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Binary interaction parameters for nonpolar systems with cubic equations of state: a theoretical approach

1. CO₂/hydrocarbons using SRK equation of state

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Abstract

This work shows that, when suitable theoretically based combining rules are used for the cross energy and cross co-volume parameters, cubic equations of state (EoS) with the van der Waals one-fluid mixing rules can adequately represent phase equilibria for the asymmetric CO₂/hydrocarbon mixtures. These combining rules lead to semi-theoretical yet simple, meaningful and successful correlations for the interaction parameters K_{ij} (of the cross-energy term) and l_{ij} (of the cross co-volume term). Unlike previous correlations, the proposed equations relate the interaction parameters only to the pure component co-volume (b_i) parameters, meaning that no additional properties (e.g. the critical volume), besides those required by the EoS itself (the critical temperature T_c , the critical pressure P_c and the acentric factor) are used. Furthermore, the form of the correlations enables us to tune easily the cubic EoS when this is required for the prediction of phase behavior of petroleum fluids. A brief theoretical analysis on the temperature dependency of the K_{ij} interaction parameter is also presented.

Keywords: Theory; Equation of state; Cubic; Vapor–liquid equilibria; Mixing and combining rules; Hydrocarbons

1. Introduction

The increased use of carbon dioxide flooding to enhance oil recovery has resulted in an increasing need for accurate predictions of phase equilibria of multicomponent mixtures containing CO₂ and hydrocarbons. Cubic equations of state (EoS) are the most common tool

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for phase equilibrium calculations of CO₂ containing mixtures. The calculations are not, however, as simple as for mixtures containing only hydrocarbons. In the case of CO₂/hydrocarbon systems at least one non-zero binary interaction parameter (often denoted K_{ij}) is needed to obtain a quantitatively correct representation of the phase behavior. The binary interaction parameters correct for the deviations between the EoS predictions and the experimental data. Provided that the pure component properties are adequately described, they mainly reveal the inadequacies of the EoS mixing and combining rules. The binary interaction parameters are generally estimated directly from experimental equilibrium data for binary systems. Experimental data are not, however, available for all mixtures of interest. On the other hand, the binary interaction parameters may not be completely empirical parameters. Teja (1978) states that, under certain conditions, they reflect genuine differences in molecular properties and that they are not correlation artifacts. In fact, the interaction parameters arise from the different simplifications and assumptions used in the derivation of the EoS mixing and combining rules, and they also take into account the various deficiencies and limitations of the EoS approach. It is difficult to predict accurately the EoS interaction parameters in a way that is theoretically justified, easy to use and also general enough to be applied to different types of mixtures. It is, however, possible to use theoretical arguments to construct semi-theoretical correlations that could be used for a variety of mixtures.

Several empirical correlations for K_{ij} have been presented in the literature. Some of these correlations are suitable for mixtures with only hydrocarbons (Katz and Firoozabadi, 1978; Nishiumi et al., 1988; Gao et al., 1992) and others for CO₂/hydrocarbon systems (Kato et al., 1981; Nishiumi et al., 1988; Darridon, 1992; Bartle et al., 1992; Kordas et al., 1994). Several correlations have been developed for “external” mixing rules, mainly for the cross critical temperature T_{cij} and the cross critical volume V_{cij} (Chueh and Prausnitz, 1967; Hiza and Duncan, 1970; Teja, 1978; Tsonopoulos, 1979). In most of the correlations presented in the literature, various pure-component properties are needed for the estimation of the interaction parameters. Only a few studies have been published for the Soave–Redlich–Kwong (SRK) EoS and they are either not reliable or they apply to only a limited number of hydrocarbons (Graboski and Daubert, 1978a; Moysan et al., 1986; Valderrama et al., 1988). Most correlations for the K_{ij} parameter presented in the literature are purely empirical and, although they are often able to correlate satisfactorily the experimental data, they are occasionally not suitable for extrapolations. Tsonopoulos (1979) shows, for example, that the parameters presented in his work can be adequately described by two different correlations which show large differences upon extrapolation. The theoretically based correlations presented by some authors (Chueh and Prausnitz, 1967; Li et al., 1985; Trebble and Sigmund, 1990; Gao et al., 1992) seem to describe the experimental data fairly well, but they use additional properties besides the ones (the critical properties and the acentric factor) required by the cubic EoS. These additional properties, like the critical volume (V_c), are often (especially for heavy hydrocarbons) not accurately known. The critical volume is a property which is often used to correlate binary interaction parameters, but as shown by Tsonopoulos and Tan (1993), and also discussed in some detail later, the values of V_c are not accurately known for *n*-alkanes larger than *n*-hexane. Actually, two different sets of experimental critical densities for *n*-alkanes exist; those of Steele and Teja (both reported by Tsonopoulos and Tan, 1993). Furthermore, the predicted critical volumes by the various group-contribution (GC) and other methods often differ significantly.

Takamiya and Nakanishi (1988) stated that the van der Waals one-fluid (vdW1f) conformal solutions mixing rules (Longuet-Higgins, 1951; Leland et al., 1968; Rowlinson and Swinton, 1986) cannot account for the computer simulation results for Lennard–Jones (LJ) mixtures with high asymmetry, especially those with large differences in size. They conclude, thus, that the vdW1f approximation cannot be applied to liquid mixtures with components differing in size. Nevertheless, Harismiadis et al. (1994) have recently shown that cubic EoS, following the vdW1f mixing rules can adequately represent the molecular simulation data for LJ mixtures, even for those with components differing significantly in size, if the correct combining rules are used. Conclusions and results for LJ mixtures also hold, up to a certain degree, for mixtures with real molecules. Many mixtures with real fluids behave similarly to hypothetical LJ mixtures, as will be discussed later.

Despite the results of Harismiadis et al. (1994), many investigators still believe that the vdW1f mixing rules cannot be used for asymmetric mixtures. This partly explains the large number of more complicated mixing rules that have appeared in the literature (Smith, 1972; Pesuit, 1978; Plöcker et al., 1978; Radosz et al., 1982). An important remark should be made for the recently proposed EoS- G^E models (Vidal, 1978; Michelsen, 1990a,b; Boukouvalas et al., 1994). These models match (in different ways and at different reference pressures) the excess Gibbs energy expression from a cubic EoS (denoted G^E) with the corresponding Gibbs energy expression from an activity coefficient model (denoted $G^{E,*}$) like UNIFAC (Fredenslund et al., 1975). Any excess Gibbs energy model can be used in conjunction with the EoS- G^E approach. In particular, the MHV2 model (Dahl and Michelsen, 1990) uses the modified UNIFAC (Larsen et al., 1987) which successfully describes asymmetric hydrocarbon mixtures. Still, the MHV2 model fails in the representation of mixtures with large differences in size, such as CO₂ with heavy hydrocarbons, as Boukouvalas et al. (1994) remark. They applied the MHV2 model for many asymmetric mixtures and showed that unreliable phase equilibrium results were obtained. This failure can be partly explained by the fact that the MHV2 (and the other similar models, like PSRK; Holderbaum and Gmehling, 1991) do not reproduce the $G^{E,*}$ of the activity coefficient model they are combined with (Kalospiros et al., 1994). This lack of reproducibility of the excess Gibbs energy is due to the approximate expression used for the $q(a)$ function (see Dahl and Michelsen, 1990) in the MHV2, MHV1 and PSRK models. The function $q(a)$ can be also calculated analytically in most cases (leading to the original “exact” model of Michelsen (1990a)). Nevertheless, for mixtures having supercritical components (like CO₂/hydrocarbons), the approximate $q(a)$ equation should be used. This leads to the lack of reproducibility of the successful $G^{E,*}$ model, which partly justifies the problems of MHV2 for such asymmetric mixtures. Boukouvalas et al. (1994) have recently proposed a new EoS- G^E model (LCVM) which performs very well in the cases where MHV2, MHV1 and PSRK fail, i.e. for highly asymmetric mixtures. The LCVM model, however, a linear combination of two other EoS- G^E mixing rules (those of Vidal (1978) and of the MHV1 model) has no explicit reference pressure and lacks theoretical justification.

Two points are clear from the above discussion. First, that the vdW1f mixing rules in combination with suitable combining rules may be successfully used for phase equilibrium calculations in asymmetric systems. Second, that other widely applied mixing rules (like the EoS- G^E models) reveal many difficulties in the description of asymmetric nonpolar systems; the EoS- G^E models were originally focused on and successfully applied to mixtures with chemically

complex and relatively symmetric compounds. Based on the above, the purpose of this work is to use the vdWlf theory and theoretically based combining rules for the description of phase equilibria for the highly asymmetric CO₂/hydrocarbon mixtures. Towards this target, theoretically based correlations for the K_{ij} and l_{ij} parameters of the SRK EoS for CO₂/hydrocarbon mixtures will be presented. The new expressions overcome some of the limitations of the existing semi-empirical correlations and, owing to their theoretical derivation, may be used for a large variety of mixtures. The correlations developed in this work follow the approach suggested by Hudson and McCoubrey (1960) for a complete form of the combining rule for the molecular cross energy parameter. The proposed correlations use only the critical properties of the compounds (T_c and P_c), which are required by the EoS for the calculation of the pure-component parameters a_i and b_i . It will be shown that the same functional form is capable of describing the interactions between CO₂ and all kinds of hydrocarbons, which represents a considerable improvement compared to most previously presented correlations. The form of the new correlation is similar to the Chueh and Prausnitz (1967) correlation for interactions between hydrocarbons and may be suitable to use for tuning the EoS when dealing with reservoir fluids (Merril, personal communication, 1993). The results presented in this work and the discussion related to on mixtures with aromatics, alkylbenzenes and mono-unsaturated molecules will provide a good insight for a physically meaningful tuning of the EoS using the binary interaction parameters.

