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Solid Phase Equation of State Application for Wax Formation Prediction in Petroleum Mixtures

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Abstract
Precipitation of solid paraffins is one of the most common problems in the oil industry, mposing high operating costs. There have been a great many efforts for the prediction of solid paraffins precipitation up to now. Most of them were based on activity coefficient models accounting to solid phase non-ideality or the multi-solid model to calculate the number of precipitated solid phases. In this work, solid phase behavior is predicted by a solid equation of state. At first, by using the thermodynamic method (subcoled liquid) for pure solid phase fugacity from pure liquid fugacity, the solid EOS parameters are tuned.
The tuned solid EOS can then be directly applied for the prediction of the amount of precipitated solid paraffins (waxes) in the oil samples. The proposed equations system in this work is solved by a proper mathematical method. The obtained results of wax precipitation in this work are in good agreement with the experimental data.

Keywords: *Solid Paraffin, Solid Phase Equation of State, Wax Precipitation, Multi-solid model*

Introduction
Wax deposition from gas and oil production facilities and pipelines is undesirable. The flow-lines and process equipment may be plugged by wax deposition. Different physical and chemical methods have been proposed to remove deposited solids, which increase operating costs. A reliable model for wax precipitation calculation is highly valued for the design and operation of flowlines.
Since the 1990s, many efforts have been made to predict conditions under which the waxes can precipitate, and find the amount of precipitated wax in functions of pressure, temperature and composition. At first, the calculations were based on the solid-liquid equilibrium assumption. Later on, the gas phase was included in the calculations [1, 2]. There are two clearly defined assumptions for the determination of the thermodynamic equilibrium wax–liquid in established multi-component hydrocarbon systems: solid solution, and the formation of multiple solid phases. In the former case, different methods were proposed based on the activity coefficient model assuming the non-ideality

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of liquid and solid phases [3, 4]. Solid phase transition and vapor phase were then considered in other works [5-7]. The non-ideality was defined using Wilson or UNIQUAC equations. Lira-Galeana et al. [8] developed the multi-solid approach in 1996. In this model, it is assumed that the solid wax consists of several pure solid phases, in where the number and nature of these phases will be obtained from phase stability analysis. Coutinho showed that the solid phase is a multi-solid solution in nature and this is supported by the experimental data [9].

In this work, the wax-precipitation model based on solid phase equation of state will be presented. The multi-solid approach is used because of its wide acceptability and limitation in using solid phase equation of state. The parameters of the equation of state are obtained in the case that vapor, liquid and solid phases are presented in the system.

Solid Phase Equation of State

There are a few EOS's which can be applied to predict solid, liquid and vapor phase behavior simultaneously [10,11]. One of these EOS types is the TST[1] equation of state that is used in this work [11]. The general form of the equation is:

$$P = \frac{RT}{v-b} - \frac{a}{(v+ub)(v+wb)} \tag{1}$$

where, *u* and *w* are 3 and -0.5 respectively. Also,

$$a_c = 0.470507 R^2 T_c^2 / P_c \tag{2}$$

$$b_c = 0.0740740 RT_c / P_c \tag{3}$$

$$Z_c = 0.296296 \tag{4}$$

1- *Twu – Sim - Tassone*

$$a = \alpha \ a_c \tag{5}$$

Alpha function for liquid and vapor phases could be used in conventional polynomial form or in exponential form. In this equation, a new alpha function is introduced for the solid phase, which will be discussed later.

In order to calculate fugacity of each component in pure solid state, the following equation is used [12].

$$d \ln f = -\frac{\Delta H}{RT^2} dT + \frac{\Delta v}{RT} dP \tag{6}$$

Where f is fugacity, ΔH is enthalpy change as result of the change in system temperature, and Δv is partial molar volume change by pressure.

