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CONCENTRATION EFFECTS IN HPLC-SEC ANALYSIS OF PETROLEUM ASPHALTENES

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ABSTRACT

The effect of concentration on the HPLC-SEC elution profile of petroleum asphaltenes has been examined in order to investigate the possible determination of critical micelle or microstructure concentrations as observed by other more laborious methods. It was observed in one case that above a certain threshold concentration (TC) the profile became constant in shape. TC was found to be in the range of previously reported CMC values by calorimetric titration. However, according to micellization theory the profile should start changing beyond the threshold concentration. Hence the association process of asphaltenes may even commence below the previously reported CMC possibly through a step-wise mechanism. A large dependence of the observed concentration effect upon wavelength of the UV-vis diode array detector is also reported. Therefore caution should be exercised when applying HPLC-SEC in deriving physicochemical information on heavy self-associating petroleum fractions.

INTRODUCTION

The use of size exclusion chromatography in the characterization and fractionation of petroleum products

such as asphalt and residua is abundant in the literature (1-5). Although the SEC technique in this area is recognized to give only relative results depending almost entirely on the calibration standards used, molecular weights based upon these results are frequently reported in the literature (5).

Especially the very heavy part of the crude oil such as the asphaltenes have a significant complexity which may affect the elution of the different compounds. Asphaltenes are briefly defined as the solid organics precipitating upon treatment of the crude oil with an excess of hydrocarbon such as n-heptane (6).

Self-association of asphaltenes in solution has been covered in a vast number of works employing different methods (7). These works have basically had the goal of determining the molecular weight of the asphaltenes (8).

Asphaltenes in solution have been shown to exhibit self-assembly, micellar and colloidal behavior in a number of works (9-13). This micellar behavior is seen in the apparent existence of a critical micelle concentration above which asphaltene "monomers" associate and form larger "micelles" (10,11,13). Based on our knowledge of asphaltene composition the critical micelle concentration should however be regarded as hypothetical, as the participating "monomers" in these mixed micelles are polydisperse in both structure and molecular weight. Hence a uniform micelle is probably non-existing (14). The magnitude of asphaltene CMCs reported in the literature is dependent upon the solvent and CMC is generally found in the range of 1 to 10 g/L depending also on the origin of the asphaltenes investigated (14).

Recent work on fractionated asphaltenes has however shown that only a small part of the asphaltenes actually participates in the association, whereas up to 60 % of

the asphaltene constituents remain unassociated when separated from the bulk asphaltenes as indicated by HPLC-SEC (15). The knowledge of the degree of association of a heavy feedstock may be of importance in the petroleum refining industry as a monomer is easy to process relative to a micelle.

Self-assembly of asphaltenes and other heavy petroleum products has been qualitatively investigated using HPLC-SEC indicating a small but significant change in the elution front as the concentration is changed (16). The association of the asphaltenes at and above a specific concentration has been monitored by both calorimetric titration (10) and surface tension measurements (11,13). This association has been related to the critical micellization concentration known from surfactants.

The present work was initiated in order to investigate whether the presence of a critical micelle or self-assembly concentration could be monitored by HPLC-SEC by examination of solutions of varying concentrations as the other methods previously used are tedious. Well characterized asphaltenes from Boscan and Kuwait oils were examined. The latter had previously been used in an extensive study of asphaltene association by calorimetric titration covering both effects of solvent and precipitation procedures for the asphaltenes (10). Due to the use of original samples in low supply only a few SEC measurements could be performed with these samples previously used in calorimetric investigations. These are used mostly as support for the results obtained using the Boscan asphaltenes. The chemical characterization of the particular asphaltenes has been reported elsewhere (15,17-20).

At this point it shall be emphasized that the term micelle is used arbitrarily due to the resemblance of the

observations to similar phenomena of reversed micelle formation in surfactant chemistry. Also the asphaltene micelles are more likely very complex aggregates of molecules, however needing a specific critical concentration in order to dominate the properties of the solution. Sheu et al. (12) have recently in detail explained the micellar resemblance of asphaltenes in solution.

