N/A	0.674	0.02	287.25-496.65	0.2	41-137.5	2	NO	Schneider et al., 1967 ⁹⁵
8	SS	99.8	N/A	%	N/A	0.730	0.02	282.95-512.15	0.2	39-144	2	NO	Schneider et al., 1967 ⁹⁵
8	SS	99.8	N/A	%	N/A	0.806	0.02	284.85-471.85	0.2	42.5-155.5	2	NO	Schneider et al., 1967 ⁹⁵
8	SS	99.8	N/A	%	N/A	0.873	0.02	293.45-428.55	0.2	53.5-152	2	NO	Schneider et al., 1967 ⁹⁵
8	SS	99.8	N/A	%	N/A	0.937	0.02	285.45-408.65	0.2	47.5-138.5	2	NO	Schneider et al., 1967 ⁹⁵
9	SS	99.9	99.9	%	%	0.941	0.014115	323.4-351.5	0.1	95.3-127.8	0.6	NO	Choi and Yeo, 1998 ²⁷
9	SS	99.9	99.9	%	%	0.925	0.013875	322.7-358.3	0.1	95.4-136.2	0.6	NO	Choi and Yeo, 1998 ²⁷
9	SS	99.9	99.9	%	%	0.878	0.01317	322.7-395.7	0.1	91.4-153.4	0.6	NO	Choi and Yeo, 1998 ²⁷
10	SA	> 99.8	> 99.0	%	%	0.675	N/A	344.2-444.4	0.1	97.4-163.8	0.3	NO	Chen et al, 1993 ⁹⁶
11	SS	99.8	99.5	%	%	0.826	0.03	257.05-279.95	0.2	58-1337	10	NO	Schneider et al., 1967 ⁹⁵
11	SS	99.8	99.5	%	%	0.862	0.03	257.65-280.45	0.2	39-1319	10	NO	Schneider et al., 1967 ⁹⁵
11	SS	99.8	99.5	%	%	0.869	0.03	257.75-280.65	0.2	32-1316	10	NO	Schneider et al., 1967 ⁹⁵
11	SS	99.8	99.5	%	%	0.880	0.03	257.65-280.25	0.2	29-1269	10	NO	Schneider et al., 1967 ⁹⁵
11	SS	99.8	99.5	%	%	0.905	0.03	257.35-279.45	0.2	52-1252	10	NO	Schneider et al., 1967 ⁹⁵
13	SS	99.8	99.8	%	%	0.772	0.04	268.65-315.15	0.2	83-1444	10	NO	Schneider et al., 1967 ⁹⁵
13	SS	99.8	99.8	%	%	0.833	0.04	272.45-334.35	0.2	40-1463	10	NO	Schneider et al., 1967 ⁹⁵

Table A6. Isolethic Data Sets of Experimental Fluid-Fluid Equilibria available for CO ₂ + n-Alkane binary mixtures													
CN	Method	Purity		Units for Purity		Composition* (z _{CO2})	Absolute composition uncertainty (mole fraction)	T range (K)	Absolute T uncertainty (K)	P range (bar)	Absolute P uncertainty (bar)	Density informed	Reference
		CO ₂	Alk	CO ₂	Alk								
13	SS	99.8	99.8	%	%	0.849	0.04	274.45-295.25	0.2	43-1435	10	NO	Schneider et al., 1967 ⁹⁵
13	SS	99.8	99.8	%	%	0.887	0.04	275.05-328.85	0.2	48-1453	10	NO	Schneider et al., 1967 ⁹⁵
13	SS	99.8	99.8	%	%	0.909	0.04	275.05-332.55	0.2	43-1435	10	NO	Schneider et al., 1967 ⁹⁵
13	SS	99.8	99.8	%	%	0.948	0.04	273.05-326.25	0.2	39-1512	10	NO	Schneider et al., 1967 ⁹⁵
16	SS	>99.9	>99	Mass %	Mass %	0.202	N/A	305.7-512.3	0.3	12.4-32.9	0.12	NO	Breman et al. 1994 ⁹⁷
16	SS	99.8	99.8	%	%	0.846	0.05	293.55-367.55	0.2	144-1346	10	NO	Schneider et al., 1967 ⁹⁵
16	SS	99.8	99.8	%	%	0.889	0.05	297.05-370.05	0.2	170-1268	10	NO	Schneider et al., 1967 ⁹⁵
16	SS	99.8	99.8	%	%	0.913	0.05	297.95-338.95	0.2	168-1463	10	NO	Schneider et al., 1967 ⁹⁵
16	SS	99.8	99.8	%	%	0.917	0.05	297.85-335.65	0.2	175-1464	10	NO	Schneider et al., 1967 ⁹⁵
16	SS	99.8	99.8	%	%	0.928	0.05	296.95-358.05	0.2	174-1266	10	NO	Schneider et al., 1967 ⁹⁵
16	SS	99.8	99.8	%	%	0.960	0.05	293.15-356.95	0.2	151-1473	10	NO	Schneider et al., 1967 ⁹⁵
28	SS	>99.9	>97	Mass %	Mass %	0.611	N/A	397.9-519.4	0.3	18.7-25	0.12	NO	Breman et al. 1994 ⁹⁷

SA: Static analytic. SS: Static synthetic. DA: Dynamic Analytic. DS: Dynamic synthetic. Mole fr.: Mole fraction. Mass fr.: Mass fraction.

