Thermodynamic Modeling of Wax Precipitation in Crude Oils[*]

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Abstract   Most of the crude oils contain waxes which precipitate when temperature drops, resulting in deposition in pipelines and production equipment. It is necessary to set up a model which can predict the wax appearance temperature and the amount of solid precipitated in the different conditions. A modified thermodynamic solid-liquid equilibrium model to calculate wax precipitation in crude oil systems has been developed recently. The assumption that precipitated waxes consist of several solid phases is adopted in this research, and the solid-solid transition is also considered in the modified model. The properties of the pseudo-components are determined by using empirical correlations. New correlations for properties of solid-solid and solid-liquid transitions are also established in this work on the basis of the data from the literature. The results predicted by the proposed model for three crude oil systems are compared with the experimental data and the calculated results from the literature, and good agreement is observed.

Keywords   waxy crude oil, solid-solid transition, solid-liquid equilibrium, thermodynamic model, wax precipitation

1   INTRODUCTION

Crude oils are mixture of light and heavy hydrocarbons. The components in crude oils can be classified into paraffin, naphthene and aromatic components[1]. Though the non-*n*-alkane components in crude oils are minor, it is essential to consider the influence of non-alkane components in the model since their properties, such as fusion temperature and fusion enthalpy, are much different from paraffin. The solubility of each component of crude oils depends on the temperature and composition of the system. When the temperature of crude oil drops, the solubility of the heavy fractions would be reduced and they will precipitate in forms of wax and asphaltene first[2]. There are problems caused by wax precipitation, such as the change in the flow behavior of crude oil from Newtonian to non-Newtonian, the decrease of production rates, the increase of energy consumed and the failure of facilities. These problems are major concerns in the production and transportation of crude oils. In petroleum industry, methods[3,4] such as thermal treatment of pipelines, use of chemical inhibitors, *etc.*, are used to prevent wax precipitation. Of course, all of the methods increase operating expenses. A model that can predict the conditions in which solids will precipitate and the amount of solids formed at different conditions can be used as a fundamental tool in preventing the solid precipitation.

In 1996, LiraGaleana *et al*.[5] presented a wax thermodynamic model in which a multi-solid phase approach was used for description of wax solids. This approach assumed that precipitated wax consisted of several solid phases, and each solid phase was a pure compound that did not mix with other solid phases. However, studies on crystal structure in recent years reveal that the miscibility of *n*-paraffins in a solid state depends strongly on differences in molecular sizes (*i.e.* carbon number). An *n*-paraffin mixture with a significant carbon number difference appears to form eutectic solids, whereas an *n*-paraffin mixture with a consecutive carbon number distribution forms a single orthorhombic solid solution[6]. So the assumption of the multi-solid phase approach is not consistent with real wax crystal behavior. Therefore，the model proposed by LiraGaleana *et al*.[5] is questionable for systems that consist of compounds of similar molecular sizes.

In this paper, the solid-solid transitions are used to explain the multi-solid phase behavior of waxes before melting. New correlations have been established to present the properties of solid solid transitions as functions of carbon number, considering the difference between odd and even carbon numbers. The fusion enthalpies of *n*-paraffin have different correlations based on the different crystal solid liquid transitions which were mentioned in Broadhurst's paper[7] and new correlations have been established for them in this paper. Molecular thermodynamics along with regular solution theory is used to describe the SLE (solid-liquid equilibrium) system. Reliable experimental data for WAT (wax appearance temperature) and the amount of wax precipitated for three crude oils under several different temperature conditions from the literature are used to validate the new wax thermodynamic model.

2 THERMODYNAMIC MODELING
2.1 Solid-liquid equilibrium modeling

When the solid and liquid phases are in thermo-dynamic equilibrium, the fugacity of component i in solid phase and liquid phase must be the same

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

The fugacity in the solid phase, based on solid solution theory, is expressed by

$$f_i^{\mathrm{S}} = \gamma_i^{\mathrm{S}} x_i^{\mathrm{S}} f_i^{\mathrm{oS}} \exp\left(\int_0^P \frac{V_i^{\mathrm{S}} \mathrm{d}P}{RT} \right) \tag{2}$$

Similarly, the fugacity in the liquid phase is

$$f_i^{\mathrm{L}} = \gamma_i^{\mathrm{L}} x_i^{\mathrm{L}} f_i^{\mathrm{oL}} \exp\left(\int_0^P \frac{V_i^{\mathrm{L}} \mathrm{d}P}{RT} \right) \tag{3}$$