2. The Soave–Redlich–Kwong (SRK) EoS

The SRK equation of state (Soave, 1972; Graboski and Daubert, 1978b):

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad (1)$$

is a two parameter cubic equation of state. The pure component parameters a_i and b_i are generally expressed as:

$$a_i(T) = \Omega_a \frac{R^2 T_{ci}^2}{P_{ci}} \alpha_i(T) \quad (2)$$

$$b_i = \Omega_b \frac{RT_{ci}}{P_{ci}} \quad (3)$$

where:

$$\alpha_i(T) = [1 + m_i(1 - \sqrt{T_{ri}})]^2 \quad (4)$$

$$m_i = 0.48508 + 1.55171\omega_i - 0.15613\omega_i^2 \quad (5)$$

The critical properties and the acentric factors for heavy n -alkanes ($N_c > 20$) were taken from the correlation proposed by Magoulas and Tassios (1990). For other heavy hydrocarbons for which critical properties and acentric factors were not presented in the literature, the acentric factors were estimated from a recent GC method (Han and Peng, 1993) and the critical properties have been estimated by the method of Constantinou and Gani (1994).

Eq. (5) has been developed by Graboski and Daubert (1978b), using experimental vapor pressure data for paraffins up to *n*-decane, and also ethylene, propylene, cyclopentane and toluene. As mentioned by Radosz et al. (1982), the performance of Eq. (5) is very similar to that of the original $m(\omega)$ expression proposed by Soave (1972). Several authors (Magoulas and Tassios, 1990; Soave, 1993), however, have stated that, when Eq. (5) or any other quadratic expression is used for $m(\omega)$ in conjunction with the Soave-temperature dependency for the energy parameter (Eq. (4)), the SRK (or any other cubic) EoS cannot represent adequately the vapor pressures (and consequently the phase equilibrium) for heavy hydrocarbons. Among other authors, Soave (1993) and Magoulas and Tassios (1990) have proposed cubic (or higher order degree polynomial) equations for the $m(\omega)$ function of cubic EoS in order to describe accurately the vapor pressures of heavy alkanes. As shown, however, by Graboski and Daubert (1978b), Radosz et al. (1982) and Kontogeorgis et al. (1994a,b), the SRK EoS with Eq. (5) yields accurate vapor pressures for heavy hydrocarbons and even for certain polar compounds as well. This conclusion is verified here by the results shown in Table 1 and in Fig. 1 for *n*-eicosane and *n*-octacosane. Excellent agreement is obtained between predicted and experimental vapor pressures. This is of particular importance for the heavy hydrocarbon (*n*-octacosane): the average absolute deviation between the vapor pressures calculated by the SRK EoS (and Eq. (5)) and the accurate experimental data of Chirico et al. (1989) is — for all the correlations of the acentric factor investigated here — less than 10%, and for most acentric factor values less than 5%.

Table 1

Average percentage absolute deviation between experimental and predicted vapor pressures for *n*-eicosane and *n*-octacosane using the SRK EoS and various methods for the estimation of the critical properties and the acentric factor

Compound	Vapor pressure range (bar)	Method for the estimation of the critical properties	Method for the estimation of acentric factor	Average percentage absolute deviation
<i>n</i> -Eicosane	1.56×10^{-4} –1.2079	Magoulas and Tassios (1990)	Magoulas and Tassios (1990)	3
<i>n</i> -Octacosane	1.31×10^{-4} –0.038847	Magoulas and Tassios (1990)	Magoulas and Tassios (1990)	3
<i>n</i> -Octacosane	1.31×10^{-4} –0.038847	Magoulas and Tassios (1990)	Hoshino et al. (1982)	2
<i>n</i> -Octacosane	1.31×10^{-4} –0.038847	Magoulas and Tassios (1990)	Kontogeorgis et al. (1994a)	2
<i>n</i> -Octacosane	1.31×10^{-4} –0.038847	Magoulas and Tassios (1990)	Robinson and Gasem (1987)	5
<i>n</i> -Octacosane	1.31×10^{-4} –0.038847	Robinson and Gasem (1987)	Robinson and Gasem (1987)	2
<i>n</i> -Octacosane	1.31×10^{-4} –0.038847	Teja et al. (1990)	Magoulas and Tassios (1990)	9

Experimental value for the critical properties and acentric factors are used for *n*-eicosane (Magoulas and Tassios, 1990). Experimental data for both compounds are taken from Chirico et al. (1989).

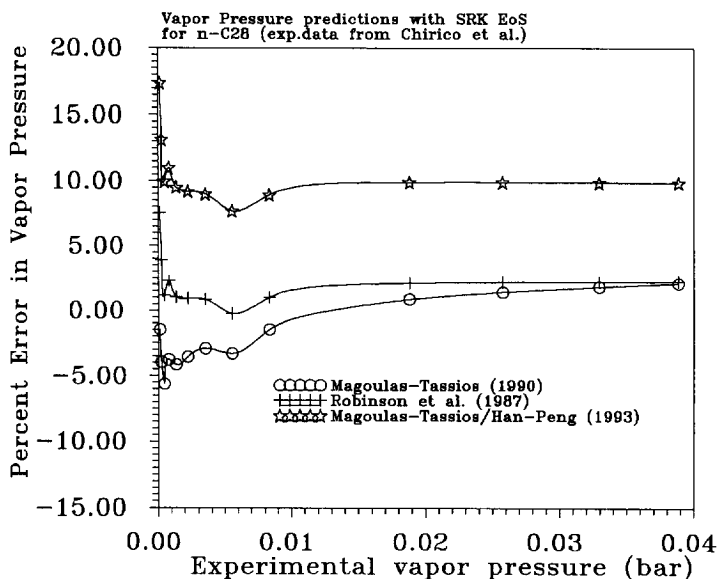


Fig. 1. Percentage error in vapor pressure with SRK–EoS for *n*-octacosane using various methods for the estimation of critical properties and acentric factors.

For the extension of the EoS to mixtures, the van der Waals one-fluid mixing and combining rules are adopted:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (6)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - K_{ij}) \quad (6a)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (7)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad (7a)$$

In order to gain understanding regarding the nature of the K_{ij} and l_{ij} parameters, a brief overview of the derivation of the vdW one-fluid mixing rules and a theoretical analysis for the cross parameters a_{ij} and b_{ij} (based on the Hudson and McCoubrey approach (1960)) will be given in the next two sections.

3. Van der Waals one-fluid quadratic mixing rules and general combining rules for the cross parameters of cubic EoS

3.1. Van der Waals one-fluid mixing rules

Following Reid and Leland (1965), the derivation of the quadratic form of the mixing rules for the a and b parameters (Eqs. (6) and (7)) in the EoS is based on the assumption that the

properties of a fluid can be derived from any pair interaction potential function $\Gamma(r)$ having the form:

$$\Gamma(r) = \epsilon f\left(\frac{r}{\sigma}\right) \tag{8}$$

where r is the intermolecular distance, ϵ is the minimum value for the interaction energy and σ is the intermolecular distance for a zero value of the interaction energy.

The final result given by Reid and Leland (1965) for the expansion of the pair and the intermolecular radial distribution functions around a hard sphere distribution function in powers of ϵ/kT , is after performing the required integrations in the equation of state for the dense fluid:

$$\begin{aligned} \sigma_m^3 f_0(\rho_m \sigma_m^3, T) + \sigma_m^3 \frac{\epsilon_m}{kT} f_1(\rho_m \sigma_m^3, T) + \dots = \\ = \sum_i \sum_j x_i x_j \sigma_{ij}^3 f_0(\rho_m \sigma_m^3, T) + \sum_i \sum_j x_i x_j \sigma_{ij}^3 \frac{\epsilon_{ij}}{kT} f_1(\rho_m \sigma_m^3, T) + \dots \end{aligned} \tag{9}$$

Eq. (9) should be valid at all temperatures and mixture densities and, thus, the coefficients of the functions f_0, f_1, f_2, \dots of both sides must be equal. This equality results in the final equations for the mixture energy and co-volume parameters:

$$\sigma_m^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \tag{10a}$$

$$\sigma_m^3 \epsilon_m = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \epsilon_{ij} \tag{10b}$$

The problem of the over-determination of the parameters ϵ_m and σ_m will not be considered here; a discussion is given elsewhere (Reid and Leland, 1965). Since $\sigma^3 \propto V_c$ or equivalently $\sigma^3 \propto b_c$, and $\epsilon/k \propto T_c$, it is easy to see that $\epsilon \sigma^3 \propto a$ and $\epsilon \propto a/b$, and Eqs. (6) and (7) can be thus obtained from Eqs. (10a) and (10b). Nothing is said until now, however, about the functional form of the combining rules that should be used for the cross parameters ϵ_{ij} and σ_{ij}^3 . A generalized form of the combining rules for the cross energy and cross co-volume parameters based on the London–Mie theory that could be used in cubic EoS is hereafter presented.

3.2. General combining rules for the cross parameters from the London–Mie theory

The London theory of dispersion forces provides an equation for the attractive potential Γ_{ij} between a pair of unlike central molecules of nonpolar fluids in the form:

$$\Gamma_{ij} = \sqrt{\Gamma_i \Gamma_j} \left(\frac{2\sqrt{I_i I_j}}{I_i + I_j} \right) \tag{11}$$

where I_i is the ionization potential of component i .

The Mie potential function may be used to describe the total intermolecular potential Γ_{ij} as a function of the molecular cross energy and size parameters ϵ_{ij} and σ_{ij} :

$$\Gamma_{ij}^{\text{Mie}} = \frac{m}{m-n} \left(\frac{m}{n} \right)^{\frac{n}{m-n}} \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^m - \left(\frac{\sigma_{ij}}{r} \right)^n \right] \tag{12}$$

When the variables m and n have the values 12 and 6, respectively, the LJ potential function is obtained.

Dispersion forces are due to the attractive part of the potential only. Inserting the attractive part of Eq. (12) in Eq. (11), an expression for the molecular cross energy parameter is derived:

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \left(\frac{\sqrt{\sigma_i \sigma_j}}{\sigma_{ij}} \right)^n \left(\frac{2\sqrt{I_i I_j}}{I_i + I_j} \right) \quad (13a)$$

The geometric mean rule for the molecular cross energy parameter ($\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$) is known as the Berthelot rule. The other two terms of the right-hand side of Eq. (13a) represent deviations from the Berthelot combining rule.

