

## Prediction of Vapor-Liquid Equilibria Using CEOS /GE Models

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### Abstract

The present study investigates the use of different GE mixing rules in cubic equations of state for prediction of phase behavior of multicomponent hydrocarbon systems. To predict VLE data in multicomponent symmetric and asymmetric mixtures such as systems that contain light gases (nitrogen, carbon dioxide, etc.) and heavy hydrocarbons, the SRK equation of state has been combined with excess Gibbs energy models. In this study, the PSRK method, developed by Holderbaum and Gmehling for VLE data prediction, is re-examined. To visualize the effect of different mixing rules in predicting VLE data, Wong and Sandler mixing rule was applied. New group and molecular interaction parameters in UNIFAC and W-S models were introduced. These parameters were obtained by regressing the available VLE data. The results of comparisons between applied models and experimental data are presented. These indicate that although all suggested models could provide reasonably good VLE information for the systems containing components of similar size in a wide range of temperatures and pressures, but only PSRK method shows minimum absolute and relative errors for both vapor and liquid compositions in asymmetric systems.

**Keywords:** VLE, State Equation, GE Models, PSRK

### Introduction

Equation of state (EOS) models, especially cubic type ones, have been extensively employed in phase equilibrium calculations for chemical process design. With the advantage of multiparameter mixing rules, especially those that incorporate the excess free energy, cubic equations of state (CEOS) are now being used for phase equilibrium calculations for complicated mixtures at high temperatures and pressures [1-7].

The idea of combining simple cubic equations of state (SRK, PR) with  $G^E$  models has been well-known since Huron and Vidal (1979) [8] published their analytical mixing rule for the attractive parameter in EOS. The original Huron-Vidal mixing rule at infinite

pressure was not largely used because the model parameters (in  $G^E$  at infinite pressure) must be adjusted, and not related to available parameter at low pressures.

The main application of CEOS/GE models is to predict high-pressure and non-ideal VLE. Application of these models in systems containing gases with large differences in size and molecular weight are a special case of this application [9-12].

Studies of the solubility of light gases such as methane, nitrogen and carbon dioxide in heavy hydrocarbons are of particular interest in the processing of coal and petroleum products, enhanced oil recovery and supercritical fluid processes.

In this work, two CEOS/GE models, namely

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PSRK (1991, 1998) and WS (1992), were re-examined for predicting VLE data in symmetric and asymmetric systems. The accuracy of WS and PSRK models with both initial (PSRK,1991) and modified (PSRK\*, Li, *et al.*,1998) [13] values of  $R_K$  and  $Q_K$  in systems containing nitrogen, carbon dioxide and hydrocarbons were compared. All group- and molecular interaction parameters were determined by regressing the available VLE data. The results for several binary and ternary mixtures are reported.

### Thermodynamic Model

The cubic equation of state Soave-Redlich-Kwong, SRK (Soave, 1972), was used to calculate VLE data. The attractive parameter in this EOS was calculated using the procedure proposed by Mathias and Copeman (1983) [14].

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

The critical constants of pure substances were taken from Magouslas and Tassios (1990) [15], and Daubert and Danner (1989) [16], and the values of constants  $c_1$ ,  $c_2$  and  $c_3$  in  $a(T_r)$  function, from Dahl, *et al.* (1991) [17].

Two different mixing rules were tested in detail with this CEOS: The Holderboun and Gmehling (PSRK, 1991) mixing rule [18], from which the EOS parameters are obtained as follows:

$$\frac{a}{bRT} = \sum_{i=1}^n x_i \frac{a_i}{RTb_i} + \frac{G_u^E / RT + \sum_{i=1}^n x_i \text{Lnb} / b_i}{-0.6466} \quad (2)$$

$$b = \sum x_i b_i \quad (3)$$

and the Wong and Sandler (WS, 1992) mixing rule [19], in which the  $a$  and  $b$  parameters are expressed by the following relations:

$$b = \frac{\sum_{i=1}^n \sum_{j=1}^n x_i x_j (bRT - a)_{ij}}{RT - \sum_{i=1}^n x_i \frac{a_i}{b_i} + \frac{A^k}{-0.6931}} \quad (4)$$

$$a = b \left( \sum_{i=1}^n x_i \frac{a_i}{b_i} + \frac{A^E}{-0.6931} \right) \quad (5)$$

$$\left( b - \frac{a}{RT} \right)_{ij} = 1/2 \left[ \left( b_i - \frac{a_i}{RT} \right) + \left( b_j - \frac{a_j}{RT} \right) \right] (1 - K_{ij}) \quad (6)$$

The excess free energy or activity coefficient model are obtained from UNIFAC activity coefficient model (Gmehling, 1993[20] and Li, *et al.*, 1998) [13,21]. Interaction parameters were optimized using Marquardt non-linear regression method.

