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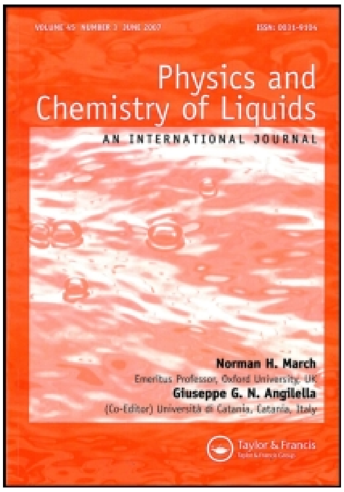

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Estimation of phase behavior in mixtures of CO_2 and C_{20}+ *n*-alkanes using predictive eos models

Ilya Polishuk[a]; Jaime Wisniak[a]; Hugo Segura[b]
[a] Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel [b] Department of Chemical Engineering, Universidad de Concepción, Concepción, Chile

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ESTIMATION OF PHASE BEHAVIOR IN MIXTURES OF CO_2 AND $C_{20}+$ *n*-ALKANES USING PREDICTIVE EOS MODELS

ILYA POLISHUK[a,*], JAIME WISNIAK[a] and HUGO SEGURA[b]

[a]*Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel;*
[b]*Department of Chemical Engineering, Universidad de Concepción, Concepción, Chile*

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The present study compares the ability of Global Phase Diagram Approach (GPDA) and Linear Combination of the Vidal and Michelsen mixing rules (LCVM) to predict equilibrium compositions and molar volumes in mixtures of CO_2–*n*-eicosane and heavier homologues. LCVM should be characterized as correlative rather than predictive model because its parameters have been evaluated by fitting the data of homologues up to *n*-octacosane. In contrast, GPDA appears as entirely predictive model because it does not resource to any experimental data of systems under consideration. Nevertheless, GPDA is much more accurate than LCVM in predicting data. These results emphasize the robustness of GPDA and evidence about its reliability for predicting of data are not available experimentally.

Keywords: Supercritical; *n*-Alkanes; Equation of state; Global phase diagram

1. INTRODUCTION

Modern process design requires thermodynamic models capable of predicting accurate results for different thermodynamic properties in both the subcritical and critical regions simultaneously, and without preliminary resource to the results of experiment. However, the present development of molecular theory does not allow an adequate evaluation of entirely predictive methods, which could yield reliable predictions for asymmetric mixtures. Therefore, the usual practice is to develop semi-predictive approaches that use some experimental data in order to predict the missing ones. Thus, quality of such approaches is defined by their accuracy and also by the relation between the amount of data input and predicted.

It is widely agreed that models characterized by high correlative ability should also be good for predictive purposes. Accordingly, it is often assumed that cubic EOSs combined with Huron–Vidal type mixing rules, which have an excellent flexibility in correlating data, will exhibit good predictive ability as well. However, it should be

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*Corresponding author. Present address: the Department of Chemical Engineering & Biotechnology, the College of Judea and Samaria, Ariel, Israel. Tel.: +972-8-6461479. Fax: +972-8-6472916. E-mail: polishyk@bgumail.bgu.ac.il

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pointed out that accuracy of these models is usually based on a large amount of experimental data. In other words, they appear to be more correlative rather than predictive.

In addition, results of our previous studies [1–3] contradict the widely accepted opinion regarding advantages of the G^E-based semi-predictive models. In particular, although their complex and multidimensional structure may have only a modest contribution to accurate description of data, it considerably hinders consideration of the overall picture of phase behavior. As a result, evaluation of parameters for such models is usually performed by the way of local data fit. The latter approach tends to ignore the fact that different regions of the thermodynamic phase space created by the EOS are closely inter-related. Thus, such models may not only generate non-realistic phase diagrams, but usually predict an incorrect balance between vapor–liquid equilibira (VLE) and liquid–liquid equilibria (LLE) and inaccurate results for the critical lines.

In order to overcome the shortcomings of the G^E-based semi-predictive models, recently [4] we have proposed the quantitative Global Phase Diagram (klGPD)-based semi-predictive Approach (GPDA). In contrast to the G^E-based equations, GPDA requires no more than just 2–3 experimental critical points to predict the entire thermodynamic phase space in whole homologues series of binary systems. In other words, the latter approach is characterized by very high ratio between the data predicted and input. The successful implementation of GPDA is based on the fact that the relation between two key properties that characterize VLE and LLE in the system, namely the relation between the Upper Critical Solution Temperature (UCST) and the Critical Pressure Maximum (CPM), is approximately constant over the majority of homologues series. Since GPDA considers not just numerous experimental points, but VLE, LLE, and the critical lines simultaneously, it produces a reasonable distribution of the inevitable deviations from the experimental data over the whole thermodynamic phase space. Hence, this approach can be reliable for prediction of data, which are not available experimentally.

At the same time, it should be realized that the only way to evaluate the accuracy of different models is comparison of their predictions with the available experimental data. The results of such comparison can evident about the robustness and reliability of predictive models. A challenging task for these models is accurate description of phase behavior in highly asymmetric systems. That is because these systems have significant practical importance and they are usually difficult for prediction. In addition, heavy compounds exhibit many different homologues and isomers. Obviously, the comprehensive experimental investigation of all possible combinations in mixtures is not always possible. Therefore the data regarding such systems is usually scarce. In particular, until the recent publication of data regarding the mutual solubility and density of carbon dioxide with eicosane and heavier paraffins [5], a very limited number of reliable datasets for these important systems were available.

The significant advantage of the data of Nieuwoudt and du Rand [5] is an accurate experimental procedure, which finds expression in their high consistency. In addition, the latter source is the only one who reports compositions and densities in both equilibrium phases. Thus, the data of Nieuwoudt and du Rand [5] is an excellent selection for evaluation of the reliability of different predictive approaches.

