

Group Contribution Method for Predicting the Phase Behavior of Binary Mixtures Containing Carbon Dioxide

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Abstract

This work deals with estimation of temperature dependent binary interaction parameters (k_{ij}) for binary systems containing CO_2 using the Soave-Redlich-Kwong equation of state with a group contribution method. In this paper six groups, namely CH_3 , CH_2 , CH , CH_4 (methane), C_2H_6 (ethane), and CO_2 (carbon dioxide) are defined and their relevant values of group interaction parameters are optimized. Using this method, it is possible to estimate the k_{ij} of any mixture containing carbon dioxide and hydrocarbons at any temperature along the coexistence curve. The results obtained in this study are, in most cases, accurate.

Keywords: *Binary Interaction Parameter, Carbon Dioxide, Equation of State, Group Contribution, Vapor – liquid Equilibria*

1. Introduction

The phase equilibria of carbon dioxide with the hydrocarbon components of natural gas mixtures are becoming increasingly important for the following reasons: (i) Industrial interest in the phase behavior of carbon dioxide, and the light paraffin hydrocarbons have grown significantly in recent years due to the increased use of carbon dioxide as an injection fluid in enhanced oil recovery (EOR) projects. (ii) The gas produced from an EOR project usually requires additional processing to meet sales gas specifications, and thus the ability to model the vapor – liquid equilibria (VLE) of the processed gas is essential for a

good design [1]. (iii) Carbon dioxide and saturated hydrocarbons are important compounds in gas processing, and the knowledge of the properties of the pure components and their mixtures is of practical importance for designing process equipment. In addition to the industrial interest, systems containing carbon dioxide are of academic interest because the large quadrupole moment of carbon dioxide makes its interaction with other molecules unusual and difficult to predict with high accuracy [1]. The carbon dioxide – ethane system is especially interesting because it forms a maximum-pressure azeotrope.

We propose in this work a methodology to

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develop a group contribution method (GCM) for van der Waals mixing rules in order to estimate the *binary interaction parameter* k_{ij} for the widely used Soave-Redlich-Kwong (SRK) equation of state (EoS) [2]. To express k_{ij} in terms of group contributions, we benefit from equations derived by Péneloux et al. [3]. The important point in this method is that the binary interaction parameter between two components i and j is a function of temperature and of the pure components critical temperatures, critical pressures and acentric factors. This means that no additional properties besides those required by the EoS itself (T_C , P_C , ω) are required.

Jaubert and Mutelet [4] applied this methodology to the Peng and Robinson EoS [5] and developed a new model named PPR78 (Predictive Peng-Robinson 1978). Since the properties of natural gas mixtures are best predicted by the SRK EoS [4,7-8], we have decided to employ a similar GCM for estimation of the temperature dependent binary interaction parameters $k_{ij}(T)$ for the widely used SRK EoS.

2. Equation of state (EoS)

EoSs are proposed to mathematically describe the relationship between pressures, volume and temperature (PVT) of fluids. An EoS can take different forms from ideal gas law to more complicated forms like that of SAFT [9]. However, the most commonly used analytical equations are the so-called cubic EoS.

Soave [2] proposed a cubic EoS of the following form for correlating the PVT behavior of pure compounds:

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

$$a = 0.42747 \left(\frac{R^2 T_C^2}{P_C} \right) \left\{ 1 + (0.480 + 1.57\omega - 0.176\omega^2) [1 - T_r^{0.5}] \right\}^2 \quad (2)$$

$$b = 0.08664 \frac{RT_C}{P_C} \quad (3)$$

where a and b are the two parameters that can be calculated using temperature, acentric factor and critical state properties. Applying the SRK EoS to mixtures, the parameters a and b must be extended to mixtures using mixing rules. These mixing rules range from the simplest, proposed by van der Waals, to more complex ones such as extended Twu and Coon[6], Wong and Sandler [22], Nasrifar and Moshfeghian [23], and Mansoori [24]. In this study the van der Waals mixing rules presented by Eqs. (4 – 5) are used not only for their simplicity, but they take less computational time for complex process simulations and group interaction parameters optimization as well. The van der Waals mixing rules read:

$$b = \sum_i x_i b_i \quad (4)$$

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (5)$$

where i, j run over all components, x_i is the mole fraction of component i in the mixture, a and b are the equation parameters and k_{ij} is the binary interaction parameter characterizing a binary mixture formed by

components i and j . When $i = j$, $k_{ij} = 0$. Binary interaction parameters take into account the difference in the interaction, size and shape of unlike molecules. These binary interaction parameters are empirical and their significance lies in their ability to make a particular model predict the correct phase behavior.

Use of a cubic EoS requires appropriate values for the above mentioned empirical parameters. Different methods have been suggested in the literature to calculate binary interaction parameters, but the interaction parameters calculated using those methods may fail to predict the complex phase behavior at high pressures [19]. The motivation behind this study was to estimate temperature dependent interaction parameters for systems of hydrocarbons and carbon dioxide using a group contribution method.

Using different equations from the previous works of Pénélox et al. [3, 10], $k_{ij}(T)$ is expressed in terms of group contributions through the following expression:

$$k_{ij} = \frac{-\frac{1}{2} \sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} \left(\frac{298.15}{T} \right)^{\left(\frac{B_{kl}}{A_{kl}} - 1 \right)} - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j(T)} \right)^2}{2 \frac{\sqrt{a_i(T)a_j(T)}}{b_i b_j}} \quad (6)$$

In Eq. (6), T is the temperature; a_i and b_i are simply calculated by Eqs. (2) and (3). N_g is the number of different groups defined by the method (for example, if six groups are defined then $N_g = 6$). α_{ik} is the fraction of molecule i occupied by group k (occurrence of group k in molecule i divided by the total number of groups present in molecule i).

$A_{kl} = A_{lk}$ and $B_{kl} = B_{lk}$ (where k and l are two different groups) are constant parameters determined in this study ($A_{kk} = B_{kk} = 0$). As can be seen, to calculate the k_{ij} parameter between two molecules i and j at a selected temperature, it is necessary to know: the critical temperature of both components, the critical pressure of both components, the acentric factor of each component and the decomposition of each molecule into elementary groups (α_{ik} , α_{jk}).

The six groups defined in this study are: group 1 = CH₃, group 2 = CH₂, group 3 = CH, group 4 = CH₄, i.e. methane, group 5 = C₂H₆, i.e. ethane, and group 6 = CO₂, i.e. carbon dioxide. The decomposition into groups of the hydrocarbons (linear or branched) is very easy. The substitution effects which were defined in the Pénélox et al. [3] work are neglected in this method.

A flash algorithm has been used to perform VLE calculations for 29 binary systems containing carbon dioxide [1,7-8,11-17,20-21,25-41] at given T and P . In this way, the composition of the liquid (x) and gas phase (y) in equilibrium are calculated. The group interaction parameters reported here are those which minimize the objective function of absolute differences between calculated and experimental vapor and liquid mole fractions for the binary isotherms using simplex method:

$$F_{\text{obj}} = \sum_{i=1}^{\text{NPT}} \left(\frac{|(x_1)_{\text{calc}} - (x_1)_{\text{exp}}|}{(x_1)_{\text{exp}}} + \frac{|(y_1)_{\text{calc}} - (y_1)_{\text{exp}}|}{(y_1)_{\text{exp}}} \right)_i \quad (7)$$

3. Results and discussion

Determination of group interaction parameters for the SRK EoS was performed. A flash algorithm was used to determine optimized group interaction parameters. Optimization of binary interaction parameters was performed for 29 binary systems containing carbon dioxide at wide ranges of temperature and pressure [1,7-8,11-17,20-21,25-41]. The obtained group interaction parameters are reported in Table 1.

In order to illustrate the accuracy of the proposed model, a decision was made to define several families of binary systems. It is indeed impossible to publish the results for all studied systems.