By combining Eqs.(1), (2) and (3) the criterion of equal fugacities can be expressed as

$$\frac{x_i^{\mathrm{S}}}{x_i^{\mathrm{L}}} = \frac{\gamma_i^{\mathrm{L}}}{\gamma_i^{\mathrm{S}}} \frac{f_i^{\mathrm{oL}}}{f_i^{\mathrm{oS}}} \exp\left(\int_0^p \frac{V_i^{\mathrm{L}} - V_i^{\mathrm{S}}}{RT} \mathrm{d}P \right) \tag{4}$$

The volume differences between solid and liquid in crude oils are less than 10%[8]; so under low and moderate pressures, the volume difference has little influence on the liquid-solid equilibrium. For this reason the exponential term is neglected in this model and the equilibrium relation can be simplified to

$$\frac{x_i^{\mathrm{S}}}{x_i^{\mathrm{L}}} = \frac{\gamma_i^{\mathrm{L}}}{\gamma_i^{\mathrm{S}}} \frac{f_i^{\mathrm{oL}}}{f_i^{\mathrm{oS}}} \tag{5}$$

The ratio of standard-state fugacity of sub-cooled liquid to solid can be calculated from the following correlations[9]:

$$\frac{f_i^{\mathrm{oL}}}{f_i^{\mathrm{oS}}} = \exp\left[\frac{\Delta H_i^{\mathrm{f}}}{RT}\left(1 - \frac{T}{T_i^{\mathrm{f}}}\right) + \frac{\Delta H_i^{\mathrm{t}}}{RT}\left(1 - \frac{T}{T_i^{\mathrm{t}}}\right) - \right.$$
$$\left. \frac{1}{RT}\int_T^{T_i^{\mathrm{f}}} \Delta c_{pi}\mathrm{d}T + \frac{1}{R}\int_T^{T_i^{\mathrm{f}}} \frac{\Delta c_{pi}}{T}\mathrm{d}T \right] \tag{6}$$

with

$$\Delta c_{pi} = c_{pi}^{\mathrm{L}} - c_{pi}^{\mathrm{S}} = 1.2739 m_i - 1.9467 \times 10^{-3} m_i T \tag{7}$$

2.2 Activity coefficients calculation

The activity coefficients for the solid and liquid phases can be written in terms of the solubility parameters based on regular solution theory:

$$\ln \gamma_i^{\mathrm{L}} = \frac{V_i^{\mathrm{L}}\left(\delta_{\mathrm{m}}^{\mathrm{L}} - \delta_i^{\mathrm{L}}\right)^2}{RT} \qquad \ln \gamma_i^{\mathrm{S}} = \frac{V_i^{\mathrm{S}}\left(\delta_{\mathrm{m}}^{\mathrm{S}} - \delta_i^{\mathrm{S}}\right)^2}{RT} \tag{8}$$

$$\delta_{\mathrm{m}}^{\mathrm{L}} = \sum \phi_i^{\mathrm{L}} \delta_i^{\mathrm{L}} \qquad \delta_{\mathrm{m}}^{\mathrm{S}} = \sum \phi_i^{\mathrm{S}} \delta_i^{\mathrm{S}} \tag{9}$$

$$\phi_i^{\mathrm{L}} = x_i^{\mathrm{L}} V_i^{\mathrm{L}} \left(\sum x_i^{\mathrm{L}} V_i^{\mathrm{L}}\right)^{-1} \qquad \phi_i^{\mathrm{S}} = x_i^{\mathrm{S}} V_i^{\mathrm{S}} \left(\sum x_i^{\mathrm{S}} V_i^{\mathrm{S}}\right)^{-1} \tag{10}$$

The solubility parameters in liquid state can be calculated from a correlation proposed by Riazi and Al-Sahhaf[10] for paraffin components in crude oils:

$$\delta_i^{\mathrm{L}} = 8.6 - \exp\left(2.219195 - 0.54907 m_i^{0.3}\right) \tag{11}$$

The solubility parameters of other compound classes are estimated by the correlations proposed by Leelavanichkul et al.[11] as follows.
For naphthenic components:

$$\delta_i^{\mathrm{L}} = 8.7 - \exp\left(2.219195 - 0.54907 m_i^{0.3}\right) \tag{12}$$

For aromatic components:

$$\delta_i^{\mathrm{L}} = 8.8 - \exp\left(2.219195 - 0.54907 m_i^{0.3}\right) \tag{13}$$