### Results and Discussion

To test and compare the ability of applied models for predicting vapor-liquid equilibrium data over a wide range of conditions, we have considered several binary and ternary mixtures containing nitrogen, carbon dioxide and hydrocarbons, for which VLE data are available over a wide range of temperatures and pressures. At first, the EOS mixing parameters are evaluated using the UNIFAC group contribution activity coefficient model in the two mixing rule models. Then, the binary and ternary systems are studied to determine their relative and absolute errors for the light component in each system.

#### Interaction Parameters

Study of systems containing gases is limited by the available group interaction parameters in UNIFAC model. In addition, the ability of these parameters in asymmetric systems to be extrapolated is not high and these models are accurate mostly in describing the data used for evaluation of their parameters (Polishuk, *et al.*, 2003 [22]). To overcome these limitations, UNIFAC interaction parameters

between unlike pairs of groups were obtained using Marquardt non-linear regression in each mixing rule. In the same procedure, the second Virial coefficient binary interaction parameters between different molecules are calculated. The results of optimization are shown in Tables 1 through 3. Group interaction parameters in UNIFAC model are calculated from:

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T}{T}\right) \quad (7)$$

where T is in K.

These interactions then can be used without any adjustments to predict VLE of multicomponent mixtures.

### Results for Binary and Ternary Systems

The binary and ternary systems that were studied are listed in Tables 4 through 6. Three types of deviations from experimental data in both phases are calculated (see Tables).

In liquid compositions:

$$\% \frac{\Delta x}{x} = \frac{100}{N_p} \sum \frac{|x_{\text{exp}} - x_{\text{cal}}|}{x_{\text{exp}}} \quad \text{and}$$

$$\% \Delta x = \frac{100}{N_p} = \sum |x_{\text{exp}} - x_{\text{cal}}|$$

In vapor compositions:

$$\% \Delta x = \frac{100}{N_p} \sum |y_{\text{exp}} \cdot y_{\text{cal}}|$$

**Table 1.** UNIFAC group interaction parameters in binary systems (PSRK model)

| Group 1         | Group 2         | a <sub>12</sub> (K) | a <sub>21</sub> (K) | b <sub>12</sub> | b <sub>21</sub> |
|-----------------|-----------------|---------------------|---------------------|-----------------|-----------------|
| CO <sub>2</sub> | CH <sub>4</sub> | 1128                | 1999                | -2.35           | 0.256           |
| CO <sub>2</sub> | CH <sub>2</sub> | -50.2               | 1012.4              | 0.31            | -8.1            |
| N <sub>2</sub>  | CO <sub>2</sub> | 340                 | 500                 | -1.85           | -0.5            |
| CH <sub>4</sub> | CH <sub>3</sub> | 103.4               | -20.4               | -0.58           | 1.85            |
| N <sub>2</sub>  | CH <sub>2</sub> | 25.6                | 304.8               | 1.82            | -0.22           |

**Table 2.** UNIFAC group interaction parameters in binary systems (WS model)

| Group 1         | Group 2         | a <sub>12</sub> (K) | a <sub>21</sub> (K) | b <sub>12</sub> | b <sub>21</sub> |
|-----------------|-----------------|---------------------|---------------------|-----------------|-----------------|
| CO <sub>2</sub> | CH <sub>4</sub> | 255                 | 185                 | 0.03            | -0.0027         |
| CO <sub>2</sub> | CH <sub>2</sub> | 192                 | 112.5               | 0.55            | 0.25            |
| N <sub>2</sub>  | CO <sub>2</sub> | 220.1               | 65.8                | 0               | 0.19            |
| CH <sub>4</sub> | CH <sub>2</sub> | 11.1                | 35.2                | 1.01            | 0.012           |
| N <sub>2</sub>  | CH <sub>2</sub> | 186.7               | 29.87               | 2.45            | -1.25           |

