An improved thermodynamic model for Wax precipitation using a UNIQUAC + PC-SAFT approach

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ABSTRACT

Wax precipitation is a serious challenge in the oil industry due to decrease in oil production and transmission efficiency. Wax precipitation modeling plays an important role to forecast the Wax appearance temperature (WAT) and the amount of precipitation. In this work, solid solution theory is used for Wax precipitation modeling. The perturbed hard chain statistical associating fluid theory (PC-SAFT) equation of state (EOS) is implemented in order to calculate the fugacity of vapor and liquid phases and their corresponding compressibility factors. UNIQUAC activity coefficient model is chosen to account for the non-ideality of solid phase. The resultant equilibrium ratios are included in the three phase equilibrium calculations and stability analysis. The proposed model is applied to calculate the amount of precipitates and WAT for six North Sea oil samples to evaluate the prediction accuracy. The crude oil samples contain several cuts and heavy fractions. The PC-SAFT EOS parameters for petroleum plus fractions are estimated using available correlations in literature. In addition, the modeling results are compared with the results of Lira-Galeana et al. [1], Pedersen et al. [2] and Dalirsefat and Feyzi [3] models. The results show improvements and demonstrate the proposed model as a comparable forecasting tool for Wax precipitation modeling in oil transmission and processing facilities.

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1. Introduction

The petroleum industries are dealing with solid precipitation during production, processing and transportation. Some of these precipitates are Waxes, Asphaltene, Gas Hydrates and Scale. Waxes are heavy hydrocarbon compounds that are mainly formed from normal paraffins with carbon numbers ranging from 15 to 75. Normal alkanes comprise 95% of Wax. There are also some other ingredients including, branched Paraffin, Naphthenics and Aromatics in small quantities [4,5]. Wax precipitation problem gets even worse if the pressure and the heavy components in the oil mixture increase. Besides, the temperature decrease also leads to Wax precipitation. Wax formation and precipitation make a number of problems including porous media blockage, production rate decline, oil pathways blockage and exploitation operation cessation, higher pressure drop in the oil pipelines, higher crude viscosity and, consequently, higher pumping costs. Therefore, prediction of formation and precipitation conditions is of great importance in petroleum industry.

The Wax appearance temperature (WAT) in a petroleum reservoir fluid at a given pressure is the highest temperature at which Wax crystallization begins. WAT prediction is a necessary element for flow assurance strategies selection. There are several techniques for WAT measurement, including visual observation, cross-polarized microscopy, filter plugging, rheometry, differential scanning calorimetry (DSC), densitometry, and spectroscopic methods. Cross-polarized microscopy (CPM) techniques can be used to observe Wax formation directly with a high resolution and therefore has emerged as one of the most commonly used industrial techniques for WAT measurement [6]. The temperature at which the Wax starts to dissolve in oil is called Wax Dissolution Temperature (WDT). Ideally, WAT and WDT should be the same, however, experimental measurements for WAT and WDT produce different values due to different rates of heat transfer to the system [7]. Usually WDT is higher than the precipitation temperature due to non-equilibrium effects during heat transfer to the experimental set up. WAT is increased as the pressure increases. This means that precipitating component solubility is decreased [2,7—9]. To predict the precipitation conditions, one needs to use a thermodynamic model. There exist several models in literature to study this phenomenon and to predict the amount of Wax precipitate and WAT.

These models can be divided into two categories: Solid-Solution and Multi-Solid. The difference between these two categories is related to the treatment of the solid phase. In the class of Solid-Solution; the model handles the solid phase as a mixture of components that are transferred into Wax phase and these components are miscible in all proportions. On the other hand, each pure or pseudo component of a Multi-Solid makes a separate phase, and these phases are insoluble in each other. Hansen et al. [10], Won [11,12], Ji et al. [13], Zuo et al. [14], Pedersen et al. [2], Farayola et al. [15] and Zhao et al. [16] models use the Solid-Solution concept. Won [11,12] model was among the early solid solution models for Wax precipitation. In their work, all the three phases were included in equilibrium calculations to study Wax precipitation. They assumed that there are only normal Paraffins in the solid phase. They neglected the liquid-solid heat capacity difference effect on the fugacity coefficients and used Scatchard-Hilderbrand theory to calculate the activity coefficients. In their work Soave-Redlich-Kwong (SRK) equation of state (EOS) is implemented to consider non-idealities in the fluid phase. Considering 17 crude samples, Hansen et al. [10] found that Won [11,12] modeling results for WAT prediction is not accurate enough. They used SRK EOS for liquid-vapor non-idealities while using Flory–Huggins solution theory for Wax precipitation. In this model, crude oil components' properties were estimated based on Riazi and Daubert correlations [17]. Hansen [10] assumed that the Wax phase contains Paraffinic, Aromatic and Naphthenic components. They divided the mixture constituents into two groups Paraffinic - Naphthenic and Aromatic. They used the group contribution method to obtain component interactions. Pedersen et al. [2] showed that Won and Hansen approaches overestimates the Wax precipitation amount. They neglected the presence of the vapor phase and used Scatchard-Hilderbrand model to account for the non-ideality of the liquid and solid. They added an adjusting parameter for solubility to the model to improve its prediction capability.

