

Observations of Sludge Formation in Group I Base Stock for Lubricants and Thermodynamic Modeling with the SAFT Equation of State

E. Pashai, M. R. Dehghani*, F. Feyzi

School of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran

ARTICLE INFO

Article history:

Received: 2016-05-25

Accepted: 2016-10-04

Keywords:

Lubricant

Degradation

Sludge

Solid-Liquid Equilibrium
(SLE)

SAFT Equation of State

ABSTRACT

Varnish and sludge formation are considered as one of the most common problems in lubrication and hydraulic systems. In order to simulate the condition of sludge formation, base stock lubricant (Group 1 API) has been selected and exposed to heat in a laboratory setup. In this work, solid-liquid equilibrium through sludge formation has been modeled using SAFT equation of state. The results for prediction of sludge formation showed that the absolute average deviations between experimental and theoretical results were less than 1.4 %. The calculated results for solubility coefficient of the oxidation byproducts from SN100 (solvent neutral Group I) base stock in fresh (un-oxidized) oil were in good agreement with the experimental data, and average deviation between calculated and experimental data was less than 6.5 %. The amount obtained for binary interaction parameter K_{ij} was -0.0447 .

1. Introduction

The presence of contaminants in the lubricants is one of the main reasons of damage in rotating machines. Lubricant degradation under operation conditions is a serious problem that leads to significant economic losses. Varnish and sludge are a more prevalent problem in most of the hydraulic and lubrication oils. When lubricant undergoes oxidative (or thermal) degradation, the relatively polar byproducts are suspended in nonpolar oil and can adhere to metal (varnish) or precipitate (sludge). Sludge and varnish have similar chemical properties.

Sludge does not deposit on the metallic surfaces; rather it is suspended in oil bulk as a semi solid black lump (something like grease) [1]. Figure 1 shows an example of sludge on reservoir [1]. Varnish is an insoluble thin brown or black layer which deposits on the inner surface of bearings and hydraulic systems such as pipelines, valves, exchangers, filters, and other easily damaged equipment.

Figure 2 shows an example of varnish deposited on an Inlet Guide Vane (IGV) valve positioner from a large-frame turbine [1]. It should be noted that sludge and varnish are

*Corresponding author: m_dehghani@iust.ac.ir

formed as a result of oil degradation. Blockage in control valves and filters is a common problem in lubrication and hydraulic systems because of sludge formation.

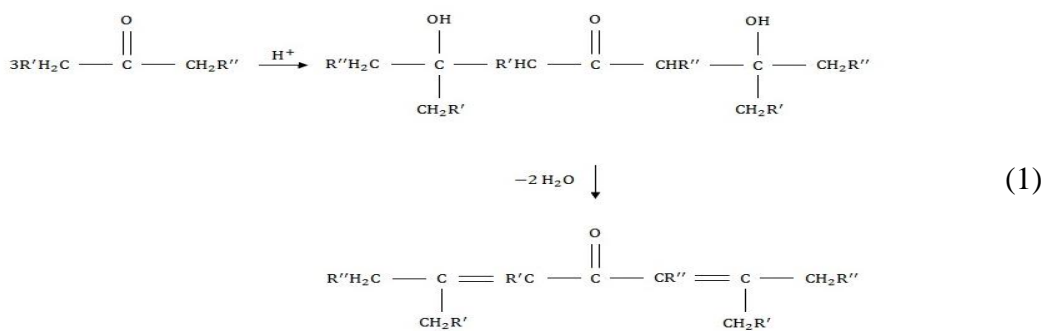


Figure 1. Sludge on Reservoir (Courtesy of Clarus Technologies).



Figure 2. Varnish formation on Inlet Guide Vane (IGV) valve from a gas turbine (Courtesy of Clarus Technologies).

Oil oxidation is the main reason for oil degradation. Several works have been concentrated on determination of mechanism and kinetic rate of oxidation reactions [2-4]. Gatto et al. [3] focused on oxidation of turbine oil. They showed that during oil oxidation, many products such as aldehyde, ketone, water, alcohol and carboxylic acid will be produced. Meanwhile aldehydes and ketones will take part in condensation reactions named as Aldol Condensation [5]. These reactions can progress leading to the formation of polar high molecular weight oligomers and low molecular weight polymers. In Eq. (1) a brief description about the nature of the sludge and varnish has been given, which shows how oligomers are produced. These materials are the main component of sludge.



Many works have focused on finding a reasonable cause for varnish or sludge formation [1, 6-10]. In this work we have tried to model sludge formation in lubricant oils utilizing a thermodynamic model. Sludge formation is a solid-liquid equilibrium (SLE) process. In the simplest case a pure crystalline solute and liquid solvent are in equilibrium. In this case solute has a finite solubility in the solvent, but the solvent solubility in the solid

is zero ($x_2^S = 1$) [11]. Sludge is a pseudo-polymer component with high molecular weight, therefore investigation of solubility of high normal alkanes and polymers such as polyethylene can be useful to select the best equation of state for prediction of solubility of sludge in oil. Sunil Kumar Maity [12] studied solubility of normal alkanes (C_{12} , C_{16} , C_{18} , C_{28} , ...) in some solvents such as C_5 , C_7 and C_{10} using PC-SAFT equation of state. Cheng

Pan and Maciej Radosz [11] presented a solid-liquid equilibrium model based on Copolymer SAFT equation of state. Copolymer SAFT was used for calculation of fugacity coefficient of solutes in liquid mixture. Solubility of naphthalene, normal alkanes and poly ethylene were studied using this model.