**Table 3.** Second Virial coefficient binary interaction parameters in WS mixing rule

| CH <sub>4</sub> with               | K <sub>12</sub> (K) | CO <sub>2</sub> with               | K <sub>12</sub> (K) | N <sub>2</sub> with                | K <sub>12</sub> (K) |
|------------------------------------|---------------------|------------------------------------|---------------------|------------------------------------|---------------------|
| C <sub>2</sub> H <sub>5</sub>      | 0.0285              | C <sub>2</sub> H <sub>6</sub>      | 0.95                | C <sub>2</sub> H <sub>6</sub>      | 0.075               |
| C <sub>3</sub> H <sub>5</sub>      | 0.0412              | C <sub>3</sub> H <sub>5</sub>      | 1.01                | C <sub>3</sub> H <sub>5</sub>      | 0.095               |
| n- C <sub>4</sub> H <sub>10</sub>  | 0.0941              | n- C <sub>4</sub> H <sub>10</sub>  | 0.998               | n- C <sub>4</sub> H <sub>10</sub>  | 0.285               |
| n- C <sub>5</sub> H <sub>12</sub>  | 0.158               | n- C <sub>5</sub> H <sub>12</sub>  | 0.895               | n- C <sub>5</sub> H <sub>12</sub>  | 0.38                |
| n- C <sub>6</sub> H <sub>14</sub>  | 0.45                | n- C <sub>6</sub> H <sub>14</sub>  | 1.02                | n- C <sub>6</sub> H <sub>14</sub>  | 0.750               |
| n- C <sub>7</sub> H <sub>16</sub>  | 0.75                | n- C <sub>7</sub> H <sub>16</sub>  | 1.115               | n- C <sub>7</sub> H <sub>16</sub>  | 0.82                |
| n- C <sub>10</sub> H <sub>22</sub> | 0.795               | n- C <sub>10</sub> H <sub>22</sub> | 1.2                 | n- C <sub>10</sub> H <sub>22</sub> | 0.99                |
| n- C <sub>20</sub> H <sub>42</sub> | 0.82                | N <sub>2</sub>                     | 1.0058              | CO <sub>2</sub>                    | 1.68                |
| n- C <sub>28</sub> H <sub>58</sub> | 0.986               |                                    |                     |                                    |                     |

These relative and absolute errors were determined for the light component in each system.

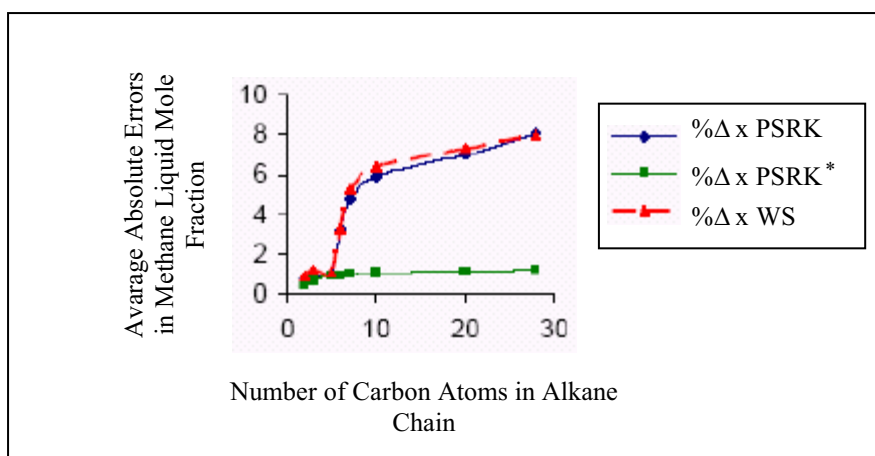
Prediction results for several binary systems are shown in Tables 4 and 5 and Figure 1. Table 4 shows the average absolute and relative errors in methane+n-alkane binary systems with both PSRK and WS models for symmetric systems. For asymmetric systems, PSRK\* (Li, *et al.*,1998) model is also considered. In Figure 1, the results of WS, PSRK and PSRK\* models are graphically compared. In this figure, the number of carbon atoms in the second components of the methane+n-alkane systems are plotted versus average absolute errors in methane liquid mole fraction. As is evident from the figure, as the number of carbon atoms increases, the performance of PSRK and WS models becomes progressively poorer, while the capability of the PSRK\* model remains unchanged.

