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APPENDICES

Appendix A Micro-centrifugation Results of A1 Asphaltenes

Figure A1 and A2 show the amount of asphaltenes precipitated as a function of time from 3 wt% and 8 wt% asphaltene-content solutions, respectively, at 60 vol% and 70 vol% heptane concentrations. It was observed that the amount of precipitated asphaltenes increases with time and asphaltene content. One hypothesis which can explain this observation is that the asphaltenes that precipitate at different times and asphaltene concentrations have different properties causing the difference in aggregation rate among each fraction. Therefore, by using these centrifugation results as a guideline, asphaltene -time-based fractionation experiments and characterization techniques were applied to investigate the influence of the properties of asphaltenes on their aggregation tendency.
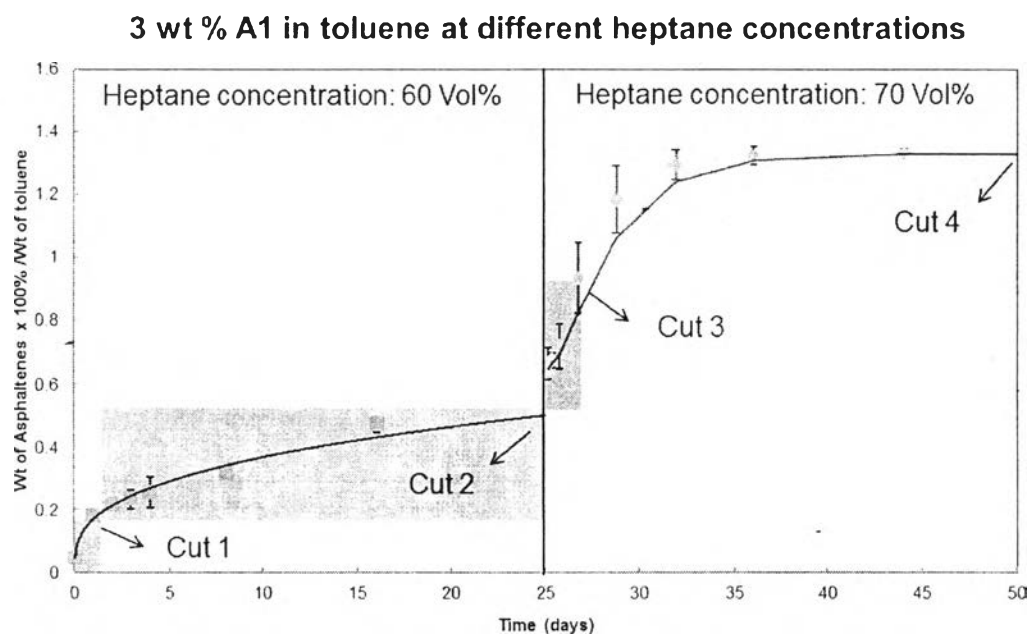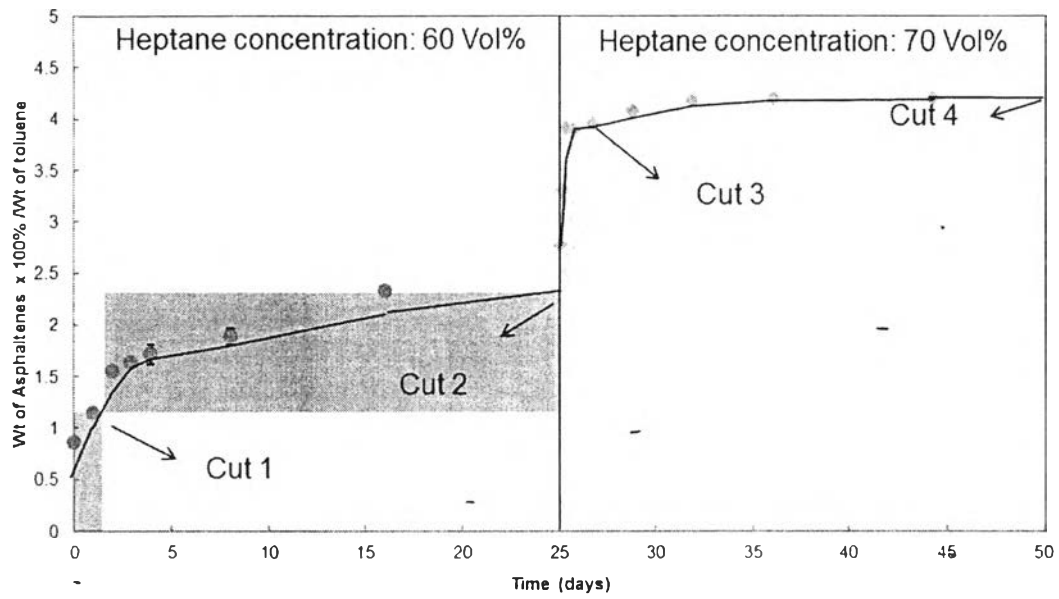
3 wt % A1 in toluene at different heptane concentrations