These studies showed that SAFT equation of state can predict equilibrium behavior of heavy hydrocarbons. Considering these results, in this work SAFT equation of state presented by Huang and Radosz [13-14] has been used for modeling of solid-liquid equilibrium in sludge-oil system. In order to check the ability of the equation of state, the experimental condition of sludge formation in the lubricant has been simulated. In the first step solubility of sludge has been measured, then in the second step solubility data have been modeled using SAFT EOS.

2. Experimental

The experimental work consists of two parts: investigation of oil degradation and measurement of sludge solubility in base oil (un-oxidized oil). In this work, the solubility data were used.

2.1. Material

In this work all materials (Toluene (99 % purity) and normal pentane (>0.95 % purity)) have been prepared from Merck Ltd. The base-stock SN100 produced by Behran Iranian Oil Company has been used as a sample. According to manufacturer's specifications, this base-stock is categorized as API I or Paraffinic group. Its physical properties have been reported as follows:

- Viscosity = 19.19 c St @ 40 °C (based on ASTM D-445)
- Viscosity Index = 100

- Specific Gravity = 0.836 @ 60 °F (based on ASTM D-4052)

2.2. Experimental setup

Thermal degradation of lubricants has been achieved in a setup similar to batch distillation setup. The goal of thermal degradation is production of sludge for obtaining solubility data. The apparatus is equipped with thermostatic bath, thermal sensor, round-bottom flask (5 liters), condenser, small round-bottom flask (0.5 liters) for collecting condensate, and an air reflux. A piece of Copper (with length of 20 cm) has been utilized to accelerate the rate of oxidation. In Fig.3, Schematic of our setup has been depicted. Base-stocks were heat-treated up to 90, 110, 130, and 150 °C. Different samples were withdrawn after different time intervals (including 3, 6, 12, 24 and 48 hours). Heating procedure continued for 48 hours. To obtain the solubility data (Solubility of sludge in fresh oil), the last samples (150 °C at 48 h) were used, because the sample was compared to other samples containing the highest amount of sludge.

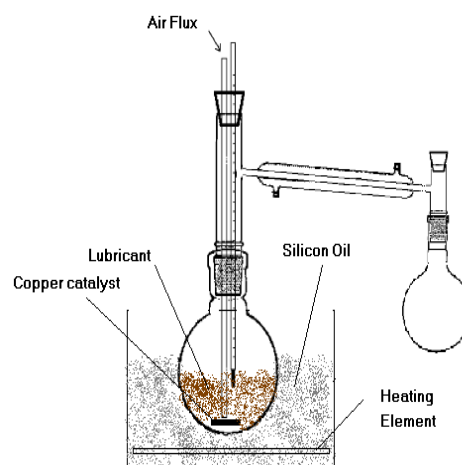


Figure 3. Schematic representation of the degradation system (Distillation system with air reflux and copper catalyst).

2.3. Measurement of sludge solubility in base oil

The obtained sludge in this work was analyzed by using an analytical package and it was found that a major part of this sludge is pseudo polymer which has already been discussed. In order to check whether the separated sludge included polar oligomer compounds or not, it was dissolved in normal pentane. Afterwards, the insoluble part was separated and dissolved in toluene as a polar solvent. It was observed that the main part of the sludge was completely soluble in toluene. Hence, it can be concluded that the main part of the sludge includes polar oligomers. This solution was then dried. The FTIR results of dried sludge confirm these results in Fig.4. A very sharp absorption was found at 1730 cm^{-1} , which suggests that the dried sludge contains polar oligomer compounds.



Figure 4. The FTIR result of dried sludge.

The solubility of the sludge in oil has been measured using refractive index experiments. To determine the refractive index, an OPTECH-RMI Refractometer has been used. The presence of contaminant in a liquid causes the refractive index to change so its value can be used as an indicator of solid phase concentration in the liquid phase. In this regard sampling has been done using a vacuum system to separate the solid phase (sludge) from the oil; all samples were filtered utilizing a 0.8 micron filter then dried in a vacuum oven. Separated sludge has been added to oil up to super saturation condition. Using a thermostatic bath, temperature of the mixture was increased gradually and refractive index of mixture was measured continuously. The refractive index of sludge–oil mixture varies versus the concentration of solid sludge in oil up to the saturation point. After saturation point the refractive index does not change with increasing the temperature. The measured solubility at different temperatures has been reported in Table1.

Table 1

Experimental SLE data for system (sludge (2) + lubricant oil (1)).

Wt Fraction (W_2)	T, K	Wt Fraction (W_2)	T, K
0.1002	303.1	0.6399	326
0.1234	304.2	0.6590	327
0.1668	306	0.7359	329.8
0.2612	309.9	0.8228	339.6
0.3327	312	0.9006	341
0.5271	318	1	344.5

3. Modeling

3.1. Solid – liquid Equilibrium

Equilibrium condition between two phases can be interpreted as the equality of the fugacities of the corresponding components in two phases. This condition also applies to the solid-liquid equilibrium.