Since $\sigma^3 \propto V_c$ and $\epsilon/k \propto T_c$, Eq. (13a) can be equivalently written:

$$T_{cij} = \sqrt{T_{ci} T_{cj}} \left(\frac{\sqrt{V_{ci} V_{cj}}}{V_{cij}} \right)^q \left(\frac{2\sqrt{I_i I_j}}{I_i + I_j} \right); \quad q = \frac{n}{3} \quad (13b)$$

Many authors (Prausnitz and Gunn, 1958; Chueh and Prausnitz, 1967; Teja, 1978; Prausnitz et al., 1986) have successfully used Eq. (13b) for high pressure VLE calculations for asymmetric mixtures, including CO₂/hydrocarbons. Upon neglecting the ionization potential term and setting $q = 1$ ($n = 3$), as suggested by Prausnitz and Gunn (1958) and other investigators, we obtain:

$$T_{cij} = \sqrt{T_{ci} T_{cj}} \left(\frac{\sqrt{V_{ci} V_{cj}}}{V_{cij}} \right) \quad (13c)$$

and since $a \propto \epsilon \sigma^3 \propto T_c V_c$, Eq. (13c) is equivalent to the classical combining rule for the cross energy parameter:

$$a_{ij} = \sqrt{a_i a_j} \quad (13d)$$

Eq. (13a) using $n = 6$ and σ_{ij} given by the arithmetic mean combining rule (Eq. (15) below) was presented and used by Hudson and McCoubrey (1960) and also by Prausnitz (1959). These authors assumed the validity of the proportionalities $\sigma^3 \propto V_c$, and $\epsilon/k \propto T_c$ to obtain an external mixing rule for T_{cij} . Hudson and McCoubrey (1960) showed that using the new mixing rule (Eq. (13a)) successful prediction of the cross second Virial coefficient was obtained for several mixtures.

Here a somewhat different method will be adopted. Considering that $\sigma^3 \propto b_c$, $\epsilon/k \propto T_c$ and $\epsilon \propto a/b$, a general form for the cross energy a_{ij} parameter of cubic EoS can be obtained from Eq. (13a):

$$a_{ij} = \sqrt{a_i a_j} \left(\frac{\sqrt{b_i b_j}}{b_{ij}} \right)^{\frac{n-3}{3}} \left(\frac{2\sqrt{I_i I_j}}{I_i + I_j} \right) \quad (14)$$

A similar combining rule has been used by Radosz et al. (1982) but in conjunction with mixing rules different than the vdWif ones.

For the σ_{ij} parameter, a combining rule with a theoretical basis, is the one which assumes the additivity of diameters for hard-sphere molecules (hard-sphere repulsion approximation):

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (15)$$

or equivalently

$$b_{ij} = \frac{1}{8}(b_i^{1/3} + b_j^{1/3})^3 \quad (16)$$

Eqs. (15) or (16) are known as the Lorentz combining rule for b_{ij} . When real molecules instead of hard spheres are considered the value of b_{ij} , as given by Eq. (16), has to be corrected by a $(1 - \lambda_{ij})$ term to take into account the possible deviations from the Lorentz combining rule (i.e. deviations from the additivity of the molecular diameters).

If the theoretical combining rules (Eqs. (14) and (16)) are now compared with the commonly used combining rules (Eqs. (6a) and (7a)), the following equations can be obtained for the typically used binary interaction parameters K_{ij} and l_{ij} :

$$(1 - K_{ij}) = \left(\frac{\sqrt{b_i b_j}}{b_{ij}} \right)^{\frac{n-3}{3}} \left(\frac{2\sqrt{I_i I_j}}{I_i + I_j} \right) \quad (17)$$

and

$$(1 - l_{ij}) = \frac{\left(\frac{b_i^{1/3} + b_j^{1/3}}{2} \right)^3}{\left(\frac{b_i + b_j}{2} \right)} (1 - \lambda_{ij}) \quad (18)$$

3.3. Correlation of the binary interaction parameters

Eqs. (17) and (18) can be used to develop correlations for the K_{ij} and l_{ij} parameters of the SRK EoS, as estimated from experimental data for CO₂/hydrocarbon mixtures.

(a) The known ionization potentials for most heavy hydrocarbons are not very accurate, although they are often considered to vary proportionally with $1/\sigma^3$ (Reid and Leland, 1965). Hudson and McCoubrey (1960) have stated that the term with the ionization potential ratio included in Eq. (17) is not significant. Nevertheless, we have found in this work that, for CO₂/hydrocarbon mixtures, this term is proportional and almost equal to $(b_i b_j)^{-1/2}/b_{ij}^{-1}$; this implies that CO₂/hydrocarbon mixtures approximately obey the LJ potential, as will be explained and discussed in detail in a later section. For the moment, the ionization potential term will be replaced by an empirical constant A . The value of the exponent n (in Eq. (17)) is 6 according to the LJ potential, but Chueh and Prausnitz (1967) and Reid and Leland (1965) found that a value of n equal to 3 describes the interactions between non-spherical molecules better. A value of n equal to 3 leads to Eq. (13c) or to the equivalent Eq. (13d) which have been extensively used in the literature. Introducing a variable $\theta = (n - 3)/3$ as the second parameter of the correlation, and solving Eq. (17) for the K_{ij} parameter, we get:

$$K_{ij} = 1 - A \left(\frac{\sqrt{b_i b_j}}{b_{ij}} \right)^\theta \quad (19)$$

(b) The correction parameter $(1 - \lambda_{ij})$ to the cross co-volume term b_{ij} is expected to vary somewhat with the size of component j (the hydrocarbon in CO₂/hydrocarbon mixtures). Replacing the term $(1 - \lambda_{ij})$ in Eq. (18) with the variable C , we get:

$$l_{ij} = 1 - C \frac{\left(\frac{b_i^{1/3} + b_j^{1/3}}{2} \right)^3}{\left(\frac{b_i + b_j}{2} \right)} \quad (20)$$

Since C is not a constant, Eq. (20) can be empirically modified:

$$l_{ij} = C_1 - C_2 \frac{\left(\frac{b_i^{1/3} + b_j^{1/3}}{2}\right)^3}{\left(\frac{b_i + b_j}{2}\right)} \quad (21)$$

Eqs. (19) and (21) relate the two binary interaction parameters with the pure component properties a_i and b_i which can be estimated directly from the critical temperature and the critical pressure of the compounds. Eqs. (19) and (21) will be used in this work to correlate and predict the K_{ij} and l_{ij} parameters which have been previously optimized from experimental VLE data for CO₂/hydrocarbon mixtures. Details for the optimization of the K_{ij} and l_{ij} parameters are given in the next section, while the results of the correlations based on Eqs. (19) and (21) are given in the Results and discussion section.

4. Optimization of the binary interaction parameters from experimental equilibrium data

The estimation of binary interaction parameters K_{ij} and k_{ij} plus l_{ij} for CO₂/hydrocarbon systems has been performed using a large data base of VLE and solubility data for mixtures of CO₂ with n -alkanes, branched alkanes, naphthenes, alkenes, alkylbenzenes, mono- and multi-ring aromatics. The data base is similar to the one presented by Garcia-Sanchez et al. (1992) and Bartle et al. (1991) and will not be further described here.

Two kinds of optimizations have been performed:

- (1) Optimization of temperature independent K_{ij} . These K_{ij} values were then correlated using Eq. (19).
- (2) Simultaneous optimization of temperature independent k_{ij} and l_{ij} . These k_{ij} values were then correlated using Eq. (19) and the l_{ij} values were correlated using Eq. (21).

The binary interaction parameters are rather sensitive to a large number of factors, including the temperature and pressure range, the composition range and the quality of the experimental data. These factors are discussed later in this section. In order to obtain reliable values for the parameters the quality of the data used was carefully investigated and the doubtful references were rejected. Data sets with a limited number of data or data sets covering a small composition range were also rejected. Since the binary interaction parameters are sensitive to the composition range of the experimental data used in their estimation, effort was made to use data sets with as similar composition ranges as possible. The temperature also affects the binary interaction parameters, as will be demonstrated in a later section. For this reason, the temperature range selected was restricted from 283 to 373 K. For the systems when only few data sets existed in the above temperature range, data sets within 50 K outside this range were accepted. Furthermore, since cubic EoS are not able to describe the critical region of mixtures properly, only data with a reduced mixture pressure below 0.95 were used, as recommended by Gasem and Robinson (1990). Furthermore, the K_{ij} values are somewhat dependent on the nature of the estimation procedure and the objective function used (Graboski and Daubert, 1978a; Darridon, 1992). No widely accepted method exists for these optimizations. Flash calculations were

performed in this work. The objective function used is the difference between the experimental and the calculated compositions.

For VLE data:

$$F_{\text{obj}} = \sum_i (x_{\text{cal}} - x_{\text{exp}})^2 + \sum_i (y_{\text{cal}} - y_{\text{exp}})^2 \quad (22)$$

For solubility data:

$$F_{\text{obj}} = \sum_i (x_{\text{cal}} - x_{\text{exp}})^2 \quad (23)$$

Estimated parameters with a very large confidence range and showing deviations from the mean value for a specific system above 30% were rejected. The finally accepted optimum K_{ij} and k_{ij}/l_{ij} parameters were fitted to Eqs. (19) and (21) by minimizing the sum of squares of residuals. The results are reported and discussed in the next section.

5. Results and discussion

5.1. K_{ij} parameters from Eq. (19)

The entire data base for CO_2 /hydrocarbon mixtures was used for the development of a correlation for the binary interaction parameter K_{ij} . Three different correlations were needed to describe the various CO_2 /hydrocarbon systems: first correlation, CO_2 with linear, branched and naphthenes; second correlation, CO_2 with aromatics; third correlation, CO_2 with 1-alkenes.

