

Sizes of vanadyl petroporphyrins and asphaltene aggregates in toluene

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Most crude oils contain traces of vanadyl porphyrins within their asphaltene fraction. Although these metals are only present in trace quantities, they have a significant detrimental impact on crude oil processing units; therefore, their selective removal is highly desirable.

The diffusion of asphaltene components through ultrafiltration membranes was used to investigate the association of vanadium compounds and asphaltene components in dilute toluene solutions. Diffusion measurements were done using model vanadyl porphyrins, asphaltenes, and native petroporphyrins in toluene using a stirred diaphragm diffusion cell equipped with ultrafiltration membranes (Ultracel YM regenerated cellulose membranes and Anopore alumina membranes). The pore sizes were varied between 3-20 nm to retain aggregates while allowing free molecules to diffuse. The permeate was continuously monitored using in situ UV/Visible spectroscopy.

The effect of pore size was tested using 4 different membranes: Ultracel YM10 (10 kDa, ~3 nm pores), Ultracel YM30 (30 kDa, ~5 nm pores), Ultracel YM100 (100 kDa, ~9 nm pores), and Anopore 20 nm membranes, and the results are shown in Fig. 1. The size of the asphaltene structures in toluene at 1 g/L are between 5 and 9 nm based on a significant jump in effective diffusivities observed between these pore sizes. This size range fits well with scattering measurements from the literature [1-3].

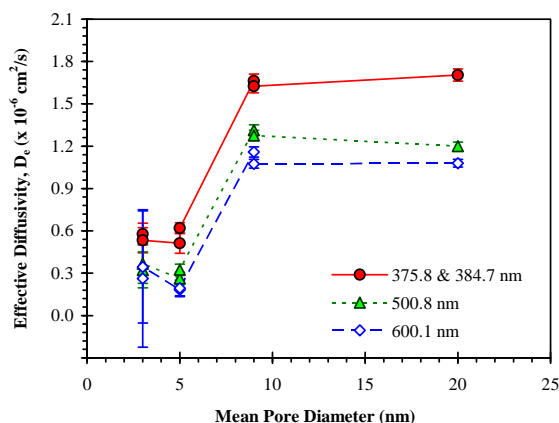


Fig. 1: Effective diffusivity of Athabasca asphaltenes as a function of membrane pore size (25°C, 1 g/L asphaltenes)

These aggregates were very stable, remaining essentially intact even after 7 days in toluene. An increase in temperature to 70°C results in an increase

in asphaltene mobility (as described by the Stokes-Einstein relationship) but does not reduce the size of the asphaltene structures below 5 nm. Likewise, a decrease in concentration to 0.1 g/L did not result in a decrease in size of the asphaltene structures to < 3 nm. The origin of the asphaltenes (Athabasca, Safaniya, and Venezuela) did not affect the results.

The native petroporphyrins present in Athabasca asphaltenes appear to be larger than the model vanadyl porphyrins studied (vanadyl octaethylporphyrin and vanadyl meso-tetraphenylporphyrin) as indicated by the presence of pore hindrance effects with the tighter membranes (see Fig 2). An increase in temperature results in an increase in petroporphyrin mobility that is proportional to the viscosity and temperature according to the Stokes-Einstein equation, while decreasing the asphaltene concentration does not result in an increase in the mobility of the vanadyl petroporphyrins. The mobility of the vanadyl petroporphyrins is affected by the origin of the sample (Athabasca, Safaniya, and Venezuela) and is therefore not universal.

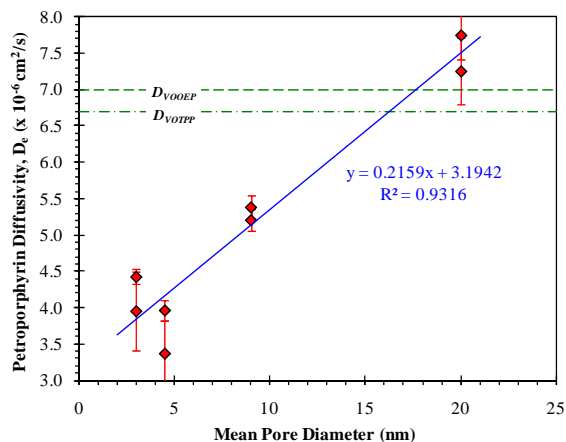


Fig. 2: Effect of Pore size on the diffusion coefficient of vanadyl petroporphyrins from Athabasca asphaltenes (25°C, 1g/L asphaltenes in toluene)

References

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- [2] Gawrys, K.; Kilpatrick, P. K., *J. Colloid Interf. Sci.* **2005**, 288, 325-334.
- [3] Fenistein, D. et al., *Langmuir* **1998**, 14, 1013-1020.