In Table 5, the results of PSRK and WS models in predicting VLE data in CO<sub>2</sub> binary systems were reported. This table also proves the previous conclusions in methane binary systems. Figure 2 shows the results for methane-octacosane binary system. It can be seen that the modified mixing rules (PSRK\*) leads to large improvements, especially at high

pressures.

The results of PSRK and WS models in predicting VLE data in ternary systems are shown in Table 6. It is noticed that PSRK\* model has reliably good results in systems consisting of components with large difference in size at high pressures. Figures 3 through 5 show the phase envelopes for methane-n-butane-n-decane, nitrogen-n-butane-n-decane and methane-nitrogen-carbon dioxide mixtures at triangular diagrams with PSRK\* model. These figures indicate that VLE prediction data of this model are in good agreement with experimental data.

The phase behavior of a methane-ethane-propane mixture and the accuracy of PSRK model is presented in Figure 6. In this figure, the phase envelope for each component in mixture was plotted at T=213 K. The peaks of these envelopes show the pressures and the mole fractions corresponding to the critical point of the mixture at mentioned temperature. As the results show the mentioned models led to accurate VLE prediction, to have better comparison of these models and other GE models mentioned references could be used.



**Figure 1.** Results of comparison for three thermodynamic models in methane-n-alkane binary system: number of carbon atoms in the second component of methane-n-alkane binary systems versus average absolute errors in methane liquid mole fraction

**Table 4.** VLE prediction results for CH<sub>4</sub>/n-alkane systems

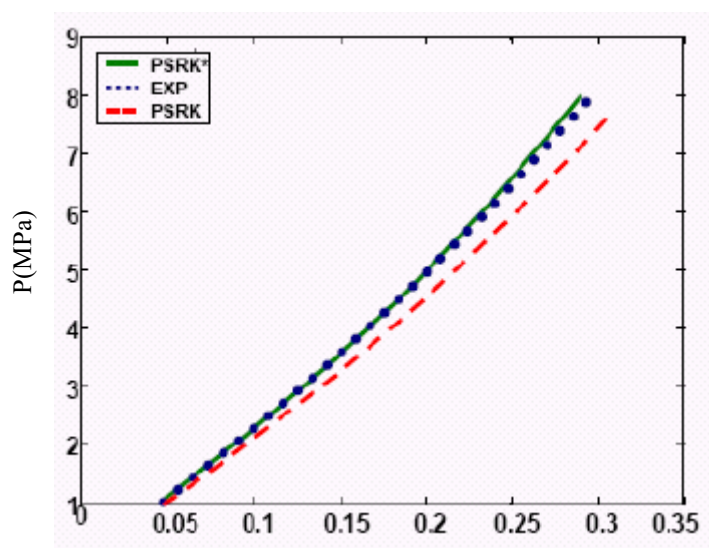
| Methane with | T (K)   | P (MPa)     | N <sub>2</sub> | PSRK Model |      |       | PSRK * Model |       | WS Model |       |       |       | Data Ref. |
|--------------|---------|-------------|----------------|------------|------|-------|--------------|-------|----------|-------|-------|-------|-----------|
|              |         |             |                | %Δy        | %Δx  | %Δx/x | %Δy          | %Δx   | %Δx/x    | %Δy   | %Δx   | %Δx/x |           |
| Ethane       | 230-270 | 0.69-6.5    | 48             | 0.91       | 0.8  | 5.2   | 0.91         | 0.8   | 5.2      | 1.098 | 0.95  | 5.65  | 23        |
| Propane      | 130-220 | 0.17-6.5    | 95             | 0.111      | 0.9  | 6.83  | 0.111        | 0.9   | 6.83     | 0.15  | 1.2   | 7.12  | 24        |
| n-Butane     | 144-277 | 3.44-12.4   | 82             | 0.09       | 0.75 | 6.49  | 0.09         | 0.75  | 6.49     | 0.12  | 1.111 | 6.89  | 25        |
| n-Pentane    | 176-273 | 0.68-13.8   | 48             | 0.48       | 1.1  | 8.2   | 0.48         | 1.1   | 8.2      | 1.23  | 1.1   | 8.2   | 26        |
| n-Hexane     | 180-273 | 0.14-18.3   | 105            | 0.113      | 3.2  | 8.51  | 0.099        | 0.95  | 1.89     | 2.1   | 3.3   | 8.71  | 27        |
| n-Heptane    | 200-255 | 0.69-17.2   | 60             | 0.101      | 4.8  | 7.5   | 0.085        | 1     | 2.58     | 0.85  | 5.2   | 8.96  | 28        |
| n-Octane     | 323-423 | 0.0469-7.1  | 31             | 0.55       | 5.1  | 7.83  | 0.055        | 1.05  | 3.28     | 2.58  | 5.42  | 8.87  | 29,30     |
| n-Nonane     | 273-423 | 1.013-23.32 | 52             | 1.52       | 5.78 | 8.25  | 0.85         | 1.08  | 7.12     | 3.2   | 6.1   | 9.1   | 31        |
| n-Decane     | 273-423 | 1.-1013     | 65             | 0.65       | 5.9  | 9.1   | 0.42         | 1.1   | 3.2      | 3.54  | 6.4   | 10.12 | 32        |
| n-Eicosane   | 373-573 | 0.96-5.1    | 15             | 0          | 7    | 9.25  | 0            | 1.145 | 4.01     | 4.1   | 7.3   | 10.5  | 33        |
| n-Octacoiane | 373-573 | 0.96-5.1    | 15             | 0          | 8.1  | 10.1  | 0            | 1.25  | 4.5      | 5.2   | 8     | 12.4  | 34        |