The solubility parameters of components i in solid solution, which is based on a cohesive energy concept, can be written as[11]

$$\delta_i^{\mathrm{S}} = \left(\frac{\Delta H_i^{\mathrm{f}}}{V_i} + \delta_i^{\mathrm{L2}} \right)^{0.5} \tag{14}$$

2.3 Density and molar volume

The liquid phase density $d_{i,25}^{\mathrm{L}}$ can be calculated from the following correlations proposed by Leela-vanichkul et al.[11]
For paraffin components:

$$d_{i,25}^{\mathrm{L}} = 0.815 + 0.06272 \times 10^{-4} m_i - 13.06/m_i \tag{15}$$

For naphthenic components:

$$d_{i,25}^{\mathrm{L}} = 0.865 + 0.06272 \times 10^{-4} m_i - 13.06/m_i \tag{16}$$

For aromatic components:

$$d_{i,25}^{\mathrm{L}} = -0.03 \ln m_i + 1.02 \tag{17}$$

The molar volume of each component can be calculated using knowledge of molecular weight and density by

$$V_i^{\mathrm{L}} = V_i^{\mathrm{S}} = m_i / d_{i,25}^{\mathrm{L}} \tag{18}$$

2.4 Properties of solid-liquid and solid-solid transitions

Won[12] proposed the following fusion correlations for normal paraffins:

$$T_i^{\mathrm{f}} = 374.5 + 0.02617 m_i - 20172/m_i \ (m_i \leqslant 450\mathrm{g \cdot mol}^{-1}) \tag{19}$$

$$T_i^{\mathrm{f}} = 411.4 - 32326/m_i \ (m_i > 450\mathrm{g \cdot mol}^{-1}) \tag{20}$$

The fusion enthalpies of paraffins can be calculated from the correlations proposed in this work. These correlations are developed based on the data listed in Broadhurst's paper[7]. In 1962, Broadhurst[7] reported about the solid phase behavior of the normal paraffins and pointed out that when the temperature of crude oil is lower than WAT, the solid phases of all n-paraffins with more than nine carbon atoms in the chain consist of four distinct crystal structures: hexagonal, triclinic, monoclinic and orthorhombic. He characterized the solid-liquid transitions of n-alkanes as follows: existing triclinic liquid transition for the even paraffins from $C_{10}H_{22}$ to $C_{20}H_{42}$, orthorhombic liquid transition for all normal paraffins above $C_{40}H_{82}$ and hexagonal liquid transition for other n-paraffins.

Similarly, the solid-solid transitions for *n*-paraffins were characterized as follows: orthorhombic hexagonal transition for the odd paraffins from C_9H_{20} to $C_{43}H_{88}$ and triclinic or monoclinic hexagonal transition for the even paraffins from $C_{22}H_{46}$ to $C_{42}H_{86}$. Odd even differences are resulted from reasonable differences in end group packing.

Consequently, the fusion enthalpies of the *n*-alkanes have different correlations according to the number of carbon atoms and the odd or even carbon number in the chain and established as follows.
n-paraffins with odd carbon number:

$$7 < C_n < 21 \quad \Delta H_i^{\mathrm{f}} = 0.5754 m_i T_i^{\mathrm{f}} \quad (21)$$

n-paraffins with even carbon number:

$$8 \leqslant C_n < 22 \quad \Delta H_i^{\mathrm{f}} = 0.8064 m_i T_i^{\mathrm{f}} \quad (22)$$

n-paraffins with all carbon number:

$$21 \leqslant C_n < 38 \quad \Delta H_i^{\mathrm{f}} = 0.4998 m_i T_i^{\mathrm{f}} \quad (23)$$

$$C_n \geqslant 38 \quad \Delta H_i^{\mathrm{f}} = 0.6741 m_i T_i^{\mathrm{f}} \quad (24)$$

In Ji's model[9], the fusion enthalpies were also divided into several parts. However, this segmentation cannot match their crystal structures correctly and the results calculated from correlations differ from the experimental data[7] a lot. The correlation for fusion enthalpies of *n*-paraffins proposed by Won[12] was adopted in most models. So this paper compares the mean squared deviation (*MSD*) between the experimental data and calculated ones based on three models. From the data listed in Table 1, it can be seen that the *MSD* using the present correlation is the best among the three models.