By integrating the above equation from the triple point pressure to the system pressure for liquid and solid phases and dividing the two equations, the following relation will be obtained. In this equation, ΔH^f and Δv are supposed to be independent of pressure and temperature.

$$\ln \frac{f^S}{f^L} = -\frac{\Delta H^f}{RT}\left(1 - \frac{T}{T^f}\right) - \frac{\Delta v P}{RT} \tag{7}$$

Where ΔH^f and T^f are melting enthalpy and melting point respectively. These parameters can be calculated as follows:

$$T^f = 374.5 + 0.02617 MW_i - 2.0172 \times 10^4 / MW_i$$

or

$$T_f = 421.63 - 1936112.63 exp\left(-7.8945 (N-1)^{0.07194}\right) \tag{8}$$

Where N and MW_i are carbon number and molecular weight respectively.

$$\Delta H^f = 0.1426 MW_i \ T^f \text{ or}$$

$$\Delta H^f = 0.05276 MW_i \ T^f \tag{9}$$

Other correlation may be used for both parameters [1, 2, 8 16].
At very low pressures (to zero pressures), eq. 7 change to:

$$\ln\frac{f^S}{f^L} = -\frac{\Delta H^f}{RT}\left(1-\frac{T}{T^f}\right) \quad (10)$$

This equation is similar to the equation that was proposed by Prausnitz et al. [13] for the calculation of solid phase fugacity. If the fugacity is calculated at zero pressure,

$$ln\left(\frac{f^S}{P}\right) = -1 - ln\,b^* - ln(v^{*S}-1) - \frac{1}{(w-u)}\frac{a^{*S}}{b^*}ln\left(\frac{v^{*S}+w}{v^{*S}+u}\right) \quad (11)$$

Where,

$$v^{*S} = \frac{1}{2}\left\{\left(\frac{a^{*S}}{b^*}-u-w\right)-\left[\left(u+w-\frac{a^{*S}}{b^*}\right)^2-4\left(uw+\frac{a^{*S}}{b^*}\right)\right]^{1/2}\right\} \quad (12)$$

$$a^* = \frac{Pa}{R^2T^2} \quad (13)$$

$$b^* = \frac{Pb}{RT} \quad (14)$$

Where u and w are the parameters of the equation of state. Combining equations 7 to 10 results in:

$$-1 - ln\,b^* - ln(v^{*S}-1) - \frac{1}{(w-u)}\frac{a^{*S}}{b^*}ln\left(\frac{v^{*S}+w}{v^{*S}+u}\right) = ln\left(\frac{f^L}{P}\right) - \frac{\Delta H^f}{RT}\left(1-\frac{T}{T^f}\right) \quad (15)$$

The only unknown variable in the above equation is a^{*S}. Therefore, the equation is solved to obtain a^{*S} for different temperatures. The parameters of predefined solid alpha function are calculated by correlating the data to the following equation

$$\alpha^S(T) = 1 + l_s(1-T_r^{0.5}) + m_S(1-T_r)^{n_s}(0.7-T_r) \quad (16)$$

In which α^S can be calculated using

$$\alpha^S = a^S / a_c \quad (17)$$

$$a^S = \frac{a^{*S}R^2T^2}{P} \quad (18)$$

In order to calculate the optimum parameters, the following function was used to minimize the difference between the experimental data and the calculated values from eq. 11.

$$F = \sum(1 + l_s(1-T_{r,i}^{0.5}) + m_s(1-T_{r,i})^{n_s}(0.7-T_{r,i}) - \alpha_i^S)^2 \quad (19)$$

The simplex-Nelder-Mead algorithm was utilized to obtain the optimum parameters, which minimizes the objecting function. Due to the nonlinearity of the function, the results will drastically depend on the initial guess for the optimal parameters. To avoid this problem, the optimization problem is run for different starting points.

Wax Precipitating Model

The vapor-liquid-solid equilibrium states are defined as follows:
Mass balance for precipitating components:

$$y_i^V n^V + x_i^L n^L + \sum_{j=}^{N_P} n_i^{Sj} - z_i^F n^F = 0 \quad (20)$$

Where,
$i = 1,...,N_c \quad , \quad j = 1,...,N_P$
N_P: Number of precipitated solid phases
N_C: Number of components
Mass balance for non-precipitating components:

$$y_i^v n^V + x_i^L n^L - z_i^f n^F = 0 \tag{21}$$

Equality of fugacities in the liquid and vapor phases for all components gives:

$$f_i^V - f_i^L = 0 \tag{22}$$

And for the liquid and solid phases for precipitating components:

$$f_i^L - f^{S_i} = 0 \tag{23}$$

Summation of mole fractions in liquid and gas phases are equal to unity

$$\sum_{i=1}^{Nc} x_i - 1 = 0 \tag{24}$$

$$\sum_{i=1}^{Nc} y_i - 1 = 0 \tag{25}$$

All the equations above constitute a system of equations, which can be solved to define the equilibrium system completely. An error function is introduced to check the convergence of the system of equations.

$$f(\delta) = \sum_{i=1}^{2N_C + N_P + 2} |\delta_i| \tag{26}$$

Where δ_i 's are the right hand expressions in equations 20 to 25.