$$f_2^L = f_2^S \quad (2)$$

Where, 2 means solute and the superscript S and L refer to the solid and liquid phases respectively. There are two approaches for calculating the liquid phase fugacity; activity coefficient (Eq. (3)) and fugacity coefficient (Eq. (4)):

$$f_2^L = \gamma_2 x_2^L f_2^{0L} \quad (3)$$

$$f_2^L = \phi_2^L x_2^L P \quad (4)$$

Solid phase has been assumed as a pure phase, so the solute fugacity in solid phase is:

$$f_2^S = f_2^{0S} \quad (5)$$

Substituting Eqs. (4) and (5) into Eq. (2), we will have:

$$\phi_2^L x_2^L P = f_2^{0S} \quad (6)$$

Then divide both sides of Eq. (6) by f_2^{0L} , which is the fugacity of pure subcooled liquid solute at constant T and P:

$$\frac{\phi_2^L x_2^L P}{f_2^{0L}} = \frac{f_2^{0S}}{f_2^{0L}} \quad (7)$$

Since f_2^{0L} is the fugacity of pure liquid, $x_2^L = 1$, so f_2^{0L} can be expressed as:

$$f_2^{0L} = \phi^0 P \quad (8)$$

Wherein f_2^{0L} is the fugacity coefficient of

pure sub-cooled liquid solute at constant T and P.

$$\text{Ln}(\phi_2^L x_2^L / \phi^0) = \text{Ln}(f_2^{0S} / f_2^{0L}) \quad (9)$$

The fugacity ratio of pure solute on the right hand side of Eq. (9) derived from a thermodynamic cycle given in Appendix A, is as follows:

$$\begin{aligned} & \text{Ln}(f_2^{0S} / f_2^{0L}) \\ &= \frac{\Delta H_m}{RT_m} \left(1 - \frac{T}{T_m}\right) - \frac{\Delta C_p}{RT_m} (T - T_m) \\ &+ \frac{\Delta C_p}{R} \text{Ln}(T/T_m) - \frac{\Delta v}{RT} (P - P^{sat}) \end{aligned} \quad (10)$$

Wherein P^{sat} is the solute saturated-vapor pressure at its melting temperature. Δv is the volume difference of liquid and solid solute ($\Delta v = v^L - v^S$). The second, third and fourth terms on the right-hand side of Eq. (10) are not of equal importance. The second and third terms can often be neglected. The last term in Eq. (10) accounts for the pressure effect. The pressure effect can be neglected at low pressures [11].

Thus at low pressures, we will have:

$$\text{Ln}(x_2^L \phi_2^L / \phi_0) = \frac{\Delta H_m}{RT_m} \left(1 - \frac{T}{T_m}\right) \quad (11)$$

Where T_m and ΔH_m are melting point and enthalpy of melting respectively. The fugacity coefficients of sludge in solution ϕ_2^L and of pure-liquid sludge ϕ_0 are calculated by SAFT equation of state presented by Huang and Radosz [13-14].

3.2. Equation of state

Molecular equations of state not only supply a beneficial thermodynamic basis for deriving chemical potentials or fugacities that are needed for phase equilibrium simulations but also allow for separating and quantifying the

effects of molecular structure and interactions on bulk properties and phase behavior [13]. Huang and Radosz [13] reported an equation of state for pure components, based on the statistical associating fluid theory (SAFT). The reference part of SAFT includes the hard-sphere, chain, and association terms which can be traced to the ideas and results of Chapman et al. [15-16] and Wertheim [17-19]. In addition, Huang and Radosz [14] extend this equation of state to mixtures of small, large, chain, and associating molecules over the whole density range using only one binary adjustable parameter that is temperature independent.

In this work, we have used these two equations of state proposed by Huang and Radosz [13-14]. They treated the effective molecular size (through hard sphere and chain terms) and molecular association as two major effects on the bulk properties of real fluids. In addition to the three pure component parameters characterizing non-associating molecules, v^{oo} , m and u^o , two association parameters, ε^{AA} and k^{AA} were used.

The residual Helmholtz energy is a sum of reference and dispersion parts:

$$a^{res} = a^{ref} + a^{disp} \quad (12)$$

The a^{ref} is a sum of hard-sphere, chain, and association terms:

$$a^{ref} = a^{hs} + a^{chain} + a^{assoc} \quad (13)$$

In this work, association term of this equation of state is neglected, because the pseudo polymer molecules of sludge are not

associated. So the residual Helmholtz energy is given by:

$$a^{res} = a^{seg} + a^{chain} \quad (14)$$

The segment Helmholtz energy a^{seg} , per mole of molecules, is:

$$a^{seg} = m a_o^{seg} \quad (15)$$

Where a_o^{seg} , per mole of segments, is the residual Helmholtz energy of nonassociated spherical segments and m is the segment number. a_o^{seg} is composed of hard sphere and dispersion parts:

$$a_o^{seg} = a_o^{hs} + a_o^{disp} \quad (16)$$

To calculate the hard sphere term, we can use proposed term by Carnahan and Starling [20]:

$$\frac{a_o^{hs}}{RT} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \quad (17)$$

Where η is the reduced density given by:

$$\eta = \left(\frac{\pi N_{Av}}{6}\right) \rho d^3 m \quad (18)$$

The dispersion term which provided the basis for the Perturbed Hard Chain Theory of Beret and Prausnitz [21] is computed by:

$$\frac{a_o^{disp}}{RT} = \sum_i \sum_j D_{ij} \left[\frac{u}{KT}\right]^i \left[\frac{\eta}{\tau}\right]^j \quad (19)$$

D_{ij} are universal constants. D_{ij} represents Chen and Kreglewski [22] constants which are listed in Table 2.