The three correlations are shown graphically in Figs. 2–4. The values for the parameters A and θ of Eq. (19) are presented for all three correlations in Table 2. Table 3 gives the code numbers (and the respective molecular weights) for the investigated compounds which appear in Figs. 2–4.

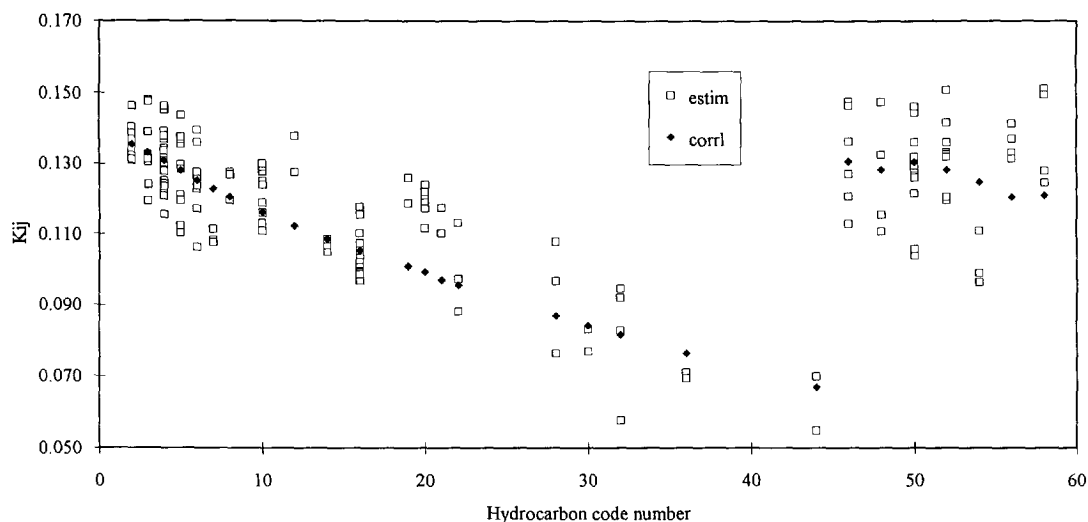


Fig. 2. Estimated and correlated values for binary interaction parameters (K_{ij}) between carbon dioxide and naphthenes, linear and branched alkanes.

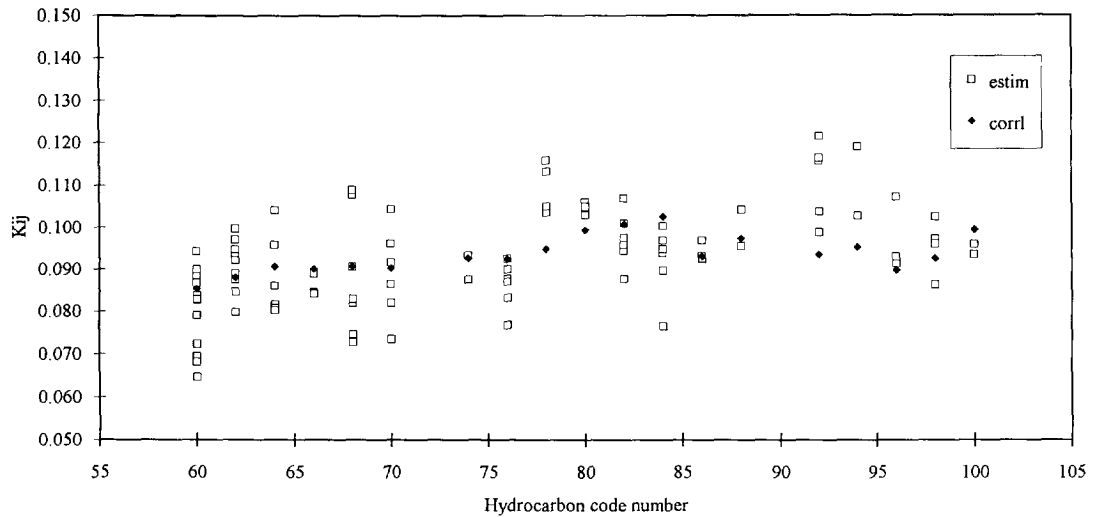


Fig. 3. Estimated and correlated values for binary interaction parameters (K_{ij}) between carbon dioxide and aromatic hydrocarbons.

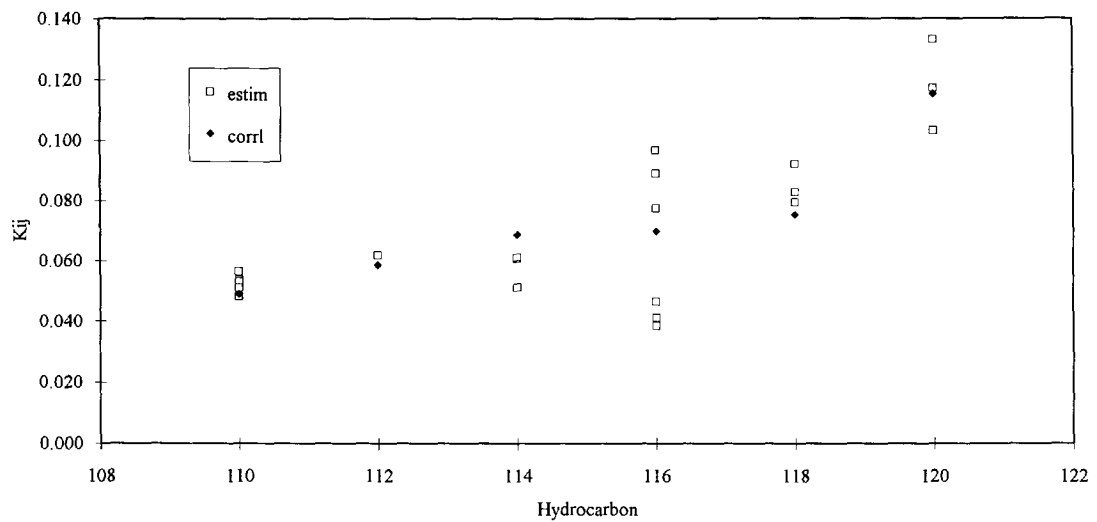


Fig. 4. Estimated and correlated values for binary interaction parameters (K_{ij}) between carbon dioxide and monoalkenes.

5.1.1. The CO_2 /methane system

It was not possible to describe the binary interaction parameter for methane with any of these correlations. This is because methane has a critical temperature lower than the critical temperature of CO_2 , and no CO_2 /methane data are available within the temperature range used in the development of the previously mentioned correlations. Using data in the temperature range between 200 and 250 K, the mean value of K_{ij} for the CO_2 /methane mixture was found to be

Table 2
 Constants for the correlations of the binary interaction parameters

K_{ij}	k_{ij}	l_{ij}	A	θ	$AAD\%^a$	C_1	C_2
Alkanes and naphthenes			0.8634	-0.05575	7		
Aromatics			0.9212	0.05441	9		
Alkenes			0.9522	0.1110	19		
	Alkanes		0.9121	0.04309			
		Alkanes				0.1015	0.1598

$$^aAAD\% = \frac{1}{N} \sum_{i=1}^N \left| \frac{K_{ij}^{\text{exp}} - K_{ij}^{\text{cal}}}{K_{ij}^{\text{exp}}} \right| \times 100$$

Table 3
 Code numbers for hydrocarbon identifications

Code number	Hydrocarbon	Mw	Code number	Hydrocarbon	Mw
1 to 44	<i>n</i> -Alkane C_x^a	—	80	Hexylbenzene	162
46	Isobutane	58	82	Heptylbenzene	176
48	Isopentane	72	84	Octylbenzene	190
50	Cyclopentane	70	86	Biphenyl	154
52	Cyclohexane	84	88	Diphenylmethane	168
54	Methylcyclohexane	98	92	1-Methylnaphthalene	142
56	Propylcyclohexane	126	94	2-Methylnaphthalene	142
58	Transdecaline	138	96	Styrene	104
60	Benzene	78	98	Tetraline	132
62	Toluene	92	100	Dibenzyl	182
64	<i>m</i> -Xylene	106	110	Ethene	28
66	<i>o</i> -Xylene	106	112	Butene	56
68	<i>p</i> -Xylene	106	114	2-Methyl-1-pentene	84
70	Ethylbenzene	106	116	1-Hexene	84
74	Propylbenzene	120	118	1-Heptene	98
76	Isopropylbenzene	120	120	1-Hexadecene	224
78	Butylbenzene	134			

^aExcept C_{30} (squalane).

equal to 0.097 which is considerably lower than the value predicted by the proposed (first) correlation for saturated hydrocarbons. The reason for this behavior seems to be related to the temperature dependency of the K_{ij} parameter. Kato et al. (1981) showed that for the Peng–Robinson (PR) EoS and at $T = 293.2$ K (the highest temperature for which experimental data are available) $K_{ij} = 0.15$, while in the temperature range 200–150 K K_{ij} is approximately equal to 0.095. In addition, Kordas et al. (1994) excluded the CO_2 /methane system from the

generalized correlation for K_{ij} that they have recently presented for the PR EoS. They present a separate temperature dependent correlation for CO₂/methane, but they recommend the constant value 0.1 for temperatures greater than 300 K.

5.1.2. The combining rule for the cross co-volume parameter

Eq. (19) depends on the combining rule for the b_{ij} . Both widely used and known definitions for the cross co-volume parameter b_{ij} (the arithmetic mean rule and the Lorentz combining rule) have been used to correlate the binary interaction parameters K_{ij} . Similar correlation results were obtained in both cases; the values of the parameter A were almost identical while the value of θ (Lorentz rule) $\approx 3\theta$ (arithmetical mean rule). For this reason, and since the arithmetic mean rule for b_{ij} is by far the most widely used in cubic EoS, the results shown in Figs. 2–4 are based on the arithmetic mean rule for the cross co-volume parameter.