Results and Discussions

The composition of oil samples and some synthetic mixtures which are used in this research, are given in Tables 1-4.

Table 1. Mole fractions for two synthetic mixtures [7]

Component	*Mixture C*	*Mixture B*
n-C_{10}	0.5876	0.5101
n-C_{18}	0.0513	0.0819
n-C_{19}	0.0486	0.0694
n-C_{20}	0.0463	0.0590
n-C_{21}	0.0440	0.0506
n-C_{22}	0.0418	0.0433
n-C_{23}	0.0397	0.0373
n-C_{24}	0.0378	0.0319
n-C_{25}	0.0359	0.0274
n-C_{26}	0.0342	0.0236
n-C_{27}	0.0327	0.0202
n-C_{28}	0	0.0176
n-C_{29}	0	0.0148
n-C_{30}	0	0.0127

Table 2. Mole fractions for a synthetic mixture [14]

Component	*Bim 13*	Component	*Bim 13*
C_{10}	80.01	C_{34}	0.61
C_{18}	7.09	C_{35}	0.53
C_{19}	6.09	C_{36}	0.45
C_{20}	5.220		

Table 3. Heavy oil fractions analysis [5]

Oil 5		
Pseudocomponent	**Mole percent**	**MW**
$P\text{-}C_{10+}$	4.4627	167.0
$N\text{-}C_{10+}$	6.4827	160.0
$A\text{-}C_{10+}$	15.126	160.0
$P\text{-}C_{15+}$	2.9096	237.0
$N\text{-}C_{15+}$	3.8627	233.0
$A\text{-}C_{15+}$	8.9664	233.0
$P\text{-}C_{20+}$	1.5426	307.0
$N\text{-}C_{20+}$	2.1514	302.0
$A\text{-}C_{20+}$	5.0199	302.0
$P\text{-}C_{25+}$	0.7856	375.0
$N\text{-}C_{25+}$	1.389	372.0
$A\text{-}C_{25+}$	3.2409	372.0
$P\text{-}C_{30+}$	0.3528	449.0
$N\text{-}C_{30+}$	1.4348	440.0
$A\text{-}C_{30+}$	1.4348	440.0
$P\text{-}C_{35+}$	0.1377	511.0
$N\text{-}C_{35+}$	1.5694	512.0
$A\text{-}C_{35+}$	0.0174	512.0
$P\text{-}C_{40+}$	0.0648	590.0
$N\text{-}C_{40+}$	1.1964	587.0
$A\text{-}C_{40+}$	0.0491	587.0
$P\text{-}C_{46+}$	0.0259	713.0
$N\text{-}CP1_{+}$	0.3143	724.0
$A\text{-}CP1_{+}$	1.8285	724.0
$N\text{-}CP2_{+}$	0.2257	901.0
$A\text{-}CP2_{+}$	1.3396	901.0

Table 4. Heavy oil fractions analysis [5]

Oil 6		
Pseudocomponent	**Mole percent**	**MW**
P-CP1	3.5922	157.0
N-CP1	4.7712	157.0
A-CP1	4.7712	157.0
P-CP2	2.7858	201.0
N-CP2	4.5495	201.0
A-CP2	4.5495	201.0
P-CP3	1.8055	252.0
N-CP3	2.9829	252.0
A-CP3	4.4744	252.0
P-CP4	1.2238	300.0
N-CP4	2.9018	300.0
A-CP4	4.3527	300.0
P-CP5	0.3674	563.0
N-CP5	2.5116	563.0
A-CP5	5.1937	563.0
P-CP6	0.0581	654.0
N-CP6	1.0319	654.0
A-CP6	1.6277	654.0
P-CP7	0.0736	666.0
N-CP7	1.0099	666.0
A-CP7	2.8634	666.0
N-CP8	0.8611	744.0
A-CP8	2.1707	744.0

