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The Performance of EOS Models in the Prediction of Vapor-Liquid Equilibria in Asymmetric Natural Gas Mixtures*

Wang Lisheng (王利生)
Department of Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China

H. Gardeler and J. Gmehling**
Department of Technical Chemistry, University of Oldenburg, P.O. Box 2503, D-26111 Oldenburg, Germany

Abstract The aim of this work is to apply cubic equations of state (EOS) to vapor-liquid equilibria calculations of gas-heavy hydrocarbon systems, which are asymmetric in molecular size and are usually found in natural gases. Investigation has been done to test the validity of the original PSRK and the cubic simplified perturbed hard-chain (CSPHC) models for global phase diagrams. The calculation results show that both equations overpredict vapor pressure in the near critical region. In the prediction of the solubilities of high molecular weight (MW) hydrocarbons in the natural gas, the PSRK model gives good agreement for the dew point pressure-vapor composition diagrams. Adjustment of the pure component parameters of the CSPHC EOS for heavy components to fit the vapor-liquid equilibrium (VLE) data has been proved to give significant promoting in prediction accuracy. However, further improvement of a van der Waals EOS, such as SRK, PT and DG models for the asymmetric systems by adjusting the three pure component properties, T_c, p_c and ω, did not achieve satisfactory results for heavy components.

Keywords equation of state, natural gas, vapor-liquid equilibria, asymmetric systems

1 INTRODUCTION

Accurate prediction for vapor-liquid equilibria for parameters in asymmetric systems (such as solubility of heavy hydrocarbons in natural gases) using thermodynamic models are very important from the industrial point of view. The van der Waals type of equations of state (EOS), such as the group contribution equation of state: the predictive Soave-Redlich-Kwong (PSRK) EOS, which combines the universal quasi-chemical functional group activity coefficients (UNIFAC) model with the Soave-Redlich-Kwong (SRK) equation of state developed with Dortmund Data Bank[1,2], can yield satisfactory predictions for vapor-liquid equilibrium (VLE) in systems with components of similar sizes, as in most systems containing polar components. However, up to now, there are still difficulties and limitations with systems with components of great differences in molecular sizes.

To improve the prediction accuracy for the equation of state model of such systems, two different colloquies of approved have greatly been adopted.

The first method is to improve the mixing rules, such as the recent work by Voutsas *et*

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** To whom correspondence should be addressed.

al.[3] and by Li *et al.*[4]. Through regression of available data, Voutsas *et al.* estimated the gas parameters R, Q and the interaction parameters A_{ij} and B_{ij} between pairs involving gaseous compounds. In the work of Li and Gmehling, effective R_k^*, Q_k^* for the subgroups $-CH_3$, $-CH_2-CH$ and $-C$ of UNIFAC in the PSRK were used to take into account the differences in molecular sizes among small and large molecules. An empirical expression has been developed for more reliable calculation of vapor-liquid equilibria in asymmetric systems. In the above mentioned works, however, the parameters involved in the mixing rule have to be regressed from binary VLE data. Since only the mixing rules are affected, the resulting behavior of the system is much similar to those of binary parameters such as k_{ij} and l_{ij} in classical mixing rules.

The second method works with a more exact description for the properties of the heavy components in concern. One example is the recent work of Bertucco and Mio[5] based on SRK-Huron-Vidal mixing rules and UNIFAC model. Experimental activity data of different solvents in binary systems with a certain polymer were used to fit the EOS parameters of the polymer. Satisfactory results have been obtained for using the regressed parameters of polystyrene (PS) in a benzene-PS system to predict the activity and VLE of chloroform-PS and acetone-PS. With this method, the difficulties of computing pure component parameters in VLE calculations with SRK EOS can be overcome.