**Table 5.** VLE prediction results for CO<sub>2</sub> binary system

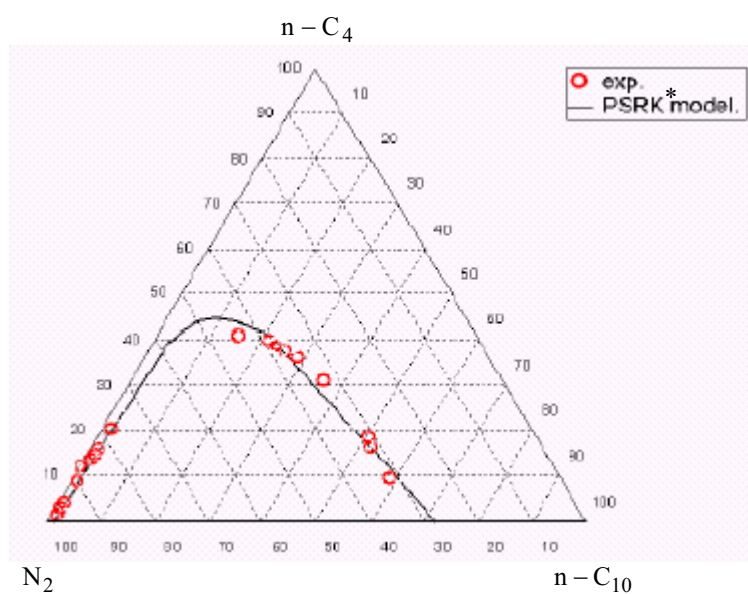
| CO <sub>2</sub> with | T (K)     | P (MPa)    | N <sub>2</sub> | PSRK Model |       |       | PSRK * Model |       | WS Model |       |       |       | Data Ref. |
|----------------------|-----------|------------|----------------|------------|-------|-------|--------------|-------|----------|-------|-------|-------|-----------|
|                      |           |            |                | %Δy        | %Δx   | %Δx/x | %Δy          | %Δx   | %Δx/x    | %Δy   | %Δx   | %Δx/x |           |
| Methane              | 173-260   | 1.1-7.07   | 75             | 0.11       | 0.623 | 1.2   | 0.11         | 0.623 | 1.2      | 0.58  | 1.14  | 2.12  | 35        |
| Ethane               | 173-273   | 0.85-11.71 | 50             | 0.095      | 0.942 | 1.015 | 0.095        | 0.942 | 1.015    | 1.14  | 1.45  | 2.98  | 36,37     |
| Propane              | 294-344   | 0.04-283   | 48             | 0.099      | 0.745 | 1.51  | 0.099        | 0.745 | 1.51     | 0.95  | 1.87  | 3.15  | 38        |
| n-Butane             | 250-418   | 0.04-283   | 83             | 0.158      | 1.52  | 2.26  | 0.158        | 1.52  | 2.26     | 0.88  | 2.25  | 4.25  | 39,40     |
| n-Pentane            | 277-310   | 0.29-9.215 | 33             | 0.189      | 1.68  | 3.84  | 0.189        | 1.68  | 3.84     | 0.921 | 2.85  | 4.12  | 41        |
| n-Hexane             | 300-323   | 2-8.74     | 30             | 0.22       | 2.54  | 4.65  | 0.15         | 1.06  | 1.32     | 1.54  | 4.12  | 6.89  | 42        |
| n-Heptane            | 394-502   | 3-1208     | 41             | 0.64       | 3.89  | 6.25  | 0.64         | 1.14  | 12.09    | 2.25  | 4.015 | 8.12  | 43        |
| n-Decane             | 343-377.4 | 4.12-12.08 | 43             | 1.2        | 5.2   | 7.623 | 0.58         | 0.85  | 1.085    | 3.46  | 5.89  | 10.1  | 44,45     |
| n-Hexadecane         | 542-550   | 2-5.07     | 18             | 2.46       | 6.35  | 9.25  | 1.12         | 0.935 | 1.78     | 4.91  | 7.58  | 12.01 | 45        |
| n-Eicosane           | 310-348   | 0.506-7.6  | 45             | 3.24       | 7.41  | 10.12 | 0.43         | 1.21  | 2.63     | 4.5   | 8.12  | 15.45 | 33,46     |
| n-Octacoiane         | 373-573   | 1.03-5.06  | 15             | 4.1        | 8.91  | 12.42 | 0.98         | 1.012 | 1.99     | 5.2   | 9.27  | 16.8  | 34        |

