



Direct adjustment of wax thermodynamic model parameter to micro Differential Scanning Calorimetry thermograms



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ABSTRACT

Among the flow assurance subjects, wax deposition plays a major role. As exploration an oil production moves towards deeper water frontiers, longer tiebacks increase the risk of wax deposition, which is assessed through modeling. In modeling schemes, the phase behavior of solid wax is essential and it is available through either a measured solubility curve or through thermodynamic models. These thermodynamic models normally need tuning and, due to the experimental difficulties of measuring solubility curves for real fluids, are tuned to the wax appearance temperature (WAT). To reduce the uncertainties of adjusting a model to just one point, a procedure to directly simulate DSC curves from a liquid-solid thermodynamic model is proposed. This new strategy allows a full thermogram adjustment without going through the empirical integration of the experimental DSC. Experimental DSC thermograms and simulated curves are presented for five standard single wax mixtures. Then, the solubility curves obtained from the model are compared to the experimental literature data and the difference between simulated wax disappearance temperature (WDT), experimental WDT and experimental wax appearance temperature (WAT) are discussed.

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1. Introduction

Wax deposition is a major issue in oil production. Among the important subjects within the flow assurance, it has received attention from the industry and the academy for years [1]. The control of wax deposition consists of retarding the oil cooling and mitigating the deposits through pigging operations or chemical interventions. To retard oil cooling, the most used strategies are cold flow, still not an option for the production of deep-water wells, and the implementation of insulated lines, which highly increases the cost of the production installations. The correct dimensioning of the insulation depends majorly on flow modeling and wax deposition simulation [1–3].

In order to model wax deposition, it is imperative to predict wax appearance conditions as well as the amount of waxy solids formed as a function of the temperature and pressure. These predictions can be carried through sundry thermodynamic models that rest on

different assumptions regarding the non-ideality of liquid mixtures and the nature of the solid phase [2,4]. The major problem with these models is that most of them cannot be used in a predictive way with crude oils. They depend on empirical parameters that should be tuned to match phase equilibrium data, as these models are extremely dependent on the sample compositional information [5]. The tuning of these parameters is a necessary first step and it has a very strong impact on the models behavior.

The models can be adjusted through different processes. Usually, the wax appearance temperature (WAT) of dead oil samples is used to tune the model parameters. However, it was shown that all current experimental techniques have shortcomings that preclude effective measurement of the thermodynamic equilibrium point (the point at which a very small crystal of paraffin is in equilibrium with the fluid at the highest possible temperature) [5]. The measurement bias is not only due to the method used but also to the fact that in cooling experiments the WAT measured is affected by the unavoidable supersaturation. On the other hand, the available methods able to quantify waxes in oil, among which the High Temperature Gas Chromatography method, renders high

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uncertainties for the quantification of heavier waxes, the molecules that dominate the simulated equilibrium temperature in any model [6]. One is then left with a biased reference to adjust the models.

The best experimental curve one might have to adjust the thermodynamic models is the solid build-up curve or solubility curve. It is defined as the amount of waxy solid precipitated versus temperature at a given pressure. It renders real equilibrium data and distributes the error among the entire wax composition. Unfortunately, wax drop out curves are not easily available by direct measurements and take long and laborious experimental efforts to be obtained. It is usually obtained through either filtration or centrifugations methods [7,8]. However, in both methods, trapped liquid prevents the complete separation of solid phase and increases the uncertainties of the experimental results. Therefore, indirect methods are usually preferred by oil companies over direct measurements to generate wax precipitation curves [4].

The most commonly used indirect method is based on the integration of Differential Scanning Calorimetry (DSC) thermograms [9–11]. This procedure rests on several assumptions for converting the area of the thermogram into the amount of solid formed. The main problem with such technique is that the enthalpy of wax crystallization needed to transform the thermogram area in solid mass is empirical. Moreover as its value changes with wax composition, it cannot be estimated with accuracy before the wax precipitation curve is known.

In order to eliminate this empirical constant, a simple change of strategy is proposed. Instead of converting the thermogram into waxy solid build-up curve, we propose the simulation of the DSC experimental curves from the model itself, allowing a full curve adjustment without going through the empirical integration of the experimental DSC thermogram. Due to the dynamic nature of the DSC experiments, differences will always be observed [12]. But they can be rendered sufficiently small if the DSC experiments are carried out with small temperature rates. Results obtained for complex wax mixtures for which experimental solubility curves are available, are presented and analyzed through the proposed procedure. In this proposed strategy, the thermodynamic model developed by Coutinho et al. [4] at atmospheric pressure that accounts for the non-ideality of the solid phase was used to simulate the liquid/solid equilibria (SLE) at atmospheric pressure.