The goals of this research include: (1) application of PSRK model to test the prediction ability of the original PSRK model for global phase diagrams and the solubilities of high-MW hydrocarbon in highly asymmetric natural gas mixtures; (2) to compare models specifically designed for hydrocarbon systems, including PT[6], CSPHCT[7], DG[8] and the original SRK[9]; (3) to test the methods similar to that suggested by Bertucco and Mioto for the prediction of highly asymmetric systems. The three parameters T^*, v^* and c of pure components in the CSPHC model and T_c, p_c and ω in the van der Waals type EOS models for the heavy components in a binary mixture are fitted to the vapor-liquid equilibrium data respectively. The calculations in this work performed with the help of the Dortmund Data Bank.

2 THERMODYNAMIC MODELS

2.1 PSRK model

PSRK model was proposed by Holderbaum and Gmehling[10], in which the PSRK mixing rule combines the UNIFAC model (Hasen *et al.*[11]) with the SRK equation of state

$$p = \frac{RT}{\nu - b} - \frac{a}{\nu(\nu + b)} \tag{1}$$

The binary mixture parameters are evaluated with PSRK mixing rules

$$\begin{aligned} \frac{a}{bRT} &= -\frac{1}{0.646\,63}\sum x_i \ln \gamma_i - \frac{1}{0.646\,63}\sum x_i \ln \frac{b}{b_i} + \sum x_i \frac{a_i}{b_i RT} \\ &= -\frac{1}{0.646\,63}\left[x_1(\ln \gamma_1 + \ln \frac{b}{b_1}) + x_2(\ln \gamma_2 + \ln \frac{b}{b_2})\right] + x_1 \frac{a_1}{b_1 RT} + x_2 \frac{a_2}{b_2 RT} \end{aligned} \tag{2}$$

$$b = \sum x_i b_i \tag{3}$$

in which the activity coefficients are calculated from the modified UNIFAC model[11]. Comparison with other group contribution equations of state showed[12] that the PSRK model presents itself with several important advantages: (1) The PSRK mixing rule has a well defined reference state

(the liquid mixture under atmospheric pressure), whereby the constant $A_0 = -0.646\,63$ in the PSRK mixing rule is basically calculated by using quasi liquid volumes of many substances at one atmosphere; (2) The PSRK model gives reliable results for vapor-liquid equilibria and gas solubility in wide temperature and pressure ranges; (3) The parameter matrix of the PSRK model is much larger than that in the other methods.

2.2 CSPHC model

An equation of state based on statistical mechanics and with molecular parameters as independent variables to fit the vapor pressure and liquid density data in the saturation phase, such as the perturbed hard-chain theory (PHCT) developed by Beret and Prausnitz[13], shows advantages in the calculation for phase behavior and thermodynamic properties in a number of different systems of industrial interest.

Due to the complexity of the equation of state derived from PHCT, there are certain restriction in its application to petroleum engineering related calculations (*e.g.*, reservoir simulation, *etc.*). A cubic simplified version of the PHCT (CSPHC EOS) was proposed by Wang and Guo[7] by reformulating the attractive portion of the canonical partition function for mixtures, and replacing the repulsive portion by a simple simulated expression. The test results on pure fluids, binary/multi-component mixtures indicate that the CSPHC EOS retains the advantages of the original PHCT, which allows satisfactory predictions of VLE and liquid density for heavy hydrocarbon-containing mixtures.

Following the derivation of the simplified perturbed hard-chain equation of state (SPHCT)[14], the CSPHC EOS was derivated from the generalized van der Waals partition function for mixtures of chainlike molecules in the following form

$$z = 1 + \langle c \rangle \left(z_r - Z_M \frac{\langle a \rangle}{v + \langle a \rangle} \right) \tag{4}$$

where z is the compressibility factor and v is the molar volume, $Z_M = 36$, and

$$\langle c \rangle = \sum_i x_i c_i \tag{5}$$

where $3\langle c \rangle_i$ and $3c_i$ stand for the average external degrees of freedom of a mixture and component i respectively, x_i is the mole fraction of component i, and

$$\langle a \rangle = \sum_i \sum_j x_i x_j v_{ji}^* [\exp(\langle T^* \rangle_i / 2T) - 1] \tag{6}$$

In this work, all calculations were carried out by setting k_{ij} equal to zero. The major objective of this work is to use the CSPHC model to predict the phase behavior for asymmetric systems in natural gases, and have it compared with other van der Waals type equations of state.

