



Mutual effects of paraffin waxes and clathrate hydrates: A multiphase integrated thermodynamic model and experimental measurements



Mohammadreza Ameri Mahabadian^a, Antonin Chapoy^{a, b, *}, Rod Burgass^a,
Bahman Tohidi^a

^a Hydrates, Flow Assurance & Phase Equilibria Research Group, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh, EH14 4AS, Scotland, UK

^b Mines Paristech, CTP – Centre Thermodynamique des procédés, 35 rue St Honoré, 77305, Fontainebleau, France

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ABSTRACT

This paper presents an extensive analysis of complex wax and hydrate forming systems employing an integrated wax-hydrate thermodynamic model. The developed model uses integration of the UNIQUAC activity coefficient model, CPA equation of state and van der Waals-Platteeuw model, for the description of waxes, fluids and hydrates, respectively. Our recently published multiphase “Gibbs energy minimization” flash algorithm [1] is extended here to identify waxy solid phase(s) and is shown to be robust in characterizing complex systems where several phases, i.e., solid wax, vapour, liquid hydrocarbon, liquid aqueous, ice and hydrate phases (structure I and II) may coexist.

The accuracy of model predictions is first validated by calculating the wax amount and composition in water-free systems for which experimental data are available. It is then used to explore the mutual effects of hydrates and waxes starting from a simple binary system of methane + n-heptadecane in the presence of water. The model is then used to analyse four multicomponent mixtures and a recombined light oil.

The analysis includes investigations into the impact of hydrate formation on wax phase boundary, amount and composition and vice versa, as well as a variety of secondary important effects including the influence of the amount of light end in the feed and impact of the free aqueous phase on the wax amount and phase boundary.

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1. Introduction

Formation of hydrates and waxes are well-known flow assurance problems causing considerable operational expenses and hazards mainly through loss of production or pipeline blockage. Experimental studies have revealed that simultaneous formation of waxes and hydrates can synergistically escalate their precipitation [2] and deposition [3]; hence promoting the possibility of pipeline blockage. Despite the high chances of formation of both hydrates and waxes at the same time (see for example [4,5]), especially in volatile oils and gas condensates under operational conditions, the

subject of mutual interactions of hydrates and waxes from a thermodynamic modelling viewpoint has been scarcely (and never in some aspects) addressed in the open literature. In view of this omission, it is critical to have an in-depth understanding of the phase behaviour of systems prone to form both waxes and hydrates, gained by utilising a robust thermodynamic model.

The only works available in the literature concerning the thermodynamic aspects of mutual interactions of hydrates and waxes are those of Tabatabaei et al. [6,7] and Ji [8]. The fluid phases in both works are described with cubic EoSs, though obviously, neglecting quasi-chemical forces due to hydrogen bonding in the presence of water would result in the poor accuracy of non-associating EoSs (see for example [9]). Also, in the work of Tabatabaei et al. [6,7], the Regular Solution Theory (RST) has been utilised to describe the waxy solid phase non-ideality. However, the RST has major drawbacks such as the overestimation of wax melting temperature [10]

* Corresponding author. Hydrates, Flow Assurance & Phase Equilibria Research Group, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh, EH14 4AS, Scotland, UK.

E-mail address: antonin.chapoy@pet.hw.ac.uk (A. Chapoy).

and inability to identify if more than one waxy solid phase has precipitated. More importantly, thorough investigation of the complex wax-hydrate systems requires a robust multiphase flash algorithm. Among the works mentioned only Tabatabaei et al. [6,7] have presented some flash calculation results. However, they have used sequential hydrate-free and wax-free flashes to calculate the phase fractions and compositions in the equilibrium state. In addition, the hydrate flash calculation algorithms utilised in the works of Tabatabaei et al. [6,7] are established on only satisfying the isofugacity criteria and are not based on a Gibbs energy minimization approach. There are many problems with these type of flash calculations in the presence of hydrates [1], as they fail to identify the presence of more than one structure of hydrate. Seemingly, this type of flash calculation algorithm has prevented the authors from analysing the mutual effect of hydrates and waxes on their compositions and amounts and only the mutual effects on the phase boundaries was investigated.