The parameters of the equation of state (ls, ms, ns) are evaluated as discussed in the previous section. The optimal values for the mentioned parameters for the oil samples are shown in Tables 5-9. The initial guess for the system of equilibrium equations is given from the results of a two-phase flash calculation. Then, the dogleg method [15] is applied to check the convergence criteria, i.e. the value of the right-hand side expression in equation 19 should be less than 1e-7. If the criterion is not met, the program will shift to simplex algorithm which uses the results of the previous step as the initial points. There is a normalizing step which filters the incoming physically unacceptable data. The physical properties data can be obtained from the concerned reference data-books and/or they can be estimated from the published correlations for thermodynamic properties. Having two parameters of the true boiling point, molecular weight and specific gravity one can estimate the thermo-physical properties of the components.

Table 5. Parameters of EOS for *mixture B*

Component	l_S	m_S	n_S
$n\text{-}C_{10}$	-9.4224	13.239	-0.18762
$n\text{-}C_{18}$	7.1395	-0.44956	-4.3144
$n\text{-}C_{19}$	-8.9293	15.535	-0.035543
$n\text{-}C_{20}$	7.9884	-0.52493	-4.2596
$n\text{-}C_{21}$	-9.2735	16.518	-0.016801
$n\text{-}C_{22}$	8.6106	-0.57798	-4.2509
$n\text{-}C_{23}$	-9.5182	17.335	-0.0037988
$n\text{-}C_{24}$	9.4021	-0.64356	-4.223
$n\text{-}C_{25}$	-9.7652	18.107	0.006465
$n\text{-}C_{26}$	10.112	-0.70408	-4.209
$n\text{-}C_{27}$	-9.7534	18.749	0.019831
$n\text{-}C_{28}$	10.816	-0.76167	-4.198
$n\text{-}C_{29}$	-9.9905	19.304	0.020441
$n\text{-}C_{30}$	11.444	-0.81451	-4.1968

Table 6. Parameters of EOS for *mixture C*

Component	l_S	m_S	n_S
$n\text{-}C_{10}$	-9.4224	13.239	-0.18762
$n\text{-}C_{18}$	7.1395	-0.44956	-4.3144
$n\text{-}C_{19}$	-8.9293	15.535	-0.035543
$n\text{-}C_{20}$	7.9884	-0.52493	-4.2596
$n\text{-}C_{21}$	-9.2735	16.518	-0.016801
$n\text{-}C_{22}$	8.6106	-0.57798	-4.2509
$n\text{-}C_{23}$	-9.5182	17.335	-0.003799
$n\text{-}C_{24}$	9.4021	-0.64356	-4.223
$n\text{-}C_{25}$	-9.7652	18.107	0.006465
$n\text{-}C_{26}$	10.112	-0.70408	-4.209
$n\text{-}C_{27}$	-9.7534	18.749	0.019831

Table 7. Parameters of EOS for *bim13*

Component	l_S	m_S	n_S
C_{10}	-10.833	14.648	-0.20581
C_{18}	7.3255	-0.47341	-4.2847
C_{19}	6.4639	-0.29946	-4.5263
C_{20}	8.0223	-0.53895	-4.2522
C_{34}	12.906	-1.0438	-4.151
C_{35}	-16.406	28.979	0.10221
C_{36}	13.603	-1.1167	-4.1423

