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Applicability of simple asphaltene thermodynamics for asphaltene gradients in oilfield reservoirs: The Flory-Huggins-Zuo Equation of State with the Yen-Mullins model

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ABSTRACT

In recent years, the Flory-Huggins-Zuo Equation of State (FHZ EoS) has been utilized to treat asphaltene gradient data in many oilfield reservoirs. The FHZ EoS employs asphaltene species from the Yen-Mullins model consisting of molecules, nanoaggregates and clusters of nanoaggregates; the specific species used depends primarily on the concentration of asphaltenes but also on the asphaltene stability. Reservoirs with equilibrated asphaltenes are repeatedly found to produce oil as a single flow unit addressing a key reservoir property. For crude oils with moderate concentrations of asphaltenes (a few%), asphaltenes are typically dispersed as nanoaggregates. In crude oils with high concentrations of asphaltenes (~10%), asphaltenes are typically dispersed as clusters of nanoaggregates. This paper examines a reservoir with a crude oil of moderate concentration of asphaltenes where a secondary charge of methane created some limited instability of asphaltenes. Many pressure and fluid measurements are made to determine that indeed the fluid column is equilibrated. The FHZ EoS and the Yen-Mullins model in this equilibrated oil column are then compared with the asphaltene gradient; excellent agreement is obtained extending the use of this thermodynamic modeling to crude oils with limited asphaltene instability. Downhole fluid analysis (DFA) is used to delineate the asphaltene gradient, and both DFA and lab data are used for determination of solution gas content of oil samples. Conventional gas chromatography, two-dimensional gas chromatography (GC × GC) and gas isotope analysis are performed to analyze the oils, all with a focus to test and ensure thermodynamic equilibrium of the oil column. The mixed charge of an oil and a secondary gas is confirmed identifying the source of asphaltene instability. The result of the asphaltene instability is to create a fraction of crude oil at the base of the oil column with asphaltenes dispersed as clusters of asphaltenes, thus exhibiting a larger asphaltene gradient there. Fluid inclusion measurements are useful to indicate the sequence of events in gas and oil charging into the reservoirs in geologic time. The Flory-Huggins-Zuo EoS and the Yen-Mullins model continue to be confirmed in oilfield studies as well as in the laboratory, even in cases of limited asphaltene instability observed here.

1. Introduction

The efficient production of crude oil requires an overall understanding of the reservoir and its contained fluids. Naturally, thermodynamic modeling of reservoir fluids is highly desirable. Reservoir crude oils consist of dissolved gases, liquids and dissolved solids, the asphaltenes. The cubic equation of state has been used for 40 years to characterize the gas-liquid equilibria of reservoir fluids [1]. Unfortunately, until recently, the modeling of asphaltenes in oilfield reservoirs has been largely absent, primarily because of the lack of thermodynamic models for asphaltenes. For a variety of reasons, it is important to model the asphaltenes. For example, the viscosity of black oils (typically with several percent of asphaltenes) and heavy oils (often with > 10% asphaltenes) varies more than exponentially on asphaltene

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content [2]. Viscosity variations in reservoirs are often associated with biodegradation and other complex processes in reservoirs which can concentrate asphaltenes [3,4]. In addition, asphaltene gradients in reservoirs are used to determine the extent of flow connectivity across oilfields [5–10], thereby addressing a critically important property of reservoirs.

A thermodynamic model for treating asphaltene gradients in reservoir crude oils requires knowledge of the size of asphaltene particles to treat the effects of gravity. There had been enormous debate in the literature about asphaltene molecular weight [11] and the nature of asphaltene nanocolloidal aggregation. Consequently, asphaltenes had not been incorporated into thermodynamic modeling of gradients in reservoirs limiting the theoretical modeling of reservoir crude oils to the cubic EoS. In addition, it is important to assess as best as possible, the extent of thermodynamic equilibrium for thermodynamic modeling of reservoirs.

Equilibrium means that there is no time dependence, even in geologic time, and that there is no entropy generation, no fluxes of any kind. (Minor thermal fluxes are not of significant concern.) With oilfield reservoirs, timelines are too long to observe time independence. Consequently, the condition of equilibrium can be validated by looking at the state of equilibrium of as many components as possible; this can include gas-liquid equilibria, gas components, gas isotopes, liquid components, extent of biodegradation (if any), biomarkers, and of course the FH EoS for asphaltene gradients. Fluid density can also be analyzed for consistency with equilibrium. Equilibrium also requires pressure communication within the reservoir.

First, in the Introduction, we briefly develop the nanoscience model and thermodynamic modeling of the asphaltenes. Simple oil reservoir cases are shown where this modeling applies. The time evolution of massive asphaltene instability is then discussed. Experimental methods are given. In the Results and Discussion, this thermodynamic modeling is applied for the first time on a well characterized oil column with limited asphaltene instability to check validity; strong confirmation is obtained.