In the present study we will compare the results predicted by GPDA and the Linear Combination of the Vidal and Michelsen mixing rules-based EOS (LCVM) [6]. At the same time, we will not consider here another important G^E-based model, namely the Predictive Soave–Redlich–Kwong (PSRK) equation [7]. That is because the inaccuracy of this model predicting the data of asymmetric systems has been discussed previously [2,6]. In addition, it has been demonstrated [2] that the attempts to correct the PSRK parameters in an artificial manner [8–10] in order to improve the accuracy of predicting data in asymmetric systems, lead to prediction of a nonphysical trend of the global phase behavior. The details of models selected for the present study are given below.

2. THEORY

The LCVM model [6] is based on the Peng–Robinson (PR) EOS [11], given as follows:

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2V_m - b^2} \tag{1}$$

where

$$a = 0.45724\frac{R^2 T_c^2}{P_c}, \qquad b = 0.07780\frac{RT_c}{P_c} \tag{2}$$

For nonpolar compounds LCVM uses the one-parameter α-functionality of Soave [12], given as follows:

$$\alpha = \left[m\left(1 - T_r^{0.5}\right)\right]^2 \tag{3}$$

where

$$m = 1 + 0.384401 + 1.52276\omega - 0.213808\omega^2 + 0.03461\omega^3 - 0.001976\omega^4 \tag{4}$$

LCVM implements the classical van der Waals mixing rule for b and following mixing rule for a:

$$a = \left[\left(\frac{\lambda}{A_V} + \frac{1-\lambda}{A_M}\right)\frac{G^E}{RT} + \frac{1-\lambda}{A_M}\sum x_i \ln\left(\frac{b}{b_i}\right) + \sum x_i \frac{a_i}{b_i RT}\right] bRT \tag{5}$$

The value of parameter λ is equal to 0.36 and it has been evaluated by fitting the experimental data in numerous binary systems. A_m is set equal to -0.52 and $A_v = -0.62$.

The success of LCVM in describing VLE data in asymmetric systems has been recently [13] explained by the fact that LCVM diminishes the difference between the combinatorial terms of UNIFAC and the cubic EOS itself, which is characteristic of other G^E-based models. Nevertheless, we have proposed a different explanation for the superiority of LCVM over PSRK in predicting the data for asymmetric systems, namely, the significantly larger base of experimental data implemented by LCVM for the evaluation of its parameters. For example, in the particular case of CO_2–*n*-alkanes, PSRK uses the data of homologues up to *n*-decane [7], and LCVM – up to *n*-octacosane [6]. However, such practice does not remove the fundamental disadvantage of the model, whose parameters are obtained by a local fit, namely, its low predictive ability.

As it has been already pointed out, the complex and multidimensional nature of G^E-based models such as PSRK and LCVM hinders the implementation of methodologies that consider the entire thermodynamic phase space instead of a local data fit. For this reason we have implemented the klGPD methodology using the simplest classical mixing rules.

Recently [14,15] it has been shown that the expressions such as Eq. (4) may generate undesirable numerical pitfalls, which are responsible for predicting nonphysical phase behavior in mixtures. Moreover, it is well known that the two-parameter equations such as PR are inaccurate in predicting thermodynamic properties such as liquid densities.

Thus, appreciation of the fact that all parts of the thermodynamic phase space are closely inter-related encourages the development of an equation of state, which would be simultaneously accurate for the largest number of properties and be free of numerical pitfalls. Recently [2] we have proposed the following EOS that meets these requirements in a satisfactory manner:

$$P = \frac{RT\,(V_m + 0.125b)}{V_m(V_m - 0.875b)} - \frac{aT_r^{\,(m_1 T_r^{m_2})}}{(V_m + c)(V_m + d)} \tag{6}$$

where m_1 and m_2 are adjustable parameters for the appropriate presentation of the vapor pressure curve. The values of these parameters for light gases, for which high quality data are available, and for complex polar compounds should be evaluated separately (for CO_2 $m_1 = -0.33595$ and $m_2 = -0.15187$). For other compounds the values of m_1 and m_2 can be generalized; for example, we have proposed that for *all* hydrocarbons m_2 be taken as 0.25 and for hydrocarbons up to and including *n*-decane, m_1 is generalized by the following expression:

$$m_1 = \frac{0.00849 - 0.29324\omega + 0.61934\omega^2 - 1.7792\omega^3}{b} \tag{7}$$

while for *n* -alkanes having a carbon numbers 11–30, m_1 is generalized as follows:

$$m_1 = \frac{-0.4162 + 1.5447\omega - 2.5285\omega^2 + 0.81466\omega^3}{b} \tag{8}$$

Although the value of b is given in L/mol, the parameter m_1 should be considered as dimensionless.

The values of a, b, c, and d are obtained solving the system of the four following equations:

$$\left(\frac{\partial P}{\partial V_m}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V_m^2}\right)_{T_c} = 0 \tag{9}$$

$$V_{m,c,\mathrm{EOS}} = (1 + V_{m,\text{triple point}})V_{m,c,\mathrm{EXPT}} \tag{10}$$

$$b = \frac{4}{3.5}V_{m,\text{triple point}} \tag{11}$$

where for light gases and heavy substances having carbon number larger that 10, Eqs. (10) and (11) correspond to the solid phase, and for others – to the liquid one. The pure compound data have been obtained from the DIPPR database [16]. However this database does not include *n*-alkanes heavier than *n*-C_{30} (with the exception of *n*-C_{32} and *n*-C_{36}) and the pertinent pure compound constants should be evaluated using the empirical correlations developed for this purpose. Kontogeorgis and Tassios [17], who have performed a comprehensive comparative investigation of the most widely used correlations for the critical constants and acentric factors, have suggested using the group-contributive correlations of Constantinou and Gani [18] for estimation of the critical temperatures and pressures of long *n*-alkanes, which are given as follows:

$$T_c = 181.128 \times \mathrm{Ln}[2 \times 1.6781 + (C_x - 2) \times 3.492] \tag{12}$$

and

$$P_c = 1.3705 + \frac{1}{(0.10022 + 2 \times 0.019904 + (C_x - 2) \times 0.010558)^2} \tag{13}$$