2.3 Pure component EOS parameters of heavy component

The pure component properties (such as vapor pressure and critical properties) of heavy hydrocabons (such as $C_{15}-C_{30}$) usually can not be measured as accurate as those of light hydrocabons. This may be caused by the much lower vapor pressure, and thermo-unstability of the heavy molecules at high temperatures. Therefore, using the EOS parameters based on these properties to predict the mixture properties might not be satisfactory. Furthermore, a reservoir fluid mixture (oil or gas condensate) contains both defined light hydrocarbons and an undefined

heavy fraction (*e.g.* C_7^+-fraction), such as methane and hexadecane mixture which shows asymmetric properties in respect to molecular size. In an undefined reservoir crude oil mixture, the properties of narrow cuts (pseudocomponents) are usually expressed in terms of average molecular weight and specific gravity. When a van der Waals type equation of state is used to predict the phase behavior of the reservoir fluids, the calculation results will vary depending on the chosen empirical T_c, p_c, ω correlation, because T_c, p_c, ω of the C_7^+-fraction can not be obtained through experiment. In practice, different T_c, p_c, ω correlations were chosen empirically to find out the ones capable of providing better results. Thus, T_c, p_c, ω may be considered to be the three independent EOS parameters.

With some of these different EOS models, calculations were carried out to investigate how the three parameters of heavy components affect the phase behavior prediction. The EOSs chosen for this test are mainly based on the CSPHC, SRK, PT and DG models.

3 CALCULATION RESULTS

3.1 Predictability of PSRK and CSPHC models

3.1.1 *Prediction for global VLE diagram*

The performances of PSRK and CSPHC models in the calculations for global VLE diagrams, compared with experimental data of a methane-decane system, are shown in Fig.1 and listed in Tablel. It can be seen that better prediction results are obtained with the PSRK equation except in the near critical region, where both equations overpredict the vapor pressure.

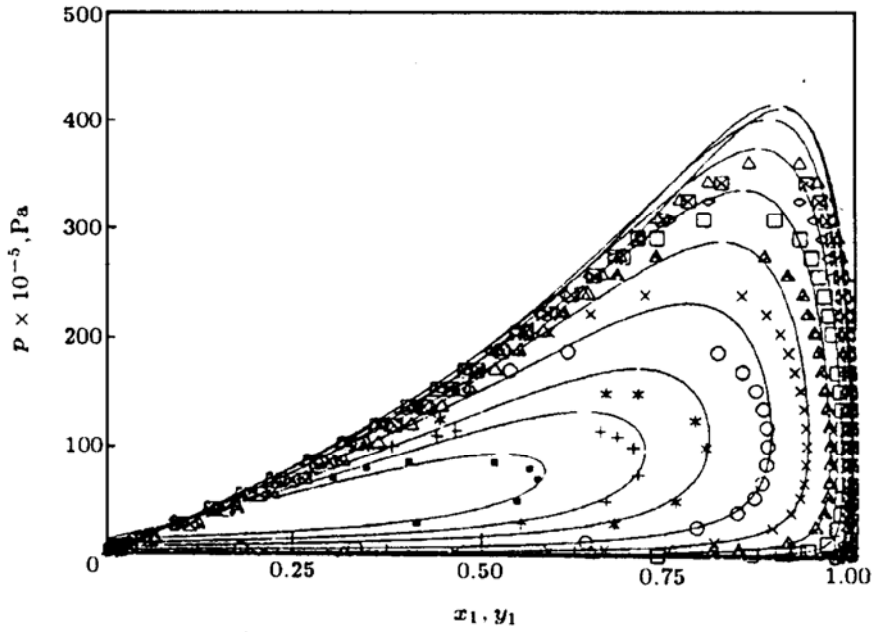

Figure 1 Prediction of global vapor-liquid equilibria for methane(1)-decane(2) system by PSRK equation of state

