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Modeling of asphaltene aggregates structure and deposition

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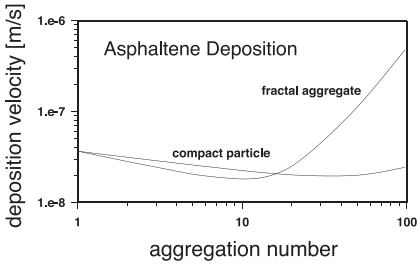
HIGHLIGHTS

- The aggregates produced by shearing of different crude oils are composed of microaggregates.
- The structure of asphaltene aggregates models the deposition in a pipeline.
- Deposition velocity shows a minimum for the aggregation number being in the range 10–100.
- It is substantially underestimated for bigger aggregates modeled as compact particles.

GRAPHICAL ABSTRACT



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ABSTRACT

A method is presented for deposition behavior prediction of asphaltene aggregates formed under shear in turbulent flow. Shearing experiments were performed in a Couette device with light and heavy crude oils and their blends. Aggregates investigated have a common fractal dimension of 1.75 and are formed by microaggregates (effective monomers) of a radius of 1.2 μm. The deposition velocity rapidly decreases with the viscosity increment. Depicted as a function of the aggregation number it shows a minimum for the aggregation number being in the range 10–100. The ratio of deposition velocities in light to heavy crude oils increases from about 4, as calculated for effective monomers, to about 40 for aggregation number equal 100. Deposition velocity of bigger asphaltene aggregates is substantially underestimated if modeled as compact particles of the same mass.

1. Introduction

Asphaltenes, a part of petroleum, are aromatic multicyclic molecules surrounded and linked by aliphatic chains and heteroatoms, of the molar mass of the range 500–2000, with average of about 750 u [1]. The polarity and complex structure lead to asphaltene self-association, flocculation and precipitation, so it is broadly agreed that asphaltenes in oil are in an aggregated state. Suspended asphaltenic particles in petroleum fluids may stick to the inner walls of oil wells and pipelines [2]. This is the major reason for fouling and arterial blockage in the petroleum industry. The investigation of asphaltene aggregation is of great practical interest [3].

Crude oil, used in previous experiments [4], was diluted by adding the toluene and *n*-heptane solution mixed at different ratios to get a variation in the asphaltene aggregate size [5] and to make the turbidity measurements possible. The obtained asphaltene aggregates were identified as aggregates with mixed statistics [6], composed of small dense primary aggregates of micrometer size. The aggregates, being the clusters of primary aggregates, were characterized by a fractal dimension of 1.6–1.7 on the scale of aggregate radius.

In reality, crude oils are often blended with another crude oil [7]. In the present study, we investigate non-diluted light and heavy crude oils and their blends with additives of 1.5% pyrolysis oil [8]

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Nomenclature

Symbols

a	Primary particle (monomer) radius (m)
d	Pipe diameter (m)
D	Aggregate fractal dimension (−)
D_r	Particle diffusivity (m^2/s)
G	Shear rate (1/s)
L	Pipe length (m)
i	Number of monomers in an aggregate (−)
Δp	Pressure drop ($kg\,s^{-2}\,m^{-1}$)
r	Hydrodynamic radius of aggregate (m)
R	Radius of aggregate (m)
Sc	Schmidt number (−)
u	Settling velocity of an individual aggregate (m/s)
u_{dep}	Deposition velocity of an individual aggregate (m/s)
u_*	Fluid friction velocity (m/s)
ϵ	Energy dissipation rate per unit mass in a pipe flow (m^2/s^3)
ϕ_{agg}	Solid volume fraction in an impermeable sphere equivalent to aggregate (−)
η	Kolmogorov microscale (m)
μ	Fluid dynamic viscosity (kg/(ms))
ν	Fluid kinematic viscosity (m^2/s)
τ	Aggregate relaxation time (s)
τ^+	Normalized particle relaxation time (−)
τ_w	Shear stress at pipe wall ($kg\,s^{-2}\,m^{-1}$)
ρ_{agg}	Equivalent aggregate density ($kg\,m^{-3}$)
ρ_f	Fluid density ($kg\,m^{-3}$)
ρ_s	Solid density ($kg\,m^{-3}$)

Table 1
Properties of crude oils and their blends $\rho_s = 1163\,kg/m^3$.