Thus, in the present study we have implemented Eqs. (12) and (13) for estimation of the critical temperatures and pressures for *all* *n*-alkanes heavier than C_{30}. At the same time, it seems that the correlation of critical volumes proposed by Tsonopoulos and Tan [19]:

$$V_c = 0.0035831 \times C_x \times \left(20.01 - \frac{59.72}{C_x} + \frac{149.7}{C_x^2}\right) \tag{14}$$

is more reliable than the pertinent correlation of Constantinou and Gani [18] and, hence, Eq. (14) is implemented by the present model. Following the recommendation of Kontogeorgis and Tassios [17], we have adopted the correlation of Constantinou *et al.* [20] for evaluating the values of acentric factors for *n*-alkanes heavier than C_{30}:

$$\exp\left[\left(\frac{\omega}{0.4085}\right)^{0.505}\right] = 0.29602 \times 2 + (C_x - 2) \times 0.14691 + 1.1507 \tag{15}$$

A further generalization of the resulting m_1 values for *n*-alkanes heavier than C_{30} yields the following expression:

$$m_1 = \frac{-0.28912 + 0.60555\omega - 0.81155\omega^2}{b} \tag{16}$$

where b is given in L/mol. Again, the parameter m_1 is considered as dimensionless.

The value of the last property necessary for evaluation of the parameters of Eq. (6), namely, the solid density at the triple point for heavy *n*-alkanes, is not available in the literature, with the exception of *n*-C_{36}. However, even for this compound there are significant deviations between the values given in the different data bases. We suppose that the slight increase in solid density with increasing the carbon number is compensated by the thermal expansion caused by the pertinent increase of the melting temperature. Hence, we assume a constant value for the solid density of 961 g/L at the triple point of *all* n-alkanes heavier than n-C_{30}. Thus, according to our model, the solid phase molar volume at this point will be dependent only on the molecular weight of the n-alkane.

Figure 1 compares the ability of Eqs. (1) (PR) and (6) to predict the pure compound data of the heavy n-alkanes considered by the present study. It should be pointed out that it is not always easy to evaluate the reliability of the polynomials that correlate the properties of these compounds in databases such as DIPPR [16] because the pertinent experimental data are insufficient. For this reason it should be understood that the points on Fig. 1 present probably only a *qualitative* approximation of real values. Thus presently we cannot say which equation predicts the vapor pressures more accurately because both yield very similar results. Nevertheless, it can be seen that Eq. (6) has a clear advantage over PR in predicting molar volumes. Obviously, fitting the parameters of Eq. (6) for particular compounds will considerably improve its accuracy in comparison with the generalized scheme presented by Eqs. (7)–(16). However, such practice will remove the predictive character of the model.

As already indicated, the parameters of Eq. (6) for mixtures are obtained using the following classical van der Waals mixing rules:

$$z = \sum_{ij} x_i x_j z_{ij} \tag{17}$$

where $z = a$, b, c, and d.

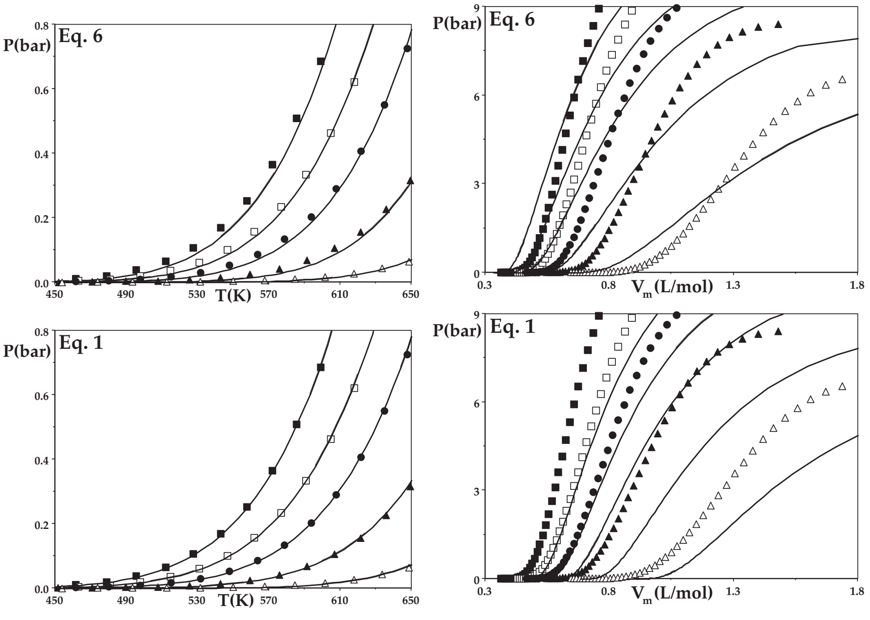

FIGURE 1 Vapor pressures and molar volumes of several n-alkanes. Black solid lines – data predicted by Eqs. (1) and (6); The generalized data of the DIPPR data base [16]: Full square – C_{22}; Hollow square – C_{24}; Full circle – C_{24}; Full triangle – C_{28}; Hollow triangle – C_{36}.

