The calculation of ternary vapor-liquid system equilibrium by using P-R equation of state

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Abstract:

By using P-R equation of state (EOS), the phase equilibrium characteristics was simulated for a system consisted of hydrogen-hexane-dicyclopentadiene (DPD). In order to improve the accuracy of the simulation, different αfunctions and mixing rules were respectively used to modify the P-R EOS. The molar concentrations in vapor and liquid phase calculated was contrasted with that of the experimental data cited in literatures. The applicability and accuracy of each modified coefficient for the system contains hydrogen at different reduced parameter conditions were presented. So this approach may be used to predict the equilibrium behaviors of a high-pressure vapor-liquid system.

Keywords: Solubility, phase equilibrium behavior, hydrogen, simulation

Introduction:

The vapor-liquid equilibrium data of ternary system is one of the most important parameters for the design of the chemical process. In thermodynamics, the simulation of phase equilibrium based on the study of experiments is the main method to resolve this kind of problem. The research of phase equilibrium behavior is a kind of very important work in supercritical fluid extraction, gas-antisolvent, chemical reaction and many other processes. Generally, P-R EOS has already been considered as the most efficient way to simulate the equilibrium behavior of a system subjected to high pressure (especially for the system contains liquid phase). The simulation of binary system by P-R EOS is very accurate, and many references [1-3] reported this kind of model. But when it is concern to ternary system or low temperature system that contains hydrogen, the calculated value does not coincide with the experimental data very well. And the literature about the simulation of ternary system by P-R EOS is not very much, and the accuracy is relatively low. So several αfunctions and mixing rules were presented to modify the P-R EOS.

Calculation:

The hydrogen-hexane-DPD system was calculated with Peng-Robinson EOS.

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \qquad (1)$$

$$a(T) = 0.45724\frac{R^2 T_c^{\,2}}{p_c}\alpha \qquad (2)$$

$$\alpha = [1 + k(1 - T_r^{0.5})]^2 \tag{3}$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{4}$$

$$b = 0.0778\frac{RT_c}{p_c} \tag{5}$$

The following are mixing rule and combining rule:

$$a = \sum_i^m \sum_j^m x_i x_j a_{ij} \tag{6}$$

$$b = \sum_i^m \sum_j^m x_i x_j b_{ij} \tag{7}$$

$$b_{ij} = \frac{b_i + b_j}{2} \tag{8}$$

$$a_{ij} = (1 - k_{ij})\sqrt{a_i(T)a_j(T)} \tag{9}$$

The P-R EOS was originally designed to model hydrocarbon systems using one interaction parameter k_{ij}, and it was obtained by regressing the experimental data. To modify the equation, many αfunctions and mixing rules were presented[4]. And we use the following function as the mixing rule instead of function (8).

$$b_{ij} = (1 - l_{ij})\frac{b_i + b_j}{2} \tag{10}$$

where l_{ij} is also an interaction parameter. And we use function (10) as the mixing rule to calculate the equilibrium data of the ternary system composed of H_2-hexane-DPD. In this system, k_{ij} and l_{ij} used in calculation are k_{12}=-0.49426, k_{13}=0.03397, k_{23}=-0.09567, and l_{12}=0.01306, l_{13}=0.0724, l_{23}=-0.01705[5].Figure 1 to 2 showed the hexane mole fraction in the gas phase from 2 to 6 MPa, the DPD mass content (wt) was 7% and 25%, at 313K and 343K respectively.

The average deviation (AAD%) of the hexane mole fraction in the gas phase at 313K is 5.1% and at 343K is 13.4%. But the AAD% of liquid phase is more than 20%. And the AAD% is defined as:

$$AAD\% = 100 \times \left| \frac{\alpha^{cal} - \alpha^{\exp}}{\alpha^{\exp}} \right| \tag{11}$$