2. Method

DSC experiments are intrinsically transient and its precise modeling requires a heat transfer scheme [12]. This heat transfer scheme, on the other hand, needs to be adjusted to experimental results. Since the goal is to use the experimental data to adjust the thermodynamic model, the simultaneous adjustment of a heat transfer model would lead to uncertainties. It is proposed, as an alternative, to use small temperature rates in order to minimize as much as possible the transient effects during the experiment. The rate was established by comparing heating and cooling experiments. It was assumed that the dynamical effects of the experiments were at a minimum once the only difference between these two experiments was the supersaturation peak in the cooling experiment. As industry standards are the cooling curves, they were used rather than the heating curves.

Supposing a static experiment, the signal calculation becomes straightforward. At a given temperature, T , the DSC signal (DSC_{EXP}) is measured as the enthalpy flux as a function of time ($\frac{\partial h}{\partial t}$), as defined in equation (1). Once the temperature rate is defined ($\frac{dT}{dt}$), the scale may be converted from time to temperature. Since the thermodynamic simulations will give out enthalpy flux as a function of the temperature (DSC_{CALC} , equation 2), to be compared with the original DSC signal, it has to be multiplied by the temperature

rate, as shown in equation (3) [13].

$$DSC_{EXP} = \frac{\partial h}{\partial t} \quad (1)$$

$$DSC_{CALC} = \frac{\partial h}{\partial T} \quad (2)$$

$$DSC_{EXP} = DSC_{CALC} \frac{dT}{dt} \quad (3)$$

At constant pressure and global composition, the heat variation is equal to the enthalpy variation, and thus can be approximated by equation (4) and the scheme depicted in Fig. 1. The models will give the compositions of the liquid and solid phases at both temperatures $T+\Delta T$ and $T-\Delta T$. With this information, the proposed equation is solved directly. In equation (2), $x_{i,b}^a$ is the molar composition of component i in the either liquid or solid phase ($a = l$ or s) and at temperature b ($T+\Delta T$ or $T-\Delta T$). $\Delta h_{i,m}$ and $\Delta h_{i,tr}$ are respectively the melting enthalpy of component i and the solid-solid transition enthalpy of component i .

$$DSC_{CALC} = \sum_i MW_i \left[x_{i,T+\Delta T}^l Cp_i^l + x_{i,T+\Delta T}^s Cp_i^s + \frac{(x_{i,T-\Delta T}^s - x_{i,T+\Delta T}^s)(\Delta h_{i,m} + \Delta h_{i,tr})}{2\Delta T} \right] \quad (4)$$

To evaluate the SLE in the samples analyzed, a thermodynamic model proposed by Coutinho et al. [4] was used. Equilibrium state is defined from the equality of fugacity of each component in the liquid and solid phase, as represented in equation (5) [14].

$$f_i^L(T, P, x_i^L) = f_i^S(T, P, x_i^S) \quad (5)$$

Equation (5) can be further extended to explicitly relate the composition of both liquid and solid phases and the thermophysical properties of their pure compounds [14]:

$$\ln \frac{x_i^s \gamma_i^s}{x_i^l \gamma_i^l} = \frac{\Delta h_{i,m}}{RT_{i,fus}} \left(\frac{T_{i,fus}}{T} - 1 \right) + \frac{\Delta h_{i,tr}}{RT_{i,tr}} \left(\frac{T_{i,tr}}{T} - 1 \right) \quad (6)$$

The thermophysical properties were calculated according to equations (7)–(11), as proposed by Coutinho et al. [4] and where developed following Maranos and Holder methods [15].

$$T_{i,fus}[K] = 421.63 - 1.936412 \times 10^6 \exp \left[-7.8945(C_{ni} - 1)^{0.07194} \right] \quad (7)$$

$$T_{i,tr}[K] = 420.42 - 1.34784 \times 10^5 \exp \left[-4.344(C_{ni} + 6.592)^{0.14627} \right] \quad (8)$$

$$\Delta h_{i,m}[kJ/mol] = 3.7791C_{ni} - 12.654 \quad (9)$$

$$\Delta h_{i,tot}[kJ/mol] = 0.00355C_{ni}^3 - 0.2376C_{ni}^2 + 7.4C_{ni} - 34.814 \quad (10)$$

$$\Delta h_{i,tr}[kJ/mol] = \Delta h_{i,tot} - \Delta h_{i,m} \quad (11)$$

Where C_{ni} , $T_{i,fus}$ and $T_{i,tr}$ are respectively the number of carbon atoms, the melting temperature and solid-solid phase transition

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