Fig. 1 shows the predicted and experimental isothermal phase diagrams for the system methane (1) +CO₂ (2) at two different temperatures 230 K and 250 K. For this system, the binary interaction parameters

were predicted 0.0968 and 0.1029, respectively. Accurate results were obtained for the VLE of the binary system, except near the critical pressures where the predictions were overestimated at these temperatures. The relevant experimental [11, 12] and predicted VLE data in the case of $k_{ij}=0$ and applying temperature dependant k_{ij} are summarized in Table 2 at $T=230$ K.

Fig. 2 shows the predicted and experimental isothermal phase diagrams for the system CO₂ (1) + ethane (2) at four different temperatures. For this system, a homogeneous positive azeotrope always exists. Clearly the proposed model is able to satisfactorily predict the phase behavior of this system. Experimental [13-16] and calculated VLE results for this binary mixture by applying temperature dependant k_{ij} is reported in Table 3. In the case of $k_{ij}=0$, no result was obtained.

Table1. Group interaction parameters: ($A_{kl} = A_{lk}$)/MPa and ($B_{kl} = B_{lk}$)/MPa

	CH₃ (group 1)	CH₂ (group 2)	CH (group 3)	CH₄ (group 4)	C₂H₆ (group 5)	CO₂ (group 6)
CH₃ (group 1)	0	A=8.06×10 ⁻³ B= -0.127	A=9.74 B=5.81	A=23.9 B=-75.0	A=0.535 B=2.35	A=-53.7 B= -22.8
CH₂ (group 2)	A=8.06×10 ⁻³ B=-0.127	0	A=13.4 B=118	A=0.560 B=4.62	A=0.512 B=-3.62	A=174 B=367
CH (group 3)	A=9.74 B=5.81	A=13.4 B=118	0	A=-74.3 B=98.7	A=4.62× 10 ⁻² B=-1.17	A=540 B=459
CH₄ (group 4)	A=23.9 B=-75.0	A=0.560 B=4.62	A=-74.3 B=98.7	0	A=9.67 B=-0.923	A=112 B=146
C₂H₆ (group 5)	A=0.535 B=2.35	A=0.512 B=-3.62	A=4.62× 10 ⁻² B=-1.17	A=9.67 B=-0.923	0	A=120 B=179
CO₂ (group 6)	A=-53.7 B=-22.8	A=174 B=367	A=540 B=459	A=112 B=146	A=120 B=179	0

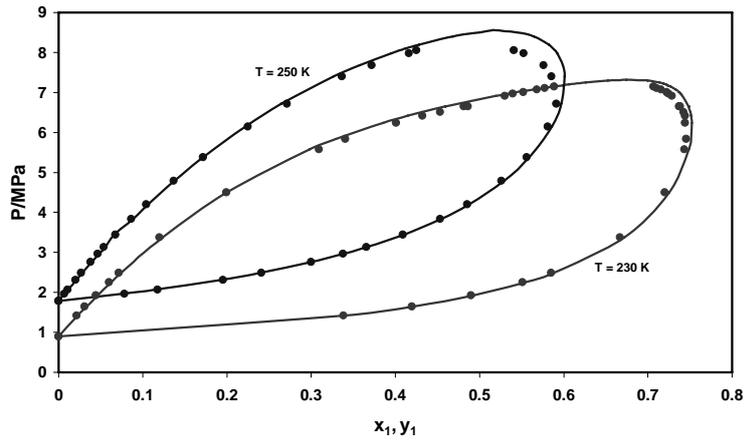


Figure 1. Predicted VLE data for the system CH₄ (1) + CO₂ (2) at $T=230\text{ K}$ ($k_{ij}=0.0968$) and $T=250\text{ K}$ ($k_{ij}=0.1029$); ● Experimental data [11, 12]; — SRK EoS with k_{ij} from GCM

