

Fractionation of Asphaltenes by Gel Permeation Chromatography

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Synopsis

Asphaltenes from three asphalts of very diverse service properties were fractionated by gel permeation chromatography (GPC) on crosslinked polystyrene gels. Broad molecular weight distributions were found spanning from 700 to more than 40,000. Each sample consisted of two portions of similar quantities, one peaking around 1000 molecular weight, the other around 14,000. The distribution of structural features measured by infrared spectroscopy is discussed briefly.

Few attempts to fractionate the asphaltene part of a crude oil residuum have been described in the literature.^{1,2} Such fractionation analyses provide valuable insight into the composition and behavior of different asphalts; however, they are difficult and time-consuming when undertaken with common techniques because of the complex nature of asphaltic compounds. The range of chemical structure spans from predominantly aliphatic molecules to highly fused aromatic ring systems, and from pure hydrocarbons to heterocyclics containing carbonyl and other polar groups. The common fractionation methods, which are based on solubility or adsorptivity, cannot separate such a mixture strictly or even predominantly by molecular weight except when applied in combinations.

Gel permeation chromatography (GPC) (also called gel filtration), being similar to a molecular sieve process, separates molecules by their size and has been used very successfully on a number of complicated mixtures, especially biological substrates. This letter describes the fractionation of the asphaltenes from three selected paving asphalts by GPC. Here we give only a brief description of the technique and some results. A detailed description of the chromatographic procedure, more experimental results, and their evaluation is in press.³

The parent asphalts of the asphaltenes under study are very divergent in chemical composition and in their use properties. They were obtained from three different crude oils, one from the California San Joaquin Valley, one from Venezuela, and one from Arabia, and had all been steam-stripped to the same penetration of 90. Their asphaltene contents were 12, 27, and 22.5 wt.-%, respectively. The asphaltenes were separated from the asphalts by repeated extraction with boiling *n*-pentane.* They were fine brown powders which could be easily dissolved in benzene.

* Asphaltenes are defined by their insolubility in pentane or in other low-boiling aliphatic hydrocarbons; the soluble portions of an asphalt are called maltenes.

Samples (1 g.) of solute in 10 ml. of benzene containing 10% methanol were fractionated at room temperature on a column of 180 cm. length and 2 cm. diameter. Because of the rather large molecular weight range found in preliminary experiments, the column was packed with two grades of heavily crosslinked polystyrene gel in series, the gel of smaller pore size following that of larger pore size. The gels were prepared following Moore's⁴ recipes for his gels C and H with slight modification. Their optimal fractionation ranges in terms of asphaltene and maltene molecular weights were < 400–8000 and 1000–40,000, respectively. The methanol was added to solvent and eluent to prevent adsorption of the more polar constituents in our samples.

Cuts of 10 ml. were taken and evaporated to constant weight under vacuum at 50°C. The fractions were kept under nitrogen in the dark until they were redissolved for further study.

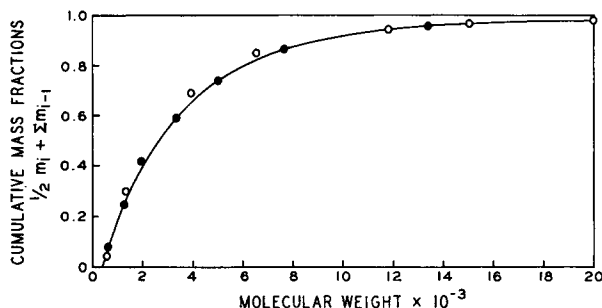


Fig. 1. Comparison of the efficiency of the gel column used in the present study with that of a Baker-Williams column for a polybutene sample: (\circ) fractionated by GPC; (\bullet) fractionated by gradient chromatography. The figure shows the corresponding integral distribution curves.

Molecular weights were determined in a Mechrolab vapor pressure osmometer. This thermoelectric instrument can be used for molecular weights up to 40,000 and yields number-average molecular weights. The measurements were carried out at 37°C. in reagent grade benzene at concentrations to give ΔR values between 1 and 3 ohms. The highest concentration was 4 g./100 g. solvent. The average deviations from the mean varied between 1% for the lowest molecular weights and 20% for values above $M = 10,000$. The concentration dependence was 12% at $c = 4$ g./100 g. benzene for $M = 20,000$ and 3% at $c = 0.5$ g./100 g. benzene for $M = 2000$. Since this is low compared to the error in molecular weights, measurements were carried out at one concentration only and the concentration dependence was neglected.

To test the gel column, one portion of a polybutene sample was fractionated under the same conditions as the asphaltenes; another portion was fractionated by gradient chromatography.* In Figure 1 the mass fractions

* I wish to thank Mr. M. J. R. Cantow for this analysis.