Table 8. Parameters of EOS for *Oil 5*

Pseudocomponent	l_S	m_S	n_S
$P\text{-}C_{10+}$	-8.6201	12.786	-0.17239
$N\text{-}C_{10+}$	3.2125	-0.08398	-5.1386
$A\text{-}C_{10+}$	3.2267	-0.12094	-4.9696
$P\text{-}C_{15+}$	5.9567	-0.27612	-4.5308
$N\text{-}C_{15+}$	-5.7139	9.9654	-0.17938
$A\text{-}C_{15+}$	-6.0577	9.9896	-0.1857
$P\text{-}C_{20+}$	7.492	-0.3908	-4.4207
$N\text{-}C_{20+}$	-6.3593	11.679	-0.15433
$A\text{-}C_{20+}$	-5.8307	10.416	-0.21188
$P\text{-}C_{25+}$	8.9575	-0.50176	-4.3724
$N\text{-}C_{25+}$	-7.4047	13.844	-0.12532
$A\text{-}C_{25+}$	-6.0942	11.417	-0.22147
$P\text{-}C_{30+}$	10.561	-0.6278	-4.3345
$N\text{-}C_{30+}$	-8.6504	16.201	-0.098267
$A\text{-}C_{30+}$	-6.588	12.693	-0.21949
$P\text{-}C_{35+}$	11.921	-0.73866	-4.3053
$N\text{-}C_{35+}$	-10.129	18.873	-0.072922
$A\text{-}C_{35+}$	-7.2483	14.239	-0.21087
$P\text{-}C_{40+}$	13.681	-0.88703	-4.2681
$N\text{-}C_{40+}$	-11.777	21.772	-0.050509
$A\text{-}C_{40+}$	-8.0138	15.977	-0.19855
$P\text{-}C_{46+}$	16.492	-1.1337	-4.209
$N\text{-}CP1_{+}$	-14.927	27.217	-0.01868
$A\text{-}CP1_{+}$	-9.4777	19.316	-0.1736
$N\text{-}CP2_{+}$	-19.061	34.309	0.0097925
$A\text{-}CP2_{+}$	-13.495	23.969	-0.20113

Table 9. Parameters of EOS for *Oil 6*

Pseudocomponent	l_S	m_S	n_S
P-CP1	-7.6701	11.668	-0.1522
N-CP1	-4.7492	7.8714	-0.16432
A-CP1	3.1885	-0.13346	-4.7521
P-CP2	-7.9844	13.428	-0.047253
N-CP2	3.8369	-0.10604	-4.8242
A-CP2	3.6483	-0.11553	-4.8232
P-CP3	6.4993	-0.37657	-4.2186
N-CP3	-4.3969	9.1252	-0.094925
A-CP3	-4.3753	8.6468	-0.11886
P-CP4	7.6419	-0.49264	-4.1055
N-CP4	-4.6555	10.188	-0.064131
A-CP4	-4.0311	8.8143	-0.12237
P-CP5	13.934	-1.2069	-3.8195
N-CP5	-7.8951	17.942	0.063654
A-CP5	-4.135	12.168	-0.078385
P-CP6	16.199	-1.4885	-3.754
N-CP6	-9.3345	20.954	0.090889
A-CP6	-4.4112	13.697	-0.055752
P-CP7	16.502	-1.5269	-3.7459
N-CP7	-9.5289	21.355	0.094017
A-CP7	-4.4491	13.904	-0.052763
N-CP8	-10.807	23.979	0.1122
A-CP8	-4.6938	15.265	-0.033513

α^S is independent of pressure and it can be used for the solid volume prediction [11]. It seems that the prediction errors for the lighter components, like C_{10}, are greater than those for the heavy fractions.