Table 2. Predicted and experimental VLE data [11] for the system CH₄ (1) + CO₂ (2) at $T=230\text{ K}$

P/MPa	$x_{1\text{exp}}$	$ \Delta x_{1\text{cal}} $ ^a $k_{ij}=0$	$ \Delta x_{1\text{cal}} $ $k_{ij}=0.0968$	$y_{1\text{exp}}$	$ \Delta y_{1\text{cal}} $ ^b $k_{ij}=0$	$ \Delta y_{1\text{cal}} $ $k_{ij}=0.0968$
0.894	0	0	0	0	0	0
1.42	0.0213	0.0193	0.0016	0.3385	0.011	0.0014
1.651	0.0307	0.0285	0.0027	0.4196	0.0131	0.0015
1.931	0.0441	0.0382	0.0025	0.49	0.0167	0.0034
2.488	0.0714	0.0593	0.0029	0.5851	0.0189	0.003
3.375	0.1199	0.0949	0.0038	0.667	0.0241	0.005
4.497	0.1994	0.1372	0.0003	0.7199	0.029	0.0056
5.573	0.3093	0.1638	0.011	0.7432	0.0341	0.0055
5.836	0.3404	0.1694	0.0112	0.7454	0.0358	0.0057
6.241	0.401	0.1686	0.0154	0.7443	0.0401	0.0078
6.417	0.4323	0.1647	0.0176	0.7442	0.0402	0.007
6.649	0.4862	0.1491	0.0274	0.7371	0.0452	0.0111
6.654	0.4815	0.1546	0.0216	0.7382	0.044	0.0099
Average		0.1036	0.0090		0.0270	0.0051

^a $|\Delta x_{1\text{cal}}| = |x_{1\text{cal}} - x_{1\text{exp}}|$

^b $|\Delta y_{1\text{cal}}| = |y_{1\text{cal}} - y_{1\text{exp}}|$

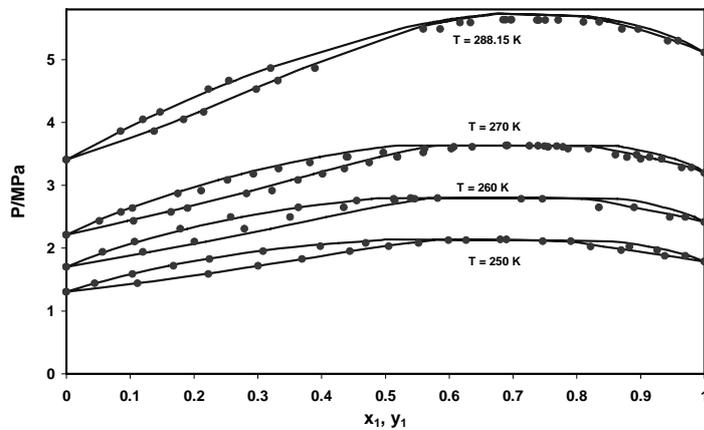


Figure 2. Predicted VLE data for the system CO₂ (1) + C₂H₆ (2) at $T=250\text{ K}$ ($k_{ij}=0.142$), $T=260\text{ K}$ ($k_{ij}=0.1436$), $T=270\text{ K}$ ($k_{ij}=0.1453$), $T=288.15\text{ K}$ ($k_{ij}=0.1485$); ● Experimental data [12- 15]; — SRK EoS with k_{ij} from GCM

Table 3. Predicted and experimental VLE data [13] for the system CO₂ (1) + C₂H₆ (2) at T=250 K