The cross-interaction parameters are obtained with the following combination rules:

$$\begin{aligned} a_{21} &= a_{12} = (1-k_{12})\sqrt{a_{11}a_{22}} \\ b_{12} &= b_{21} = (1-l_{12})\frac{b_{11}+b_{22}}{2} \\ c_{12} &= c_{21} = \frac{c_{11}+c_{22}}{2} \\ d_{12} &= d_{21} = \frac{d_{11}+d_{22}}{2} \end{aligned} \tag{18}$$

where k_{12} and l_{12} are binary adjustable parameters. Proper evaluation of their values is the objective of the GPDA. As we have already pointed out, experience shows that the balance between VLE and LLE does not significantly change along a homolog series. In other words, intersection between the CPM isobar and the LCST isotherm, which is necessary for the appropriate and overall description of mixtures [4], usually takes place at similar values of k_{12} and l_{12}. This observation reveals the basis of the GPDA. Thus, to predict the entire thermodynamic phase space of a complete homolog series, it is necessary to know only the experimental value of UCST together with the pressure (and sometimes the temperature of CPM) of one of the homologs. It is helpful to consider as reference systems those homologs that exhibit the Type II behavior and which have been intensively investigated. In the series under consideration the best candidate is the system CO_2–*n*-decane. Here the binary parameters of the series have been evaluated using the klGPD of this system.

The range of applicability of GPDA can be substantially enlarged if the values of binary interaction parameters change proportionally to the values of the corresponding pure-compound parameters. Such proportionality can be easily established for the case of a linear combination rule for the covolume, as follows:

$$l_{12} = \frac{b_{22}-b_{11}}{b_{22}+b_{11}} L_{12} \tag{19}$$

where L_{12} is a value characteristic for a given homologs series.

The following proportional relation for the binary interaction parameter k_{12}, including the appropriate temperature dependency, has been developed:

$$k_{12} = \left(K_{11} - l_{12}\frac{T_{c2}}{T_{c1}}\right)(1-t) + K_{22}t \tag{20}$$

where K_{11} and K_{22} are characteristic values for a given homologues series and t is given by the following dimensionless functionality:

$$t = \tanh\left[\left(\frac{T-T_{c1}}{T^*_{c2}-T_{c1}}\right)^2\right] \tag{21}$$

For homologs heavier than the reference homolog (CO_2–*n*-decane), $T^*_{c2} = T_{c2}$. For lighter homologs T^*_{c2} is equal to the T_{c2} of the reference homolog. Therefore, for all lighter homologs T^*_{c2} will be taken as 617.7 K, the T_c of *n*-decane [16]. This will allow keeping the same temperature dependency of k_{12} along the homologues series. For the series CO_2–alkanes $K_{11} = 0.1$, $K_{22} = 0.35$, and $L_{12} = 0.02$.

Thus, in contrast to LCVM, which parameters have been obtained by fitting the experimental VLE data of carbon dioxide with *n*-eicosane and some heavier *n*-alkanes, GPDA does not resource to that data and appears here as entirely predictive model. We will now compare the ability of LCVM and GPDA to predict phase equilibria and volumetric properties of the mixtures under consideration.

3. RESULTS AND DISCUSSION

A very important test for thermodynamic models is their ability to predict the critical data. Such data are particularly important for the carbon dioxide mixtures because this fluid is frequently used as a supercritical solvent and the processes of the supercritical extraction become very effective in the vicinity of the critical line. The experimental critical data relevant for the present study are available only for the system CO_2–*n*-docosane [21]. Figure 2 compares the prediction of these data given by GPDA and LCVM. It can be seen that although GPDA does not succeed in predicting the critical points quantitatively, its robust character is evident in comparison with the results of LCVM. The figure demonstrates that the latter model tends to overestimate the immiscibility region of the system. Obviously, the ability of the models to predict the critical data has a very important impact on their accuracy in predicting the sub-critical data as well, which will be considered below.

Figures 3–10 compare the experimental and the calculated phase equilibria data of CO_2–*n*-eicosane, *n*-tetracosane, *n*-octacosane, and *n*-hexatriacontane. It can be seen that the increasing molecular weight of *n*-alkanes does not exhibit a serious influence on the regularities characteristic for the data.

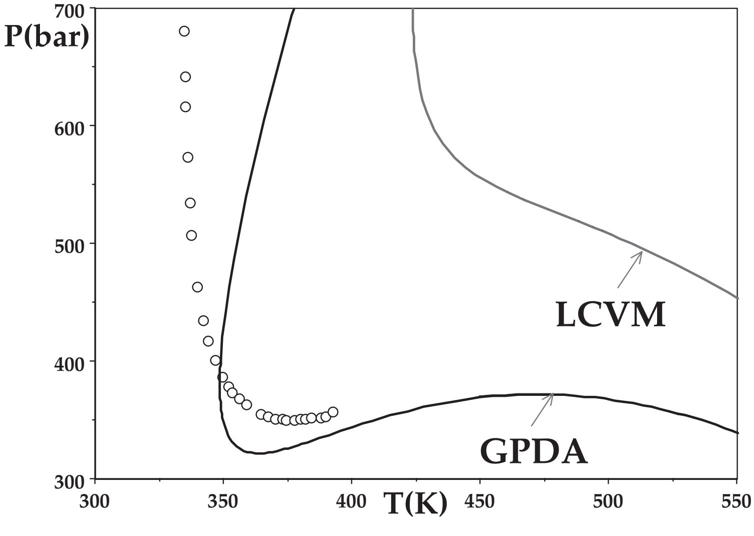

FIGURE 2 Critical data of CO_2–C_{22}. Black solid line – data predicted by PSRK; Gray solid line – data predicted by LCVM; Hollow circles – experimental data of Scheidgen [21].