— PSRK(UNIFAC) modle; ■ + * ○ × △ □ ◇ ⊠ ⧋ experimental data (DDB[1,2])

T,K: ■ 583.05; + 563.00; * 542.25; ○ 510.93; × 477.59; △ 477.26; □ 410.93; ◇ 377.59; ⊠ 344.26; ⧋ 310.93

The predicted results of CSPHC for the methane-hexadecane system are also listed in Table 1. The $AAD\%$ for saturation pressure and vapor composition predicted with the CSPHC model are 5.94% and 1.25% respectively. Compared with the fitted results of other models, these figures appear to be satisfactorily accurate.

Table 1 Summery of different EOS parameters and corresponding calculation results for gases(1)-hydrocarbons(2) vapor-liquid eqilibria

System	Data points	T K	$p \times 10^{-5}$ Pa	CSPHC					SRK				
				$AADp$ %	$AADy_1$ %	$T^*(2)$ K	$v^*(2) \times 10^5$ $m^3 \cdot mol^{-1}$	$c(2)$	AAD_p %	$AADy_1$ %	$T_c(2)$, K	$p_c(2)$ $\times 10^{-5}$,Pa	$\omega(2)$
$CH_4(1)$-$nC_{10}H_{22}(2)$	172	310.93–583.05	1.0–395.0	6.75	1.78	192.16	10.015	2.8584	15.88	10.31	617.74	24.74	0.4600
				3.52[a]	2.03[a]	203.52[a]	10.521[a]	2.3401[a]	6.66[a]	7.78[a]	659.55[a]	22.06[a]	0.7730[a]
$CH_4(1)$-$nC_{16}H_{34}(2)$	121	373.15–703.55	20.0–577.24	5.94	1.25	217.57	15.464	3.5544	27.10	3.24	731.80	17.24	0.6710
				1.09[a]	1.49[a]	225.37[a]	15.362[a]	2.6820[a]	23.00[a]	3.37[a]	732.12[a]	16.66[a]	0.6586[a]
$N_2(1)$-$nC_{10}H_{22}(2)$	94	310.93–410.93	20.44–340.69	5.23	0.25	192.16	10.015	2.8584	30.01	0.22	617.74	24.74	0.4600
				5.23[a]	0.25[a]	203.52[a]	10.521[a]	2.3401[a]	5.21[a]	0.39[a]	652.13[a]	23.66[a]	0.7955[a]
$N_2(1)$-$nC_{16}H_{34}(2)$	112	308.15–623.55	6.9–258.1	8.45	0.70	217.54	15.464	3.5544	15.88	10.31	731.80	17.24	0.6710
				5.83[a]	4.03[a]	225.37[a]	15.362[a]	2.6820[a]	6.50[a]	7.91[a]	660.30[a]	21.96[a]	0.7791[a]
$CO_2(1)$-$nC_{16}H_{34}(2)$	92	313.15–663.75	6.9–258.1	14.63	1.61	217.54	15.464	3.5544	28.30	11.68	731.80	17.24	0.6710
				6.83[a]	3.90[a]	203.75[a]	15.337[a]	3.6786[a]	25.13[a]	18.01[a]	762.58[a]	18.96[a]	0.3885[a]