P/MPa	x _{1exp}	$ \Delta x_{1cal} ^a$ $k_{ij}=0.1420$	y _{1exp}	$ \Delta y_{1cal} ^b$ $k_{ij}=0.1420$
1.3020263	0	0	0	0
1.4418548	0.0444	0.0003	0.1115	0.0027
1.588776	0.1035	0.0012	0.2226	0.0058
1.827903	0.2245	0.0049	0.3697	0.0007
1.9484798	0.3083	0.0093	0.4447	0.0002
2.0295398	0.398	0.0302	0.5056	0.0085
2.1268118	0.599	0.1092	0.6265	0.0528
2.1349178	0.69	0.1854	0.6802	0.0982
1.965705	0.926	0.0164	0.8696	0.0133
1.8755258	0.9701	0.0062	0.9378	0.0059
1.7853465	1	0	1	0
Average		0.0330		0.0171

$$^a |\Delta x_{1cal}| = |x_{1cal} - x_{1exp}|$$

$$^b |\Delta y_{1cal}| = |y_{1cal} - y_{1exp}|$$

Table 4 presents the experimental data [17] and calculated values for the system CO₂ (1) + C₅H₁₂ (2) at 273.41 K and 252.67 K, respectively. As can be seen, there are good agreements between the experimental values and the predicted ones. The deviations between the experimental and predicted values in Fig. 3 have proven the necessity of using temperature dependant k_{ij} . Clearly the proposed model compares well with the experimental values for both the vapor phase and the liquid phase. The same calculations were also performed for the system CO₂ (1)

+ C₁₁H₂₄ (2) at two temperatures of 418.3 K and 373.13 K. The results are shown in Figs. 4 and 5, respectively. As can be seen, the model predicts the experimental data [17] quite satisfactorily compared with the situation when $k_{ij}=0$. In order to illustrate the accuracy of the calculated parameters for the systems containing branched hydrocarbons, the VLE of the binary system CO₂ (1) + Isopentane (2) at three different temperatures is given in Fig. 6 as an example. The agreement is clearly good.

Table 4. Predicted and experimental VLE data [16] for the system CO₂ (1) + C₅H₁₂ (2) at T=273.41 K

P/MPa	x _{1exp}	$ \Delta x_{1cal} ^a$ $k_{ij}=0$	$ \Delta x_{1cal} $ $k_{ij}=0.1009$	y _{1exp}	$ \Delta y_{1cal} ^b$ $k_{ij}=0$	$ \Delta y_{1cal} $ $k_{ij}=0.1009$
0.269	0.0451	0.0488	0.0096	0.8798	0.031	0.0279
0.538	0.0968	0.0958	0.0186	0.9443	0.0119	0.0086
1.048	0.2014	0.1658	0.0324	0.9701	0.0086	0.0048
1.558	0.3206	0.2053	0.0391	0.9821	0.0048	0.0006
2.179	0.5006	0.1981	0.0334	0.9868	0.0055	0.0008
2.406	0.5882	0.1682	0.0201	0.9882	0.0056	0.0008
2.668	0.7012	0.1181	0.004	0.9883	0.007	0.0022
2.772	0.7517	0.0915	0.0046	0.9906	0.0053	0.0006
2.965	0.8303	0.0556	0.0035	0.992	0.0049	0.0005
3.103	0.8802	0.035	1E-04	0.9932	0.0044	0.0006
3.247	0.9274	0.0171	0.001	0.9946	0.0038	0.0008
Average		0.1090	0.0151		0.0084	0.0044