Table 2

Chen and Kreglewski [22] constants D_{ij} used in Eq. 19.

	i=1	i=2	i=3	i=4
j=1	-8.8043	2.9396	-2.8225	0.34
j=2	4.1646270	-6.0865383	4.7600148	-3.1875014
j=3	-48.203555	40.137956	11.257177	12.231796
j=4	140.43620	-76.230797	-66.382743	-12.110681
j=5	-195.23339	-133.70055	69.248785	0.0
j=6	113.51500	860.25349	0.0	0.0
j=7	0.0	-1535.3224	0.0	0.0
j=8	0.0	1221.4261	0.0	0.0
j=9	0.0	-409.10539	0.0	0.0

The chain term can be computed from:

$$\frac{a^{chain}}{RT} = (1 - m) \ln \frac{1 - \frac{1}{2}\eta}{(1 - \eta)^3} \quad (20)$$

Since Huang and Radosz [13] approximate their segments as hard spheres, they considered $g(d)^{hs}$ as the hard sphere radial distribution function:

$$g(d)^{hs} = \frac{1 - \frac{1}{2}}{(1 - \eta)^3} \quad (21)$$

This equation of state (SAFT) can be expressed as sum of compressibility factors (Appendix B).

Two reference terms of Eq. (12) can be extended to mixtures based on rigorous statistical mechanics [13]. As mentioned, in this work, association term is neglected.

Huang's hard-sphere term for mixtures is based on a theoretical result of Mansoori et al. [23], in which for the Helmholtz energy the equation is given by:

$$\frac{a^{hs}}{RT} = \frac{6}{\pi\rho} \left[\frac{(\xi_2)^3 + 3\xi_1\xi_2\xi_3 - 3\xi_1\xi_2(\xi_3)^2}{\xi_3(1 - \xi_3)^2} - \left[\xi_0 - \frac{(\xi_2)^3}{(\xi_3)^2} \right] \ln(1 - \xi_3) \right] \quad (22)$$

Where $\xi_{i=0-3}$ is a function of molar density ρ . This parameter was defined by Chapman et al. [16]:

$$\xi_k = \left(\frac{\pi N_{Av}}{6} \right) \rho \sum_i X_i m_i (d_{ii})^k \quad (23)$$

Where X is the mole fraction, m is the number of segments per molecule, and d is the effective, temperature-dependent segment diameter calculated from Eq.(24):

$$d = \sigma (1 - 0.12 \exp(-3u^0/T)) \quad (24)$$

Mansoori et al. [23] derived a useful expression for the pair correlation function for a mixture of hard spheres:

$$g_{ij}(d_{ij})^{seg} \approx g_{ij}(d_{ij})^{hs}$$

$$= \frac{1}{1 - \xi_3} + \frac{3d_{ii} d_{jj}}{d_{ii} + d_{jj}} \frac{\xi_2}{(1 - \xi_3)^2}$$

$$+ 2 \left[\frac{d_{ii} d_{jj}}{d_{ii} + d_{jj}} \right]^2 \frac{\xi_2^2}{(1 - \xi_3)^3} \quad (25)$$

With d_{ij} representing $d_{ii} d_{jj} / d_{ii} + d_{jj}$, Eq. (25) for like segments becomes:

$$g_{ii}(d_{ii})^{seg} \approx g_{ii}(d_{ii})^{hs}$$

$$= \frac{1}{1 - \xi_3}$$

$$+ \frac{3d_{ii}}{2} \frac{\xi_2}{(1 - \xi_3)^2}$$

$$+ 2 \left[\frac{d_{ii}}{2} \right]^2 \frac{\xi_2^2}{(1 - \xi_3)^3} \quad (26)$$

The chain term for mixture of hard spheres is given by:

$$\frac{a^{hs}}{RT} = \sum_i X_i (1 - m_i) \ln(g_{ii}(d_{ii})^{hs}) \quad (27)$$

Where g_{ii} is evaluated for the interaction of two spheres i in a mixture of spheres, evaluated at the hard-sphere contact, given by Eq. (26).

A general expression for the dispersion term is:

$$\frac{a^{disp}}{RT} = m \frac{a_0^{disp}}{RT} \quad (28)$$

Wherein m is the segment number and a_0^{disp} is the dispersion Helmholtz energy, per mole of segments. The a_0^{disp} term is a function of the segment energy $/kT$.

The mixing rule presented by Huang [16] for u/kT is:

$$\frac{u}{kT} = \frac{\sum_i \sum_j X_i X_j m_i m_j \left[\frac{u_{ij}}{kT} \right] (v^0)_{ij}}{\sum_i \sum_j X_i X_j m_i m_j (v^0)_{ij}} \quad (29)$$

Where

$$(v^0)_{ij} = \left[\frac{1}{2} \left[(v^0)_i^{1/3} + (v^0)_j^{1/3} \right] \right]^3 \quad (30)$$

$$u_{ij} = (1 - k_{ij})(u_{ii} u_{jj})^{1/2} \quad (31)$$

Wherein k_{ij} is an empirical binary parameter, fitted to experimental data.

This equation of state can be expressed as sum of compressibility factors (Appendix C). The used set of equations to calculate the fugacity coefficient can be found in Appendix C. Bisection method was used to solve equation of state. The fugacity coefficients of sludge in solution φ_2^L and of pure-liquid sludge φ_0 can be calculated by Eq. (C-12).

4. Results and discussion

According to complexity of the sludge-oil system, we made some assumptions for modeling:

- Sludge and oil are considered as a pure substance.
- Sludge is a heavy pseudo-polymer compound.
- According to assumption (2), association term in SAFT EOS can be ignored.