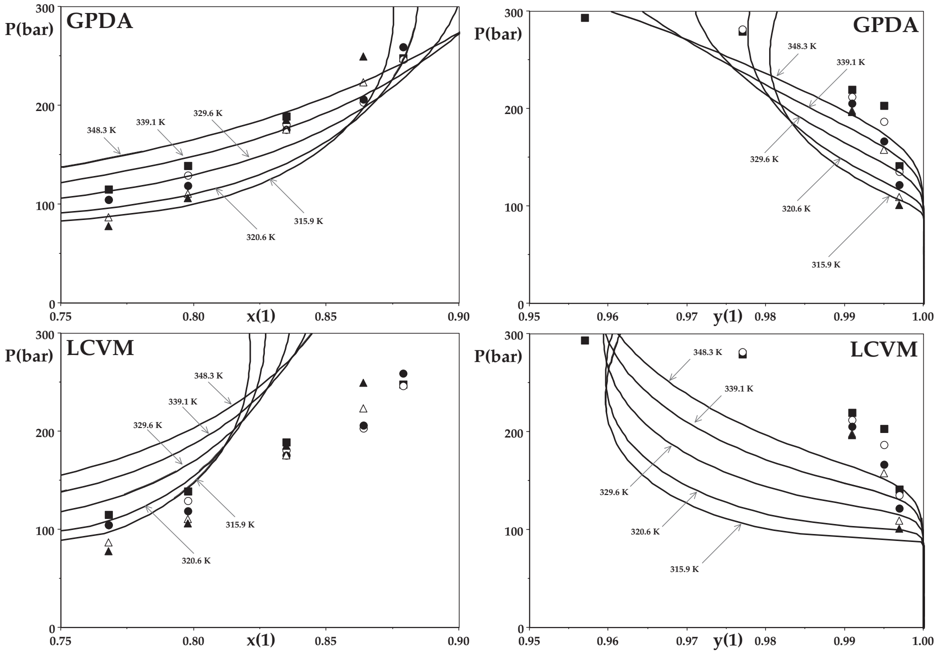

FIGURE 3 Equilibrium compositions in the system CO_2–C_{20}. Black solid lines – data predicted by GPDA and LCVM. Experimental data of Nieuwoudt and du Rand [5]: Full triangles – 315.6 K; Hollow triangles – 320.6 K; Full circles – 329.6 K; Hollow circles – 339.1 K; Full squares – 329.6 K.

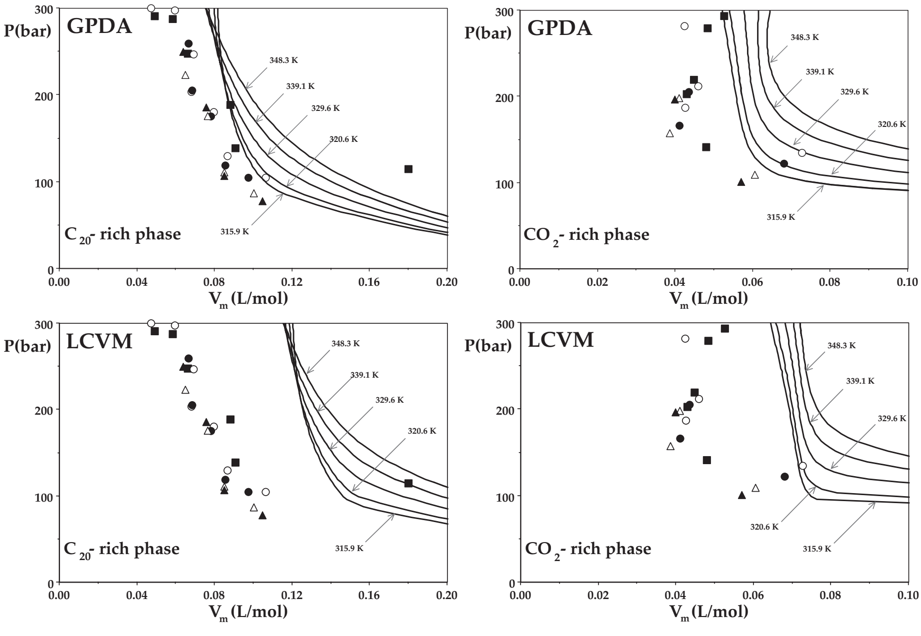

FIGURE 4 Equilibrium molar volumes in the system CO_2–C_{20}. Black solid lines – data predicted by GPDA and LCVM. Experimental data of Nieuwoudt and du Rand [5]: Full triangles – 315.6 K; Hollow triangles – 320.6 K; Full circles – 329.6 K; Hollow circles – 339.1 K; Full squares – 329.6 K.

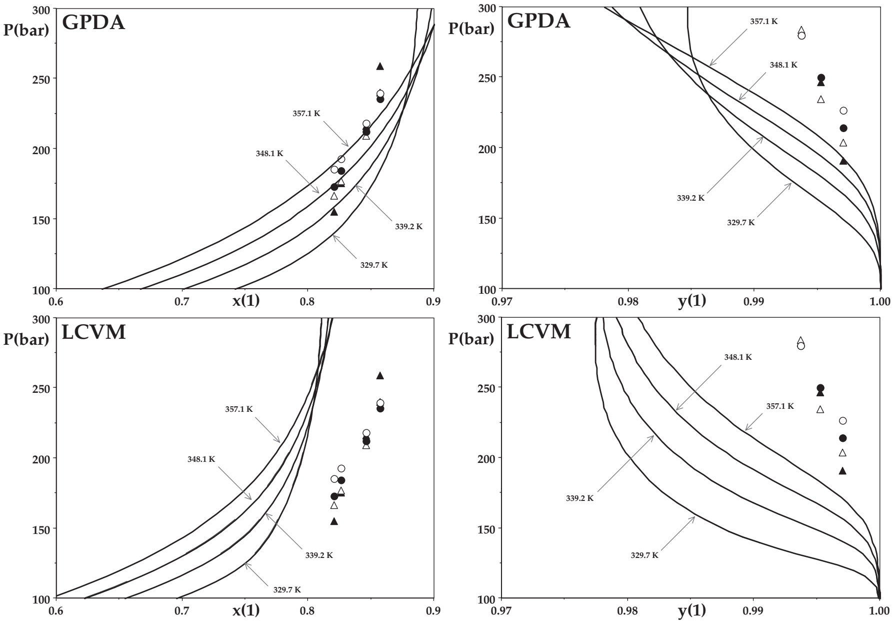

FIGURE 5 Equilibrium compositions in the system CO_2–C_{24}. Black solid lines – data predicted by GPDA and LCVM. Experimental data of Nieuwoudt and du Rand [5]: Full triangles – 329.7 K; Hollow triangles – 339.2 K; Full circles – 348.1 K; Hollow circles – 357.1 K.