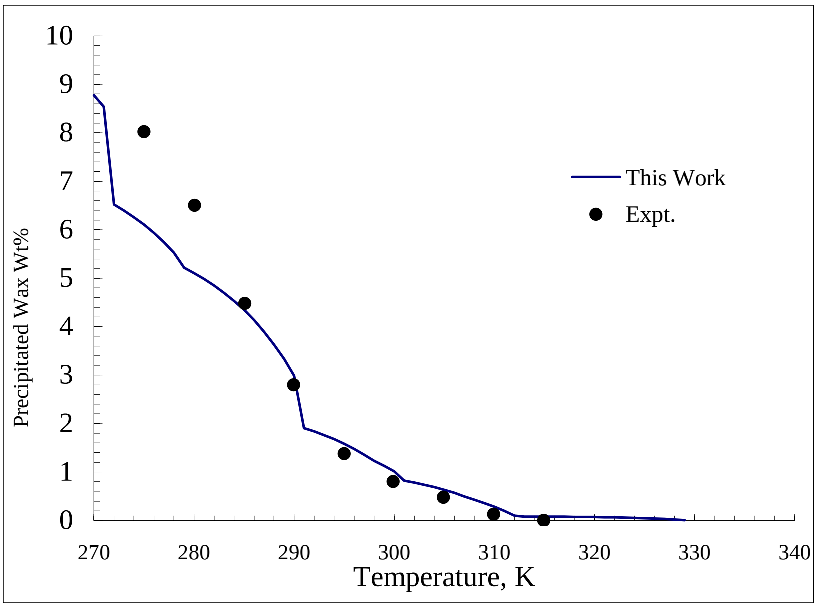

Figure 1. Experimental and calculated amount of precipitated wax for *Oil 5*

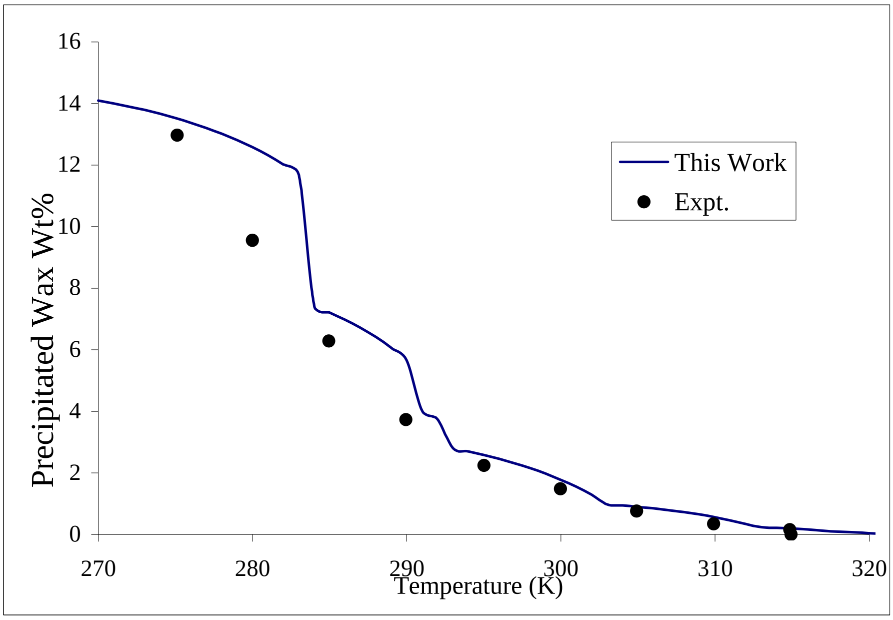

Figure 2. Experimental and calculated amount of precipitated wax for *Oil 6*

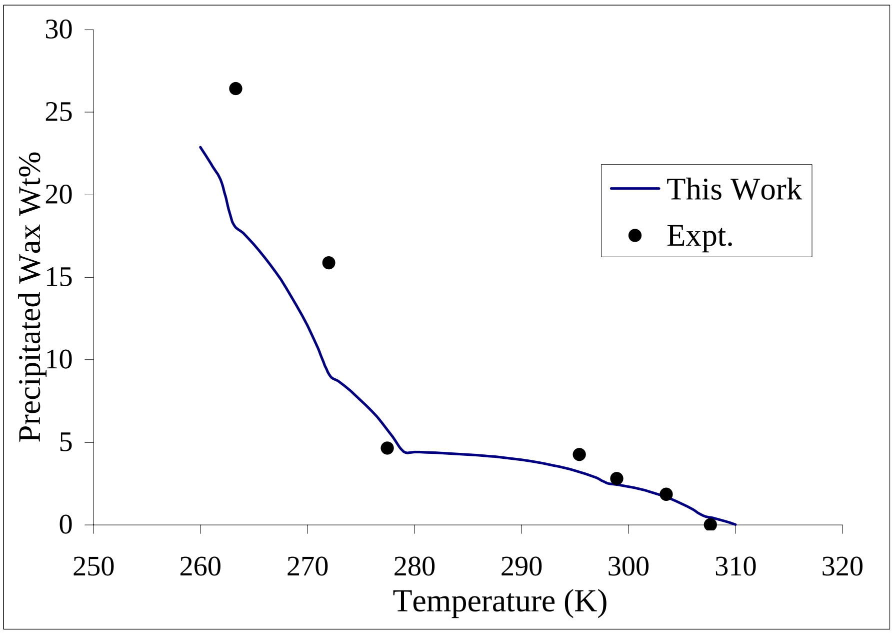

Figure 3. Experimental and calculated amount of precipitated wax for *bim13*

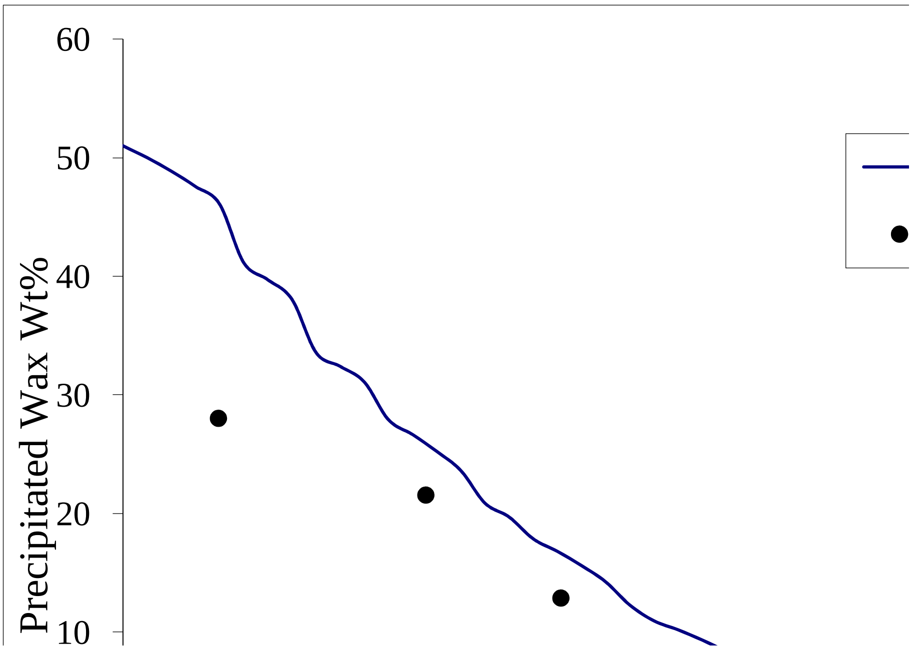

Figure 4. Experimental and calculated amount of precipitated wax for *mixture B*

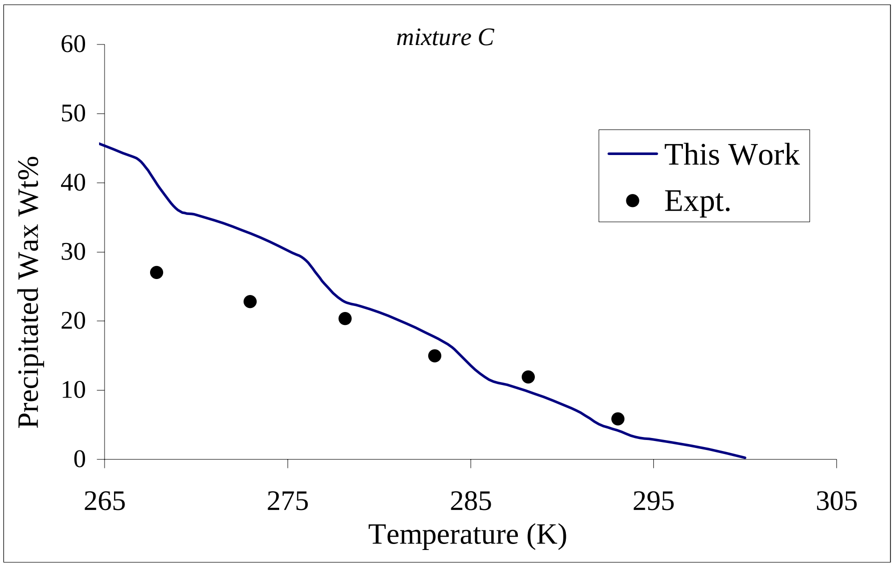

Figure 5. Experimental and calculated amount of precipitated wax for *mixture C*

Conclusion

Complex behavior of a solid phase in an oil mixture and the wide range of its application in solid precipitation and deposition petroleum fluids (wax, asphaltene, …) need to be modeled via applicable and efficient methods. Here, the application of a solid EOS for the description of solid phase was tested for wax precipitation in petroleum mixtures. In this work, TST solid equation of state is used for describing wax precipitation phenomena in some synthetic and real oil mixtures. This solid equation of state is based on an alpha function. Using thermodynamic method for pure solid fugacity from pure liquid fugacity, the TST EOS parameters were tuned before its application for wax precipitation prediction. The multisolid phase approach is used for determination of the nature and number of solid phases. As can be seen in the previous sections, the obtained results in this work are in good agreement with the experimental data.

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