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The Thermodynamic Model on Paraffin Wax Deposition Prediction

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Abstract

In process of crude oil production and transportation, wax and other solid deposition issues have a significant impact on oilfield production. Solid precipitation not only reduces the production efficiency and increases the cost of production. Therefore, there is a need to study the rate of paraffin wax deposition and cloud point temperature in order to guide the oil field control the paraffin wax deposition. In this paper, we use the Flory theory of polymer solution to correct the liquid activity coefficients, and regular solution theory to correct for the non ideality of the solid mixture, and we consider the impact of isoparaffin. Finally, thermodynamic model is established. The actual example calculation shows that the forecast results of this model are more accurate.

Keywords

Paraffin Wax, Deposition, Thermodynamic Model, Activity Coefficients

1. Preface

Paraffin wax deposition issues have a significant impact on oilfield production. The deposition of paraffin wax in the tubing and pipe can reduce the production efficiency. In the meantime, removing the deposition of paraffin wax will increase a lot of expenses. The process of paraffin wax deposition is a very complicated problem. On one hand, because the composition of the oil and gas system is very complex, there needs further research on the effect of various components on paraffin deposition. On the other hand, many theoretical issues are involved in the process of paraffin deposition as solubility, crystal, fluid dynamics, mass transfer dynamics, heat transfer, etc. The mechanism of paraffin deposition is not yet fully understood; there are many kinds of explanation theory as solubility theory, crystallization theory, diffusion theory, and phase equilibrium theory [1]. At present, phase equilibrium theory was widely accepted. According to this theory, reason of paraffin wax deposition is the thermodynamic condition of oil and gas system, such as the change of oil and gas system composition, compo-

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nent, temperature, and pressure [2].

Model established in this paper can be used to determine cloud point of paraffin wax and the deposited amount of paraffin with the lowering of the temperature, which has important reference value for oilfield to solve paraffin deposition problems.

2. The Thermodynamic Model

When the phase equilibrium of gas, liquid, solid phase is reached [3].

$$f_i^V = f_i^L = f_i^S \tag{1}$$

where

$$f_i^V = x_i^V \varphi_i^V p \,. \tag{2}$$

$$f_i^L = x_i^L \gamma_i^L f_i^{OL} \,. \tag{3}$$

$$f_i^S = x_i^S \gamma_i^S f_i^{OS} \,. \tag{4}$$

If considering the heat tolerance of the liquid and solid, fugacity of solid standard state and liquid standard state has the following relationship.

$$\ln \frac{f_i^{OS}}{f_i^{OL}} = -\frac{\Delta H_i^f}{RT}\left(1-\frac{T}{T_i^f}\right)+\frac{1}{RT}\int_T^{T_i^f}\Delta C_{pi}\mathrm{d}T-\frac{1}{R}\int_T^{T_i^f}\frac{\Delta C_{pi}}{T}\mathrm{d}T \,. \tag{5}$$

where

$$\Delta C_{pi} = C_{pi}^L - C_{pi}^S = b_1 M_i + b_2 M_i T \tag{6}$$

where b_1, b_2 get from the experimental fitting. In the absence of experimental data b_1, b_2 can get

$$b_1 = 0.3033 \,. \tag{7}$$

$$b_2 = -4.635\times 10^{-4} \,. \tag{8}$$

Take (6) into (5), (5) becomes

$$\ln \frac{f_i^{OS}}{f_i^{OL}} = -\frac{\Delta H_i^f}{RT}\left(1-\frac{T}{T_i^f}\right)+\frac{b_1 M_i}{R}\left(\frac{T_i^f}{T}-1+\ln\frac{T}{T_i^f}\right)+\frac{b_2 M_i}{R}\left(\frac{\left(T_i^f\right)^2}{2T}+\frac{T}{2}-T_i^f\right) \,. \tag{9}$$

The non ideal of the solid mixture is corrected by using the regular solution theory, then derived the calculation formula for the activity coefficient of solid phase.

