



# Regular solution based approach to modeling asphaltene precipitation from native and reacted oils: Part 1, molecular weight, density, and solubility parameter distributions of asphaltenes



D.P. Powers<sup>a</sup>, H. Sadeghi<sup>a</sup>, H.W. Yarranton<sup>a,\*</sup>, F.G.A. van den Berg<sup>b</sup>

<sup>a</sup>Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr. NW, Calgary, Alberta T2N 1N4, Canada

<sup>b</sup>Shell Technology Centre Amsterdam, Shell Global Solutions International BV, PO Box 38000, 1030 BN Amsterdam, The Netherlands

## HIGHLIGHTS

- Property distributions determined for native and cracked asphaltenes.
- Asphaltene molecular weights follow exponential mole frequency distribution.
- Asphaltene densities and solubility parameters correlated to cumulative mass fraction.

## ARTICLE INFO

### Article history:

Received 31 December 2015

Received in revised form 1 March 2016

Accepted 2 March 2016

Available online 19 March 2016

### Keywords:

Asphaltenes

Self-association

Molecular weight

Density

Solubility parameter

Modified regular solution theory

## ABSTRACT

Asphaltenes self-associate and their molecular weight, density, and solubility parameter distributions are factors in asphaltene precipitation. Thermo- and hydrocracking alter these distributions and these changes must be accounted for when modeling solubility. To determine these distributions for reacted asphaltenes, heptane extracted asphaltenes from native, thermo-cracked, and hydrocracked crude oils were fractionated into solubility cuts. The asphaltenes were dissolved in toluene and then partially precipitated at specified ratios of heptane-to-toluene to generate sets of light (soluble) and heavy (insoluble) cuts. The molecular weight and density were measured for each cut.

The molecular weight data were fitted with a self-association model in order to predict the distributions at any given concentration. The asphaltenes were found to contain a significant fraction of neutral (non-associating) species and the molecular weight distribution were represented with an exponential mole frequency distribution. The density distributions were determined directly from the data and were correlated to the cumulative mass frequency. Solubility parameters were calculated using a modified regular solution model with the measured density and molecular weight distributions as inputs. The solubility parameters were also correlated to the cumulative mass frequency distribution. These distributions provided fits to asphaltene yield data within the error of the measurements. Guidelines are provided to predict asphaltene solubility when fraction data are not available, and the model using the guidelines matched the experimental data in this study with an average deviation of 4 wt%.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Asphaltenes can precipitate upon a change in temperature, pressure, or composition and this precipitation can lead to deposition and fouling in reservoirs, wellbores, or surface facilities. Asphaltene precipitation can occur during the depressurization of light crude oils [1,2], when diluting heavy oils for recovery or transport processes [3], and when different streams are blended to obtain desired feed or product properties in refinery processes

[4,5]. In refineries, some issues include the reduction of the overall rates of hydrotreating reactions, deactivation of catalysts from surface deposition, and increased coke formation (asphaltenes are a coke precursor). In general, asphaltene precipitation limits the ultimate level of conversion [6,7]. Hence, it is necessary to prevent or mitigate asphaltene precipitation and, as a starting point, a reliable method to predict asphaltene precipitation at different conditions is required for both upstream and downstream operations.

Asphaltene precipitation from native (non-reacted) dead crude oils and crude oil blends has been modeled with both equation of state and regular solution approaches [8–16]. These models

\* Corresponding author.

## Nomenclature

$A(T)$	asphaltene monomer enthalpy of vaporization	<i>Greek symbols</i>	
$A, B, C, D$	constants in cumulative mass frequency equation	$\delta$	solubility parameter
$A_1, A_2$	non-ideality constants in VPO calibration equation	$\lambda$	exponential parameter in cumulative mole frequency equation
$C$	concentration	$\rho$	density
$c, d$	constants in solubility parameter correlation	$\tau$	fitting parameter in density equation
$f$	cumulative mass fraction	<i>Subscripts</i>	
$f^*$	cumulative mole fraction	0	initial condition
$\Delta E$	voltage difference in VPO	A	asphaltenes
$K$	association “reaction” constant	$i$	component
$K_i^{HL}$	equilibrium constant of component $i$ between light and heavy liquid phases	$mix$	mixture
$K_{VPO}$	VPO calibration constant	$min$	minimum
$\dot{m}_{524^\circ C+}$	mass flow rate of the 524 °C+ boiling cut	$max$	maximum
$MW$	molecular weight	$N$	neutrals
$N$	neutral molecule	$P$	propagators
$R$	universal gas constant	$S$	solvent
$P_i$	propagator aggregate of $i$ molecules	$T$	terminators
$T$	temperature	<i>Superscripts</i>	
$T_1$	terminator molecule	$H$	heavy phase
$v$	molar volume	$L$	light phase
$w$	mass fraction	$n$	shape factor for solubility parameter correlation
$x$	mole fraction		
$X$	fractional conversion		