$$^a |\Delta x_{1cal}| = |x_{1cal} - x_{1exp}|$$

$$^b |\Delta y_{1cal}| = |y_{1cal} - y_{1exp}|$$

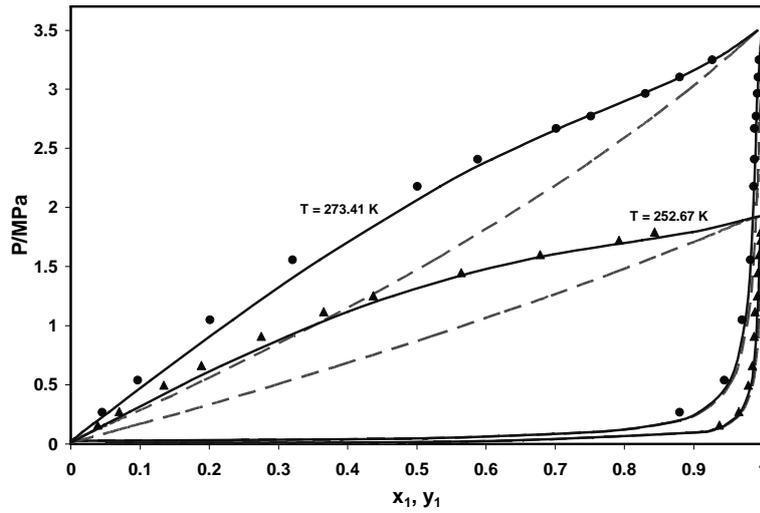


Figure 3. Predicted VLE data for the system CO₂ (1) + C₅H₁₂ (2) at $T_1=273.41$ K ($k_{ij}=0.1009$) and $T_2=252.67$ K ($k_{ij}=0.1079$); ●, ▲ Experimental data [16]; ---- SRK EoS with $k_{ij}=0$; ___ SRK EoS with k_{ij} from GCM

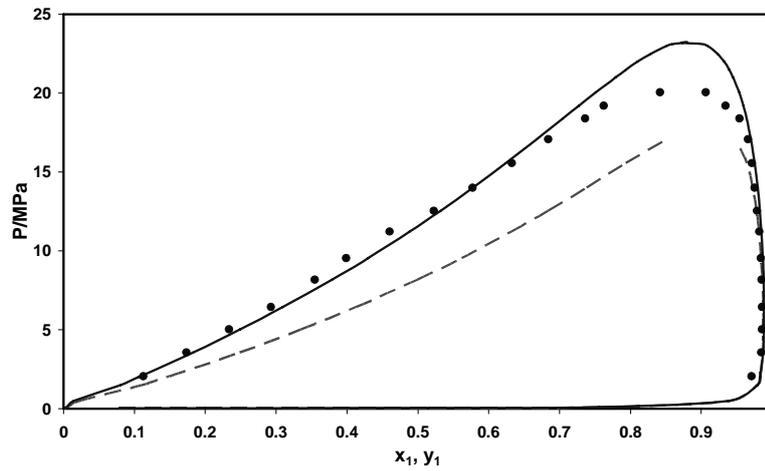


Figure 4. Predicted VLE data for the system CO₂ (1) + C₁₁H₂₄ (2) at $T=418.3$ K ($k_{ij}=0.1415$); ● Experimental data [17]; ---- SRK EoS with $k_{ij}=0$; ___ SRK EoS with k_{ij} from GCM

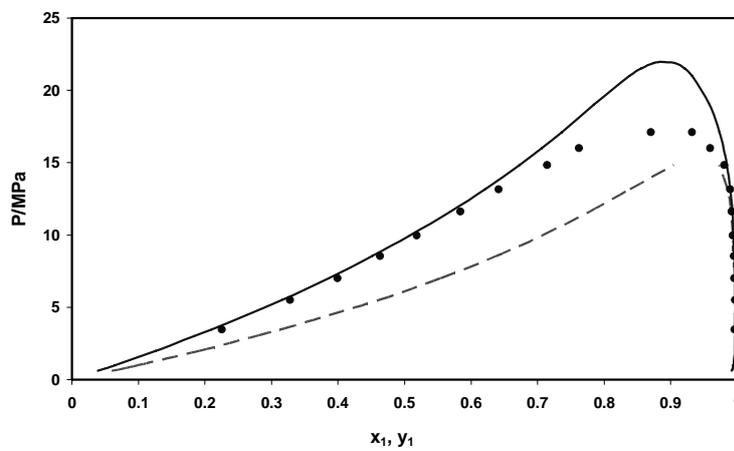


Figure 5. Predicted VLE data for the system CO₂ (1) + C₁₁H₂₄ (2) at $T=373.13$ K ($k_{ij}=0.1461$); ● Experimental data [17]; ---- SRK EoS with $k_{ij}=0$; ___ SRK EoS with k_{ij} from GCM