$$\ln \gamma_i^S = \frac{V_i^S\left(\delta_m^S-\delta_i^S\right)^2}{RT} \tag{10}$$

where

$$\delta_m^S = \sum \phi_i^S \delta_i^S \,. \tag{11}$$

$$\phi_i^S = \frac{x_i^S V_i^S}{\sum x_i^S V_i^S} \,. \tag{12}$$

$$\delta_i^S = \delta_0 - \left(0.000325+0.00232\ln M_i\right)\left(T-25\right) \,. \tag{13}$$

$$\delta_0 = 8.021-\frac{59.5}{M_i}+0.0008 M_i^{0.6677} \,. \tag{14}$$

$$V_i^S = \frac{0.9M_i}{0.8155 + 0.6272\times10^{-4}M_i - \frac{13.06}{M_i}}. \tag{15}$$

Use the Flory theory of polymer solution to correct the liquid activity coefficients, the calculation formula as follows [4].

$$\ln\gamma_i^L = \ln N_i + 1 - N_i - \sum_{j\neq i}\frac{c_i}{c_j}N_i + \sum_{j\neq i}N_i k_{ij}\sum_{m\neq i}N_m - \sum_{j\neq i}\sum_{m<j}\frac{c_i}{c_j}N_m N_i k_{mj} \tag{16}$$

where

$$N_i = \frac{c_i n_i}{\sum c_j n_j}. \tag{17}$$

Molecular interaction is divided into three categories: (1) PN—PN (2) PN—A (3) A—A. Among which P stands for alkane, N stands for cycloalkane, A stands for aromatic. Their molecular interaction coefficients are as follows:

$$(1): k_{ij} = 3.05037\times10^{-2}\left|c_i - c_j\right|. \tag{18}$$

$$(2): k_{ij} = -3.46841\times10^{-2}\left(c_i c_j\right). \tag{19}$$

$$(3): k_{ij} = -1.19469\times10^{-1}\left|c_i - c_j\right|. \tag{20}$$

Paraffin wax is mainly composed by the n-alkane, but contains a small amount of isoparaffin, cycloalkane and aromatic. For these non-normal paraffin, their melting point and other properties are very different from the n-alkane, the melting point of normal paraffin wax decreases obviously when a branch is added. For example: the melting point of $C_{43}H_{88}$ is 188˚F, it is generally believed that the melting point of $C_{52}H_{104}$ is relatively high. But because there is a branched chain in $C_{52}H_{104}$, its melting point will be lower than $C_{43}H_{88}$ nearly 100˚F, it's 91˚F. Therefore, it is necessary to consider the effect of non-normal paraffin [5].

For normal structure paraffin wax:

$$T_i^f = 374.5 + 0.02617M_i - \frac{20172}{M_i}. \tag{21}$$

$$\Delta H_i^f = 0.162564M_i T_i^f. \tag{22}$$

For non-normal structure paraffin wax:

$$T_{i,non}^f = T_{i,normal}^f - \left(90 - \frac{80c_i}{100 + c_i}\right). \tag{23}$$

For isoparaffin, cycloalkane:

$$\Delta H_i^f = 0.0527M_i T_i^f. \tag{24}$$

For aromatic:

$$\Delta H_i^f = 11.2T_i^f. \tag{25}$$

3. The Example Calculation and Results

In order to validate the model, calculated by using the data of [6] (see **Table 1**) (SRK state equation is used in calculation). Calculation results are shown in **Figure 1** and **Figure 2**.

From **Figure 1** we can see that the cloud point temperature is different under different pressures. This difference is because of the combined effect of pressure and composition. Temperature decreases with increasing pressure. Under 1.5 MPa, the measured cloud point temperature is 318.7 K, calculating cloud point temperature is 318 K, measured and calculating results are quite close. It can be seen from the **Figure 2** that the theoretical results are in good agreement with the actual results.

Table 1. The components of a kind of crude oil in the Beihai Oilfield.