In the current study, the CPA EoS, originally presented by Kontogeorgis et al. [11], is utilised to describe the non-ideality of fluids. In the case of analysis of the systems containing water, it is vital for the applied EoS to take into account the associative hydrogen bonds contributions due to water associations in the fluids non-ideality. Additionally, the well-known and widely used model of van der Waals and Platteeuw (vdWP) [12] has been applied to describe the non-ideality of hydrate phases of different structures (here sI and sII). The accuracy of the coupled CPA-vdWP model for the description of the number and nature of the hydrates formed in equilibrium, in systems under hydrate forming conditions, has been validated in our previous work [1]. Finally, the UNIQUAC activity coefficient model, initially developed by Abrams and Prausnitz [13], and applied for the first time by Coutinho [14] for calculating paraffinic solids non-ideality, is exploited here to describe the waxy solid phase(s). The UNIQUAC is proven to be one of the most accurate thermodynamic models, to date, to evaluate *Wax Disappearance Temperature* (WDT_p), *Wax Precipitation Curve* (WPC) and composition of precipitates [15,16]. In the present study, to avoid confusion between the wax phase boundary data calculated by the model with the same value measured experimentally, which can either be *Wax Appearance Temperature* (WAT) or *Wax Disappearance Temperature* (WDT), the term WDT_p is referring to model predictions. This is because of several uncertainties while measuring these variables [17]. Obviously, if WDT is measured properly, it should correspond to the true wax melting point (thermodynamic liquidus point) [18] mainly due to less chance of superheating compared to subcooling [19].

Here, these three accurate thermodynamic models for the corresponding phases are integrated into a single framework: “UNIQUAC-CPA-vdWP” model which is abbreviated as UCV. The description of the model formulations will be presented in section 2.2.

In the present work, our recently published multiphase “Gibbs energy minimization” flash algorithm [1] is extended to identify the presence of wax phase(s). Such a flash algorithm coupled with a strong stability analysis scheme has a proven record of robustness [20]. The robustness of the devised algorithm is tested here with several examples with up to 8 phases of different natures may coexist. This robust flash algorithm is an essential requirement for the analysis of complex hydrate-wax forming systems, in particular for identifying the mutual effect of waxes and hydrate on their amount and composition. The steps required to extend the flash algorithm to take paraffin solid phases into consideration will be presented in the “Methodology” section.

This work also includes experimental measurement of Hydrate Dissociation Points (HDP) for three synthetic multicomponent mixtures of diverse phase behaviours as well as a recombined light

oil. These data are used to check the accuracy of the model.

The “Analysis and Discussions” section present the interpretations, based on several different types of calculations on the mutual interactions of hydrates and waxes, in particular:

- Effect of the overall composition distribution (heavy end and light end impacts) on the phase diagrams of hydrates and waxes
- Influence of the hydrates on the wax phase boundary
- Impact of the waxes on the hydrate dissociation line
- Influence of the hydrates on the amount and composition of wax precipitated
- Impact of waxes on the amount and compositions of hydrates formed

The analysis is first performed to understand how the wax phase boundary is influenced by the formation of sI hydrate (HI) in a binary system of methane + n-heptadecane in the presence of different water to hydrocarbon molar ratio in the feed (W/H). The aspects mentioned above are then evaluated in the three multicomponent synthetic mixtures for which experimental wax phase boundary data are available [8] as well as SHF4 mixture of Ungerer et al. [21]. Finally, the analysis of the effect of hydrates on the wax amount and phase boundary for a recombined light oil mixture is carried out. This is performed to assess the validity of analysis for a real mixture.

2. Methodology

Accurate determination of the number and nature of phases at equilibrium requires not only precise thermodynamic models, capable of describing corresponding phases but also a robust multiphase flash calculation algorithm. Accordingly, this section is devoted first to describe the flash calculation algorithm. Then the formulation of the exploited thermodynamic models will be presented.

2.1. Multiphase flash calculation

The flash calculation used here is an extension of our recently published multiphase flash calculation in the presence of hydrates [1] to systems where wax phase(s) may be present. The devised flash algorithm includes a combination of a Gibbs free energy minimization approach, with the Michelsen [22] multiphase algorithm applied in the inner loop, and the Michelsen [23] tangent plane distance (TPD) stability analysis to perform the initial “No-Hydrate Flash” (NHF) step [1]. Similar to the original work [1] the stability analysis here uses the BFGS algorithm [24] to find stationary points of the Michelsen TPD function starting with trial compositions defined in by Li and Firoozabadi [25]. The NHF step results are then employed as a part of the initial guess compositions for the “Hydrate Flash” (HF) step [1].

In the current work, the following changes have been made to the original algorithm to model the presence of waxes correctly:

- 1) Initialization of the compositions for the NHF step
- 2) Initialization of the compositions for the HF step
- 3) Considerations for components non-precipitating in the wax phase(s)

Details of each of these changes are presented below.

2.1.1. Initialization of the compositions for the “No-Hydrate Flash” step

For the initial guess of compositions in the presence of water, it is assumed that for the first flash calculation in the NHF step, at

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