**Table 6.** Results of models for some ternary systems

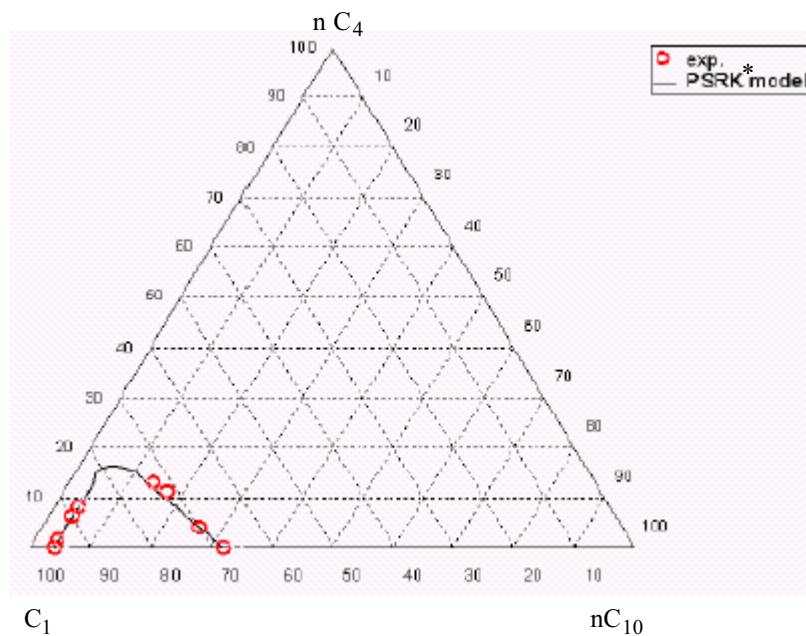
| System                          | T (K)     | P (MPa)      | N <sub>2</sub> | PSRK Model |           |       | PSRK* Model |      | WS Model |      |      | Data Ref. |       |
|---------------------------------|-----------|--------------|----------------|------------|-----------|-------|-------------|------|----------|------|------|-----------|-------|
|                                 |           |              |                | %Δy        | %Δx       | %Δx/x | %Δy         | %Δx  | %Δx/x    | %Δy  | %Δx  |           | %Δx/x |
| Methane-ethane – propane        | 158-213   | 0.386-5.514  | 11<br>2        | 0.65       | 2.01<br>2 | 7.98  | -           | -    | -        | 0.84 | 3.4  | 10        | 47    |
| Methane-propane-n-butane        | 277-377.4 | 1.375-11.717 | 88             | 0.98       | 0.91      | 6.5   | -           | -    | -        | 1.1  | 0.98 | 5.45      | 48    |
| Ethane-n-butane-n-heptane       | 421.8-450 | 3.44-827     | 36             | 2.91<br>8  | 1.65<br>3 | 4.8   | 0.91        | 0.85 | 2.85     | 1.12 | 1.85 | 5.44      | 49    |
| Methane-n-butane-carbon dioxide | 230-450   | 0.14-5.5     | 69             | 5.2        | 2.52      | 59    | -           | -    | -        | 7    | 3.11 | 7.12      | 23,37 |
| Methane-n-butane-methane        | 352       | 27.5         | 6              | 7.52       | 3.6       | 7.8   | 1.25        | 0.98 | 1.82     | 9.94 | 3.73 | 7.98      | 50    |
| Nitrogen-carbon dioxide-methane | 270       | 4.55-9.62    | 38             | 0.95       | 4.2       | 8.1   | -           | -    | -        | 1.8  | 4.5  | 8.7       | 51    |
| Nitrogen-n-butane-n-decane      | 352.6     | 27.5         | 16             | 3.52       | 2.89      | 5.6   | 0.85        | 1.18 | 4.3      | 3.95 | 4.5  | 7.5       | 50    |