The correlations proposed by Huang and Radosz [13] have been used to obtain SAFT parameters of oil. These correlations are given by:

$$m = A^{(1)} + A^{(2)} MM \quad (32)$$

$$mv^{oo} = A^{(1)} + A^{(2)} MM \quad (33)$$

$$u^o/k = A^{(1)} - A^{(2)} \exp[-A^{(3)} MM] \quad (34)$$

Where $A^{(1)}$, $A^{(2)}$ and $A^{(3)}$ are coefficients which were reported by Huang and Radosz [13] and MM is molecular weight which is 380 g/mole for oil (using GPC method). Since liquid density and vapor pressure experimental data of sludge were not found, SLE experimental data have been used to fit SAFT parameters of sludge.

The results of calculations are shown in the

Table 3. For sludge-oil system, absolute average deviations (AAD %) of calculated

SAFT parameters are less than 1.4 %.

Table 3

SAFT parameters for sludge and oil.

Material	u^o/k (K)	M	v^{oo} (mL/mol)
Sludge	257.7085	10.2398	11.036
Oil	257.4317	16.3005	13.1024

Values of melting temperature (T_m) and enthalpy of melting (ΔH_m) for obtained sludge (using DTA method) in this work can be seen in Table 4. These values have been obtained by using thermal analysis.

Table 4

Values of enthalpy of melting and melting temperature of sludge.

ΔH_m (J/mol)	T_m (K)
56520	344.5

In modeling work by using MATLAB software, Nelder-Mead simplex method (Lagarias et al. [24]) has been used for optimization and our objective function (OF) is:

$$OF = \sum_{i=1}^N \left[\frac{(\text{Calculated}(i) - \text{Experiment}(i))}{\text{Experiment}(i)} \right]^2 \quad (35)$$

Where N is the number of data points. The calculated results for sludge solubilities are in good agreement with the experimental data, and average deviation between calculated and experimental data is less than 6.5 %. Modeling results can be seen in Fig. 5. As can be seen, solubility increases with temperature increment and our modeling predicted this treatment well. This figure shows that SLE data fits better with SAFT model with $K_{ij} = -0.0447$ rather than ideal solubility values.

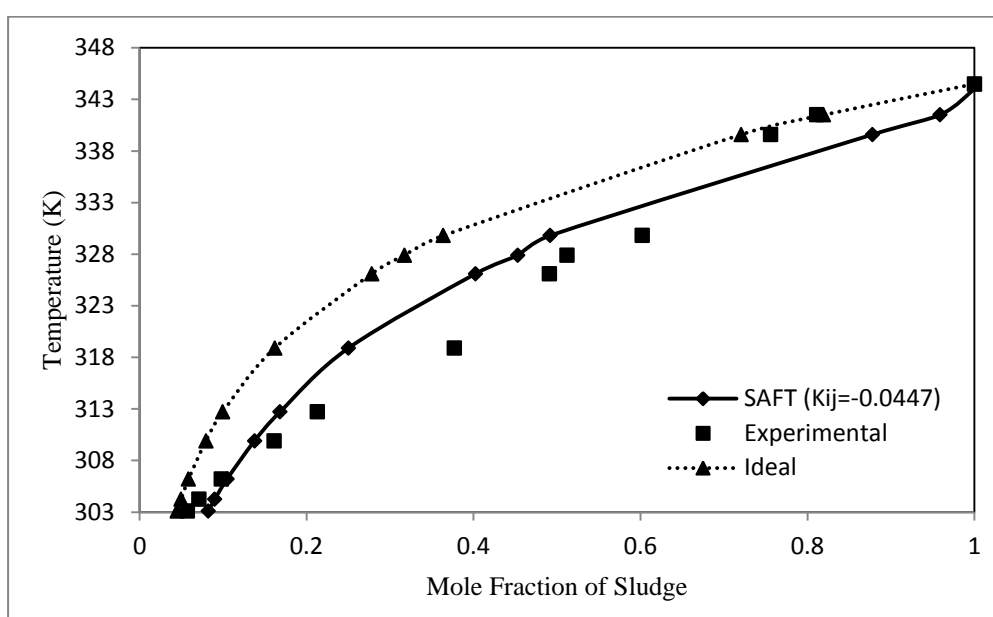


Figure 5. SLE for system (Sludge + Lubricant oil) at 1 bar.

4. Conclusions

In this work, Sludge formation in lubricant oil (SN-100 base stock) has been simulated by using distillation-like set-up, and then solubility-temperature experimental data of sludge-oil system has been obtained. Different samples were withdrawn after different time intervals (including 3, 6, 12, 24 and 48 hours). Heating procedure was continued for 48 hours. To obtain the solubility data, the last samples (150 °C at 48 h) were used. FTIR result and determination of molecular weight indicated that the solid obtained from samples was polymeric. So it has been assumed that sludge is a heavy pseudo-polymer compound. Solid-Liquid equilibrium (SLE) of this system has been investigated. According to this assumption that sludge is a heavy pseudo-polymer compound, association term in SAFT EOS was ignored. SAFT parameters for oil and sludge have been obtained by some correlations and SLE data fitting respectively. By using these parameters, modeling results have good agreement with obtained solubility experimental data. This means that increase in the solubility with temperature increment of the oil has been well predicted. Average deviation between calculated and experimental data was less than 6.5 %. The amount obtained for binary interaction parameter K_{ij} was -0.0447 .