The correlation for 1-alkenes was based on a limited number of systems and using data of rather poor quality, as reported by Wagner and Wichterle (1987). For this reason, the correlation for 1-alkenes should be used with caution. The same conclusion for CO₂/1-alkene systems holds for other correlations presented in the literature, like that of Kordas et al. (1994).

As can be seen from Figs. 2–4, the same functional form for the correlation can describe the three different types of CO₂/hydrocarbon systems and the same correlation constants are used for all saturated hydrocarbons. The value of θ was found to be approximately equal to zero for these correlations, as can be seen in Table 2. Based on the derivation of the combining rule, this means that the exponent n of the Mie potential (Eq. (12)) has a value of approximately 3, instead of value equal to 6, as suggested by the LJ potential. Chueh and Prausnitz (1967), Reid and Leland (1965) and, more recently, Trebble and Sigmund (1990) have shown that a value of $n = 3$ often provides a better representation of the binary interaction parameters for mixtures with real compounds. The same authors argue that for complex molecules the relations $\epsilon \propto T_c$ and $\sigma^3 \propto V_c$ are not strictly valid. This effect combined with the uncertainty in the calculation of the cross co-volume parameter (Leland, 1976) partly explain the discrepancy between the value of n found from theory and experiment. We have found in this work, however, a different explanation for this apparent (but not actually true) difference between $n(\text{theory})$ and $n(\text{experiment})$. The explanation we propose is based on the inclusion of the ionization potential term in the calculations. When this is done, the value of n , which is in agreement with the experimental results, is approximately equal to 6. A thorough explanation and discussion of this important observation is given in the section prior to Conclusions.

5.1.3. Trends of the interaction parameter K_{ij} with respect to hydrocarbon size and degree of saturation

Some additional interesting information can be obtained from Figs. 2–4. In spite of what might be expected, the interaction parameters for CO₂/saturated hydrocarbons mixtures decrease with increasing size difference. No apparent physical explanation can be easily provided for this effect. It has nevertheless been observed by other investigators as well (Kato et al. 1981; Moysan et al., 1986; Valderrama et al., 1987 for H₂S–hydrocarbon mixtures; Valderrama et al., 1988; Darridon, 1992). If this effect is real, the recent correlation presented by Trebble and Sigmund (1990) cannot predict reliable values for the interaction parameters between CO₂ and saturated hydrocarbons, since it always predicts K_{ij} values which increase with increasing

hydrocarbon size. Trebble and Sigmund (1990) recognized this problem and modified their original correlation accordingly to account for the decreasing K_{ij} with increasing carbon number. Nevertheless, the modified Trebble–Sigmund correlation only provides a very slightly decreasing K_{ij} trend and still overpredicts the interaction parameters for CO₂/heavy alkanes. Furthermore, the modified Trebble–Sigmund correlation has not been extensively used, and these authors retain the original form of their correlation in some recent applications (Sigmund and Trebble, 1992; Trebble et al., 1993). In addition, both the original and the modified Trebble and Sigmund correlations are restricted to only moderately asymmetric systems, and according to the authors (Sigmund and Trebble, 1992), the CO₂/hexadecane systems is thought to be the upper limit of molecule size difference where the correlation can be successfully applied. K_{ij} parameters for CO₂/aromatics systems, however, seem to increase slightly with molecular size, and similar behavior is observed for CO₂/monoalkene mixtures. Again, no physical explanation is found for this behavior. Another interesting conclusion drawn from Figs. 2–4 is that the magnitude of the binary interaction parameters decreases with increasing degree of unsaturation of the hydrocarbon. This seems to hold for systems with both 1-alkenes and aromatics. The correlation for CO₂/saturated hydrocarbons shown here (Fig. 2) provides an upper limit for the binary interaction parameters. It seems from the results that when the aliphatic character of a molecule overrides — in terms of K_{ij} parameters — the unsaturated or aromatic character, the molecule starts to behave like a saturated hydrocarbon. We note that 1-hexadecene has the same K_{ij} value as *n*-hexadecane. Furthermore, for alkylbenzenes above butyl-benzene, the K_{ij} value does not increase any more with the molecular size, but in fact starts decreasing. This behavior is similar to that observed in the case of the CO₂/saturated hydrocarbon interaction parameters. These results clearly show that in the case of a petroleum fraction the K_{ij} value that should be used for interactions with CO₂ is smaller than the interaction parameter values used for a mixture with only saturated hydrocarbons and it becomes even smaller as the content of oil in aromatics increases. Hence, the K_{ij} value for a petroleum fraction lies between the interaction values of the equivalent saturated and aromatic hydrocarbons.

5.1.4. The problem of the critical volume

The critical volume of the pure components is often used in correlations for the K_{ij} parameter. When such correlations are derived from or applied to mixtures of CO₂ (or another gas) with heavy hydrocarbons, a very important problem arises: how should the critical volume of the medium and high molecular weight hydrocarbons be calculated? Accurate experimental data for the critical volume of *n*-alkanes, were, until very recently, available only up to *n*-hexane. Steele (see Tsonopoulos and Tan, 1993) has presented data up to *n*-decane which reveal an increasing trend of the critical density with the number of carbon atoms in the *n*-alkane. According to the data of Steele, the critical density seems to reach a constant value for heavy alkanes. Ambrose however, recommends (on behalf of the IUPAC) the recent data of Teja et al. (1990) which show that the critical density of *n*-alkanes goes through a maximum at $N_c = 6$ or 7 and then decreases with the molecular weight. Most predictive methods (Lydersen, 1955; Ambrose, 1979; Fedors, 1979; Tsonopoulos, 1987; Vetere, 1987; Elbro et al., 1991; Tsonopoulos and Tan, 1993; Constantinou and Gani, 1994) predict an increasing trend of the critical density with the number of carbon atoms, and lead to a limiting value of the density around 0.22–0.26 g cm⁻³ at infinitely long chain. The predictions of many of these methods are shown in Fig. 5 together with the two

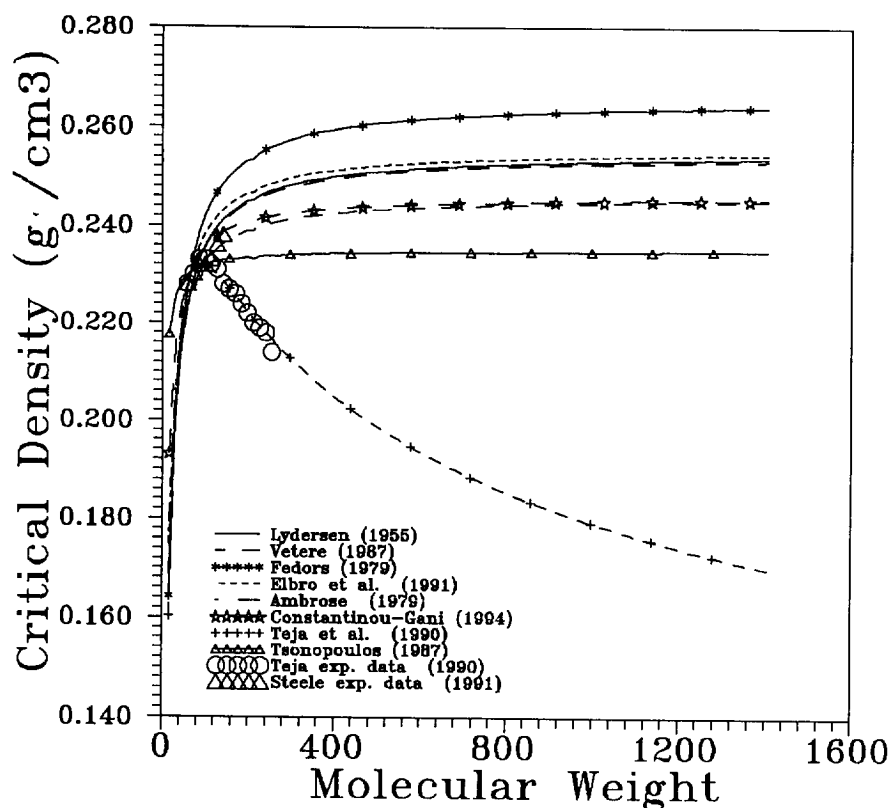


Fig. 5. Experimental and predicted critical densities vs. molecular weight for n -alkanes (up to n -C₁₀₀) using various estimation methods.

different series of experimental data. It is obvious that these predictive methods agree with the trend suggested by the data of Steele. On the other hand, the correlations of Teja et al. (1990) and Anselme et al. (1990) have been derived based on the data of Teja et al. (1990), and tend to a zero value of critical density at infinitely long chain. The experimental data of Teja et al. (1990) are further supported by recent molecular simulation results (Siepmann et al., 1993).

Experimental and correlated phase equilibrium (P - xy) diagrams for three CO₂/ n -alkane mixtures (with n C5, n C10 and n C22) are shown in Figs. 6(a)–(c). The correlated phase diagrams have been generated with the SRK EoS using Eq. (19) and the parameters of Table 2. Fig. 7 presents a typical phase diagram with the proposed correlation for an aromatic containing CO₂ system. Finally, Fig. 8 shows the experimental and calculated phase diagram for CO₂/ n -hexadecane using several correlations, in addition to the one presented here. These figures present typical results and suggest that the proposed correlation — though temperature independent and using a small number of parameters — accurately describes phase equilibrium for CO₂ containing mixtures. Furthermore, as suggested by Fig. 8, the proposed method generally performs better than other correlations for asymmetric CO₂ systems.