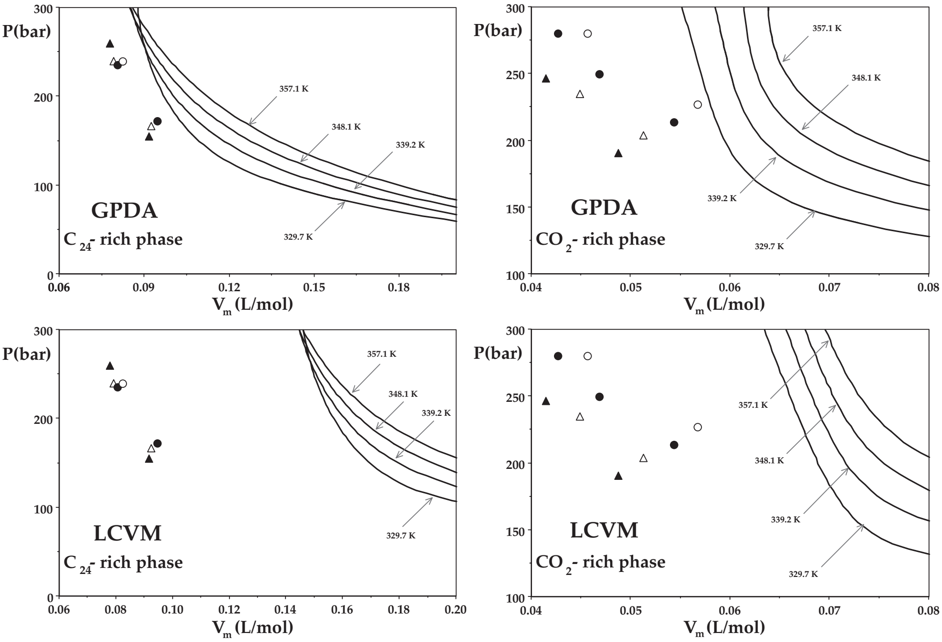

FIGURE 6 Equilibrium molar volumes in the system CO_2–C_{24}. Black solid lines – data predicted by GPDA and LCVM. Experimental data of Nieuwoudt and du Rand [5]: Full triangles – 329.7 K; Hollow triangles – 339.2 K; Full circles – 348.1 K; Hollow circles – 357.1 K.

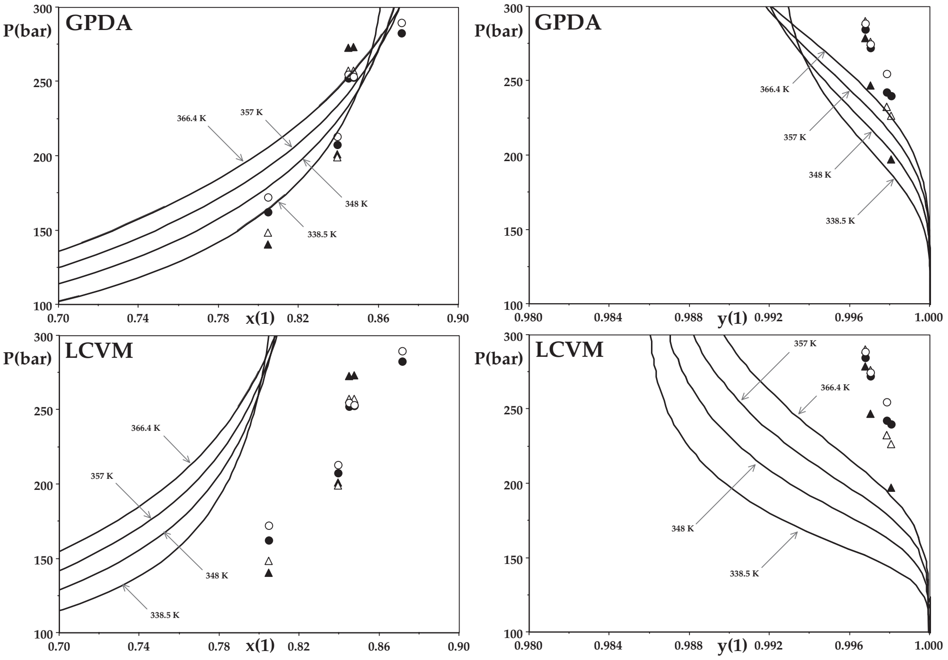

FIGURE 7 Equilibrium compositions in the system CO_2–C_{28}. Black solid lines – data predicted by GPDA and LCVM. Experimental data of Nieuwoudt and du Rand [5]: Full triangles – 338.5 K; Hollow triangles – 348 K; Full circles – 357 K; Hollow circles – 366.4 K.