Nomenclature

a	molar Helmholtz energy (total, res, seg, bond, assoc, etc.) [per mole of molecules].
a_o	segment molar Helmholtz energy (seg) [per mole of segments].
d	temperature-dependent segment diameter [Å^0].

f	fugacity [bar].
k	Boltzman's constant $\approx 1.381 \times 10^{-23}$ J/K.
m	effective number of segments within the molecule (segment number).
M	number of association sites on molecule.
N	total number of molecules.
N_{AV}	Avogadro's number $\approx 6.02 \times 10^{23}$ molecules per mol.
P	pressure [bar].
R	gas constant.
T	temperature [K].
u/k	temperature-dependent dispersion energy of interaction.
v	molar volume.
v^L	liquid molar volume [mL/mol of solute].
v^S	solid molar volume [mL/mol of solute].
v^{00}	temperature-independent segment volume [mL/mol of segments].
X	mole fraction.
$Z = Pv/RT$	compressibility factor.
$\eta = \left(\frac{\pi N_{AV}}{6}\right) \rho d^3 m$	pure-component reduced density, the same for segments and molecules.
ρ	molar density [mol/A^3].
Φ	fugacity coefficient.
γ	activity coefficient.

Subscripts

res	residual.
hs	hard sphere.
seg	segment.
$assoc$	associating, or due to association.

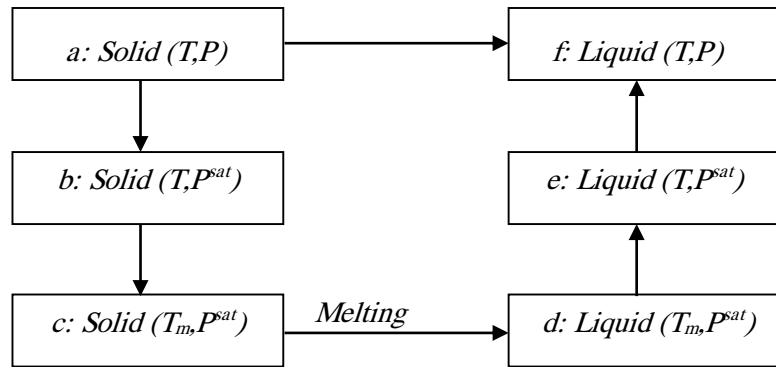
Abbreviations

API	American Petroleum Institute.
EOS	Equation of State.
PC-SAFT	Perturbed Chain Statistical Associating Fluid Theory.
SAFT	Statistical Associating Fluid Theory.

Appendix

Appendix A. Derivation of the pure-solute f_2^{0L}/f_2^{0S}

The fugacity ratio of pure solute is concluded from a thermodynamic cycle. Similar to what Prausnit et al. [25] did for the temperature effect, Pan and Rasosz [11] produced a loop for both temperature and pressure effects. The detailed derivations are shown below.



The molar Gibbs energy change for solute from state (a) to state (f) is related to the fugacities of solid and subcooled liquid.

$$\Delta G(a \rightarrow f) = RT \ln\left(\frac{f_2^{0L}}{f_2^{0S}}\right) \quad (\text{A-1})$$

It is also related to the corresponding enthalpy and entropy changes by:

$$\Delta G(a \rightarrow f) = \Delta H(a \rightarrow f) - T \Delta S(a \rightarrow f) \quad (\text{A-2})$$

For the enthalpy change from state (a) to state (f), we have:

$$\Delta H(a \rightarrow f) = \Delta H(a \rightarrow b) + \Delta H(b \rightarrow c) + \Delta H(c \rightarrow d) + \Delta H(d \rightarrow e) + \Delta H(e \rightarrow f) \quad (\text{A-3})$$

Using the Maxwell relations,

$$\left(\frac{\partial H}{\partial P}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_P \quad \text{and} \quad \left(\frac{\partial H}{\partial T}\right)_P = C_P \quad (\text{A-4})$$

Eq. (A-3) can be rewritten in terms of the heat capacity, C_P , and the enthalpy of melting, ΔH_m , as follows:

$$\begin{aligned} \Delta H(a \rightarrow f) = & \int_P^{P^{sat}} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right]^S dP + \int_T^{T_m} C_P^S dT + \Delta H_m + \int_T^{T_m} C_P^S dT \\ & + \int_{P^{sat}}^P \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right]^L dP \end{aligned} \quad (\text{A-5})$$

For the entropy change from state (a) to state (f), we have:

$$\Delta S(a \rightarrow f) = \Delta S(a \rightarrow b) + \Delta S(b \rightarrow c) + \Delta S(c \rightarrow d) + \Delta S(d \rightarrow e) + \Delta S(e \rightarrow f) \quad (\text{A-6})$$

Using the Maxwell relations again,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P \quad \text{and} \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad (\text{A-7})$$

We rewrite the entropy change given by Eq. (A-6) as:

$$\begin{aligned} \Delta H(a \rightarrow f) = & \int_P^{psat} \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right]^S dP + \int_T^{T_m} C_P^S dT + \Delta H_m + \int_T^{T_m} C_P^S dT \\ & + \int_{psat}^P \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right]^L dP \end{aligned} \quad (A-8)$$