System	Data points	T K	$p \times 10^{-5}$ Pa	PT					DG				
				$AADp$ %	$AADy_1$ %	$T_c(2)$ K	$p_c(2)$ $\times 10^{-5}$,Pa	$\omega(2)$	AAD_p %	$AADy_1$ %	$T_c(2)$ K	$p_c(2)$ $\times 10^{-5}$,Pa	$\omega(2)$
$CH_4(1)$-$nC_{10}H_{22}(2)$	172	310.93–583.05	1.0–395.0	18.01	5.13	617.74	24.74	0.4600	15.47	11.84	617.74	24.74	0.4600
				13.59[a]	4.01[a]	612.98[a]	24.17[a]	0.5607[a]	5.88[a]	8.10[a]	660.64[a]	17.81[a]	0.6421[a]
$CH_4(1)$-$nC_{16}H_{34}(2)$	121	373.15–703.55	20.0–577.24	15.33	2.76	731.80	17.24	0.6710	13.50	2.20	731.80	17.24	0.6710
				b	b	b	b	b	12.74[a]	2.17[a]	731.98[a]	16.95[a]	0.6748[a]
$N_2(1)$-$nC_{10}H_{22}(2)$	94	310.93–410.93	20.44–340.69	16.07	0.21	617.74	24.74	0.4600	7.60	0.19	617.74	24.74	0.4600
				3.88[a]	0.27[a]	656.84[a]	23.77[a]	0.5255[a]	3.64[a]	0.27[a]	648.14[a]	22.30[a]	0.5436[a]
$N_2(1)$-$nC_{16}H_{34}(2)$	112	308.15–623.55	6.9–258.1	13.15	11.42	731.80	17.24	0.6710	11.57	11.48	731.80	17.24	0.6710
				b	b	b	b	b	5.75[a]	8.23[a]	661.81[a]	17.77[a]	0.6423[a]
$CO_2(1)$-$nC_{16}H_{34}(2)$	92	313.15–663.75	6.9–258.1	31.57	22.13	731.80	17.24	0.6710	21.75	9.41	731.80	17.24	0.6710
				b	b	b	b	b	25.74[a]	4.24[a]	730.98[a]	17.41[a]	0.6828[a]

$$AAD_n = \sum_i |(n_{exp} - n_{cal})/n_{exp}|_i \times 100\%, n = p \text{ or } y_1$$

[a] referred to the regressed results; [b] No better results found through regression.

3.1.2 *Prediction of solubilities of high-MW hydrocarbon in the natural gas*

Fig.2 shows the predicted results for the relationship between the dew point pressure and vapor composition in the near pure nitrogen region in N_2-decane system as calculated with the two equations. From this figure it can be seen that both PSRK and CSPHC models give reliable results. These data are regarded as key factors for the solubility of heavy hydrocarbons in natural gas production and transportation.

The relationship between dew point pressure and vapor composition in the near pure nitrogen region for N_2-hexadecane system calculated from the PSRK equation has also been found quite satisfactory, as shown in Fig.3. It can be concluded, therefore, PSRK and CSPHC equations can be used to predict the phase behavior of natural gases with very good accuracy.

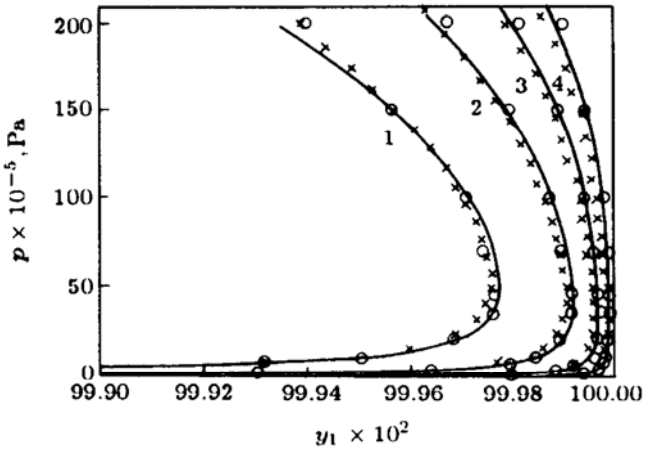

Figure 2 Prediction of dew point pressure *vs.* vapor phase composition (y) for the system nitrogen(1)-decane(2) by PSRK (UNIFAC) and CSPHC equations of state
— CSPHC model; × PSRK (UNIFAC) model; o experimental data (DDB[1,2])
T, K: 1–310.85; 2–293.15; 3–278.15; 4–263.15

