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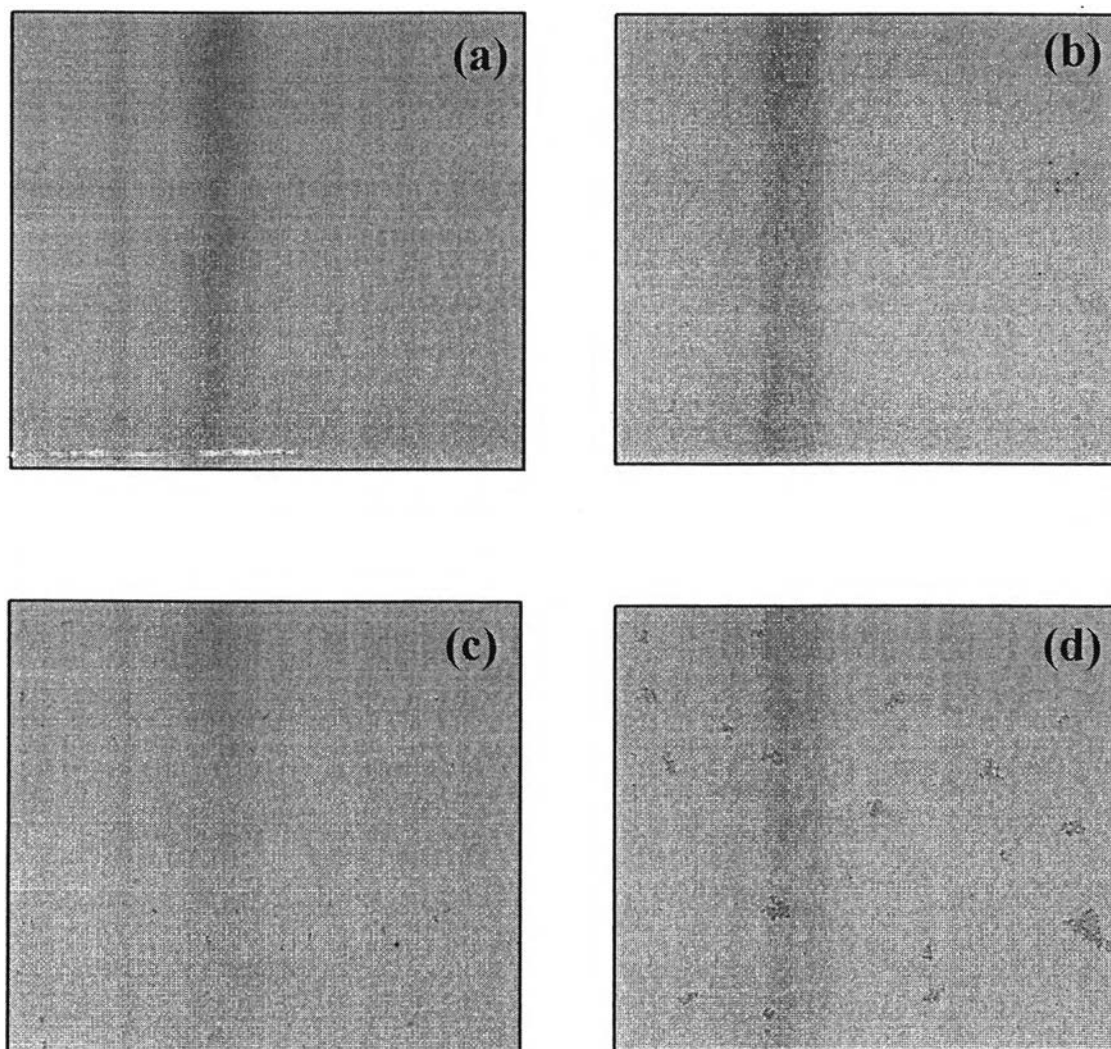
## APPENDICES

### APPENDIX A Microscopy Analysis

The asphaltene aggregation kinetics was investigated using detection time, which was obtained by the microscopy. The precipitant, which is n-heptane, was slowly added to either crude or model oil. The mixture was kept stirred evenly along the addition process. The time when last drop of n-heptane was added to the mixture is defined as initial time or zero. After the addition, small amount of the mixture was sampled on a pair of 18×18 and 25×25 mm cover glasses. The sample was monitored under a microscope specified in Chapter III. A camera was used to capture the image at each time. The images captured were used to determine the detection time, which is the average time between the time at which haze and particles was detected. The detectable particle size in this study is 0.5 microns.

Figure A1 shows the images captured at different times and stages of aggregation. “Clear” is the stage where nothing was detected under microscope. The mixture will stay clear until the particles growth has reached the detectable size, which is the “haze” stage. At haze stage, particles will form a cloud that is barely detectable. The particle will continue to grow until reach 0.5 microns, which is where they climb to “detected” stage. The detection time is then determined from these two stages. After a certain time, the particle will start to agglomerate to bigger clusters in “agglomerated” stage.

The uncertainties of this experiment contributed by both experimental and systematic errors. In experimental aspect, size of droplet is a main cause of error because it highly adjust the density of detected particle, including the haze. To minimize this problem, the droplet was sampled using small pipette tips to equate the droplet volume and thus equate the density of particles. In systematic aspects, different experimenter will have different discretion and that results in bad reproducibility. However, despite of that, the trends observed still be the same for all.