Substituting Eqs. (A-5) and (A-8) into Eq. (A-2), we obtain

$$\begin{aligned} \Delta G(a \rightarrow f) = & \Delta H(a \rightarrow f) - T \Delta S(a \rightarrow f) \\ = & \int_{psat}^P (v^L - v^S) dP \\ & + \int_{T_m}^T (C_P^L - C_P^S) dT \\ & - T \int_{T_m}^T (C_P^L - C_P^S) \frac{dT}{T} + \Delta H_m \left(1 - \frac{T}{T_m} \right) \\ = & \Delta v (P - P^{sat}) + \Delta C_P (T - T_m) - T \Delta C_P \ln \left(\frac{T}{T_m} \right) + \Delta H_m \left(1 - \frac{T}{T_m} \right) \end{aligned} \quad (A-9)$$

Wherein $\Delta C_P = C_P^L - C_P^S$, and $\Delta v = v^L - v^S$. Since pressure has little effect on Δv , Δv can be taken out of the integration directly. Substituting Eq. (A-9) into Eq. (A-1), we get the fugacity ratio given in Eq. (7).

Appendix B. The compressibility factor of pure liquid

The final equation of state can be presented as a sum of the compressibility factor terms:

$$Z - 1 = Z^{seg} + Z^{chain} \quad (B-1)$$

$$Z^{seg} = m \left[\frac{4\eta - 2\eta^2}{(1 - \eta)^3} + \sum_i \sum_j j D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{\eta}{\tau} \right]^j \right] \quad (B-2)$$

$$Z^{chain} = (1 - m) \frac{\frac{5}{2}\eta - \eta^2}{(1 - \eta)(1 - \frac{1}{2}\eta)} \quad (B-3)$$

Appendix C. The compressibility factor of solution

A general parameterization concept used in Huang's work [14] is that proposed by Topliss [26]. The parameterization of the SAFT equation will introduce eight parameters, A-H, whose definitions are:

$$A = \sum_i X_i m_i (d_i)^0 \quad (C-1)$$

$$B = \sum_i X_i m_i (d_i)^1 \quad (C-2)$$

$$C = \sum_i X_i m_i (d_i)^2 \quad (C-3)$$

$$D = \sum_i X_i m_i (d_i)^3 \quad (C-4)$$

$$E = \sum_i X_i m_i \quad (C-5)$$

$$F = a^{chain}/RT = \sum_i X_i (1 - m_i) \ln(g_{ii}(d_{ii})) \quad (C-6)$$

$$G = \frac{u}{kT} = \frac{\sum_i \sum_j X_i X_j m_i m_j \left[\frac{u_{ij}}{kT} \right] (v^0)_{ij}}{\sum_i \sum_j X_i X_j m_i m_j (v^0)_{ij}} \quad (C-7)$$

$$H = \frac{a^{assoc}}{RT} = \sum_i X_i \left[\sum_{A_i} \left[\ln X^{A_i} - \frac{X^{A_i}}{2} \right] + \frac{1}{2} M_i \right] \quad (C-8)$$

After parameterization, the residual Helmholtz energy can be expressed simply by:

$$\begin{aligned} \frac{a^{res}}{RT} = & \frac{3 \frac{BC}{D} \xi - \frac{C^3}{D^2}}{1 - \xi} + \frac{\frac{C^3}{D^2}}{(1 - \xi)^2} + \left[\frac{C^3}{D^2} - A \right] \ln(1 - \xi) + F \\ & + E \sum_i \sum_j D_{ij} G^i \left[\frac{\xi}{\tau} \right]^j + H \end{aligned} \quad (C-9)$$

Using these eight parameters, Compressibility factor, Z , can be expressed by:

$$Z = 1 + \rho \left[\frac{\partial \bar{a}}{\partial \rho} \right]_{T,X} = 1 + \rho \left[\frac{\partial \bar{a}}{\partial \rho} \right]_{T,\beta} + \sum_{i=1}^8 \left[\frac{\partial \bar{a}}{\partial \beta_i} \right]_{T,\rho,\beta_{i \neq j}} \left[\frac{\partial \beta_i}{\partial \rho} \right]_{T,X} \quad (C-10)$$

Where

$$\bar{a}(\rho, T, X) = \bar{a}[\rho, T, \beta(\rho, T, X)] = \frac{a^{res}}{RT} \quad (C-11)$$

An expression for log fugacity coefficient $\ln \phi_i(\rho, T, X)$ is:

$$\ln \phi_i = \left[\frac{\partial (N\bar{a})}{\partial n_i} \right]_{\rho, T, n_{i \neq j}} + (Z - 1) - \ln Z \quad (C-12)$$

Where N is the total number of moles and the residual is defined with respect to a mixture of ideal gases at the same ρ , T , and X .

$$\left[\frac{\partial (N\bar{a})}{\partial n_i} \right]_{\rho, T, n_{k \neq i}} = \bar{a} + \left[\frac{\partial \bar{a}}{\partial X_i} \right]_{T,\rho, X_{k \neq i}} - \sum_j X_j \left[\frac{\partial \bar{a}}{\partial X_j} \right]_{T,\rho, X_{k \neq j}} \quad (C-13)$$

Where

$$\left[\frac{\partial \bar{a}}{\partial X_i} \right]_{T,\rho, X_{k \neq i}} = \sum_{l=1}^8 \frac{\partial \bar{a}}{\partial \beta_l} \frac{\partial \beta_l}{\partial x_i} \quad (C-14)$$

$$\left[\frac{\partial \bar{a}}{\partial X_j} \right]_{T,\rho, X_{k \neq j}} = \sum_{l=1}^8 \frac{\partial \bar{a}}{\partial \beta_l} \frac{\partial \beta_l}{\partial x_j} \quad (C-15)$$