Figure A1 Centrifugation plots for different cuts at 60 vol% and 70 vol% heptane from 3 wt% asphaltene solution.

8 wt % A1 in toluene at different heptane concentrations

Figure A2 Centrifugation plots for different cuts at 60 vol% and 70 vol% heptane from 8 wt% asphaltene solution.

Appendix B Plausible Explanation for Effect of Concentration

As discussed in results and discussions section, it showed that effect of asphaltene content has influence on the difference in aggregation kinetics of fractioned asphaltenes from different asphaltene concentrations. The results from scattering and microscopy experiments are successfully utilized to characterize difference in asphaltene stability among asphaltene fractions. However, those techniques cannot provide the evidence explaining why fractionated asphaltenes extracted from higher asphaltene concentration have higher stability than the ones fractioned from lower asphaltene concentration.

Figure B1 demonstrates the ratio of precipitated asphaltenes to total asphaltenes from 3 wt% and 8 wt% asphaltene concentrations as a function of heptane concentration after one month and two months, respectively. It was observed that, at high heptane concentrations (above 50 vol% heptane) for both asphaltene concentrations, amounts of precipitated asphaltenes do not change significantly between one and two months indicating that their thermodynamic equilibrium of asphaltene precipitation were approached after one month. Whereas, at precipitant concentration below 50 vol% heptane, amount of precipitated asphaltenes increased significantly from one