Application of Group Contribution Method in Predicting V-L Equilibrium of ShengLi Heavy oil

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Preface

Group contribution methods have been used to calculate the properties of pure components, such as viscosity, surface tension, critical property etc.。Recently，group contribution methods are also used to predict vapor liquid equilibrium of the systems in which the composition of the components can be known exactly.

In this paper, the group contribution method is used to predict the vapor liquid equilibrium of the heavy oil which is a complex mixture.

Experiment

With the flow equilibrium unit, the V-L equilibrium data were obtained. The experiments were done under two different pressures and five different temperatures. At the same time, the feed was cut by TBP instrument into narrow fractions of which the properties were measured.

Group Contribution Method

Assume that the narrow fractions can be thought as pseudo-components, thus petroleum is considered as a mixture of these components. Then the V-L equilibrium relation can be treated as that of the mixture.

With the given flow and composition of the feedstock, under a certain pressure, if flashing temperature is defined, the vaporization ratio can be calculated and if the vaporization ratio is defined the flashing temperature can be calculated.

The application of group contribution method in predicting V-L equilibrium of petroleum requires that the group compositions of petroleum must be determined. The methods such as Model Compounds method，n-d-M-LP method and Model Molecule method are available. Although these methods are effective to a certain extent in the predicting of V-L equilibrium, they need much more properties and the process is complex. In this paper, normal paraffin model molecule method is used to determine the group composition and the procedure is

Cut the oil into narrow fractions with TBP data;

Assume that every narrow fraction consists of normal paraffin which has the same properties as the fraction's;

The number of group - CH_3 in each model molecule always equals 2, and that of - CH_2 -group can be any positive number.

Then the group composition can be determined by the molecular weight or the boiling point of the narrow fraction.

In general, under atmospheric and vacuum conditions, the V-L equilibrium constants K can be calculated as follow,

$$K_i = \frac{\gamma_i P_i^s}{P} \tag{1}$$

In the equation, P_i^s is the saturated vapor pressure of component i under the system temperature, γ_i is the activity coefficient of component i in the liquid phase，P is the system pressure. P_i^s is calculated by the method for predicting saturated vapor pressure of pure compounds proposed by Jensen. γ_i is calculated using modified UNIFAC(Larsen and Kikic) method.

Saturated Vapor Pressure Model of Group Contribution—Jensen Model

$$RT\ln(\phi_i^s P_i^s) = \sum \nu_k^{(i)} \Delta g_k + RT\sum \nu_k^{(i)} \ln \Gamma_k^{(i)} \tag{2}$$

$$\sum \nu_k^{(i)} \Delta g_k = \sum \nu_k^{(i)} \Delta g_k^{'} + \Delta G_i^{'} \tag{3}$$

$$\Delta g_k^{'} = A_{k,1} / T + A_{k,2} + A_{k,3} T + A_{k,4} \ln T \tag{4}$$

$$\Delta G_i^{''} = \sum\sum \nu_{kj}^{(i)} \Delta g_{kj}^{''} \tag{5}$$

In the above relations, ϕ_i^s is the fugacity coefficient of saturated vapor of component i，and it is approximately equals 1.0.；Δg_k is the Gibbs energy function of group k，depending on the temperature and the structure of the molecule; $\Gamma_k^{(i)}$ is the activity coefficient of group k in component i ,calculated by the residue term in UNIFAC activity coefficient model；$\nu_k^{(i)}$ is the number of group k in component i ；$\nu_{kj}^{(i)}$ is the contribution number of *j* type structure in group *k* of component *i*, $A_{k,1}$ is the group parameter of group *k*。

When normal paraffin model molecule method is used to determine the group composition, there are only two types of group in pseudo components,—-CH_3 and -CH_2-, thus