Table 1 The comparison of *MSD* among three models

Model	*MSD*
Won model	1.959×10^8
Ji model	2.572×10^8
present model	1.689×10^7

The *MSD* is defined as follows:

$$MSD = \frac{1}{n} \sum_{i=7}^{50} (\Delta H_i^{\mathrm{fexp}} - \Delta H_i^{\mathrm{fcal}})^2 \quad (25)$$

The properties for solid-solid transition have not been regressed into correlations in many papers. Ma and Guo[13] and Ji *et al.*[9] did this work in their model. However, in Ma's paper the correlations were just established for odd normal parafins, and in Ji's paper the latent heats for transitions were correlated with the product of molecular weight and fusion temperature using a linear function. The data listed in Corriou's paper[14] indicated that the enthalpies of the solid-solid transition are a function of the carbon number and the curve is parabola instead of beeline. Several third-order polynomial functions have been established in this model.

n-paraffins with odd carbon number:

$$9 \leqslant C_n \leqslant 43$$

$$T_i^{\mathrm{t}} = 0.0039 C_n^3 - 0.4249 C_n^2 + 17.2812 C_n + 93.1012 \quad (26)$$

$$\Delta H_i^{\mathrm{t}} = 39805.146 - 6180.1417 C_n + 347.9015 C_n^2 - 4.9602 C_n^3 \quad (27)$$

n-paraffins with even carbon number:

$$22 \leqslant C_n \leqslant 42$$

$$T_i^{\mathrm{t}} = 0.0032 C_n^3 - 0.3249 C_n^2 + 12.7811 C_n + 157.1936 \quad (28)$$

$$\Delta H_i^{\mathrm{t}} = 44019.633 - 6181.7767 C_n + 348.7432 C_n^2 - 4.9661 C_n^3 \quad (29)$$

The fusion properties of non-*n*-alkane components are calculated from the following correlations proposed by LiraGaleana *et al.*[5]:

$$T_i^{\mathrm{f}} = 333.46 - 419.01 \exp(-0.00855 m_i) \quad (30)$$

For naphthenic components:

$$\Delta H_i^{\mathrm{f}} = 0.2216 m_i T_i^{\mathrm{f}} \quad (31)$$

The following correlation developed by Pan *et al.*[5] is used to estimate the change in heat of fusion for aromatic components:

$$\Delta H_i^{\mathrm{f}} = 47.04 T_i^{\mathrm{f}} \quad (32)$$

For C_7^- components, the properties of hydrocarbons have been given in the literature. However, for C_7^+ fractions, their properties are estimated from all of the above correlations.

2.5 Computational process

(1) Initialize the system and input data x_i and m_i for each component, including T_i^{f}、ΔH_i^{f}、d and V for C_7^- components;

(2) The first iteration, estimate first solid mole fraction=0.5, $\gamma_i^{\mathrm{L}} = \gamma_i^{\mathrm{S}} = 1.0$;

(3) Calculate initial solid liquid equilibrium constant (K^{SL}) objective function and its derivative;

(4) Calculate next solid phase mole fraction, *S*;

(5) Calculate component mole fractions in liquid and solid phases;

(6) Calculate parameters: molar volumes, volume fractions and solubility parameters for solid and liquid phases;

(7) Calculate activity coefficients for solid and liquid phases;

(8) Calculate next K^{SL} objective function and its derivative;

(9) Check whether the sum of objective function is less than 0.001; if yes, calculate solid mass percent of each component and total mass percent solid, if not return to (4).

Here, the objective function and its derivative are

calculated by

$$F_{obj} = \sum \left[\frac{x_i \left(K_i^{SL} - 1 \right)}{1 + S \left(K_i^{SL} - 1 \right)} \right]$$

$$\frac{d(F_{obj})}{dS} = -\sum \left\{ \frac{x_i \left(K_i^{SL} - 1 \right)^2}{\left[1 + S \left(K_i^{SL} - 1 \right)^2 \right]} \right\} \qquad (33)$$

3   MODELING RESULTS AND DISCUSSION

In order to prove the accuracy of the present modified model of wax precipitation in crude oils, the experimental data for the WAT and the amount of wax precipitated for three crude oils under several temperature conditions obtained by Leelavanichkul *et al.*[11] are used to compare with the results predicted by the Leelavanichkul model and the present modified model, respectively. The three crude oils have detailed compositional characterization[11] including a total of 148 pseudocomponents for each crude oil. These pseudocomponents are determined based on carbon number ranges and hydrocarbon group types. The light end fractions (C_7^-) are attributed to single carbon number. Each carbon number of the solvent fractions (C_7—C_{25}) is classified into paraffin, naphthene and aromatic fractions. The solute fractions, which include C_{26}—C_{50} are differentiated as saturate (*n*-alkane, non-*n*-alkane) and aromatic fractions. Finally the heavy fractions are lumped into one C_{50}^+ fraction, two resin fractions, and three asphaltene fractions. All the components of oil mixtures cannot be identified since crude oils are the mixtures of thousands of different components. Therefore, the lumping characterization is usually for predicting the thermodynamic properties of the crude oils. These characterization data are used as input for the modeling of solids precipitation at present research.