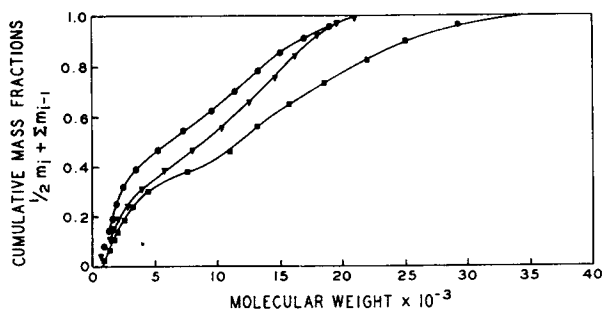


Fig. 2. Integral distribution curves of three asphaltenes: (●) California San Joaquin Valley asphaltene; (■) Venezuelan asphaltene; (▼) Arabian asphaltene.

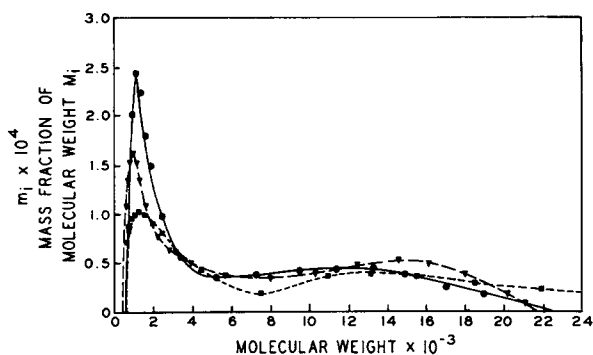


Fig. 3. Differential distribution curves of three asphaltenes: (●) California San Joaquin Valley asphaltene; (■) Venezuelan asphaltene; (▼) Arabian asphaltene.

are plotted versus the molecular weight according to Schulz's method.⁵ The integral molecular weight distribution curves obtained by the two techniques match very satisfactorily.

In Figure 2 the integral distribution curves of the three asphaltene samples are compared in the same plot. Graphical differentiation of these curves yielded the differential molecular weight distribution curves in Figure 3. Details, such as the narrow peaks in the low molecular weight range, were obtained by a new evaluation method based on the elution curve. A fuller account of this method, which was suggested by O. L. Harle,⁶ is in preparation.¹

An important result of this study is the rather wide molecular weight distribution of the asphaltene. The largest span of molecular weights reported before was from an unspecified lower limit to about 6000.¹ Now we find that each of the samples has a distinct portion in the low molecular weight range of 700–4000 and a second portion spread over a larger molecular weight range of up to 40,000 in case of the Venezuelan asphalt. This type of distribution accounts for part of the discrepancy of asphaltene molecular weights reported in the literature^{7,8} because it accentuates the

different averaging processes by the methods of boiling point elevation and ultracentrifugation. The number-average molecular weights of our three samples are in the range of 3000–4000, in close agreement with values found by boiling point elevation.^{7,8} The weight-average molecular weights calculated from the distributions vary from 7000 to 13,000. These numbers are considerably higher than the number-averages, although they do not match the molecular weights found with the ultracentrifuge^{7–9} and with diffusion¹⁰ at room temperature. Probably, the measured molecular weights of our high fractions are somewhat low because of some residual low molecular weight contamination which has a great effect on \bar{M}_n . On the other hand, the ultracentrifuge molecular weights tend to be too high because they are based on the optical density of asphaltene samples. We found that the optical density of asphaltene molecules increases with molecular weight by a factor of more than 3. This can lead to serious errors in the evaluation of sedimentation patterns obtained with a light absorption method.

The chemical structure of the asphaltene samples as a function of the molecular weight was studied with infrared spectroscopy. Again, some features common to the three asphaltenes were observed. The abundance of polar groups, such as hydroxyl (band at 2.90 μ) and carbonyl (5.8–5.9 μ) is greatest in the low molecular weight range and decreases with increasing molecular weight. The aromaticity (6.2 μ) of asphaltenes is significantly greater than that of maltenes but increases very little with molecular weight. The number of aliphatic chains with more than three C atoms (13.9 μ) also changes little with molecular size.

In this study we were not specifically concerned with aggregation. Preliminary experiments indicate that aggregation did not occur under the conditions of fractionation and molecular weight measurements.

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Résumé

Des asphaltènes, provenant de trois asphaltes, ayant des propriétés très diverses ont été fractionnés par chromatographie sur gels de polystyrène ponté (GPC). On a trouvé une large distribution du poids moléculaire s'étendant de 700 à plus de 40,000. Chaque échantillon était composé de deux portions de quantités égales, l'une se groupant autour d'un poids moléculaire de 1000, l'autre d'environ 14,000. La distribution des caractéristiques structurales, mesurées par IR, est discutée brièvement.

Zusammenfassung

Asphaltene aus drei Asphaltproben mit sehr verschiedenen Verweudungseigenschaften wurden durch Gelpermeationschromatographie (GPC) an vernetzten Polystyrolgelen fraktioniert. Breite Molekulargewichtsverteilungen mit einem Bereich von 700 bis mehr als 40,000 wurden gefunden. Jede Probe bestand aus zwei Teilen von etwa ähnlicher Grösse, die eine mit einem Maximum bei Molekulargewicht 1000, die andere mit einem solchen bei 14,000. Die Infrarotspektroskopisch bestimmte Strukturverteilung wird kurz diskutiert.

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