Zhao et al. [16] developed their model according to solid solution theory and used SRK EOS to account for liquid and vapor equilibrium and UNIQUAC model for solid phase. Moreover, they used a new correlation [18] for latent heat calculation in their approach and an improved version of the SRK EOS (Wang and Gmehling [19]). Farayola et al. [15] used Patel and Teja [20] EOS to describe vapor-liquid behavior and UNIQUAC model to describe solid behavior in a solid solution approach and compared their results with a situation in which the Peng-Robinson (PR) EOS was used instead of Patel and Teja [20] EOS for liquid-vapor non-idealities. They showed that use of Patel and Teja EOS leads to a higher prediction capability.

Multi-solid model, however, only uses an EOS to calculate fugacity in the all phases in equilibrium. Pan and Firoozabadi [21], Nichita et al. [22], Escobar-Remolina [23], Lira-Galeana et al. [1], Derakhshan and Shariati [24] and Dalirsefat and Feyzi [3] used this approach. Lira-Galeana et al. [1] used the multi-solid approach for Wax precipitation for the first time. In their work, Wax is assumed to be comprised of different pure solid phases for which there are also some experimental evidences. They used PR EOS and Pedersen correlation [2] for ΔC_p [2]. Pan and Firoozabadi [21] split each petroleum cut into Paraffinic, Naphthenic and Aromatic parts and employed Lira-Galeana et al. [1] workflow to obtain Wax precipitation amount. They used Cavett and Lee and Kesler [25] correlations for critical properties and acentric factor. In addition, they estimated the PNA properties for parts with molecular weight greater than 300 from Riazi and Al-Sahhaf correlation [26]. UNIQUAC approach which is appropriate for complex mixtures, was implemented by Coutinho et al. [27] for Wax precipitation. However, it was not able to provide a good representation of simple systems and overestimates the crystallization of light compounds

in mixtures of paraffins with a broad range of chain lengths.

Dalirsefat and Feyzi [3] presented a modeling approach based on solid solution theory and split the plus fractions using Whitson approach to improve the petroleum cut parameters estimation during EOS calculations. Based on Pan and Firoozabadi [21] results, they assumed that the components heavier than C_{15} can exist in Wax phase. They correlated the melting temperature from Lira-Galeana et al. [1] and Won [11,12] relations and used Pedersen et al. [2] correlations for $\Delta C_{p,i}$. Three phases were assumed to be included in their approach. The liquid vapor non-idealities were considered using a modified version of PR EOS [28].

According to the phases in the equilibrium, these models can be divided into two categories. The first category of models, considers the presence of the three phases: vapor, liquid and solid. The other category neglects the presence of the vapor phase and examines

Table 1
Compositions and properties of oil mixtures [1].

Oil no.	5		8		10	
Component	Mw	Mole %	Mw	Mole %	Mw	Mole %
C_1		0.056		0.000		0.016
C_2		0.368		0.113		0.145
C_3		1.171		1.224		1.392
IC_4		0.466		0.645		1.180
NC_4		1.486		2.832		3.088
IC_5		0.961		1.959		2.980
NC_5		1.396		3.335		3.802
C_6		2.251		5.633		7.207
C_7	88.800	6.536	92.800	9.933	94.100	11.333
C_8	101.000	8.607	106.300	10.750	107.000	12.465
C_9	116.000	4.882	120.000	7.179	122.000	7.784
C_{10}	133.000	2.830	134.000	6.561	136.000	5.314
C_{11}	143.000	3.019	148.000	5.494	147.000	5.033
C_{12}	154.000	3.119	161.000	4.547	161.000	3.989
C_{13}	167.000	3.687	175.000	4.837	175.000	3.869
C_{14}	181.000	3.687	189.000	3.700	189.000	3.627
C_{15}	195.000	3.637	203.000	3.520	203.000	3.165
C_{16}	207.000	3.079	216.000	2.922	214.000	2.311
C_{17}	225.000	3.657	233.000	3.072	230.000	2.472
C_{18}	242.000	3.289	248.000	2.214	244.000	2.815
C_{19}	253.000	3.109	260.000	2.493	258.000	2.110
$C_{20}+$	423.000	38.400	544.000	17.000	418.000	14.400
Sp.Gr.	0.893		0.934		0.88	

Table 2
Compositions and properties of oil mixtures [1].

Oil no.	11		12		15	
Component	Mw	Mole %	Mw	Mole %	Mw	Mole %
C_1		0.000		0.000		0.021
C_2		0.100		0.173		0.254
C_3		0.118		1.605		1.236
IC_4		0.106		1.148		0.588
NC_4		0.099		3.596		2.512
IC_5		0.162		3.086		1.955
NC_5		0.038		4.171		3.485
C_6		0.458		7.841		6.842
C_7	90.800	2.194	94.100	11.110	92.200	12.850
C_8	106.500	2.847	105.400	13.430	105.400	13.980
C_9	122.300	1.932	119.000	9.419	119.000	9.190
C_{10}	135.000	5.750	135.000	5.583	134.000	6.435
C_{11}	149.000	4.874	148.000	4.890	148.000	5.118
C_{12}	162.000	5.660	162.000	3.864	161.000	4.111
C_{13}	176.000	6.607	175.000	4.298	175.000	4.231
C_{14}	189.000	6.149	188.000	3.272	188.000	3.682
C_{15}	202.000	5.551	203.000	2.274	202.000	3.044
C_{16}	213.000	5.321	216.000	2.791	214.000	2.255
C_{17}	230.000	5.022	232.000	2.311	230.000	2.405
C_{18}	244.000	4.016	246.000	1.960	245.000	2.006
C_{19}	256.000	4.176	256.000	1.821	257.000	1.766
$C_{20}+$	473.000	38.800	388.000	11.300	399.000	12.000
Sp.Gr.	0.963		0.872		0.887	