month to two months. Interesting observation is that amount of precipitated asphaltenes from both asphatlene concentrations are approximately the same at first month for both asphaltene concentrations. However, 3 wt% solution provides larger amount of precipitated asphaltenes than 8 wt% solutions after two months which is their expected equilibrium time. As discuss earlier, at high asphaltene concentration, soluble asphaltene dispersed in the solution behave as stabilizing agents by altering solvency power of solution. With the support of soluble asphaltenes, once asphaltenes are destabilized by adding precipitant, unstable asphaltenes in higher asphaltene concentration required more time to precipitate and therefore have longer detection time than asphaltenes in lower asphaltene content. This finding also agree in our K1 fractionation work because the first precipitant concentration added to destabilize asphaltenes in both asphaltene concentrations was
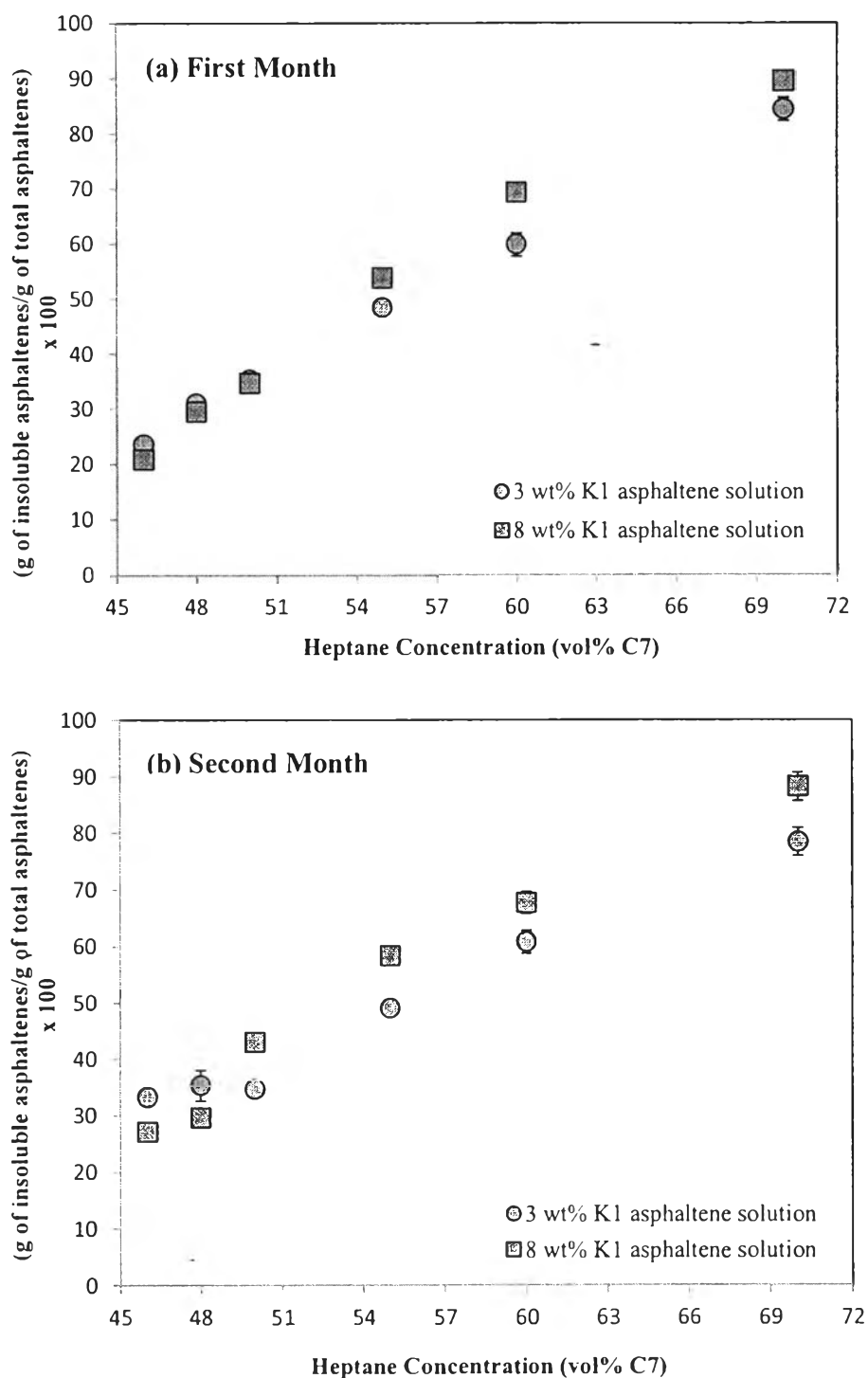
Figure B1 Fraction of asphaltenes precipitated to total asphaltenes at (a) one month and (b) two months as a function of heptane concentration.

48 vol% heptane which is at instantaneous onset volume for 3 wt% solution and is below instantaneous onset volume for 8 wt% solution (inst. onset volume for 8 wt% solution is 50 vol% heptane), which has approximated detection time of 2.5 hours.

The results indicate that soluble asphaltenes in high asphaltene content solution can still stabilize and retain more asphaltenes in solution up to slightly above instantaneous onset heptane concentration.