3.1   WAT

Table 2 shows the comparison between WAT from experiment, the results predicted from the Leelavanichkul model and present modified model. It can be seen that the results predicted by the present model shows slightly higher values than the experimental results and the deviations are within experimental error. But then, Hamouda and Viken[16] reported that the wax get deposited in the pipeline at a higher temperature than those measured in the laboratory since pipeline wall roughness and the presence of nucleation

sites, such as solid, corrosion products, play a great role in deposition of wax in under-saturated fluids.

3.2   Amount of wax

At a given temperature, the wax mass percent that precipitates from crude oil is calculated for 1 mol of mixtures from

$$\text{Wax mass \%} = \frac{\text{total precipitated mass}}{\text{mass of crude oil}} = \frac{\sum\limits_{j=1}^{N^S} m_j \cdot x_j^S \cdot S}{\sum\limits_{i=1}^{N} m_i \cdot x_i} \qquad (34)$$

The mass percent of solids precipitated as a function of temperature for crude oils A, B, and C are presented in Figs.1, 2, and 3, respectively. From the figures, we find out that the predicted amount of solid precipitated with the present model is more in agreement with the experimental data than the Leelavanichkul model. Good predicting results benefit from taking account of the solid-solid transitions of paraffins and establishing new correlations for solid solid transition and fusion enthalpies in the present model.
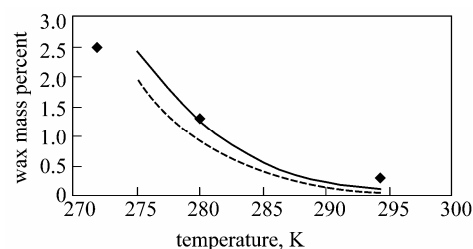

Figure 1   Wax precipitation as a function of temperature for crude oil A
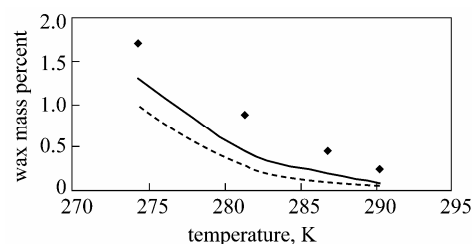◆ experiment; ——— modified model;
---- Leelavanichkul model

Figure 2   Wax precipitation as a function of temperature for crude oil B
◆ experiment; ——— modified model;
---- Leelavanichkul model

Table 2   Experimental WAT data and model predictions for crude oils

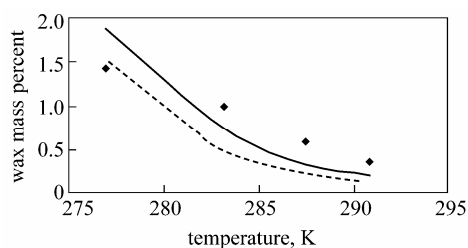| Sample	Experimental results	Leelavanichkul model	Deviation	Present model	Deviation
crude oil A	298.2K	298.6K	0.4K	301.3K	3.1K
crude oil B	295.2K	293.4K	−1.8K	295.4K	0.2K
crude oil C	294.2K	296.0K	1.8K	297.8K	3.6K

Figure 3   Wax precipitation as a function of temperature for crude oil C
◆ experiment; —— modified model;
- - - - Leelavanichkul model

4   CONCLUSIONS

This work has focused on the development of a thermodynamic model to estimate solid precipitation as a function of temperature and composition. A molecular thermodynamic approach based on regular solution theory is adopted for the modeling work.

(1) Taking account of the effects of the solid solid transitions on the equilibrium constants, the calculated amount of wax which was precipitated at different temperatures in the present model approaches the experimental results better than that of the Leelavanichkul model.