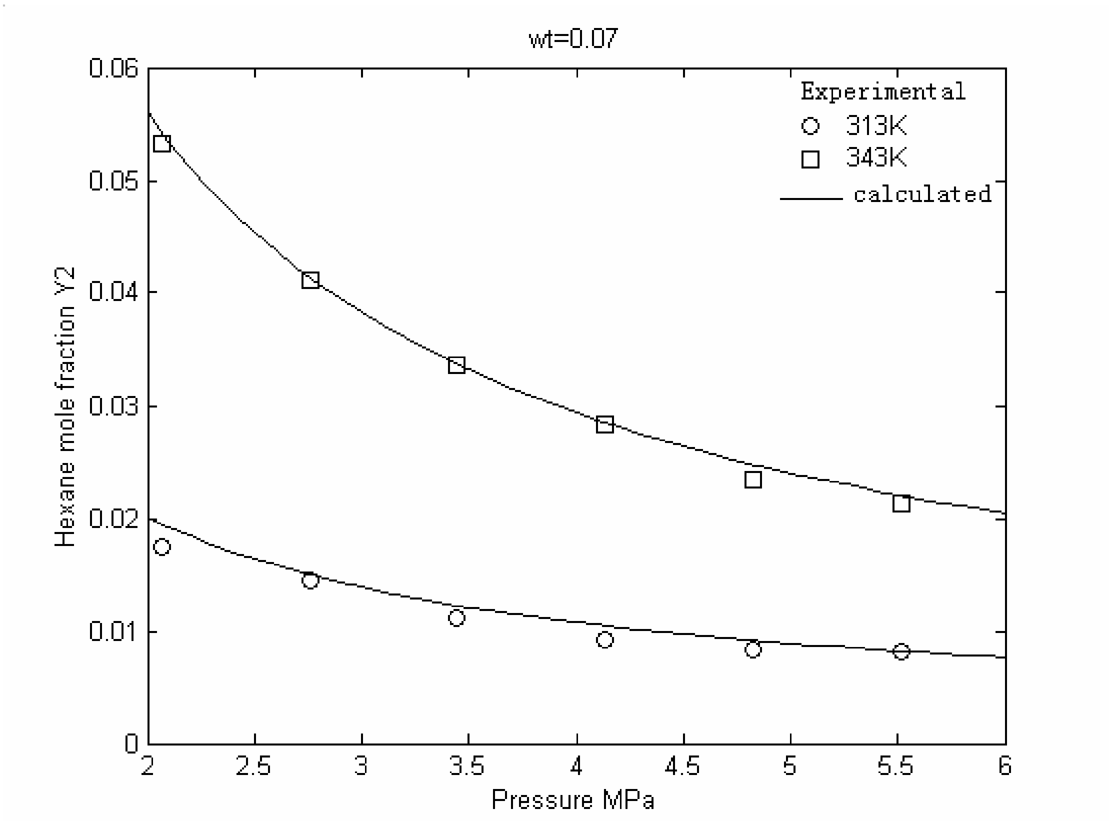

Fig.1 Composition of hexane in the gas phase for DPD in liquid feed at 7 wt%

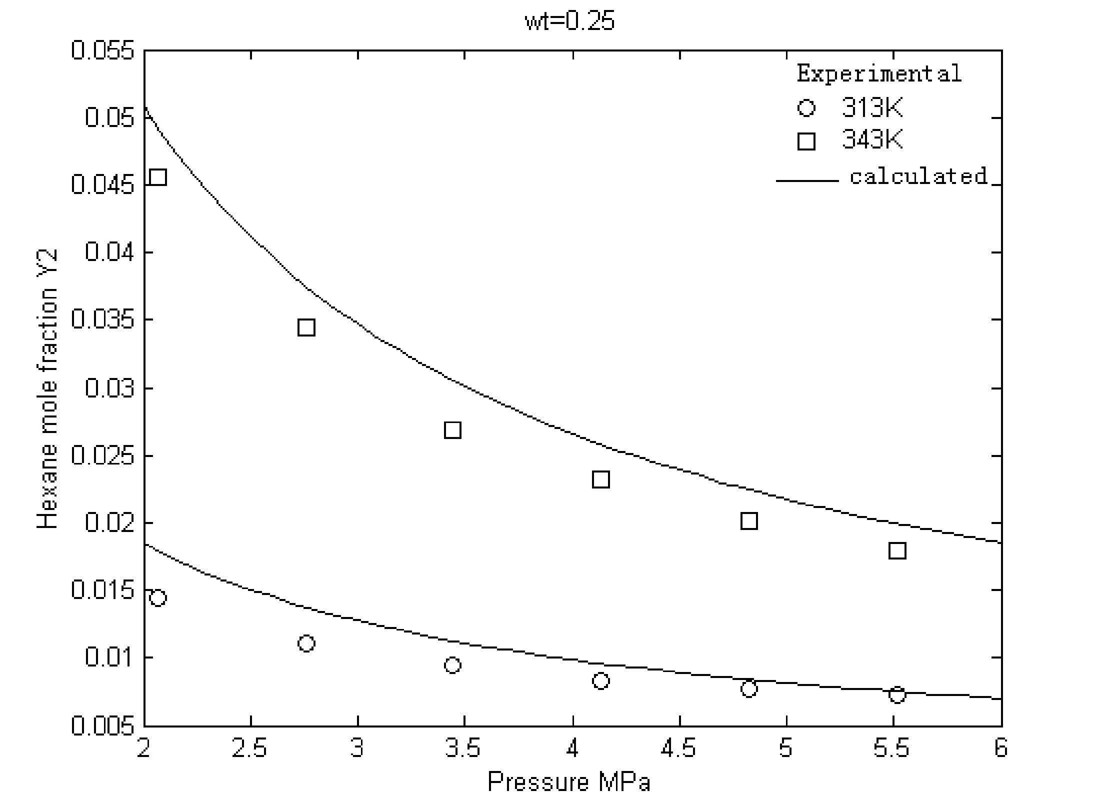

Fig.2 Composition of hexane in the gas phase for DPD in liquid feed at 25 wt%

Harmens and Knapp[6] presented one α function as the following to improve the P-R EOS:

$$\alpha = [1 + k_1(1 - T_r^{0.5}) - k_2(1 - \frac{1}{T_r})]^2 \qquad (12)$$