EXPERIMENTAL.

Asphaltenes were separated according to a modified IP 143 procedure (18, 19) at ambient temperature followed by a thorough washing of the precipitated material to ensure removal of co-precipitated components. As precipitants n-heptane and mixtures of 10%toluene in n-heptane were used for respectively Kuwait and Boscan asphaltenes. Also a Kuwait asphaltene precipitated at 43°C in n-octane was examined. The addition of toluene to the precipitant was used to prepare more complex asphaltenes as low molecular weight species are dissolved in the precipitant (19). Asphaltene solutions of increasing concentration in toluene were prepared by weight (+/-0.01 mg) in sealed vials and left overnight to ensure solution equilibrium.

The chromatographic equipment consisted of a Hewlett-Packard 1090 HPLC with a diode array detector with 8 wavelengths. Freshly distilled toluene was used as eluant at a flow rate of 2mL/min at 30°C. The column was a Phenomenex Phenogel 5 μm , 10^4\AA , 30 cm 7.9 mm i.d. The DAD wavelengths examined were 305, 340, 380, 410, 420, 450, 500, and 575 nm. Only a few of these responses are reported herein. 50 μL sample solution was injected automatically.

Calibration was performed by examining polystyrene standards (PS) of known molecular weight in order to establish the non-excluded volume. $\log MW(PS) = 7.4848 - 0.7836t_R$.

RESULTS AND DISCUSSION.

Several non-size effects are known to affect SEC of petroleum derived components such as polyaromatic hydrocarbons, and hence the elution volume cannot be directly correlated to the molecular size of the individual compounds (21). The tailing of SEC chromatograms of petroleum products often reported (22) can be due either to adsorption through charge-transfer interactions with the stationary phase or to other non-size effects where even large PAHs elute later than a non-excluded compound (21). This is also seen in the present case where a significant tailing can be observed beyond the non-exclusion volume of ca. 7.0 min (calculated from MW of toluene) as determined by the polystyrene standards.

In the present work the possible association of petroleum products into micro or micelle-like structures may also affect the retention behavior. The investigation of micellar solutions by size exclusion chromatography has been reported to be complex in nature. This is caused by the dilution effects in the column as the sample propagates through it. This dilution affects the dynamic equilibrium involved in the micellization process especially close to the critical micelle concentration (CMC). In order to exist micelles have to be in equilibrium with a monomer concentration equal to CMC. As micelles and monomers will have different elution velocities through the column, they will be separated and hence micelles must dissociate in order to reestablish the local monomer

concentration of CMC. Hence the chromatographic profile becomes complex. For simple systems in aqueous solution, however, the determination of CMC and the equilibrium constants has been possible by SEC. The theory for SEC of aqueous micellar solutions has been reviewed by Birdi (23). The above effects are expected to increase the threshold concentration relative to the "true" CMC. It is assumed that the dilution effect may be minimized by using a single column configuration as employed herein.

Chromatograms of the Boscan asphaltenes recorded at 305 nm are given in Figure 1 as a function of concentration between 2.6 and 20.2 g/L. A distinct increase in the total exclusion peak at 3.5 min is observed while the peak at 4.6 min is relatively constant. A quantitative measure is given in figure 2 where the ratio of absorbances at 3.5 and 4.6 min. are plotted versus concentration for two detector wavelengths. The relative size of the 3.5 min peak becomes constant above ca. 8 g/L. The constant profile observed above 8 g/L is in contradiction to the expected change beyond a certain concentration as seen in aqueous SEC of micellar solutions (23). This may indicate that asphaltenes do associate below CMC. However, it could as well indicate that the dilution effect is minimized above this threshold value.