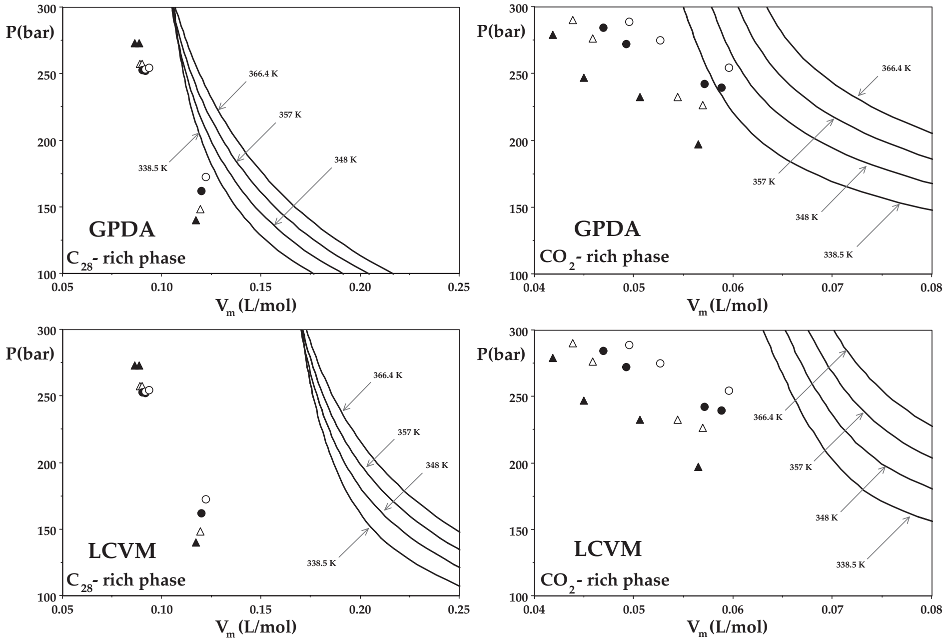

FIGURE 8 Equilibrium molar volumes in the system CO_2–C_{28}. Black solid lines – data predicted by GPDA and LCVM. Experimental data of Nieuwoudt and du Rand [5]: Full triangles – 338.5 K; Hollow triangles – 348 K; Full circles – 357 K; Hollow circles – 366.4 K.

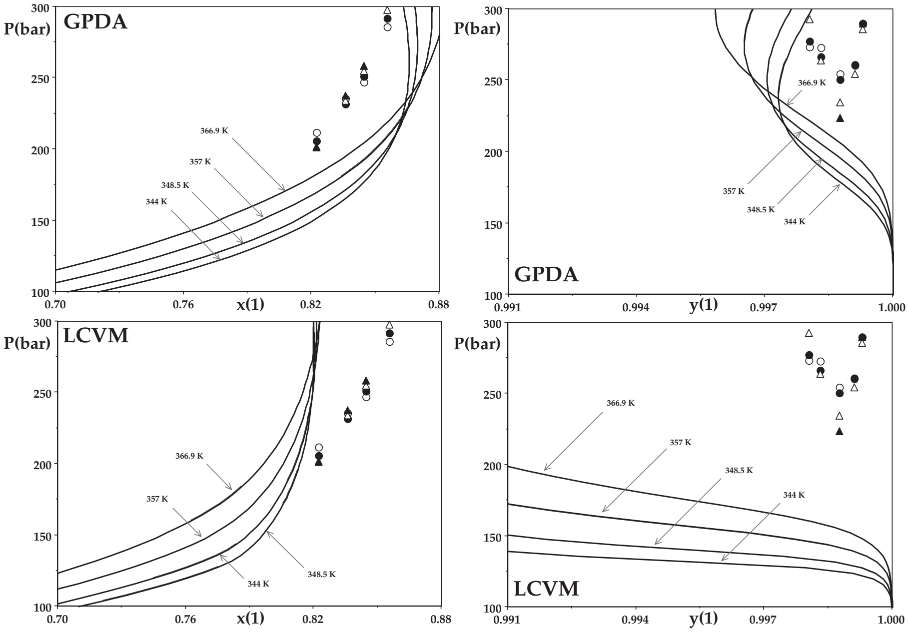

FIGURE 9 Equilibrium compositions in the system CO_2–C_{36}. Black solid lines – data predicted by GPDA and LCVM. Experimental data of Nieuwoudt and du Rand [5]: Full triangles – 344 K; Hollow triangles – 348.5 K; Full circles – 357 K; Hollow circles – 366.9 K.

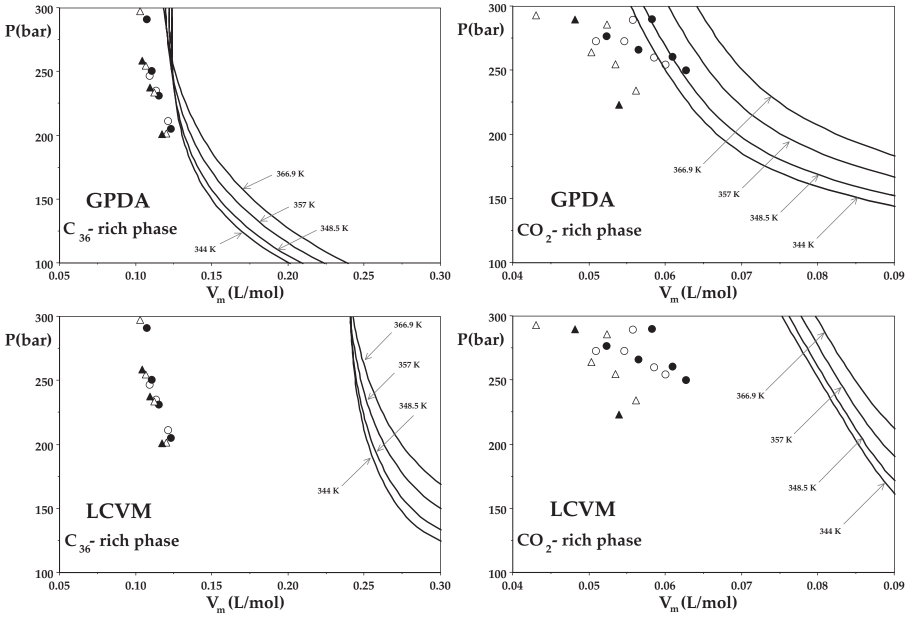

FIGURE 10 Equilibrium molar volumes in the system CO_2–C_{36}. Black solid lines – data predicted by GPDA and LCVM. Experimental data of Nieuwoudt and du Rand [5]: Full triangles – 344 K; Hollow triangles – 348.5 K; Full circles – 357 K; Hollow circles – 366.9 K.