* In mole fraction of CO₂.

APPENDIX B: Other tables to which the main text of the article refers

Table B1. Pure compound parameters* for the RK-PR EOS (This work)

Compound	Compound ID	a_c (bar*L ² /mol ²)	b (L/mol)	δ_1	K
Carbon Dioxide	CO ₂	3.9809	0.026440	2.509688	2.04173
METHANE	C1	2.3570	0.029392	1.244398	1.44042
ETHANE	C2	5.8024	0.043368	1.583623	1.75359
PROPANE	C3	9.8513	0.059399	1.764917	1.93370
n-BUTANE	C4	14.6687	0.075559	1.904346	2.09604
n-PENTANE	C5	20.3887	0.092397	2.118901	2.24755
n-HEXANE	C6	26.7882	0.109456	2.313637	2.39124
n-HEPTANE	C7	33.7503	0.126979	2.465532	2.53450
n-OCTANE	C8	41.5046	0.145042	2.633607	2.67573
n-NONANE	C9	49.6476	0.163111	2.763240	2.80022
n-DECANE	C10	58.4693	0.182177	2.875941	2.94303
n-UNDECANE	C11	68.2601	0.201038	3.046729	3.02959
n-DODECANE	C12	77.8716	0.220190	3.134497	3.16265
n-TRIDECANE	C13	89.5311	0.241046	3.316538	3.25130
n-Tetradecane	C14	102.0200	0.259970	3.541600	3.27688
n-Pentadecane	C15	113.3595	0.279939	3.620746	3.39568
n-Hexadecane	C16	125.5040	0.299846	3.717471	3.46921
n-Heptadecane	C17	135.7470	0.319486	3.694975	3.63771
n-Octadecane	C18	148.1487	0.339557	3.788625	3.74081
n-Nonadecane	C19	160.5037	0.359993	3.845494	3.84899
n-Eicosane	C20	171.8450	0.380561	3.842323	4.01140
n-Heneicosane	C21	184.4799	0.402123	3.865807	4.10806
n-Docosane	C22	198.9758	0.420783	4.019107	4.15471
n-TRICOSANE	C23	210.9991	0.444393	3.959352	4.32337
n-TETRACOSANE	C24	223.9849	0.467426	3.952760	4.45024
n-PENTACOSANE	C25	236.1051	0.485341	3.995209	4.53313
n-HEXACOSANE	C26	250.9000	0.510475	4.009181	4.66289
n-HEPTACOSANE	C27	262.6818	0.531827	3.979683	4.82872
n-OCTACOSANE	C28	278.8538	0.549011	4.150393	4.84541
n-NONACOSANE	C29	291.5623	0.567363	4.187813	4.90774
n-TRIACONTANE	C30	305.8439	0.588238	4.225805	5.00535
n-DOTRIACONTANE	C32	333.3214	0.640966	4.119647	5.21010
n-HEXATRIACONTANE	C36	384.8594	0.720154	4.163653	5.56525

*They reproduce the experimental (DIPPR,⁹⁸) critical temperature T_c , critical pressure P_c , acentric factor and liquid molar volume at 0.70 reduced temperature. Only for the case of CO₂, instead, the saturated liquid molar volume is reproduced at 270 K.

Table B2. Experimental fluid phase compositions under two-phase equilibrium conditions, at specified T and P, for some CO₂(1) + n-alkane(2) systems, considered in the objective function.