A Kuwait n-heptane asphaltene was also examined but as only a very small or no total exclusion peak (3.5 min) was found a similar analysis could not be performed. Chromatograms at 305 and 575 nm of this asphaltene at a concentration of 10 g/L are given in Figure 1. The three concentrations examined were 5.64, 10.44, and 20.09 g/L which are all above the CMC (3.24 g/L) in toluene at 25.02°C of this specific sample determined by calorimetry (10). Only minor changes can be detected in the normalized chromatograms supporting the findings of constancy for the Boscan asphaltenes. The changes were seen to be

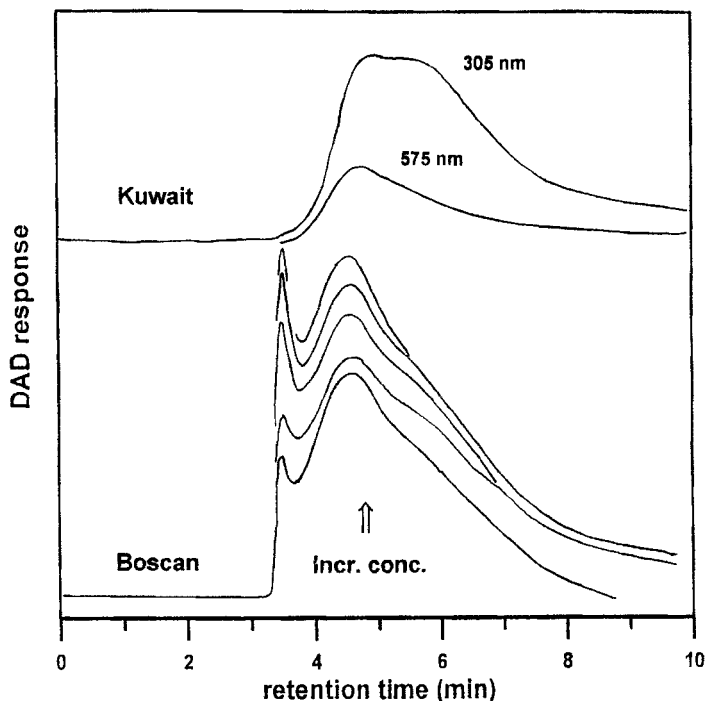


Figure 1. SEC Chromatograms of Boscan asphaltenes at 305 nm, concentrations 2.6, 5.0, 10.4, 16.0 & 20.4 g/L. Also given Kuwait n-C7 asphaltenes 10 g/L at 305 and 575 nm.

a small increase in response at short retention times and less at longer. The normalized area of the eluting front between 3.3 and 6 min was, however, found to increase about 8 % at all detector wavelength for 10 g/L where as a significant wavelength effect was observed for 20 g/L solution. In the latter case the response increased from 8 to 30 % between 305 and 500 nm as seen in Figure 3, where the 10 and 20 g/L responses are given relative to the 5 g/L response as a function of detector wavelength. Standard deviations on areas were less than 2 %. As can

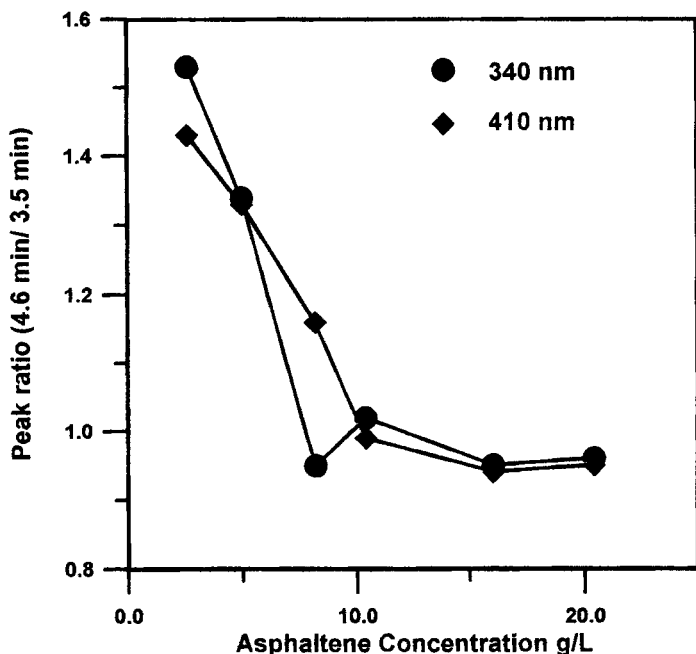


Figure 2. Ratio of detected absorbances at 4.6 to 3.5 minutes at 340 and 410 nm versus concentration of boscan asphaltenes in injected sample.