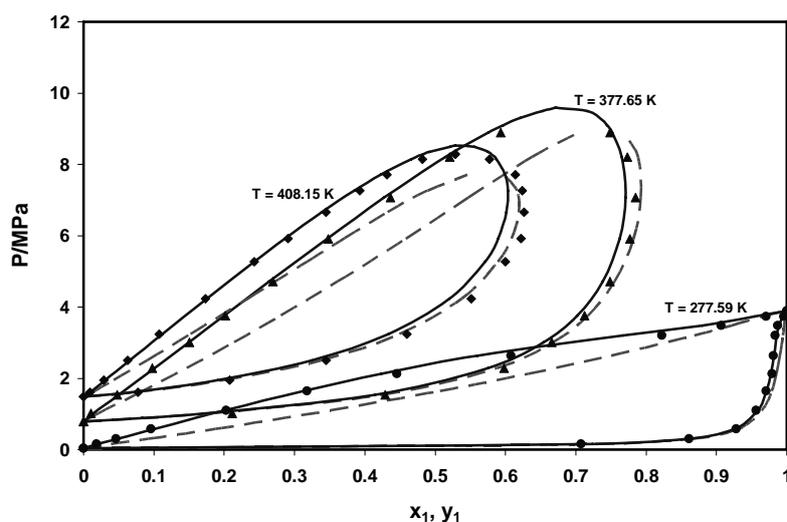


Figure 6. Predicted VLE data for the system CO₂ (1) + Isopentane (2) at $T_1=277.59$ K ($k_{ij}=0.1262$), $T_2=377.65$ K ($k_{ij}=0.1568$) and $T_3=408.15$ K ($k_{ij}=0.1672$); ●, ▲, ■ Experimental data [20, 21]; ---- SRK EoS with $k_{ij}=0$; ___ SRK EoS with k_{ij} from GCM

4. Conclusions

In this paper, the SRK EoS with k_{ij} calculated from a GCM model has been extended to systems containing carbon dioxide. In other words, it is likely to estimate the k_{ij} for any mixtures containing CO₂ + alkanes (linear or branched) at any temperature along the VLE. The results obtained in this study are satisfactory.

This work presents an engineering way to calculate the VLE of binary systems containing CO₂. It gives us a technique to directly determine the binary interaction parameters between two components.

A group contribution method allowing estimation of the temperature dependent binary interaction parameters for the widely used SRK EoS has been developed. A key point in our approach is that the k_{ij} between two components i and j is a function of temperature, the critical temperatures, the critical pressures and the acentric factors of the two components. This means that no

additional properties besides those required by the EoS itself are required.

In this paper, six groups are defined: CH₃, CH₂, CH, CH₄ (methane), C₂H₆ (ethane), and CO₂ (carbon dioxide), which means that it is possible to estimate the k_{ij} for any mixture of saturated hydrocarbons (n -alkanes and branched alkanes) and carbon dioxide at different temperatures.

To sum up, this model describes the VLE of binary mixtures and carbon dioxide and hydrocarbons quite well.

Nomenclature

$a(T)$	temperature dependent function of the equation of state (Pa.m ³ /K.mol ²)
A_{kl}, B_{kl}	constant parameters allowing the calculation of the binary interaction parameters (MPa)
b	co-volume (m ³ /kmol)
F	objective function
k_{ij}	binary interaction parameter
N_g	total number of groups

NPT	number of experimental points
P	pressure (MPa)
P _C	critical pressure (MPa)
R	Universal gas constant (kJ/kmol K), 8.314×10 ⁻³ MPa m ³ /K.kmol
T	temperature (K)
T _C	critical temperature (K)
v	molar volume (m ³ /kmol)
x, y	mole fraction

Greek letters

α_{ik}	fraction occupied by group k in molecule i
ω	acentric factor

Subscripts

C	critical value
calc	calculated value
exp	experimental value
i, j	related to the components i and j
obj	objective value
r	reduced value

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