Based on the results presented by several authors (Chueh and Prausnitz, 1967; Li et al., 1985), it seems that the methodology and principles followed for the correlation of the K_{ij} parameter

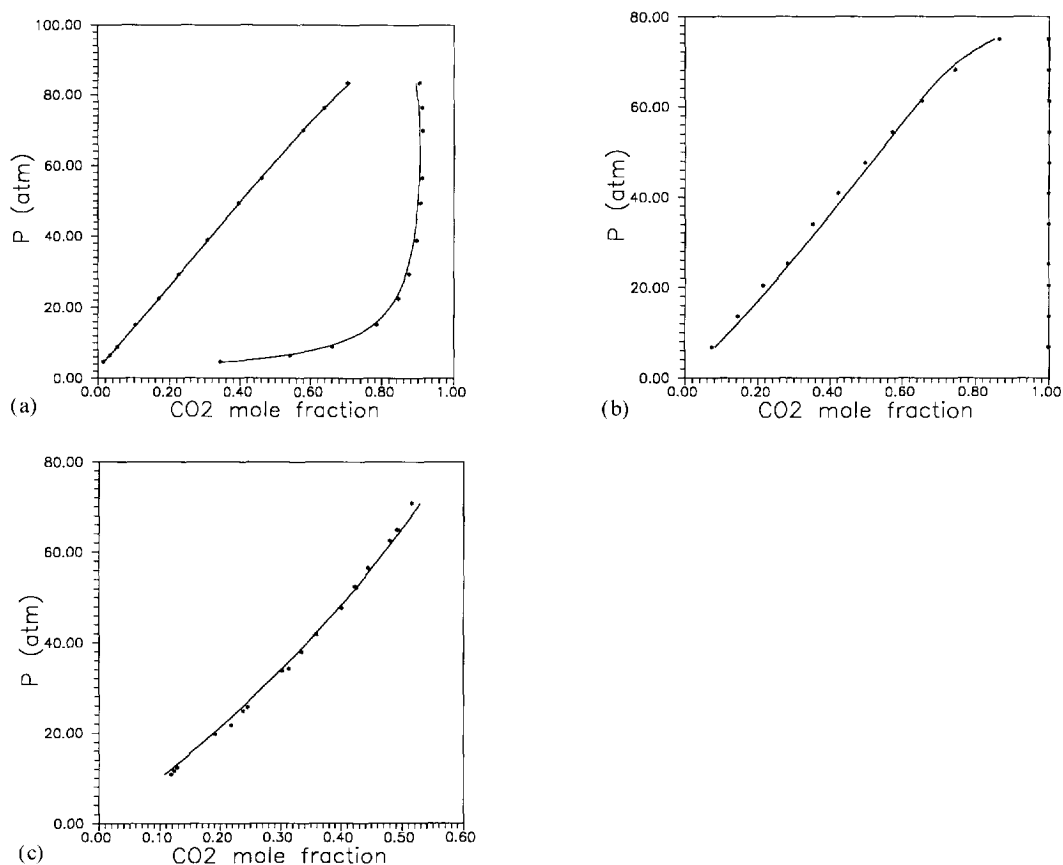


Fig. 6. (a) Predicted phase diagram for the system CO_2/n -pentane at 344.34 K (Cheng et al., 1989) using the binary interaction parameter K_{ij} calculated using Eq. (19). (b) Predicted phase diagram for the system CO_2/n -decane at 310.9 K (Reamer and Sage, 1963) using the binary interaction parameter K_{ij} calculated using Eq. (19). (c) Predicted phase diagram for the system CO_2/n -docosane at 348.15 K (Fall and Luks, 1984) using the binary interaction parameter K_{ij} calculated using Eq. (19).

presented in this work may be used to describe the binary interaction parameters for other kinds of systems, besides CO_2 /hydrocarbons, like methane/hydrocarbon and ethane/hydrocarbon mixtures. Different values of the parameters should however be used. All the conclusions and results presented in this work are valid, at least qualitatively, for the PR and other cubic EoS as well. The conclusions concerning the relative magnitude of the binary interaction parameters for CO_2 with aromatics and saturated hydrocarbons, as well as the trends with respect to molecular size and degree of saturation, are believed to hold for all cubic EoS (Valderrama et al., 1988; Nutakki, 1991; Darridon, 1992).

5.2. k_{ij} and l_{ij} parameters from Eqs. (19) and (21)

The correlations for the simultaneously optimized k_{ij} and l_{ij} are, owing to lack of enough reliable data, presented for mixtures with CO_2 and only linear and branched alkanes. The results

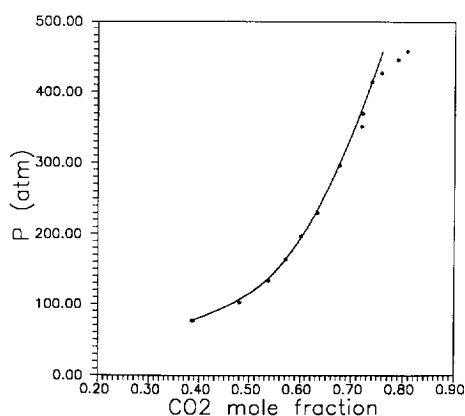


Fig. 7. Predicted phase diagram for the system CO₂/biphenyl at 333.15 K (Zhang et al., 1991) using the binary interaction parameter K_{ij} calculated using Eq. (19).

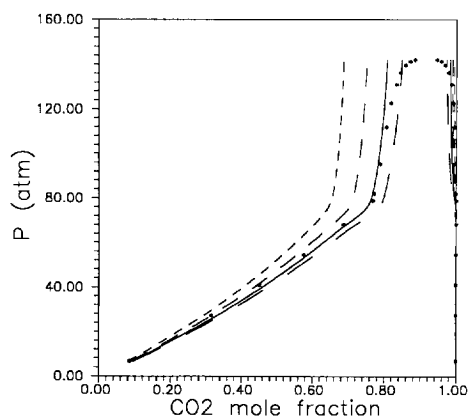


Fig. 8. Predicted phase diagram for the system CO₂/*n*-hexadecane at 308.15 K (Charoensombut-Amon et al., 1986) using the binary interaction parameter K_{ij} calculated using Eq. (19) (solid line), Kordas et al. (1994) (long dash), Kato et al. (1981) (medium dash) and Trebble and Sigmund (1990) (short dash).

are shown in Figs. 9 and 10 and the constants of Eqs. (19) and (21) are given in Table 2. The estimation of the optimum k_{ij} and l_{ij} parameters was performed based on the same rules described previously for the estimation of the k_{ij} parameters, but larger deviations were allowed. It should be emphasized that the optimum k_{ij} and l_{ij} values resulted from a simultaneous estimation of both parameters. (We use the symbol k_{ij} to designate the interaction parameters of the attractive term optimized together with the l_{ij} parameters; it is used to distinguish from the K_{ij} values optimized and correlated independently in the previous sections.) It is well known (Anderson et al., 1978) that simultaneous estimation of both l_{ij} and k_{ij} parameters leads to more than one set of parameters which have the same confidence range and can represent the experimental data equally well. For this reason, the parameters k_{ij} and l_{ij} are not actually independent but intercorrelated. It is important to mention that this intercorrelation of parameters leads to large scatter of data. Fig. 11 presents a typical phase diagram for CO₂/*n*C₃₆ using the proposed correlations (for K_{ij} alone and for both k_{ij} and l_{ij}) and the model of Gasem and Robinson (1990) which uses correlations for both interaction parameters. As can be seen, the

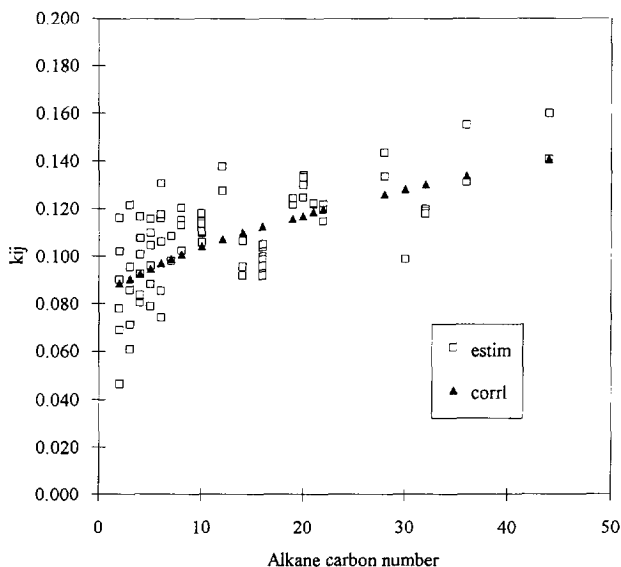


Fig. 9. Estimated and correlated values for binary interaction parameters (k_{ij}) between carbon dioxide and linear and branched alkanes.

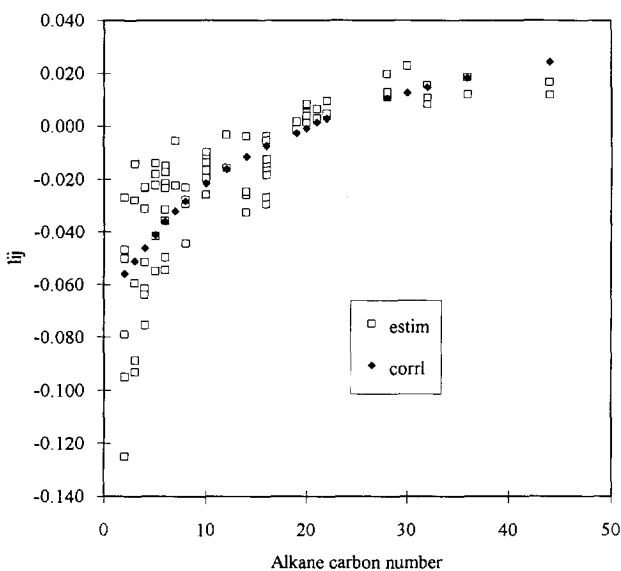


Fig. 10. Estimated and correlated values for binary interaction parameters (l_{ij}) between carbon dioxide and linear and branched alkanes.

proposed correlations for both interaction parameters offer, for this highly asymmetric system, an improvement over the previous correlation for only K_{ij} presented in this work, as well as a better performance than the Gasem and Robinson (1990) method. Nevertheless, the correlation for K_{ij} alone given here provides satisfactory results in most cases and is preferred. The correlations for both k_{ij}/l_{ij} are restricted to CO_2 /alkane systems and should be used with caution due to the

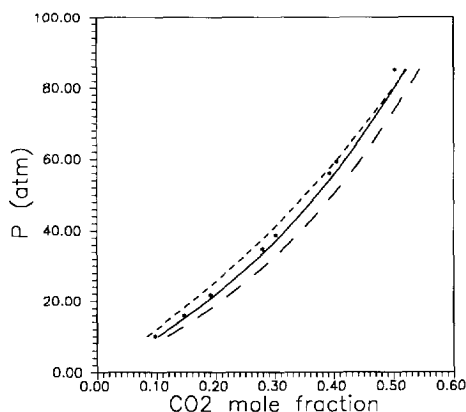


Fig. 11. Predicted phase diagram for the system CO_2/n -hexatriacontane at 423.2 K (Gasem and Robinson, 1985a) using the binary interaction parameters k_{ij} and l_{ij} calculated using Eqs. (19) and (21) (solid line), Gasem and Robinson (1985b) temperature independent k_{ij} and l_{ij} (long dash), and K_{ij} from Eq. (19) (short dash).

inevitable intercorrelation of the parameters. The latter correlations are, however, particularly useful for highly asymmetric systems where the use of the second interaction parameter may be required.