be seen the observations are significantly dependent upon the detector wavelength. The detector response could be caused by association of smaller molecules with larger ones that absorb light at higher wavelengths, hence rendering these even larger, giving them a shorter elution time. Also the species absorbing light at higher wavelength are more complex and may be the true associating species in asphaltenes. This is confirmed by the chromatograms as the bimodal type seen in Figure 1 dominates at low detector wavelengths, whereas only the 4.7 min peak with a significant tailing is observed at longer wavelengths for the Kuwait derived asphaltenes.

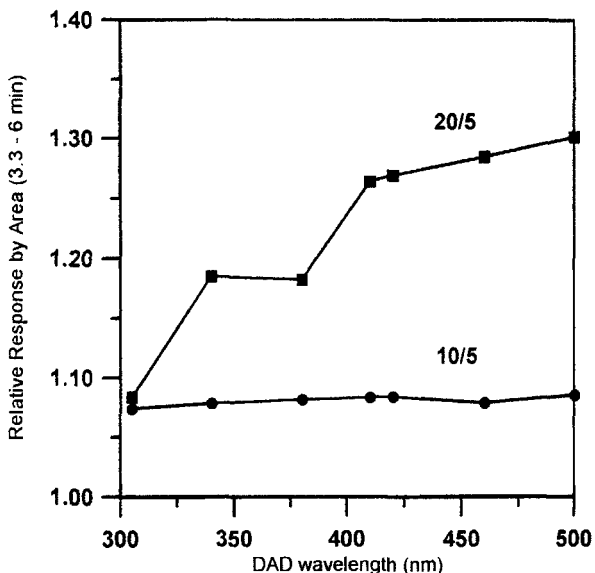


Figure 3. Relative response of main front of chromatograms versus detector wavelength. Response calculated for 10 and 20 g/L relative to signals for 5 g/L. Areas from integrator.

For the heavier Kuwait asphaltene obtained by precipitation in n-octane at elevated temperature two concentrations were examined at both side of CMC (1.55 g/L) as detected previously by calorimetry (24). Note that this asphaltene sample has a lower CMC than the one precipitated at 20°C by n-heptane from the same crude oil. In Figure 4 the two normalized chromatograms recorded at 305 nm and 500 nm between 3.3 and 9.0 min are subtracted giving a differential indication of the changes observed. As can be seen for the 305 nm response a significant relative increase in the low retention time side is observed hence a significant association is taking place between 1.22 and 4.33 g/L of this asphaltene

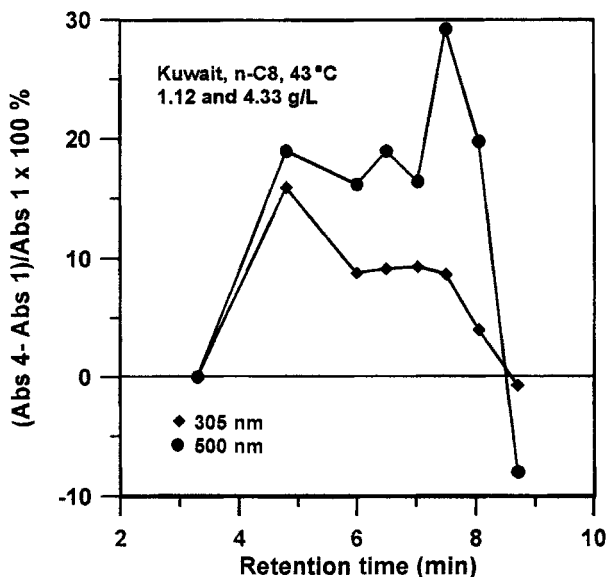


Figure 4. Differential chromatograms for Kuwait asphaltene injected in concentrations of 1.12 and 4.33 g/L. Signal were normalized with respect to the injected concentrations. Two detector wavelengths investigated.