References

- [1] Fitch, J. C., and Gebrain, S., "Review of degradation Mmechanisms leading to sludge and varnish in modern turbine oil formulations", *Journal of ASTM International*, **3** (8), 1 (2006).
- [2] Stark, M. S., Wilkinson, J. J., Smith, J. R. L., Alfahad, A. and Pochopien, B. A.,

- “Autoxidation of branched alkanes in the liquid phase”, *Ind. Eng. Chem. Res.*, **50** (2), 817 (2011).
- [3] Gatto, V. J., Moehle, W. E., Cobb, T. W. and Schneller, E. R., “Oxidation fundamentals and its application to turbine oil testing”, *Journal of ASTM International*, **3** (4), 1 (2006).
- [4] Ingold. K. U., “Inhibition of the autoxidation of organic substances in the liquid phase”, *Chem. Soc. Rev.*, **61** (1), 563 (1961).
- [5] March. J., *Advanced organic chemistry*, 3rd ed., John Wiley & Sons Inc., New York, USA, p. 172 (1985).
- [6] Thompson, B. T. and Livingstone, G., “Using quantitative spectrophotometric analysis as a predictive tool to measure varnish potential”, *Proceedings of Lubrication Excellence 2004 Conference*, Nashville, USA, pp. 23-25, (2004).
- [7] Sasaki, A., Uchiyama, S. and Yamamoto, T., “Free radicals and oil auto-oxidation due to spark discharges of static electricity”, *Lubr. Eng.*, **55** (9), 24 (1999).
- [8] Sasaki, A., Uchiyama, S. and Yamamoto, T., “Generation of static electricity during oil filtration”, *Lubr. Eng.*, **55** (9), 14 (1999).
- [9] Sasaki, A., Uchiyama, S. and Kawasaki, M., “Varnish formation in the gas turbine oil systems”, *Journal of ASTM International*, **5** (2), 1 (2008).
- [10] Kouame, S. D. and Liu, E., “Characterization of fully and partially additized lubricant deposits by temperature programmed oxidation”, *Tribology International*, **72** (1), 58 (2014).
- [11] Pan, C. and Radosz, M., “Modeling of solid–liquid equilibria in naphthalene, normal-alkane and polyethylene solutions”, *Fluid Phase Equilibria*, **155** (1), 57 (1999).
- [12] Maity, S. K., “Modeling and simulation of solid-liquid equilibrium by perturbed-chain statistical associating fluid theory”, M-Tech Thesis, Indian Institute of Technology, Kharagpur (2003).
- [13] Huang, S. H. and Radosz M. “Equation of state for small, large, polydisperse and associating molecules”, *Ind. Eng. Chem. Res.*, **29** (11), 2284 (1990).
- [14] Huang, S. H. and Radosz, M., “Equation of state for small, large, polydisperse and associating molecules: Extension to fluid mixtures”, *Ind. Eng. Chem. Res.*, **30** (8), 1995 (1991).
- [15] Chapman, W. G., Gubbins, K. E., Jackson G. and Radosz, M., “Equation-of-state solution model for associating fluids”, *Fluid Phase Equilibria.*, **52** (1), 31 (1989).
- [16] Chapman. W. G., Gubbins, K. E., Jackson, G. and Radosz, M., “New reference equation of state for associating liquids”, *Ind. Eng. Chem. Res.*, **29** (8), 1709 (1990).
- [17] Wertheim, M. S., “Fluids with highly directional attractive forces: I. Statistical thermodynamics”, *J. Stat. Phys.*, **35** (1), 19 (1984).
- [18] Wertheim, M. S., “Fluids with highly directional attractive forces: III. Multiple attraction sites”, *J. Stat. Phys.*, **42** (3), 459 (1986).
- [19] Wertheim, M. S., “Fluids of dimerizing hard spheres and fluid mixtures of hard spheres and dispheres”, *J. Chem. Phys.*, **85** (5), 2929 (1986).
- [20] Carnahan, N. F. and Starling, K. E. J., “Equation of state for nonattracting rigid spheres”, *Chem. Phys.*, **51** (2), 635

- (1969).
- [21] Beret, S. and Prausnitz, J., "Perturbed hard-chain theory: An equation of state for fluids containing small or large molecules", *M. AZChE J.*, **21** (6), 1123 (1975).
- [22] Chen, S. S. and Kreglewski, A., "Applications of the augmented van der Waals theory of fluids: I. Pure fluids", *Ber. Bunsen-Ges. Phys. Chem.*, **81** (10), 1048 (1997).
- [23] Mansoori, G. A., Carnahan, N. F., Starling, K. E. and Leland T. W., "Equilibrium thermodynamic properties of the mixture of hard spheres", *J. Chem. Phys.*, **54** (4), 1523 (1971).
- [24] Lagarias, J. C., Reeds, J. A., Wright, M. H., and Wright, P. E., "Convergence properties of the Nelder-Mead simplex method in low dimensions", *SIAM Journal of Optimization.*, **9** (1), 112 (1998).
- [25] Prausnitz, J. M., Lichtenthaler, R. N. and Azevedo, E. G. D., *Molecular thermodynamics of fluid-phase equilibria*, 3rd ed., Prentice Hall PTR, New Jersey, USA, p. 641 (1999).
- [26] Topliss, R. J., "Techniques to facilitate the use of equations of state for complex fluid-phase equilibria", Ph.D. Thesis, University of California, Berkeley, (1985).