In particular, it is remarkable to note that below certain pressure the solubility of carbon dioxide in *n*-paraffins increases with the increase of temperature. However above that pressure the temperature dependency of the solubility becomes opposite. It can be seen that both models are able to predict this phenomena. However in contrast to GPDA, which always yields reliable predictions, LCVM is able to describe the data only qualitatively. That is because LCVM consistently tends to underestimate the content of CO_2 in the hydrocarbon-rich phase. Such result can probably be explained by the fact that the present recent experimental data [5] have not been included so far by the parameter fitting of LCVM, which evidences about low reliability of this model.

Similar conclusions can be drawn considering the solubility of *n*-alkanes in the supercritical CO_2. Although yet GPDA does not always success to yield the exact predictions of data, it is more accurate than LCVM. Although importance of the data regarding the solubility of heavy organic substances in supercritical fluids is evident, the parameter evaluation of EOSs is usually performed considering the bubble point data. However, due to the fact that the predictive ability of the models evaluated by the local data fit is in many cases not high, they tend fail in description of the dew point data.

Since all thermodynamic properties are closely inter-related, it seems difficult to achieve robust description of certain properties neglecting other ones. In other words, one can hardly expect a reliable prediction of phase behavior from the model, which is inaccurate in description of molar volumes. Nevertheless, the accuracy of models is usually examined by their ability to describe the compositions of phases in equilibrium, while the accuracy of predicting volumetric properties is sometimes neglected. In addition, it should be realized that the volumetric properties of those phases are usually not less important for process design.

The quality of predicting volumetric properties in mixtures is defined by two factors, namely the exactness with which the equations describe pure compounds and reliability in prediction of compositions. Since GPDA has a superiority over LCVM in these two points, it does not seems surprising that it is much more accurate predicting molar volumes of mixtures as well (see Figs. 4, 6, 8, and 10). In particular, since PR EOS considerably overestimates the molar volumes of pure heavy paraffins, LCVM overestimates this property also in their mixtures. The inaccurate predictions of compositions only multiply the error. As a result, LCVM describes volumetric properties of the hydrocarbon-rich phase with deviations that usually exceed 100%. LCVM is also less accurate than GPDA predicting the molar volumes of the CO_2–rich phase.

Figure 11 presents the results predicted by LCVM and GPDA for the system Co_2–*n*-tetracontane (C_{44}). It can be seen that both models yield almost identical results, which are relatively accurate.

These results demonstrate a doubtless advantage of the approach that considers an entire thermodynamic phase space over the model, which parameters have been evaluated by the way of local data fit.

4. CONCLUSIONS

The present study compares the ability of two EOS models, GPDA and LCVM to predict equilibrium compositions and molar volumes in mixtures of Co_2–*n*-eicosane and heavier homologs. Implementation of both models to the systems under

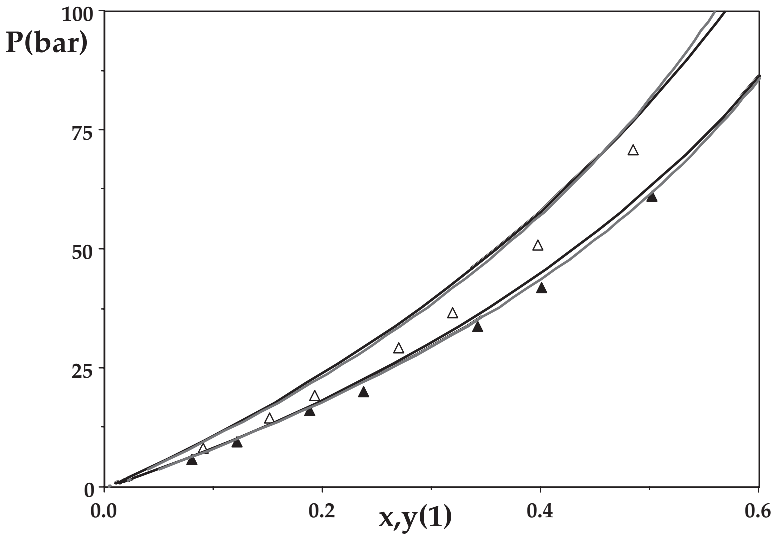

FIGURE 11 Dew point data in the system CO_2–C_{44}. Black solid line – data predicted by PSRK; Gray solid line – data predicted by LCVM; Experimental data of Gasem and Robinson [22]: Full triangle – 373.2 K; Hollow triangle – 423.2 K.

consideration does not require any parameter fitting. Therefore both of them are ready for engineering computations. However the LCVM should be characterized as correlative rather than predictive model because its parameters have been evaluated by fitting the data of homologues up to *n*-octacosane. In contrast, GPDA appears as entirely predictive model because it does not resource to any experimental data of systems under consideration. Nevertheless, GPDA is much more accurate than LCVM in predicting data. In particular, while LCVM tends to overestimate the immiscibility in the system and its error in predicting volumetric properties may exceed 100%, GPDA usually generates only minimal deviations from the experimental data. These results emphasize the robustness of the GPDA and evidence about its reliability for predicting of data, which are not available experimentally.

NOMENCLATURE

a = Cohesion parameter
b = covolume
c, d = attraction density dependence parameters in Eq. (1)
G^E = excess Gibbs energy
P = pressure
R = universal gas constant
T = temperature
x = mole fraction of the lighter compound in liquid phase
y = mole fraction of the lighter compound in vapor phase
V = volume

Greek letters

ω = acentric factor

Subscripts

C = critical state
m = molar property

Abbreviations

CPM = Critical Pressure Maximum
EOS = Equation Of State
GPD = Global Phase Diagram
GPDA = Global Phase Diagram Approach
klGPD = Global Phase Diagram in the $k_{12} - l_{12}$ projection
LCST = Lower Critical Solution Temperature
LCVM = Linear Combination of the Vidal and Michelsen mixing rules
LLE = Liquid–Liquid Equilibria
PSRK = Predictive-Soave-Redlich-Kwong Group Contribution EOS
UCST = Upper Critical Solution Temperature
VLE = Vapor-Liquid Equilibria

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