6. On the temperature dependency of the K_{ij} parameter

In spite of what has been stated by some authors (Tsonopoulos, 1979; Lin, 1984), it is generally accepted that the binary interaction parameter K_{ij} of the cross energy term depends somewhat on temperature, which partly explains the scatter of the K_{ij} data in Figs. 2–4 (Leland, 1980; Kato et al., 1981; Moysan et al., 1986; Valderrama et al., 1988; Bartle et al., 1992; Kordas et al., 1994). Kato et al. (1981) tried to describe this temperature dependency in an empirical way and found that a quadratic function could adequately describe the K_{ij} parameters for CO_2/n -alkanes systems, for n -alkanes smaller than n -decane. A similar quadratic temperature dependency is presented by Moysan et al. (1986) and Ohe (1990), while recently Kordas et al. (1994) suggested a cubic temperature dependency of the interaction parameters. It is the objective of this section to show that a consistent temperature dependency can be found for all kinds of mixtures of alkanes with CO_2 and other gases, and that there seems to be a theoretical explanation for this temperature behavior.

Cook and Rowlinson (1953) and Rowlinson and Sutton (1955) showed using the theory of noncentral forces between nonspherical molecules, that:

$$\epsilon_{ij} = \epsilon_{ij}^0 \left(1 + \frac{\eta_{ij}}{kT} \right) \quad (24)$$

where ϵ_{ij}^0 is the value of ϵ_{ij} at infinite temperature. The other symbols are explained in the nomenclature.

It is apparent from Eq. (24) that the potential energy parameter bears a linear dependency with the inverse temperature.

Fisher and Leland (1970) showed, however, in the process of deriving the quadratic form of the mixing rules for σ_m^3 and $\sigma_m^3\epsilon_m$ (Eqs. (10a) and (10b)) that a better approximation can be made by finding ϵ_m using the second two terms of the right-hand side of Eq. (9) and then dividing by f_1/kT :

$$\sigma_m^3\epsilon_m = \sum_i \sum_j x_i x_j \left(\sigma_{ij}^3 \epsilon_{ij} + \sigma_{ij}^3 \epsilon_{ij}^2 \frac{f_2}{f_1 T} \right) \tag{25}$$

The parameter f_2/f_1 will be determined empirically. It can be shown that Eq. (6) will now be given by:

$$a = \sum_i \sum_j x_i x_j a_{ij} \left(1 + \epsilon_{ij} \frac{f_2}{f_1 T} \right) \tag{26}$$

and consequently

$$(1 - K_{ij})^T = (1 - K_{ij})^0 \left(1 + \epsilon_{ij} \frac{f_2}{f_1 T} \right) \tag{27}$$

where $(1 - K_{ij})^0$ is the value of $(1 - K_{ij})$ at infinite temperature. Substituting Eq. (24) in Eq. (27), an expression showing a quadratic dependency of the binary interaction parameter K_{ij} with the inverse temperature results:

$$(1 - K_{ij})^T = \left(1 + \frac{\mu}{T} + \frac{\nu}{T^2} \right) (1 - K_{ij})^0 \tag{28}$$

where $\mu = \epsilon_{ij}^0 f_2/f_1$ is given in K and $\nu = (\eta_{ij} \epsilon_{ij}^0 f_2)/(k f_1)$ is given in K².

The values of the parameters of the above temperature dependent correlation of K_{ij} are given for some of the investigated systems in Table 4 and some typical results are shown graphically in Figs. 12(a)–(c). Similar plots with respect to temperature can be obtained for mixtures with only hydrocarbons as well, such as methane or propane with light alkanes. Figs. 12(a)–(c) present plots of K_{ij} with respect to temperature, similar to the ones shown by Kato et al. (1981) and Kordas et al. (1994) for CO₂/light alkanes systems. Note that the temperature dependency of the K_{ij} , as revealed by Eq. (28), is quadratic with respect to $1/T$. Note, also from Table 4, the similarity of the parameter values for CO₂/hydrocarbon systems and for mixtures with only hydrocarbons.

The effect of temperature is not very significant at low reduced temperatures but it is pronounced at high reduced temperatures. At low reduced temperatures, the quadratic function

Table 4
Parameters for the quadratic dependence of the binary interaction parameters with temperature (Eq. (28))

System	$(1 - K_{ij})^0$	$\mu(1 - K_{ij})^0$	$\nu(1 - K_{ij})^0$
CO ₂ /propane	0.35874	264.14	–33552
CO ₂ /butane	0.40018	247.69	–31604
CO ₂ /decane	0.51584	251.35	–42090
CO ₂ /docosane	0.58880	277.40	–58529
CO ₂ /octacosane	0.74845	186.20	–47600
Methane/decane	0.72812	173.12	–29447
Ethane/decane	0.65951	233.08	–40421
Propane/decane	0.66528	241.49	–42620

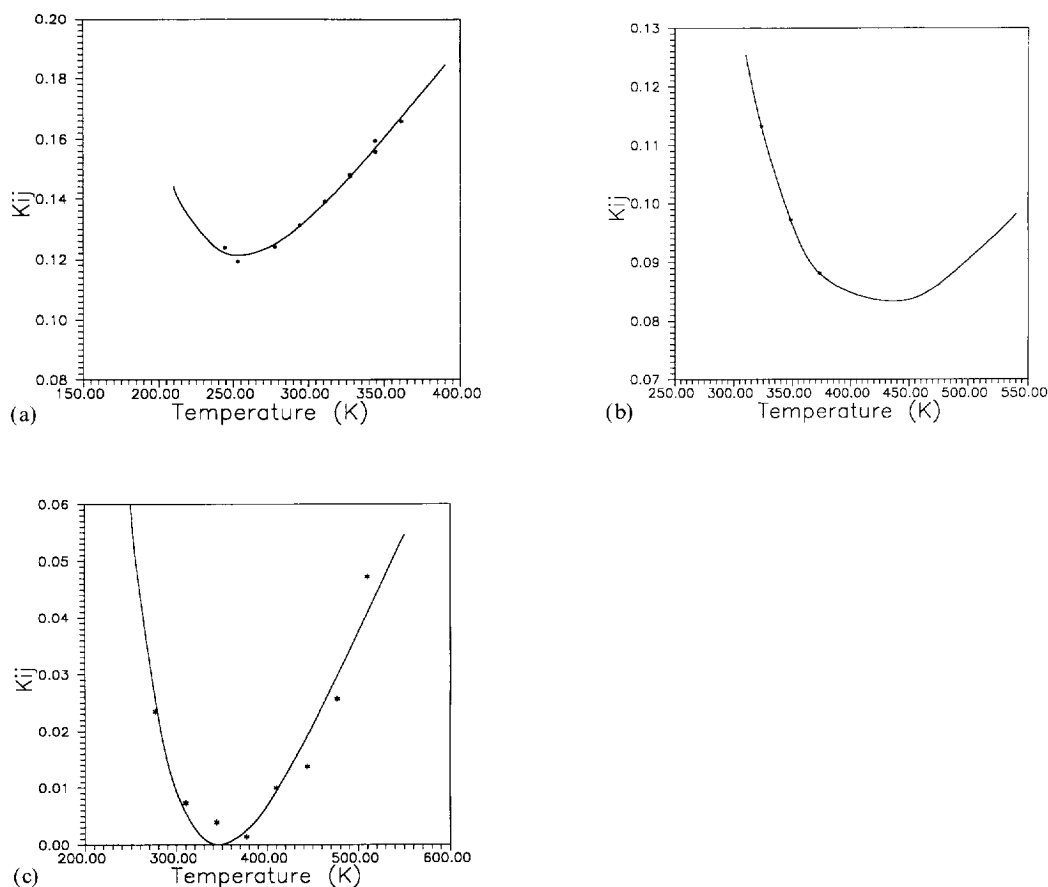


Fig. 12.(a) Temperature dependence of estimated binary interaction parameters (K_{ij}) between carbon dioxide and propane and its correlation by means of Eq. (28). (b) Temperature dependence of estimated binary interaction parameters (K_{ij}) between carbon dioxide and docosane and its correlation by means of Eq. (28). (c) Temperature dependence of estimated binary interaction parameters (K_{ij}) between ethane and decane and its correlation by means of Eq. (28).

is close to a minimum which hides the temperature dependency and leads to the conclusion that the temperature has a negligible effect on the binary interaction parameters. Note, however, that the differences in the reported experimental data and in the composition range reported by different authors are often more significant than the effect of temperature at low reduced temperatures. For this reason, only data from the same source or data from different authors in reasonable agreement with each other and covering similar ranges of compositions were used to study the temperature dependency of the K_{ij} parameter.

