

Short Communication

Diffusivity of coal and petroleum asphaltene monomers by fluorescence correlation spectroscopy

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Abstract

Using fluorescence correlation spectroscopy (FCS) we measure the translational diffusion coefficient of Iino coal asphaltenes and UG8 petroleum asphaltenes dispersed in toluene at extremely low concentrations (0.03–3.0 mg/L). Using a simple scaling argument we compare them with several molecules of known size and molecular weight. We find that Iino coal asphaltene molecules – which have a comparatively small alkane fraction – have a diffusion constant of $1.5 \times 10^{-5} \text{ cm}^2/\text{s}$ and corresponding hydrodynamic radius close to 0.25 nm: making them significantly smaller than petroleum asphaltenes.

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The supply of gasoline, diesel fuel, heating oil, plastics, chemicals, electricity, etc. all depend on a stable flow of crude oil. With steadily increasing demand for these products and the seeming inevitability of the so called “Peak Oil” of available supply, it is clear that the world’s reliance on crude oil will have to end sooner or later. Fortunately, a wide variety of carbonaceous materials – including shale, coal, and bitumen – may be upgraded to produce so called ‘synfuels’. These feedstocks are abundant and readily available. For example, Canada’s tar sands contain the largest known hydrocarbon reserves and the United States alone have close to 500 billion metric tonnes of demonstrated recoverable coal reserves. Moreover, synthetic fuels thus produced may in principle be processed using the same infrastructure that is already in place for crude oils.

The precise chemical composition of these feedstocks is still different from that of crude oil and the existing infrastructure and methods have to be adapted. One such differ-

ence common to shale, coal, and bitumen, is the larger aromatic carbon content when compared to lighter crude oils. The compositional difference is especially important for the heaviest, most aromatic fraction of crude oil, where physical properties become increasingly complex and complicate production and refinement. For crude oils in particular, these heavy, aromatic molecules tend to aggregate and precipitate out of the liquid phase: leading to clogged formations and pipelines. This behavior has earned it the title of ‘bad cholesterol’ of oil. However, these problems are not exclusive to crude oils. Materials derived from coal liquefaction are also known to form similar aggregates in organic solvents [1,2]. The fraction of crude which contains most of the responsible heavy aromatics – so called *asphaltenes* – is generally defined as a solubility class: the fraction soluble in toluene and insoluble in *n*-heptane (or *n*-pentane).

Since the alternative feedstocks have an even higher aromatic content, understanding this fraction is crucial to reliable and economically viable supply. In case of heavy oil bitumen, the asphaltene fraction probably has similar chemical composition to that of already studied lighter

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crude oils. Other important feedstocks have different asphaltene composition. Liquified coal asphaltenes, for example, have substantially less alkane carbon content and a higher density of heteroatoms. The absence of long alkane chains (as seen by ^{13}C NMR [3]) and increased polarity emphasize different aspects of aggregation. Shorter alkane substituents provide reduced steric repulsion and increased diffusivity; increased diffusivity implies increased rates for aggregation and increased polarity may manifest itself in stronger molecular interactions and higher surface activity.

It is thus important to study asphaltenes from different sources to understand governing chemical principles that determine their phase behavior. The first step is determination of chemical properties. Although the atomic and functional analysis of such compounds is performed routinely [4,5], determination of molecular weight – particularly for crude oil asphaltenes – is still a difficult and delicate task. Instead, rotational hydrodynamic radii of a number of coal asphaltenes have recently been measured by time-resolved fluorescence depolarization (TRFD) [6,3]. This technique measures polarization anisotropy decay times, which lead to rotational diffusion constants. This information leads to approximate diffusion constants which are useful to estimate reaction rates.

Unfortunately, this technique was unable to resolve decay times for molecules smaller than octaethyl porphyrin. In particular, it was not able to resolve the radius of the Iino coal sample because the decay times, and thus its dimension, were too small. Alternatively, this coal sample was previously characterized using Taylor dispersion [2], however, high concentrations were employed (0.1 g/L). At this concentration asphaltenes already show signs of aggregation [7,8] and may bias the result. Similarly, previous measurements utilizing vapor pressure osmometry [4,5] performed on other coal asphaltene samples may also have been affected by this effect.

In order to resolve the size of apparently small coal asphaltenes, we must employ a technique that is both non-destructive and remains sensitive at concentrations orders of magnitude below any presumed onset of aggregation. We use confocal fluorescence correlation spectroscopy (FCS) to study the translational diffusion of asphaltene molecules derived from Iino coal and dispersed in toluene at extremely low concentrations (0.03–3.0 mg/L). This is accomplished by measuring correlations in the fluctuations of total fluorescence intensity due to fluorophores diffusing in and out of a confocally defined observation volume. We require low fluorophore concentrations to emphasize single molecule contributions to the fluctuations of the fluorescence signal and to remove ambiguities arising from asphaltene aggregation or fragmentation. The strength and applicability of the technique to the case of asphaltene diffusion was demonstrated by measuring the diffusivity of petroleum asphaltenes (UG8, Kuwait) [9].

In order to compute these correlation functions, we first record time-dependent fluctuations in fluorescence inten-

sity collected from a sample driven either by Brownian motion or chemical reactions. For purely diffusive, non-interacting particles, the relaxation of local fluctuations in concentration $\delta C(r, t)$ around the ensemble average C is governed by the diffusion equation:

$$\frac{\partial \delta C(r, t)}{\partial t} = D \nabla^2 \delta C(r, t), \quad (1)$$

where D is the translational diffusion coefficient. The normalized autocorrelation function of this signal $G(t)$ is defined as a time average of the products of collected fluorescence intensity fluctuations $\delta F(t)$ [10]

$$G(t) = \frac{\langle \delta F(t) \delta F(t + \tau) \rangle}{\langle F(t) \rangle^2}. \quad (2)$$

In order to maximize signal to noise, current FCS experiments utilize a confocal illumination and detection setup which restricts the collection of light to a small observation volume. This diffraction limited volume reduces the number of particles under observation and maximizes the relative amplitude of these fluctuations. The instantaneous fluorescence intensity recorded from the sample can be most generally expressed as

$$F(t) = q \int \phi(x) C(x, t) d^3x, \quad (3)$$

where q is a molecular brightness and $\phi(x)$ a normalized collection profile that depends only on optical setup and emission and excitation wavelengths.

To fit the data using Eq. (3) one needs to determine both excitation and emission spatial profiles, convolve, and calculate $\phi(x)$. Fortunately, for pure diffusion this is not necessary. Noting that $G(t)$ is inversely proportional to C , and that time only appears when multiplied by diffusion constant D , we use simple scaling to infer the diffusivity of the sample under investigation. By scaling axes of the measured correlation functions so that they collapse on top of a chosen reference fluorophore [9], two scaling parameters are obtained for each sample. The scaling parameter for the time axis, γ , corresponds to the diffusivity of sample molecule relative to the reference. By multiplying γ with the diffusivity of the reference compound we obtain an absolute measurement of the diffusivity of unknown molecules: regardless of details of optics used and without introducing any additional assumptions or artifacts ([11–14] and references therein).

$$D_{\text{abs}} = \gamma D_{\text{ref}}, \quad (4)$$

The remaining scaling parameter is related to the concentration and not relevant to determining D .

Measurements are performed on a home built apparatus depicted in Fig. 1 and similar to that described in [15] in detail. A diode laser (Power Technology) operating at 405 nm and peak power 4 mW is connected through a single mode fiber (OZ Optics) to the optical assembly. It is further collimated to a diameter that slightly under-fills the back aperture of the oil immersion objective (Olympus,

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