Asphaltene mass concentration	ν [m^2/s]20 °C	ρ_f [kg/m^3]20 °C
0.05%	6.53×10^{-6}	842
0.25%	8.01×10^{-6}	849
0.50%	9.60×10^{-6}	856
0.75%	1.22×10^{-5}	863
1.15%	1.77×10^{-5}	868

and 2 ppm Kemelix™ 7415X, both acting as asphaltenes dispersants. The aggregation of asphaltenes is induced by shear which, if sufficiently high, can cause aggregation even stable colloids [9]. The shear conditions existing in a pipe flow is modeled in a Couette device.

The structure of produced aggregates is determined by the method using the power-law dependence of the radius of aggregate on the number of effective monomers. The full form of this dependence is employed, so it is possible to determine not only the fractal dimension but also the radius of effective monomers. The latter is compared to that determined analyzing microscope images of asphaltene aggregates. Another method is also proposed to determine the average effective monomer in population of aggregates.

2. Experimental

URAL BLEND heavy crude oil and DĘBNO light crude oil with additives of 1.5% pyrolysis oil [8] and 2 ppm Kemelix™ 7415X were investigated separately and blended to get liquids of different mass concentrations of asphaltenes ranging from 0.05% to 1.15%. The characteristics of crude oils investigated, determined by the methods described previously [4], are presented in Table 1.

The samples of crude oil were sheared in a Couette device. It consists of the inner cylinder of radius $r_1 = 39.6$ mm and the outer cylinder of inner radius $r_2 = 40.2$ mm. The height of the cylinders is 200 mm and the annular gap between them is $\Delta r = 0.65$ mm. The outer cylinder is fixed, while the rotational speed of the inner cylinder can be adjusted. It was taken equal to 108 revolutions per minute, which corresponds to the shear rate 688 1/s if calculated directly from the relative rotation speed, the cylinder radii, and the width of the gap. This value is in the middle of the range used for the transported crude oil [4]. The Taylor number is defined as [10].

$$\mathrm{Ta} = \frac{\omega \Delta r^{3/2} r_1{}^{1/2}}{\nu} \tag{1}$$

For a fluid of kinematic viscosity $\nu = 1 \times 10^{-5}\,m^2/s$, which is the order of magnitude of the viscosity of the crude oils used, and angular frequency ω applied, the Taylor number is about 4. It is lower than the critical value (41), which means that the Couette flow is laminar and the mean of shear rate calculation is proper.

After introducing the additives, the crude oil were sheared during 30 min and a drop of sample was placed on slide and dried in free air to observe under microscope. Dried drop on a slide was observed under optical microscope Nikon Alphaphot 2YS2 equipped with JCC-8201-CCD Color Camera making possible to register the images.

3. Determination of the fractal dimension and the radius of effective monomers

The structure of aggregates is formed in the process of aggregation. One can imagine that individual asphaltene molecules stick together, first in pairs, then form nanoaggregates which can form clusters. Two main mechanisms are associated with irreversible asphaltene aggregation in crude oil [11]. The reaction-limited aggregation, in which not every contact between two particles results in their aggregation, produces more compact aggregates. This mechanism is characteristic for early stage of the process. Then the aggregation is limited by diffusion. The transition takes place at the aggregate size of the order of micrometers. In such a model relatively loose aggregates are obtained consisting of more dense microflocs. Such objects are known as aggregates with mixed statistics and constituent microaggregates are termed as effective monomers [6]. The images reported [12,13] confirm the mixed statistics character of asphaltene aggregates. The typical images of aggregates produced in this study in the Couette device, presented in Fig. 1, have the same structural character.

The structure of aggregates formed in three-dimensional space is often analyzed from its plane projection. In the case of a perfect, infinite fractal the projection has the dimension $\boldsymbol{D}$ of the fractal if $D < 2$, but is compact with dimension 2, if $D \geq 2$. Real fractals, however, are limited by an inner and an outer scale, arising from the finite size of both the monomers and of the cluster. Such effects can be detected if the fractal dimension of an image is measured from its density correlation function behavior [14]. When applied to a sample of electron micrographs of diesel soot particles whose apparent dimension is 1.83, the theory gives 1.90 as the true fractal dimension of the soot, so the change seems not to be essential.

The mass-radius relation makes it possible to determine the fractal dimension of a population of aggregates of the same fractal structure, whereas their internal structure is not analyzed. The slope of the relation depicted in a log–log plot is the fractal dimension, assuming that the projection does not modify neither the number of detectable constituent particles, which is acceptable if $D < 2$, nor the size of aggregate.

The images of aggregates produced in the Couette device were analyzed to read the number of monomers i in an aggregate and the aggregate size R. Then plotted in a log–log system they form a