No attempt to include this (or any other) temperature dependency in the previously presented correlations was made owing to lack of accurate data, especially outside the range studied by Kato et al. (1981). We believe that, within the temperature used in this study ($283\text{--}373 \pm 50$ K), such a temperature dependent correlation would offer no significant gain in accuracy as compared to the proposed temperature independent correlations.

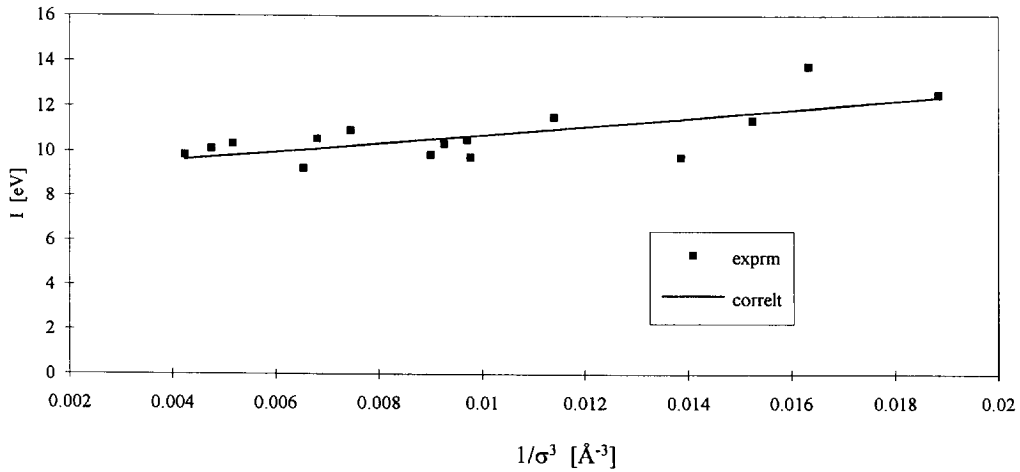


Fig. 13. Correlation of the ionization potentials as linear function of $(1/\sigma^3)$.

7. Relation between the ionization potential and the molecular diameter of the Mie potential function

It is often stated in the literature (see e.g. Prausnitz and Gunn, 1958; Chueh and Prausnitz, 1967; Teja, 1978; Prausnitz et al., 1986) that the classical geometric mean rule for the cross energy parameter of cubic EoS ($a_{12} = (a_1 a_2)^{1/2}$) can be derived from the London–Mie theory (described previously) in an empirical way. This is done by setting the exponent n (of the attractive part of the Mie potential function) to an empirical value equal to 3, and further assuming that the ionization potential ratio (appeared in Eqs. (11), (13a) and (13b)) is approximately unity. We will show in this section that, when making the plausible assumption that the ionization potential is proportional to σ^{-3} , the classical geometric mean rule for a_{ij} can be derived by setting the exponent n to 6, which is a theoretically justified value since it leads to the LJ form of the Mie potential function.

Reid and Leland (1965) stated that the ionization potential (I) can be expressed as a linear function of $(1/\sigma^3)$. Using I data from Lide (1993) and σ data from Reid et al. (1987) (for CO_2 and hydrocarbons), a linear plot of I with σ^{-3} can be obtained:

$$I = 8.835 + \frac{188.63}{\sigma^3} \tag{29}$$

where the ionization potential is in eV and σ is in \AA . Eq. (29) is shown graphically in Fig. 13.

Replacing Eq. (29) in the ionization potential ratio term (appearing in Eqs. (11), (13a) and the other similar ones), this term can be written as:

$$\frac{2\sqrt{I_i I_j}}{I_i + I_j} = \Pi \left(\frac{2\sqrt{\sigma_i \sigma_j}}{\sigma_i + \sigma_j} \right)^{-3} = \Pi \left(\frac{\sqrt{\sigma_i \sigma_j}}{\sigma_{ij}} \right)^{-3} = \Pi \left(\frac{\sqrt{b_i b_j}}{b_{ij}} \right)^{-1} \tag{30}$$

where Π is a function of i and j with a value smaller than unity and typically around 0.9.

Replacing Eq. (30) in Eqs. (14), (17) and (19), the following expressions are easily derived:

$$a_{ij} = \sqrt{a_i a_j} \Pi \left(\frac{\sqrt{b_i b_j}}{b_{ij}} \right)^{\frac{n-6}{3}} \quad (31)$$

$$(1 - K_{ij}) = \Pi \left(\frac{\sqrt{b_i b_j}}{b_{ij}} \right)^{\frac{n-6}{3}} \quad (32)$$

$$K_{ij} = 1 - A \left(\frac{\sqrt{b_i b_j}}{b_{ij}} \right)^{\frac{n-6}{3}} \quad (33)$$

Using the values presented in Table 2 it can be seen that A has a value around 0.9 as expected and that, to the value of θ presented (between -0.05 and 0.11), the corresponding value of n is approximately equal to 6, which is exactly the exponent used in the LJ potential. Replacing $n = 6$ in Eqs. (31) and (32), the geometric mean combining rule for a_{ij} is recovered and the value of k_{ij} is approximately equal to zero (to the extent that the function Π approaches unity). Eq. (31) (with $n = 6$) (or similarly Eq. (13d)) is equivalent to the following expression for the cross critical temperature used by Chueh and Prausnitz (1967):

$$T_{c_{ij}} = \sqrt{T_{c_i} T_{c_j}} (1 - K_{ij})$$

$$K_{ij} = 1 - \left[\frac{2\sqrt{V_{c_i}^{1/3} V_{c_j}^{1/3}}}{V_{c_i}^{1/3} + V_{c_j}^{1/3}} \right]^3 = 1 - \left[\frac{8\sqrt{V_{c_i} V_{c_j}}}{(V_{c_i}^{1/3} + V_{c_j}^{1/3})^3} \right] = 1 - \frac{\sqrt{V_{c_i} V_{c_j}}}{V_{c_{ij}}} \quad (34)$$

Chueh and Prausnitz (1967) derived Eq. (34) from the London–Mie theory assuming that $n = 3$. We have shown in this section that the same equation (or, equivalently, the geometric mean rule for a_{ij}) can be derived from the London–LJ theory, i.e. n is approximately equal to 6 for the CO_2 and hydrocarbon molecules considered here. It is well-known that the geometric mean rule for a_{ij} describes approximately well the interactions for many types of (non-polar) mixtures. Its derivation from the London–LJ theory implies that many of the real non-polar molecules encountered in nature can be, to a certain degree, described by the LJ potential. This is an important conclusion since it indicates that discussion of simulation results and other theoretical considerations for mixtures with LJ molecules can be applied to mixtures with real relatively non-polar molecules, as well.

8. Conclusions

Theoretically based expressions were successfully used to correlate the binary interaction parameters K_{ij} and (simultaneous optimized) k_{ij}/l_{ij} of the SRK EoS for CO_2 /hydrocarbon mixtures. Correlations for the K_{ij} parameter are given for all kinds of hydrocarbons (saturated, unsaturated and aromatics). For the simultaneous optimized k_{ij} and l_{ij} parameters, correlations which apply only to CO_2 /saturated hydrocarbon mixtures are provided. The proposed correlations seem to be of wide application, even for the most asymmetric CO_2 /hydrocarbon mixtures. Unlike previously presented expressions for the K_{ij} , they do not need any additional information

to those already required by the EoS (critical properties and acentric factor). The functional form of the correlations enables us to easily tune the EoS when dealing with reservoir fluids. The conclusions for the CO₂/aromatics systems presented here can help the user to develop a physically meaningful method to tune the EoS. It has been shown that the estimated values of K_{ij} follow a temperature dependency as predicted by the theory of noncentral forces between nonspherical molecules. The present correlations and the insight about the behavior of the binary interaction parameters is expected to improve the ability and facilitate the use of cubic EoS in predicting phase equilibria for systems using CO₂ to enhance oil recovery. Finally, the theoretical derivation for the K_{ij} correlation (based on the London–LJ theory) helps us gain understanding on the nature of the attractive interaction parameter used in cubic EoS. Indeed, neglecting any other possible deficiencies in the cubic EoS, K_{ij} , as shown here, clearly represents the deviations between the classical geometric mean rule for a_{12} and the theoretically “exact” combining rule derived from the London–LJ theory. These conclusions are correct only for relatively non-polar mixtures (like the ones studied in this work), for which London theory is assumed to be valid.

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List of symbols

a	equation of state parameter
A	parameter in Eq. (19)
b	equation of state parameter
c_i	cohesive energy
C_1	parameter in Eq. (21)
C_2	parameter in Eq. (21)
F_{obj}	objective function
G^E	excess Gibbs free energy
I	ionization potential
k	Boltzmann’s constant
k_{ij}	binary interaction parameter for the energy parameter of the EoS for $l_{ij} \neq 0$
K_{ij}	binary interaction parameter for the energy parameter of the EoS for $l_{ij} = 0$
l_{ij}	binary interaction parameter for the co-volume parameter of the EoS
m	exponential for the repulsive part of the Mie potential function
Mw	molecular weight
n	exponential for the attractive part of the Mie potential function
n, N	number of points
N_c	carbon number
P	pressure

r	intermolecular distance
R	universal gas constant
T	temperature
V	molar volume
x	molar fraction (liquid phase)
y	molar fraction (vapor phase)

Greek letters

α	mixture energy parameter
δ_i	solubility parameter
Γ	intermolecular potential
ϵ	interaction energy
η	parameter of non-central energy
θ	parameter in Eq. (19)
λ_{ij}	interaction parameter
μ	parameter in Eq. (28) [K]
ν	parameter in Eq. (28) [K ²]
Π	parameter in Eq. (30)
ρ	density
σ	intermolecular distance for a zero value of ϵ
ω	acentric factor
Ω_a	constant of a cubic EOS related to energy parameter
Ω_b	constant of a cubic EOS related to co-volume parameter

Subscripts

c	critical
cal	calculated
corr	correlated
estim	estimated
exp	experimental
i	component i
j	component j
m	mixture
n	number of components
r	reduced

Superscripts

0	temperature independent
T	temperature dependent

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