require property distributions for the crude oil constituents and particularly for the asphaltenes. For example, the regular solution approach, which is the focus of this work, requires the molecular weight, density, and solubility parameter distributions. Determining asphaltene properties is challenging because asphaltenes are a solubility class (insoluble in  $n$ -alkanes, such as  $n$ -pentane and  $n$ -heptane, and soluble in aromatic solvents, such as toluene) containing hundreds of thousands and perhaps millions of species [17], some of which tend to self-associate into nano-aggregates [18,19]. While functional groups within the asphaltenes have been identified, molecular structures and size distributions have proven difficult to determine.

The measured apparent molecular weights of native (unreacted) asphaltenes range from a few hundred to a few hundred thousand g/mol, depending on the technique used. Vapor pressure osmometry (VPO) measurements show that the apparent molecular weight increases with increasing asphaltene concentration and decreases with increasing temperature [20–22]. The changes in molecular weight are attributed to asphaltene self-association where the reported molecular weight corresponds to an average molecular weight of the asphaltene nano-aggregates. Calorimetric titration [23,24], small angle neutron scattering [25,26], and interfacial tension measurement [21,27] confirm self-association in asphaltenes.

Asphaltenes molecular weight measured from different methods and sources provide a consistent average monomer molecular weight of approximately 1000 g/mol [18,19,28–30]. For example, molecular weights from VPO suggest monomer molecular weights of 1000–2000 g/mol [20,31]. Fluorescence depolarization (FD) gives asphaltene molecular weights between 500 and 1000 g/mol [32]. Diffusion measurements such as Taylor dispersion, nuclear magnetic resonance (NMR), and fluorescence correlation spectroscopy are consistent with these values [33–36].

VPO measurements indicate that the asphaltene nano-aggregate molecular weight distribution ranges from approximately 2000 g/mol to more than 30,000 g/mol with average molecular weights from 3000 to 10,000 g/mol depending on the source

asphaltenes. The VPO data are in good agreement with those measured by gel permeation chromatography (GPC) and molecular film methods [29,37,38]. GPC has the advantage of not being limited by the low vapor pressure of asphaltenes; however, the results obtained from this method can be affected by asphaltene adsorption which can cause calibration error for higher molecular weights [39]. Recent time-of-flight data for nanoaggregate molecular weight are consistent with VPO measurements [17]. On the other hand, observed molecular weight of aggregates from combination of ultracentrifugation and X-ray scattering measurements are an order of magnitude larger than VPO results [40].

Agrawala and Yarranton [41] modeled asphaltene association analogously to linear polymerization. They used this “terminator/propagator” model and estimated the molecular weight distribution of asphaltene nano-aggregates. Barrera et al. [31] fitted this association model to molecular weight data for fractionated native asphaltenes and demonstrated that the fitted molecular weight distributions could be represented with a Gamma distribution function. The Gamma distribution is a more convenient form in which to represent the molecular weight distribution and is used in the regular solution model that forms the basis of this study [11,12]. Density distributions have also been measured for several asphaltenes from native crude oils and a solubility parameter correlation has been developed for native asphaltenes [11,12,31].

Most research in asphaltene precipitation modeling has focused on native asphaltenes. However, cracking by definition will alter the size distribution and properties of the asphaltenes including the  $H/C$  ratio, metal content, aromaticity factor, density, and molecular weight [42–48]. Typically, in both thermo- and hydrocracking, aliphatic chains are cracked off the asphaltenes and, at high conversions, highly condensed structures are expected with lower molecular weight, lower  $H/C$  ratio, higher density, and increased aromaticity. Conversion also appears to decrease the average molecular weight of the asphaltene aggregates [6]. However, it is unknown if reacted asphaltenes self-associate in the same manner as upstream asphaltenes since their molecular structure has been altered. Lababidi et al. [49] found that thermal

Download English Version:

<https://daneshyari.com/en/article/205015>

Download Persian Version:

<https://daneshyari.com/article/205015>

[Daneshyari.com](https://daneshyari.com)