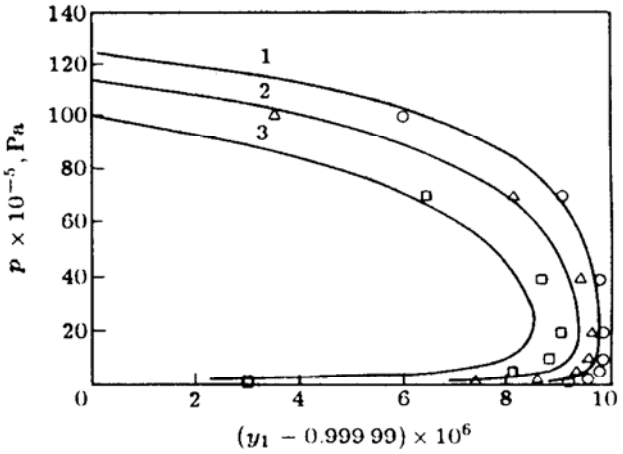

Figure 3 Prediction of dew point pressure *vs.* vapor phase composition (y) for system nitrogen(1)-hexadecane(2) by PSRK (UNIFAC) equation of state
— PSRK (UNIFAC) model; o △ □ experimental data (DDB[1,2])
T, K: 1–293.15; 2–303.15; 3–313.15

3.2 Adjusting the pure component parameters to fit with VLE data

The CSPHC equation is tested first as an example in this report. We first fit in the VLE data of a mathane-decane system for the regression of the three new parameters T^*, v^* and c of decane. Table 1 lists the fitted results. The three new parameters are then used to predict the VLE of a N_2-decane system. Fig.4 shows the prediction results with original parameters and with the new parameters of decane regressed from methane-decane mixture respectively. It can be seen that the more accurate predictions, especially in the near critical region, have been obtained with the regressed data.

Fig.5 shows the prediction of the CSPHC equation for a methane-hexadecane system, calculated from the original parameters of hexadecane, is not satisfactory. Fig.5 also shows the regressed results for the same system. The improvement is significantly even in the near critical region. These parameters of hexadecane in the CSPHC equation are regressed from a methane-hexadecane system and then used to predict the VLE data of a propane-hexadecane system (Fig.6). The predicted results are found to be quite satisfactory as compared with the predicted results from CSPHC EOS with the original parameters.

However, through these tests we can not extend a conclusion that the way of further improving