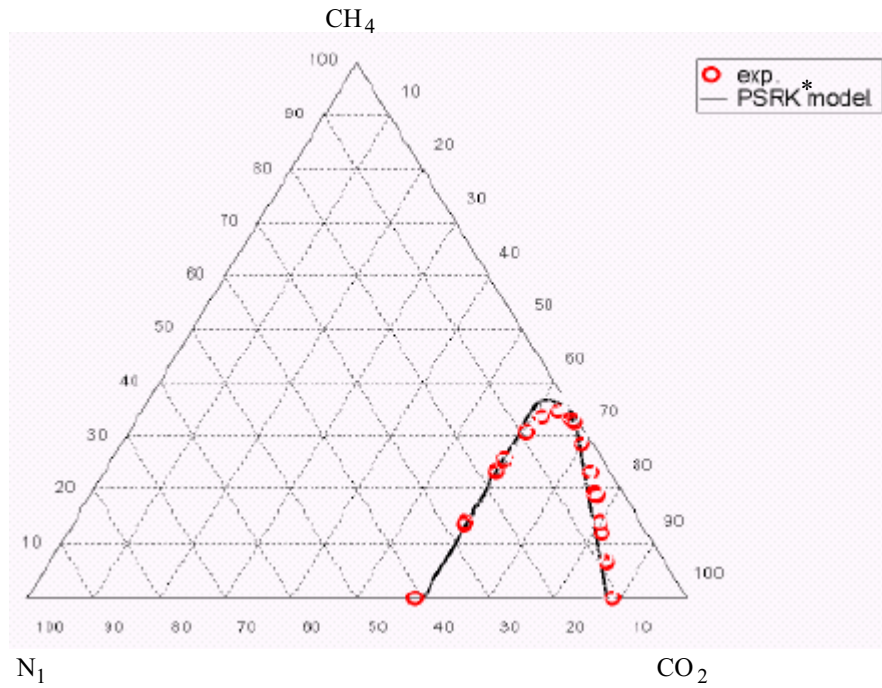
**Figure 2.** Solubility of methane in methane-n-octacosane system at T = 420 K