in toluene. This is in good agreement with the above CMC value. However, for the 500 nm response a fairly constant increase is observed through out the chromatogram with a maximum at about 7.4 min. Again the result is significantly dependent upon the detector setting. These normalized chromatograms were constructed from points taken from the integration program and the specific concentration of the injected solution. Note that the relative error on the 500 nm signal is comparably larger as the detector response at this wavelength is one fifth of the response at 305 nm.

For the Boscan asphaltene the total integrated DAD signal at various wavelength was examined as a function of concentration and found to obey Beer's law. This was

also found for the Kuwait n-heptane asphaltene. Hence the changes observed in the chromatograms are strictly related to the association or rearrangement of asphaltene constituents. However the findings herein does not provide evidence of a specific critical concentration above which association starts, but rather indicate the step-wise association leading to a certain limit above which association in some way is constant or in equilibrium.

Qualitative concentration effects has also been reported by Jennings et al. (16) for two asphalts injected in concentrations between 1 and 7 g/L, where the intensity of the high molecular weight side of the chromatogram increased and apparently became constant. In the work of Donaldson et al. (2) a concentration effect between concentrations as high as 30 and 70 g/L toluene was reported for an asphalt but apparently without a limiting concentration. In asphalts, however, other non-asphaltene types are present to a large extent, which may affect the actual result of the analysis. The current author has also observed an increase in the total exclusion peak of both Kuwait and Boscan asphaltenes as these are solvent extracted removing compounds with low molecular weight (15, 20). In that case the true concentration of the associating compounds is increased relatively when the injected solution concentration is kept constant as the content of complex molecules in the asphaltenes increases. And therefore the apparent CMC is expected to decrease as observed with the Kuwait asphaltenes used in this work (10).

The picture of the asphaltene self-assembly emmerging from the present HPLC-SEC study is very complex. Not only is a CMC obscured by dilution effects and changes in monomer-micelle equilibria but the difference in response also makes the conclusions

difficult. The origin of the asphaltene and the pretreatment of this may also have a large effect as observed for the different samples investigated herein.

The concentration region investigated herein is often used in characterization of asphalts which may contain large quantities of asphaltenes, hence it is evident that care must be taken in the interpretation of the obtained data as molecular weights, colloidal indices and other SEC derived magnitudes will be concentration dependent. Also it is important to emphasize the dependence of the result obtained by different DAD wavelengths as is evident from Figure 3. This significant wavelength dependence has also been reported by others (25).

CONCLUSION

The possibility of observing an asphaltene concentration effect in HPLC-SEC that could be related to previously reported critical micellization processes in these petroleum fractions has been investigated. Although a strong asphaltene origin dependence is evident and no unambiguous trends could be deduced we may conclude as follows. A threshold concentration (TC) is observed above which no further changes takes place in the chromatogram. This cannot be related directly to the micellization where association starts above the critical micelle concentration (CMC). TC values are however well in agreement with the range of CMC magnitudes for asphaltenes reported in the literature. This was confirmed by examination of asphaltenes with known CMCs from investigations by calorimetric titration. Although the HPLC-SEC procedure is fast compared to other methods applied in association studies of asphaltenes the method is hampered by the dilution effects in the column. More

quantitative work as presented herein compared to other of the above mentioned methods are however needed before definite conclusions can be drawn.

This work also confirmed that chromatograms of heavy petroleum products are highly dependent upon both concentration and wavelength. This should be kept in mind when using HPLC-SEC for analytical determination of physicochemical properties of petroleum products to avoid ambiguous results.

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