Tan gave the k_1 and k_2 value of hydrogen. That is k_1=0.30298 and k_2=0.07889.By using the equation (12), we get a more accurate result that the AAD% of hydrogen in liquid phase at 313K is 5.4% and at 343K is 8.6%.Figure 3 and 4 shows that the hydrogen mole fraction in the liquid phase using function (12) instead of function (3).

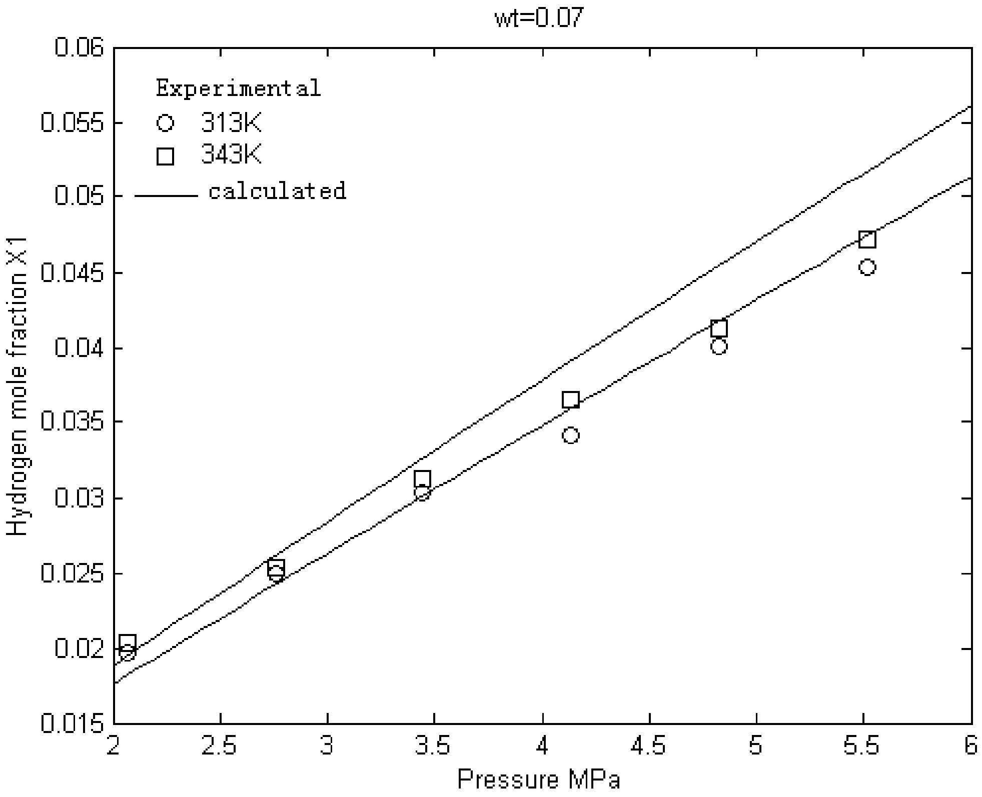

Fig.3 Composition of hydrogen in the liquid phase for 7 wt% DCPD

Conclusion and discussion:

The phase equilibrium behavior for the ternary system hydrogen-hexane-DPD were simulated by using P-R EOS at pressure from 2 to 5 MPa and temperature at 313K and 343K. From figure 1 to 4, it can be concluded that if we care the equilibrium behavior in the gas phase of the system composed of hydrogen-hexane-DCPD, we can use function (3), otherwise we the better use function (12). It was also found that using the P-R EOS model to calculate the equilibrium behavior is accurate. And using P-R EOS incorporate with a modified αfunction to simulate the equilibrium behavior of a ternary system can get a satisfactory result.

List of symbols:

Letters

a , b	constants in P-R EOS	T	temperature (K)
P	pressure (MPa)	T_r	reduced temperature

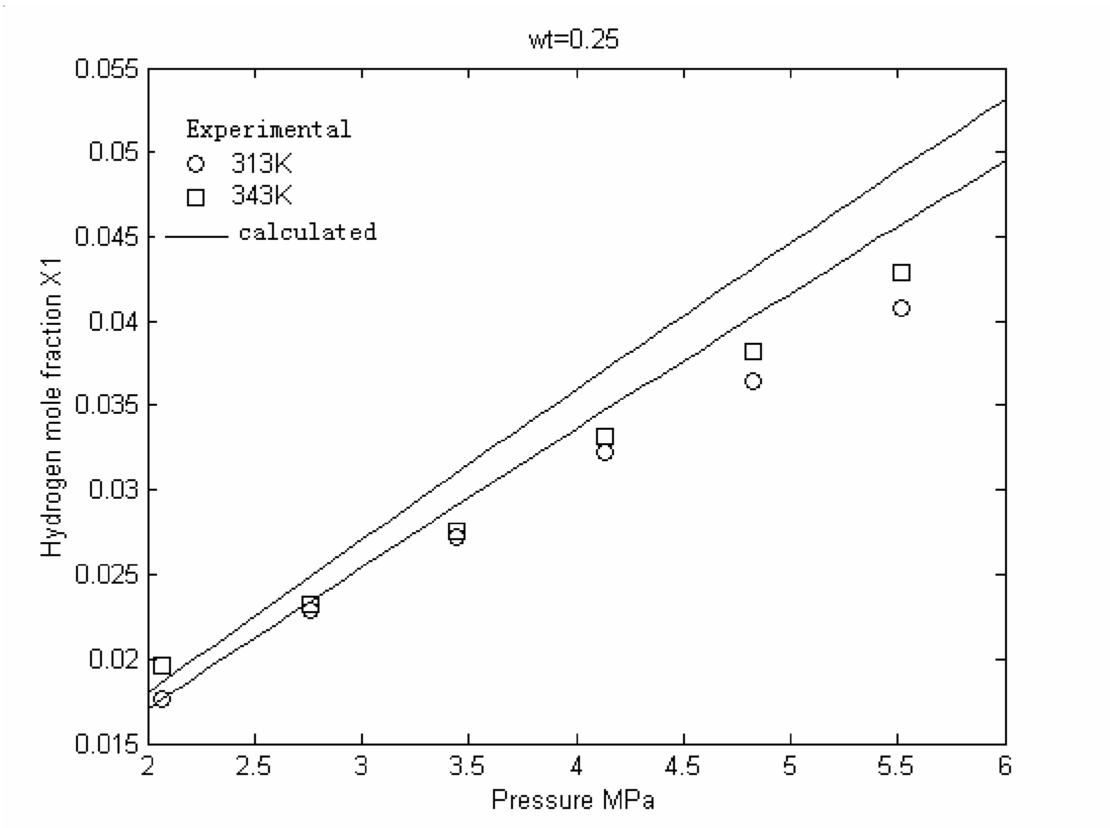

Fig.4 Composition of hydrogen in the liquid phase for 25 wt% DPD

x	mole fraction in liquid phase	k	constants in P-R EOS
y	mole fraction in gas phase	ω	acentric factor
kij ,lij	parameter in mixing rule		

Subscripts

1	hydrogen	2	hexane	3	DPD

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