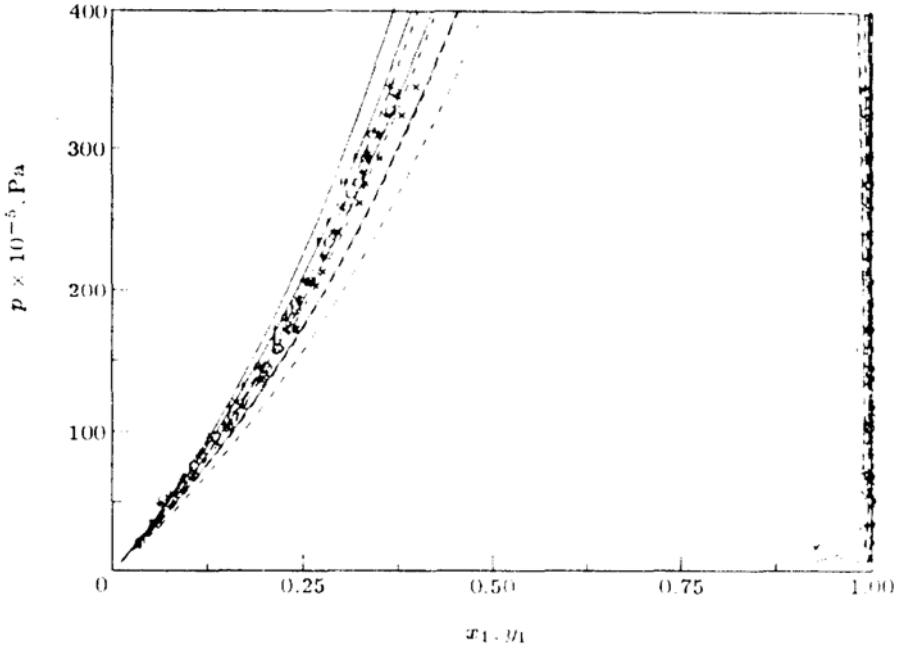

Figure 4 Prediction of vapor-liquid equilibria for nitrogen(1)-dencane(2) system by CSPHC equation of state

– – – CSPHC EOS with original parameters; —— CSPHC EOS with the parameters of decane regressed from methane-decane system; + * ○ × experimental data (DDB[1,2])

T,K: + 310.93; * 311.26; ○ 377.59; × 410.93

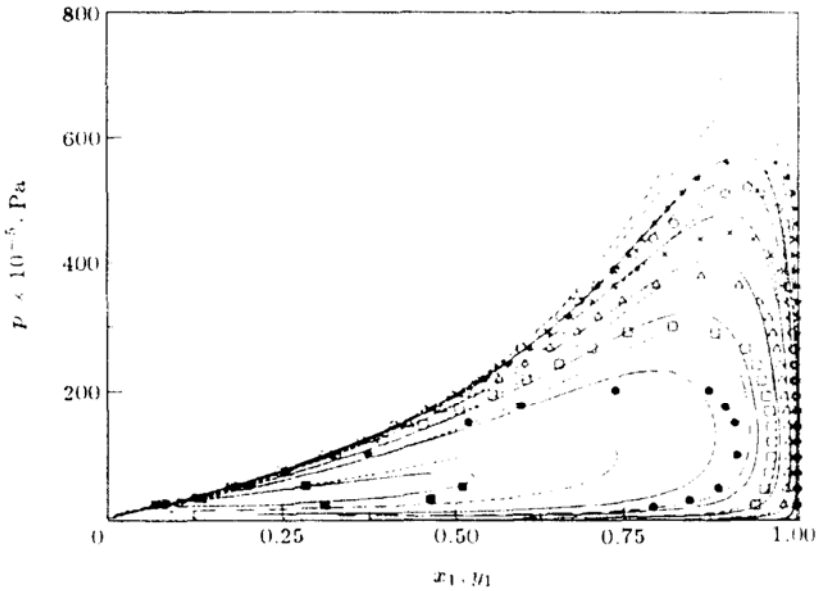

Figure 5 Calculation of global vapor-liquid equilibrium for methane(1)-hexadecane(2) system by CSPHC equation of state

—— CSPHC with new parameters; – – – CSPHC with original parameters;

■ ● □ △ × ○ * experimental data (DDB[1,2])

T,K: ■ 703.55; ● 623.15; □ 572.15; △ 523.15; × 473.15; ○ 423.15; * 373.15

a van der Waals EOS for the asymmetric systems is to adjust the three pure component properties, T_c, p_c and ω. Table 1 lists a summery of different EOS parameters and their corresponding VLE calculation results for a number of asymmetric gases(CH_4, N_2, CO_2) and hydrocarbon systems.

It may be noted that the results with the PSRK model are not included in the table because very poor results with PSRK were obtained for the hexadecane containing systems (It may be worth to metion that recent work by Li *et al.*[4] employed the regression of available data to give effective R_k^*, Q_k^* and succeeded in obtaining good calculated results for asymmetric systems). From Table 1 it can be seen that the CSPHC model gives the smallest average absolute deviation ($AAD, \%$) in this work. From Table 1 we can conclude that the adjustment of pure component parameters of heavy hydrocarbons to fit the VLE data has been found to be satisfactory with the CSPHC model only, and not for other van der Waals types of EOS.