Components	Mole fraction	Density	Molecular weight
N_2	0.000		
CO_2	0.028		
C1	0.128		
C2	0.240		
C3	1.186		
IC4	1.235		
NC4	3.792		
IC5	1.586		
NC5	2.567		
C6	5.235	0.6701	84.40
C7	8.152	0.7260	93.58
C8	9.418	0.7346	109.21
C9	7.024	0.7621	124.00
C10+	60.730	0.8997	345.63

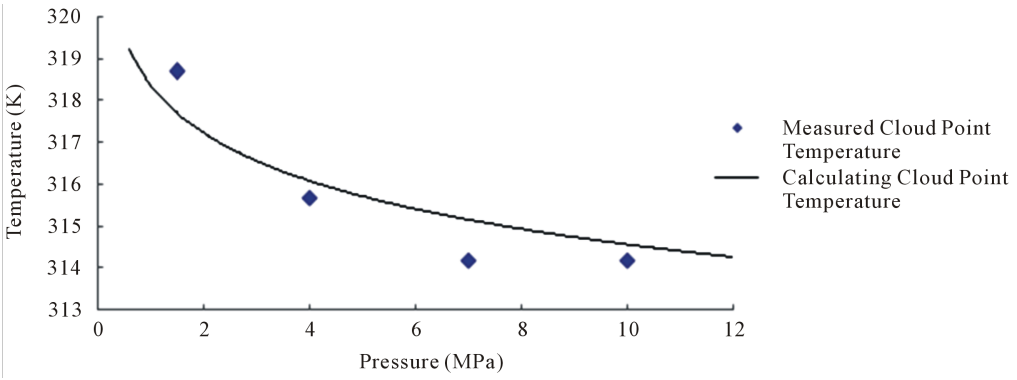

Figure 1. The diagram of cloud point temperature.

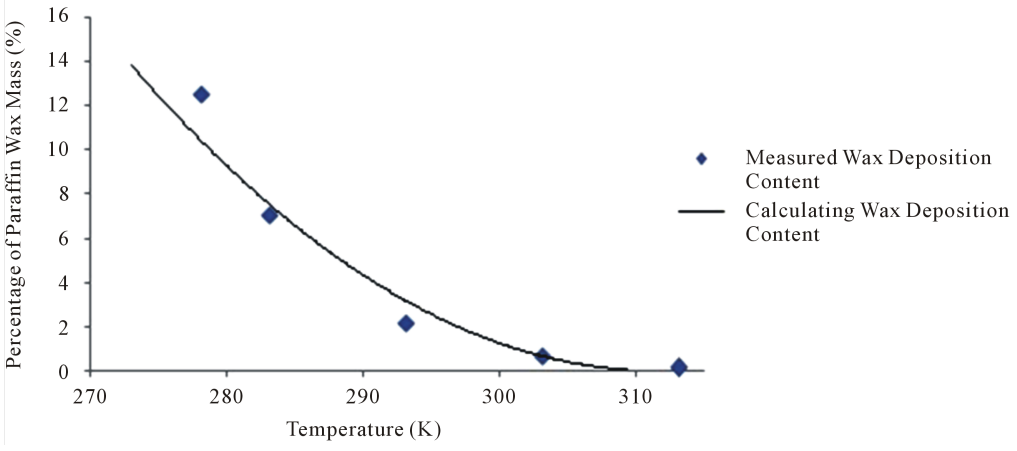

Figure 2. The diagram of wax deposition content.

4. Conclusions

1) The model proposed in this paper is more accurate, and the prediction results are in good agreement with the practical data.

2) The model considers the non ideality of the solid phase mixture, and the activity coefficients of solid phase are corrected by using the regular solution theory.

3) The model considers the influence of the non-normal paraffin; it makes the results more accurate.

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Explanation of Nomenclature

f	fugacity;
f_i^{OS}	fugacity of solid standard state;
f_i^{OL}	fugacity of liquid standard state;
x	mole fraction;
γ	activity coefficient;
φ	fugacity coefficient;
ΔH_i^f	molar enthalpy of fusion;
T_i^f	melting point temperature;
C_p	specific heat under constant pressure;
b_1, b_2	coefficient;
M	molecular weight;
V_i	molar volume of component;
δ	solubility parameter;
c_i	carbon number of component i;
n_i	mole number of component i;
k	coefficient of molecular interaction;
p	pressure;
R	gas constant;
T	temperature.

Superscript:

V	gas phase;
S	solid phase;
L	liquid phase;
O	standard state;
f	liquate.

Subscript:

i	pure component;
p	constant pressure.