CN	<i>T</i> (K)	<i>P</i> (bar)	<i>x</i> ₁	<i>y</i> ₁	Reference
1	219.3	41.37	0.782	0.204	Mraw et al, 1978 ¹⁸ (Interpolated point)
1	270.0	65.37	0.8521	0.6298	Webster and Kidnay, 2001 ⁴⁸
2	230.0	9.48	0.1548	0.3225	Wei et al, 1995 ⁵¹
2	230.0	10.23	0.9326	0.8389	Wei et al, 1995 ⁵¹
2	270.0	31.51	0.2907	0.4116	Wei et al, 1995 ⁵¹
3	270.0	17.0	0.3107	0.7658	Yucelen and Kidnay, 1999 ⁵⁵
4	344.3	55.3	0.4180	0.7770	Hsu et al., 1985 ²³
6	313.15	40.52	0.4446	0.9748	Wagner and Wichterle, 1987 ⁶³
10	344.3	85.5	0.5936	0.9968	Iwai et al., 1994 ⁷⁰
10	377.6	137.9	0.7173	0.9789	Reamer and Sage, 1963 ³¹
16	393.2	101	0.4968	0.9982	Spee and Schneider, 1991 ³⁹
16	393.2	200	0.7473	0.9909	Spee and Schneider, 1991 ³⁹
16	573.2	101	0.428	0.962	Brunner et al., 1994 ⁸⁰
16	573.2	201	0.700	0.938	Brunner et al., 1994 ⁸⁰
20	353.2	250	0.78534	0.97959	Kordikowski and Schneider, 1993
20	393.2	250	0.70577	0.99422	Kordikowski and Schneider, 1993
22	373.2	199.55	0.76603	0.9963	Pohler and Schneider, 1995 ⁴²
22	373.2	299.47	0.86965	0.9862	Pohler and Schneider, 1995 ⁴²
24	573.2	50.66	0.2533	0.9961	Tsai and Yau, 1990 ⁸⁹
28	573.5	50.57	0.270	0.9983	Huang et al., 1988 ⁹¹
32	573.2	50.66	0.2839	0.9996	Tsai and Yau, 1990 ⁸⁹

CN: Carbon number of the n-alkane. *x*₁ and *y*₁ are mole fractions of CO₂ in the heavy and light phases respectively.

Table B3. Experimental fluid-fluid saturation pressures at given temperature and liquid phase composition for some CO₂(1) + n-alkane(2) systems, considered in the objective function.

CN	T (K)	x_1	P (bar)	Reference
13	338.6	0.80	125	Enick et al., 1985 ³³
13	377.4	0.80	178	Enick et al., 1985 ³³
16	313.2	0.227	21.33	Tanaka et al., 1993 ⁷⁹
20	310.2	0.253	20.265	Huie et al., 1973 ⁴⁷
20	373.2	0.147	20.265	Huie et al., 1973 ⁴⁷
24	373.2	0.172	20.265	Tsai and Yau, 1990 ⁸⁹
24	573.2	0.1127	20.265	Tsai and Yau, 1990 ⁸⁹
28	373.4	0.184	20.40	Huang et al., 1988 ⁹¹
28	573.5	0.122	20.33	Huang et al., 1988 ⁹¹
28	373.2	0.7298	161.9	Sato et al., 1998 ⁸⁶
28	423.2	0.8972	408.5	Sato et al., 1998 ⁸⁶
32	348.2	0.2279	20.92	Fall and Luks, 1984 ⁸⁸
32	573.2	0.126	20.265	Tsai and Yau, 1990 ⁸⁹

CN: Carbon number of the n-alkane. x_1 is the mole fraction of CO₂ in the liquid phase.

Table B4. CMRs interaction parameters optimized for some CO₂(1) + n-alkane(2) systems individually

		SYSTEM						
		CO ₂ + C1	CO ₂ + C2	CO ₂ + C8	CO ₂ + C10	CO ₂ + C13	CO ₂ + C16	CO ₂ + C20
Interaction Parameters	k'_{112}	0.02070	0.14971	0.20995	0.18520	0.22924	0.25047	0.27139
	k'_{122}	0.10795	0.25751	0.54902	0.52164	0.51408	0.48952	0.32785
	k^{∞}_{112}	0.00016	-0.04951	-0.18521	-0.22561	-0.22652	-0.25631	-0.31299
	k^{∞}_{122}	-0.02720	-0.14304	-0.59344	-0.64650	-0.67716	-0.74875	-0.83642
	l_{112}	-0.03829	-0.05656	0.00013	-0.01382	0.06752	0.09066	0.09198
	l_{122}	0.00732	0.00565	0.03503	0.02501	0.03952	0.05533	0.05224
	T^*_{112} /K	321.14	367.95	250.80	237.29	222.24	199.20	141.65
	T^*_{122} /K	1475.42	1857.5	980.64	720.28	799.39	981.09	1879.65
	OF	0.1933	0.3416	0.652	1.683	0.715	1.759	1.842
	OF_{corr}	-	-	0.958	1.860	0.972	2.040	3.220

OF is the objective function value corresponding to a single binary system optimization. Although some extra terms were used while fitting the “binary system-specific” interaction parameters for CO₂+C10, CO₂+C13, CO₂+C16 and CO₂+C20 (see section 3.3), the OF values reported here correspond only to the terms accounting for data in tables 2 to 5, B2 and B3, in order to be comparable to OF_{corr} .

OF_{corr} is the partial objective function value, corresponding to a given binary system, in the optimum found for the CO₂ + n-alkane series, covering simultaneously systems from C3 to C32 in tables 2 to 5, B2 and B3 (Eq. 11 and Table 6).

Model: RKPR-EOS + CMRs

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