**Figure A1** Images of mixture captured from microscope. (a) clear (b) haze (c) detected (d) agglomerated

## APPENDIX B Viscosity and Diffusivity Calculation

There are other possible effects that at a first glance could explain the stability of asphaltenes at high concentration, beside the role of soluble asphaltenes. Increase in asphaltene concentration could consequently increase viscosity. Furthermore, the presence of soluble asphaltenes could decrease the effective diffusivity of insoluble asphaltenes. Both could boost the stability of insoluble asphaltenes.

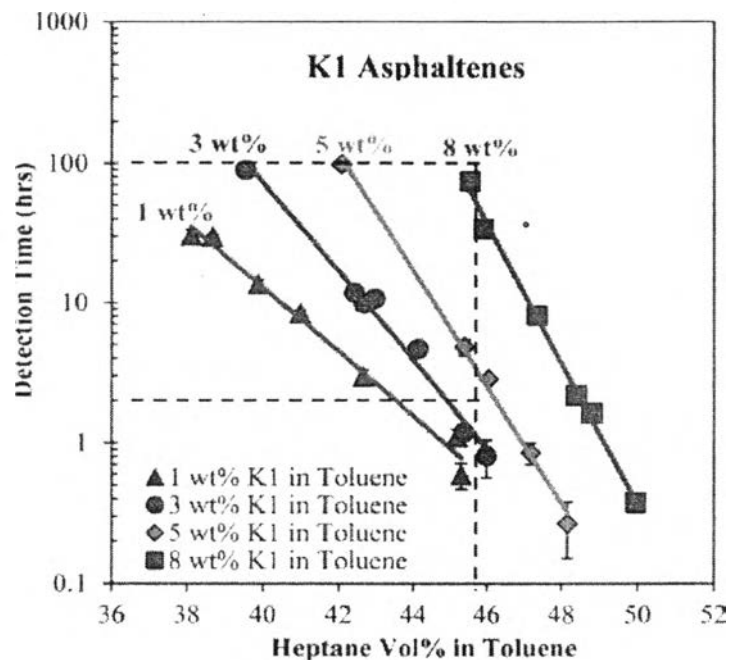
### B.1 Viscosity increase due to increase in total asphaltene concentration

For a system of constant solution composition and asphaltenes origin, the detection time of asphaltene aggregation is proportional to viscosity and inversely proportional to the asphaltene concentration squared.

$$t_{\text{det}} \propto \frac{\mu}{\sqrt{C_1(0)}} \quad (\text{B1})$$

As it can be seen in Figure B1, as the asphaltene content increases above 1 wt% the detection time increases. The point 1, where the total asphaltene concentration in model oil is 5wt%, the detection time is 2 hours and the volume fraction of unstable asphaltenes is  $6.4656 \times 10^{-4}$ . The point 2, where the total asphaltene concentration model oil is 8wt%, the detection time is 100 hours and the volume fraction of unstable asphaltenes is  $7.0150 \times 10^{-3}$ . If the change in detection time is due to viscosity, the increase in the viscosity from solution 1 to solution 2 would have to be comparable to the value calculated using Equation B1. In this case,  $\frac{\mu_2}{\mu_1} \sim 160$ .

According to Barré *et al.* (2008), as the concentration of asphaltenes increase in asphaltene + toluene mixture, the viscosity increases. However, the increase in concentration is not as great as 160 times. In fact, for their asphaltenes the viscosity increases of solution increases 50 times the most, in the case where volume fraction of asphaltenes is 0.20. Therefore, the increase in viscosity cannot explain the increase on the onset time as concentration of asphaltenes increases in solution.



**Figure B1** Detection time of K1 asphaltenes at different concentration as a function of heptane concentration.

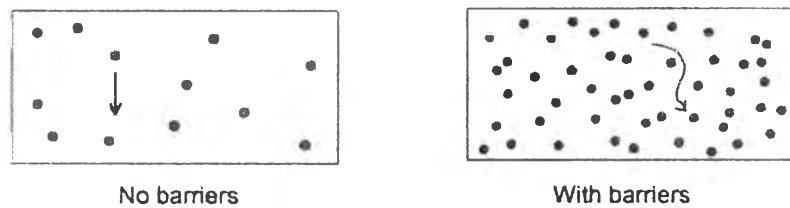
### B.2 Diffusivity decrease as soluble asphaltenes act as diffusion barrier

Another possible explanation for the increase in detection time as asphaltene concentration increases is the decrease of effective diffusivity of aggregating asphaltenes due to the presence of soluble asphaltenes that act as diffusion barriers. Schematics of the phenomenon are shown in Figure B2.

In order to decrease in effective diffusivity to explain the increase in onset time, the ratio  $D_2/D_1$  (i.e., effective diffusivity in point 2 over effective diffusivity in point 1) would have to be of similar value to the ratio of viscosities, i.e.,  $\mu_1/\mu_2$ . This conclusion is supported by the Stokes-Einstein equation that related the diffusivity of spheres to the viscosity of solution. The problem of reduction in effective diffusivity due to solid non-interacting periodic composite barriers has been solved and the decrease in effective diffusivity is a function of the volume fraction of barriers.

$$\frac{D_{\text{eff}}}{D_{\text{single}}} = \frac{2(1-\phi)}{2+\phi} \quad (\text{B2})$$

Using this equation, the volume fraction what would cause the ratio  $\frac{D_{\text{eff}}}{D_{\text{single}}} = \frac{1}{160}$  would be  $\phi=0.9969$ . The volume fraction of soluble asphaltenes in solution is about 0.006, three orders of magnitude lower than the one estimated. Therefore, decrease in diffusivity due to presence of barriers cannot explain the increase in onset time as asphaltene concentration increases.



**Figure B2** Schematic of soluble and insoluble asphaltenes in mixture (Left) No barriers (Right) With barriers.



