

Differential aggregation of asphaltene probed with time-resolved fluorescence

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The aggregation behavior of asphaltenes is still poorly understood because of the complexity of the compounds that make up this material. Asphaltenes contain polyaromatic hydrocarbons, which can undergo π -stacking, and abundant heteroatoms, which can associate by polar interactions. Some of the asphaltene components are fluorescent and different fluorescence techniques were employed in the past to characterize asphaltenes, such as steady-state[1], time-resolved[2] and anisotropy depolarization measurements [3] Aggregation leads to decreases in the steady-state emission intensity, to shifts in the emission spectra and to the shortening of lifetimes, therefore, fluorescence spectroscopy can be used to study asphaltene aggregation.

We combined time-resolved lifetime with time-resolved emission spectrum (TRES) measurements to characterize the aggregation of Athabasca asphaltene precipitated from pentane (AA-5, with 50% heptane insoluble material). The emission of asphaltenes corresponds to the emission of several chromophores with different emission spectra and lifetimes. Therefore, the emission decays were fit to a sum of exponentials and average lifetimes ($\langle \tau \rangle$) were calculated (eq. 1) where A is the pre-exponential factor associated to the lifetime (τ) of each species "i".

$$\langle \tau \rangle = \sum_1^i A_i \tau_i \quad (1)$$

TRES spectra (Fig. 1) at short delays after excitation include the emission from short-lived and long-lived excited states, while only the spectra for the long-lived excited states are observed for long delays. A small shift for the TRES at short delays is observed when the AA concentration is raised from 1 mg/L to 10 g/L, while a marked red shift is observed for the

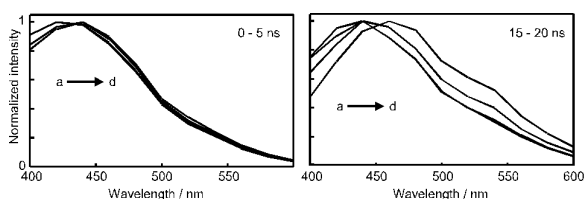


Fig. 1. Normalized TRES for the emission ($\lambda_{ex} = 335$ nm) of AA-5 collected between 0 and 5 ns (left) and 15 and 20 ns (right) after the excitation pulse ([AA-5]: (a) 1 mg/L, (b) 10 mg/L, (c) 1g/L, (d) 10 g/L).

TRES at long delays. These results are consistent with the quenching inside aggregates of the

asphaltene fluorophores with higher excited state energies and this effect is more prominent for long lived excited states.

The number of exponentials used for the fit of the emission decay of AA-5 indicates the number of lifetimes that can be discriminated and not the number of different molecules detected. Therefore, average lifetimes were compared instead of individual lifetimes. The lifetimes for AA-5 samples excited at 335 nm were measured for the decays at 420 nm or 520 nm (Fig. 2). A decrease of the average lifetime due to the formation of aggregates was observed above 10 mg/L for the emission at 420 nm, while this decrease was only observed above 5 g/L for the emission at 520 nm. In both cases the samples were excited at 335 nm and the same excited states were formed. Therefore, the different dependence observed indicates that different fluorophores are incorporated in different aggregates.

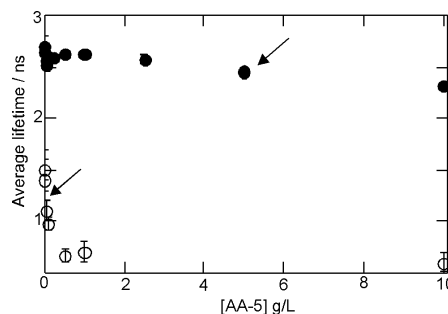


Fig. 2. Dependence of the AA-5 average lifetime with the AA-5 concentration excited at 335 nm and with the emission collected at 420 nm (O) or 520 nm (●). The decrease in the lifetime is indicated by the arrow (> 10 mg/L for O and > 5 g/L for ●).

In conclusion, our results show that different asphaltene components aggregate in different concentration ranges. Therefore, asphaltene aggregates have different compositions depending on the asphaltene concentration and asphaltene aggregation cannot be described within the framework of a critical nano-aggregate concentration.

References

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