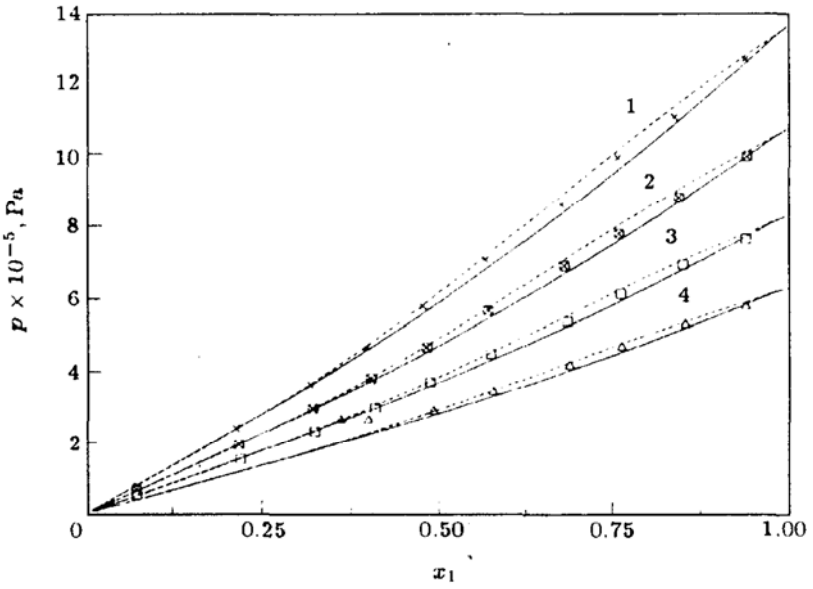

Figure 6 Prediction of saturation pressure *vs.* liquid composition for propane(1)-hexadecane(2) system by CSPHC equation of state

— CSPHC model with new parameters of hexadecane regressed from methane-hexadecane VLE data; – – – CSPHC model with original parameters; ×□ ⊠ △ experimental data (DDB[1,2])

T,K: 1–313.15; 2–303.15; 3–293.15; 4–283.15

4 CONCLUSIONS

The predictability of the original PSRK and CSPHC models were tested. Special attention was paid to global phase diagrams and dew point pressure-vapor composition diagrams of asymmetric binary mixtures in natural gas. The calculation results show that both equations overpredict vapor pressure in the near critical region. Adjustment of the pure component parameters of heavy hydrocarbons to fit the VLE data has been tested in different EOS. The prediction accuracy with the CSPHC model can be then improved significantly in this way. While for other van der Waals type EOS, however, the adjustment of pure component parameters (T_c, p_c and ω) of heavy hydrocarbons does not seem to be capable of improving the prediction accuracy for asymmetric systems.

NOMENCLATURE

a	SRK EOS parameter defined by Eq.(1)
b	SRK EOS parameter defined by Eq.(1)
$3c$	number of external degrees of freedom per moleculer
k_{ij}	binary interactive energy coefficient

l_{ij} binary interactive size coefficient
p_c critical pressure, MPa
Q_k^* UNIFAC combinatal parameter
R universal gas constant
R_k^* UNIFAC combinatal parameter
T_c critical temperature, K
T^* characteristic temperature for intermolecular interaction, K
v molar volume, $m^3 \cdot mol^{-1}$
v^* characteristic volume per mole, $m^3 \cdot mol^{-1}$
x mole fraction in liquid phase
y mole fraction in gas phase
Z_M maximum coordination number
z compressibility factor
ω acentric factor
$\langle\ \rangle$ mixture

Subscripts

c critical
i component
ij pertaining to binary pairs of molecules/segments i and j
M maximum
r repulsion

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