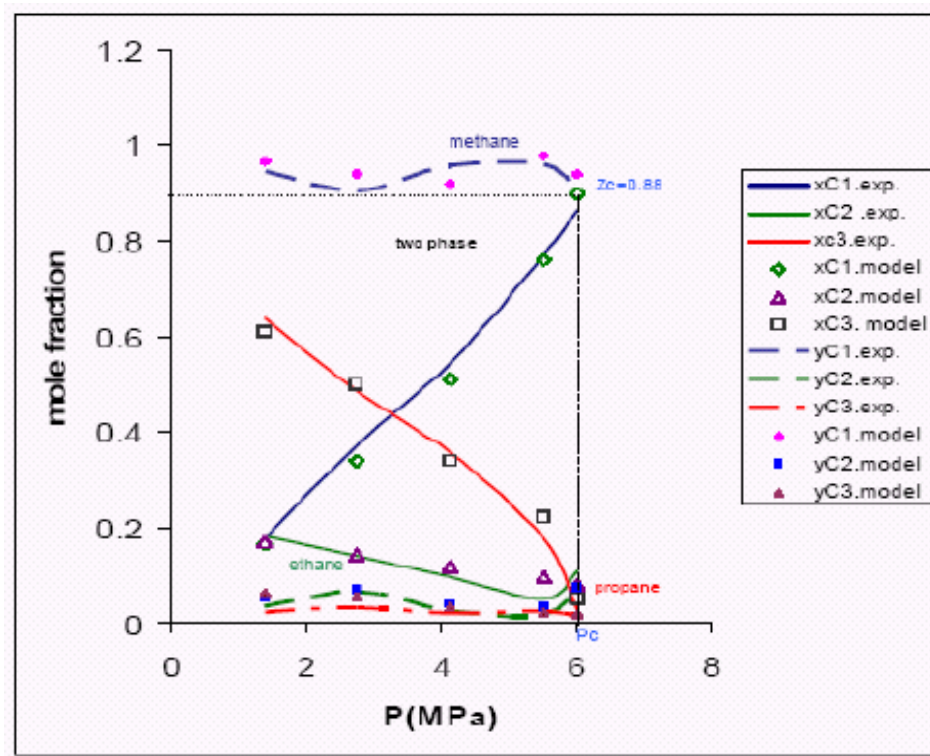
**Figure 3.** VLE prediction for nitrogen-n-butane-n-decane mixtures at 350 K and 27.58 MPa (Exp. data from Ref. 50)



**Figure 4.** VLE prediction for methane-n-butane-n-decane mixtures at 350 K and 27.58 MPa (Exp. data from Ref. 50)



**Figure 5.** VLE prediction for methane-nitrogen-carbon dioxide mixtures at 270 K and 8.612 MPa (Exp. data from Ref. 42,51)



**Figure 6.** Phase behavior for methane-ethane-propane mixtures at 213 K (Exp. data from Ref. 47)



## Conclusion

It is observed that the performance of PSRK and PSRK\* models in mentioned systems are better than WS for the following reasons: Better VLE prediction can be obtained in wide range of conditions; These models can be simply applied in alkane-alkane systems because of the zero value of the interaction parameters; Using modified parameters for  $Q_k$  and  $R_k$  in these models leads to good VLE prediction in a wide range of molecular sizes.

## Notation

|                  |   |
|------------------|---|
| a                | Attraction energy parameter of an EOS ( $\text{dm}^6 \text{ bar mol}^{-2}$ )                |
| $a_i$            | Attractive parameter in cubic EOS for pure component ( $\text{dm}^6 \text{ bar mol}^{-2}$ ) |
| $A^E$            | Excess molar Helmholtz energy ( $\text{J mol}^{-1}$ )                                       |
| b                | Repulsive parameter in cubic EOS ( $\text{dm}^3 \text{ mol}^{-1}$ )                         |
| $b_i$            | Repulsive parameter in cubic EOS for pure component i ( $\text{dm}^3 \text{ mol}^{-1}$ )    |
| $G^{E0}$         | Excess molar Gibbs energy at zero pressure or at normal pressure ( $\text{J mol}^{-1}$ )    |
| $k_{ij}$         | Binary parameter for second Virial coefficient mixing rule                                  |
| $N_p$            | Number of data points   |
| P                | Pressure (bar)  |
| $Q_k$            | Group surface area constant   |
| $R_k$            | Group volume constant   |
| R                | Universal gas constant ( $\text{J mol}^{-1} \text{ K}^{-1}$ )                               |
| T                | Temperature (K)   |
| $V_k^{(i)}$      | Number of group k in molecule i   |
| $x_i$            | Liquid composition (mole fraction) of component i   |
| $x_{\text{cal}}$ | Calculated liquid composition (mole fraction) of component i                                |
| $y_i$            | Vapor or gas phase composition of component i   |
| $y_{\text{cal}}$ | Calculated vapor or gas phase composition of component i                                    |
| v                | Molar volume ( $\text{dm}^3 \text{ mol}^{-1}$ )   |
| EOS              | Equation of state   |
| PR               | Peng –Robinson equation   |
| SRK              | Soave –Redlich –Kwong equation  |
| UNIFAC           | Universal functional group  |

VLE Vapor liquid equilibrium

WS Wong – Sandler

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