1.1. Yen-Mullins model

The Yen-Mullins model codifies the asphaltenes species in crude oils and laboratory solvents as shown in Fig. 1 [12,13]. In light crude oils with low asphaltene concentrations, asphaltenes are dispersed as molecules [12–14]; in black oils with moderate asphaltene concentrations, asphaltenes are dispersed as nanoaggregates [7,8,12–14]; and in heavy oils with high asphaltene concentrations, asphaltenes are dispersed as clusters [12–15]. Relatively small asphaltene molecular weights are found in a variety of molecular diffusion experiments [16–20], and mass spectrometry experiments [21–29]. Island molecular architecture, with a single polycyclic aromatic hydrocarbon ring system (PAH) per molecule, dominates asphaltene molecular structures as shown in diffusion measurements [16–18], and unimolecular decomposition in mass spectrometry [26,28]. Control experiments were performed to validate that laser-desorption, laser ionization methods (L^2MS) can detect all fractions of asphaltenes with relatively uniform cross section [27], thereby validating L2MS results on the dominance of island architecture for asphaltenes.

Recently, ultrahigh resolution molecular imaging confirmed previous results on the substantial dominance of island architecture for a very diverse set of asphaltenes [30,31]. Not even one traditional archipelago molecule was observed, with PAHs crosslinked by an alkane bridge, in hundreds of images in these diverse samples from ExxonMobil, Chevron, Shell, and Schlumberger [31]. Most importantly, experiments were performed to validate that the imaging methods could resolve traditional archipelago molecules [32]. Excellent images of even 1,2-di(pyren-1-yl)ethane with no fragmentation at all despite the presence in this molecule of one of the weakest C—C bonds, the ethane linkage with bond strength 65.2 kcal/mol [33].

The critical nanoaggregate concentration (CNAC) of asphaltenes has been measured by many methods including high-Q ultrasonics [34,35], DC-conductivity [36,37], AC-conductivity [38], NMR [39,40], centrifugation [41] and mass spectrometry [42]. In all these studies, the aggregation concentration in toluene is approximately 10^{-4} mass fraction or roughly 10^{-4} M. The aggregation number of the nanoaggregate is obtained using surface assisted laser desorption ionization mass spectrometry (SALDI MS) which is a gentle desorption technique which can preserve the fragile nanoaggregate at low desorption energies [27,43,44]. The aggregation number of ~6 is obtained in SALDI MS studies is consistent with many other studies [27,43,44]. For example, live black oil centrifugation gave similar results [45].

Weak asphaltene nanoaggregate binding energy implied in the SALDI MS studies is consistent with the CNAC. Using the standard approximation for the free energy of formation of nanoaggregates (or micelles), $\Delta G \sim RT\ln(cmc)$ or $\Delta G \sim RT\ln(CNAC)$ [46], the resulting estimate is $\Delta G_{CNAC} \sim -6$ kcal/mol. Moreover, there is a significant entropic component favoring nanoaggregate formation as gleaned from the small temperature dependence of the CNAC, thus the enthalpic component is not large [37,47]. The structure of the nanoaggregate is given by the divergence and analysis of combined small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) [48,49], which is consistent with molecular dynamics modeling results [50]. These measurements and modeling show that the core of the nanoaggregate is concentrated in aromatic carbon (with its high atomic number) and the periphery is enriched in alkane with its high hydrogen content [48–50].

Clusters of nanoaggregates form at several grams per liter concentration in toluene as shown by kinetic studies of floc growth with asphaltene instability [51,52], as well as DC-conductivity and centrifugation [53]. The size of asphaltene clusters are likewise given by DC-conductivity [53], centrifugation [53], SANS and SAXS analyses [48,49], and NMR [54–56].

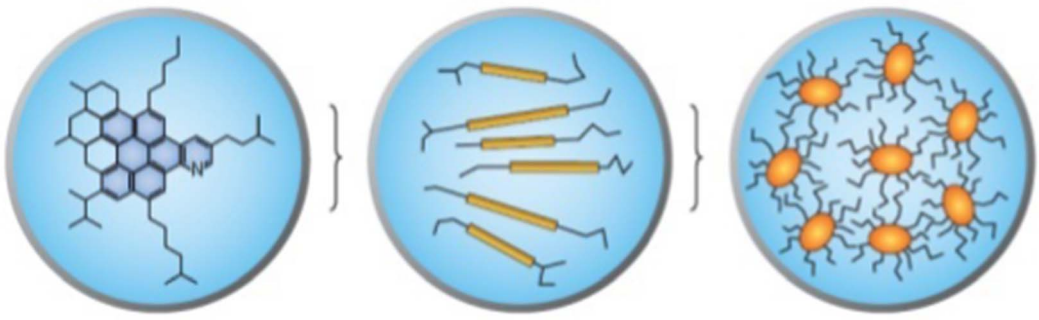

Fig. 1. The Yen-Mullins model specifying the centroids of distributions for asphaltene molecules (left), nanoaggregates (center) and clusters of nanoaggregates (right) [12,13]. Asphaltenes are dispersed as molecules in light crude oils, as nanoaggregates in black oils, and as clusters in heavy oils [12,13].