From this point, regarding time-based fractionation, fractions precipitated from lowest solubility are expected to exhibit approximately the same aggregation tendency in microscopy experiments. Moreover, after remaining asphaltenes from low heptane concentration were precipitated and fractionated at higher heptane concentration, the ones from higher asphaltene concentration are attributed to wider range of stable asphaltenes compared to the ones from lower asphaltene concentration. The evidence of this explanation can be observed from larger amount of asphaltenes precipitated at high heptane concentration (above 50 vol% heptane) for 8 wt% solution which indicates that stabilizing power of soluble asphaltenes are diminished and no longer significant at very high heptane concentrations. Therefore, latter fractions separated at higher heptane concentrations from higher asphaltene concentration are expected to be more stable than fractions precipitated from lower asphaltene concentration.

Considering fractions separated at different times, quantity of asphaltenes precipitated at different times was used to explain the reason why higher instability of fractionated asphaltenes from 8 wt% solution over 3 wt% solution. Figure 12 illustrates mass ratio of precipitated asphaltenes at first day to total asphaltenes precipitated at 1 day and 25 days at heptane concentrations used to destabilize asphaltenes in K1 fractionation study, respectively. Therefore, all fractions precipitated from 8 wt% solution at one day and 25 days are reasonably more stable than fractions precipitated from 3 wt% solution for all investigated heptane concentrations. For effect of concentration on A1 asphaltene fractionation, 60 vol% heptane concentration was initial precipitant concentration performed in this study. This concentration is slightly above instantaneous onset volume for both 3 and 8 wt% solutions (inst. onset volume of 3 and 8 wt % solutions are 57 and 59 vol% heptane respectively) which are similar conditions used in K1 fractionation.
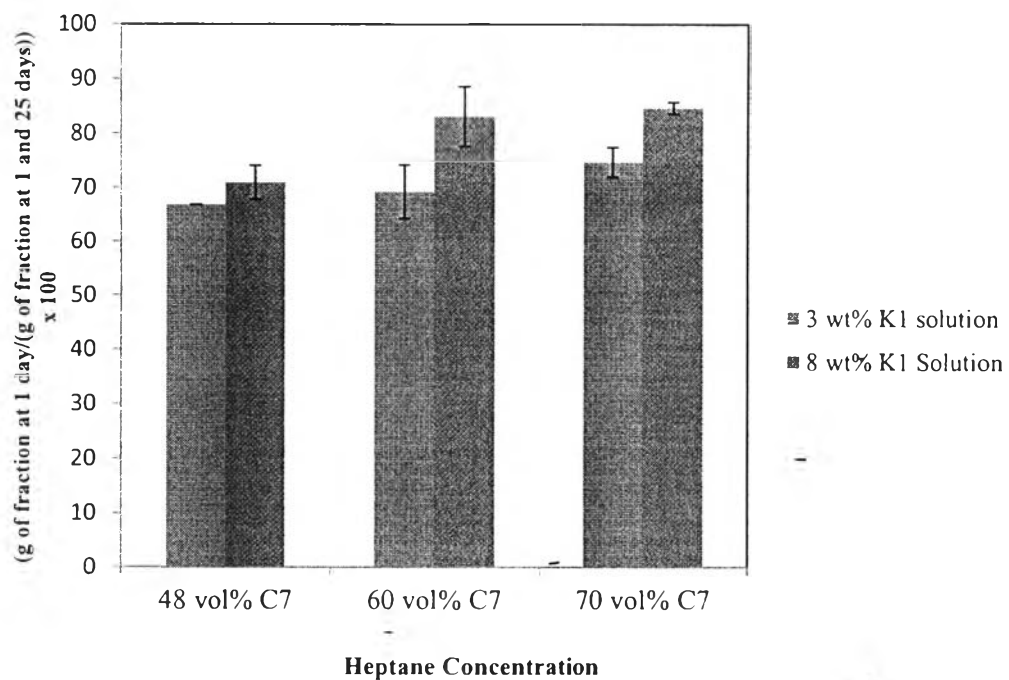
Figure B2 Fraction of asphaltenes precipitated at 1 day to total asphatlenes precipitated after 25 days as a function of heptane concentration.

Therefore, similar stability trends on the effect of asphaltene concentration observed from A1 and K1 fractionation can support our explanation mentioned earlier.

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