(2) New correlations for the fusion enthalpy and solid solid transition temperature and enthalpy of n-alkanes have been established in this research. The fusion enthalpies of the n-alkanes are divided into four components corresponding to the four crystal structures, so the fusion enthalpies are in good agreement with the data listed in the literature. For the properties of solid-solid transitions, new third-order polynomial correlations have been established as functions of carbon number by considering the difference between odd and even carbon numbers on the basis of the data presented by Dirand *et al.*[6].

NOMENCLATURE

C_n carbon number
c_p heat capacity, $J \cdot mol^{-1} \cdot K^{-1}$
$d_{i,25}^L$ liquid phase density at 25℃, $g \cdot cm^{-3}$
f fugacity
H enthalpy, $J \cdot mol^{-1}$
MSD mean squared deviation of the fusion enthalpy, $J^2 \cdot mol^{-2}$
m molecular weight, $g \cdot mol^{-1}$
P pressure, MPa
R ideal gas constant
S solid phase mole fractions
T temperature, K
V volume, cm^3
x mole fraction
γ activity coefficient
δ solubility parameter
ϕ volume fraction

Superscripts

f   fusion
L   liquid phase
o   standard-state
S   solid phase
t   solid-solid transition

Subscripts

m   average value

REFERENCES

1   Mazee, WM., "Thermal analysis of normal alkanes", In: "Modern Petroleum Technology, 4", Hobson, G.D., Pohl, W., eds., Barking: Applied Science Publishers, 782—803(1973).
2   Misra, S., Baruah, S.K.P., "Paraffin problems in crude oil production and transportation: a review", In: SPE Prod Facilities., 50—54(1995).
3   Hunt, A., "Uncertainties remain in predicting paraffin deposition", *Oil Gas J.*, **7**(29), 96—103(1996).
4   Bernadiner, M.G., "Advanced asphaltene and paraffin control technology", In: Int. Symp. on Oilfield Chem. of SPE, New Orleans, LA, 2—5(1993).
5   LiraGaleana, C., Firoozabadi, A., Prausnitz, J.M., "Thermodynamics of wax precipitation in petroleum mixtures", *AIChE J.*, **42**, 239—248(1996)
6   Dirand, M., Chevallier, V., Provost, E., Bouroukba, M., Petitjcan, D., "Multicomponent paraffin waxes and petroleum solid deposits: structural and thermodynamic state", *Fuel*, **77**, 1253—1260(1998).
7   Broadhurst, M.G.J., "An analysis of the solid phase behavior of the normal paraffins", *J. Res. Natl. Bur. Stand. (US).*, **66A**, 241—249(1962).
8   Pedersen, S.K., Skovborg, P., Hans, P.R., "Wax precipitation from north-sea crude oils (4). Thermodynamic modeling", *Energy Fuels*, **5**, 924(1991).
9   Ji, H.Y., Bahman, T., Ali, D., Adrian, C.T., "Wax phase equilibria: developing a thermodynamic model using a systematic approach", *Fluid Phase Equilibria*, **216**(2), 201—217(2004).
10   Riazi, M.R., Al-Sahhaf, T.A., "Physical properties of heavy petroleum fractions and crude oils", *Fluid Phase Equilibria*, **117**, 217—224(1996).
11   Leelavanichkul, P., Deo, M.D., Hanson, F.V., "Crude oil characterization and regular solution approach to thermodynamic modeling of solid precipitation at low pressure", *Petrol. Sci. Technol.*, **22**(7/8), 973—990(2004).
12   Won, K.W., "Thermodynamics for solid-liquid-vapor equilibria: wax phase formation from heavy hydrocarbon mixtures", *Fluid Phase Equilibria*, **30**, 265—279(1986).
13   Ma, Q.L., Guo, T.M., "Application of composition model to calculation of wax precipitation from crude", Journal of the University of Petroleum, China (Edition of Natural Science), **27**(5), 99—102(2003). (in Chinese)
14   Corriou, J.P., "Temperatures and enthalpies of (solid+solid) and (solid+liquid) transitions of n-alkanes", *J. Chem. Thermodyn.*, **34**, 1255—1277(2002).
15   Pan, H., Firoozabadi, A., Fotland, P., "Pressure and composition effect of wax precipitation: experimental data and model results", SPE 26740, 579—592(1996).
16   Hamouda, A.A., Viken, B.K., "Wax deposition mechanism under high pressure and in presence of light hydrocarbons", In: Int. Symp. on Oilfield Chem. SPE, New Orleans, LA, 2—5(1993).