$RT\sum \nu_k^{(i)} \ln \Gamma_k^{(i)} = 0$ ， $\Delta G_i^{''} = 0$ ， the method is simplified,

$$RT\ln P_i^s = \sum \nu_k^{(i)} \Delta g_k^{'} \tag{6}$$

Activity Coefficient Model

In UNIFAC activity coefficient model

γ_i is consisted of two parts γ_i^c and γ_i^R ,

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R \tag{7}$$

For normal paraffin model molecule method $\ln \gamma_i^R = 0$, thus,

$$\ln \gamma_i = \ln \gamma_i^c \tag{8}$$

Larsen suggested that γ_i^c could be calculated with the two relations below,

$$\ln \gamma_i^c = 1 - \omega_i + \ln \omega_i \tag{9}$$

$$\omega_i = r_i^{2/3} / \sum_j x_j r_j^{2/3} \tag{10}$$

Kikic suggested that γ_i^c could be calculated with another two relations ,

$$\ln \gamma_i^c = \ln \frac{\omega_i}{x_i} + 1 - \frac{\omega_i}{x_i} - 5q_i (1 + \ln \frac{\Phi_i}{\theta_i} - \frac{\Phi_i}{\theta_i}) \tag{11}$$

$$\omega_i = r_i^{2/3} / \sum_j x_j r_j^{2/3} \quad (12)$$

Predicting Results

By the above method, calculation of flashing temperature and vaporization ratio was made for ShengLi heavy oil and the results are shown in table 1 and table 2.

Table 1 Deviations of flashing temperature predicted by group contribution methods

Model	Kikic	Larsen
AAD，ΔT,K	11.47	11.54
ARD，(%)	1.92	1.93

Table 2 Deviations of flashing vaporization ratio predicted by group contribution methods

Model	Kikic	Larsen
AAD，ΔE,%	4.00	4.02
ARD，(%)	23.62	23.81

$$\text{AAD}=\frac{1}{N}\Sigma\left|calculated-\exp erimental\right|$$

$$\text{ARD}=\frac{1}{N}\Sigma\left[\left|\frac{calculated-\exp erimental}{\exp erimental}\right|\right]\times 100\%$$

The results in the above tables are not satisfactory and so the model parameter are to be modified.

Modification of the Parameter in Jensen Model and the Predicting Results

The parameters provided by the vapor pressure model are obtained from the Antoine equation，and the data involving that of C_3 to C_{18}. However, for Shengli heavy oil, the carbon numbers of the fractions are from 22 to 76, far beyond the application range. Therefore twelve normal hydrocarbons whose carbon numbers are from 22 to 76 are chosen to get the new parameters. The data involve 72 points which are obtained under different experimental temperatures. The modified parameters are shown in table 3. With Larsen and Kikic model, the flashing temperatures and vaporization ratios are predicted and the results are shown in table 4.

Table 3 Modified parameters of Jensen model

Item	Parameters for $-CH_3$	Parameters for $-CH_2-$
$A_{k,1}$	2.03122×10^4	9.03611×10^4
$A_{k,2}$	-8.49432×10^3	-7.11573×10^3
$A_{k,3}$	2.21895	-0.788164
$A_{k,4}$	1.55162×10^3	1.11290×10^3

Table 4 Deviation of predicting results with modified parameters

Item	Flashing temperature		vaporization ratio	
	Kikic K	Larsen K	Kikic K	Larsen K
AAD	4.72	4.74	1.49	1.50
ARD,%	0.79	0.79	7.69	7.77

From the data in table 4，It can be found that with the modified parameter，the AAD and ARD of predicted temperatures by Kikic model are reduced from 11.47K and 1.92% to 4.72K and 0.79% respectively；and that of predicted vaporization ratios are reduced from 4.00% and 23.62% to 1.49% and 7.69% respectively. The AAD and ARD of predicted temperatures by Larsen model are reduced from 11.54K and 1.93% to 4.74K and 0.79%；and that of predicted vaporization ratios are reduced from 4.02% and 23.81% to 1.50% and 7.77% respectively. The deviations are descended obviously, i.e., the accuracy is enhanced greatly.

Conclusion

With the normal paraffin model molecule to determine the group composition, Larsen and Kikic group contribution models for γ_i were used to predict the V-L equilibrium of ShengLi reduced crude. It was found that the results were not satisfactory. By modifying the parameter in the vapor pressure model, the results of flashing temperatures and vaporization ratios match the experimental data satisfactorily. The AAD and ARD of predicted temperatures by Kikic model are 4.72K and 0.79% respectively；and that of predicted vaporization ratios are 1.49% and 7.69% respectively. The AAD and ARD of predicted temperatures by Larsen model are 4.74K and 0.79%；and that of predicted vaporization ratios are 1.50% and 7.77% respectively.

Reference

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