

Using the fluorescence of DBO to study the aggregation of asphaltenes

Zixin Yang*, Cornelia Bohne

Department of Chemistry, University of Victoria (*corresponding author: xyang@uvic.ca)

Asphaltenes, which are operationally defined as the fraction of bitumen that is insoluble in heptane (or another alkane) but soluble in toluene [1], is the least characterized component of crude oil. Asphaltenes can aggregate even at low concentrations, which causes problems both in the reservoir and during transport and processing of oil.

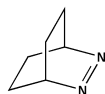


Fig. 1. The structure of DBO.

Fluorescence techniques have been employed to characterize asphaltenes, by either exploring the intrinsic emission from asphaltene solutions [2] or by adding external probes [3]. DBO (2,3-diazabicyclo[2.2.2]oct-2-ene, Fig. 1) is a fluorescence probe molecule where the lifetime is shortened through an aborted hydrogen abstraction, making the probe's lifetime sensitive to the presence of aliphatic C-H bonds. In addition, DBO has a long fluorescence lifetime. These properties were previously explored to study the binding dynamics of DBO with host systems, such as cyclodextrins [4]. In this work, we used DBO as an external fluorescent probe to characterize the aggregation of Athabasca asphaltene. (AA-5, containing 50% heptane insoluble material).

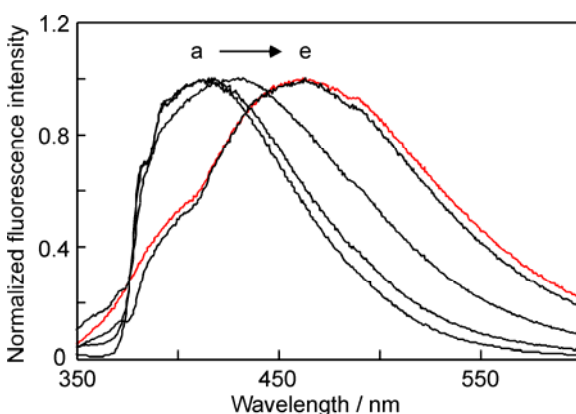


Fig. 2. Normalized fluorescence spectra: **a** to **d**: DBO (2 mM) in toluene in the presence of increasing concentrations of AA-5 (**a**=0, **b**=1, **c**=10, **d**=100 mg/L); **(2) e**: (red) asphaltene emission in toluene, [AA-5]= 100 mg/L. The samples were deaerated by bubbling nitrogen and were excited at 335 nm.

DBO has a broad emission spectrum with a maximum around 420 nm, while AA-5 has an emission spectrum with a maximum around 460 nm (Fig. 2). With the addition of AA-5 the emission intensity for DBO was quenched leading to a red shift of the normalized spectra. At an AA-5 concentration of 100 mg/L the emission of DBO cannot be differentiated from the AA-5 emission in the steady-state experiment. The observed quenching indicates that DBO interacted with AA-5.

The lifetime of DBO was measured using single photon counting. Asphaltenes have an intrinsic emission and the fluorescence decay for AA-5 does not follow a mono-exponential function indicating that several chromophores with different lifetimes (< 15 ns) are present. The advantage in using DBO is that its emission lifetime in toluene is 217 ns and it can be differentiated from the lifetimes associated with the emission of AA-5. Our preliminary lifetime measurements show that AA-5 quenches the emission of DBO leading to a shortening of the DBO lifetime (Table 1). The abrupt decrease in lifetime between 10 mg/L and 100 mg/L maybe related to the interaction of DBO with the AA-5 aggregate and detailed AA-5 concentration studies are being performed to test this hypothesis.

Table 1 Lifetime for the singlet excited state of DBO (2 mM) in deaerated toluene solutions. The lifetimes correspond to the longest lifetime component of a fit of the decay to a sum of exponentials. The samples were excited at 335 nm and the emission was collected at 420 nm.

[AA-5] / mg L ⁻¹	Lifetime/ ns
0	217
1	215
10	150
100	13.5
1000	12.3

In conclusion, our preliminary experiments showed that DBO interacts with asphaltene components and DBO has the potential for being used as a probe to study the aggregation of asphaltene.

References

- [1] Mitchell, D. L.; Speight, J. G. (1973) *Fuel*, 52, 149-152.
- [2] Groenzin, H.; Mullins, O. C. (1999) *J. Phys. Chem. A*, 103, 11237-11245.
- [3] Pietraru, G. M.; Cramb, D. T. (2003) *Langmuir*, 19, 1026-1035.
- [4] Nau, W. M.; Zhang, X. (1999) *J. Am. Chem. Soc.* 121, 8022-8032.