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Characterising high mass materials in heavy oil fractions by size exclusion chromatography and MALDI-mass spectrometry

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Abstract

Several petroleum vacuum residues and a Maya asphaltene have been examined using size exclusion chromatography (SEC), using 1-methyl-2-pyrrolidinone as eluent. Aliphatic components are not dissolved in this solvent. All the samples showed a bimodal distribution. Material under the early eluting peak, excluded from column porosity corresponded to apparently very large molecular masses. The later eluting peak corresponded to molecules with a smaller range of masses and was relatively intense. The material excluded from column porosity is concentrated in the heptane-insoluble fraction; the peak of this fraction corresponding to smaller molecules shifted to earlier times than was found for the whole sample. In UV-fluorescence spectrometry, the heptane-insoluble materials did not fluoresce strongly. Materials excluded from column porosity showed no fluorescence, indicating that UV-fluorescence based methods are unable to detect high mass materials. MALDI-mass spectrometry indicated a bimodal distribution for the Maya asphaltene with a mass range up to *m/z* 40,000. Comparison of the low mass range of the spectrum with the small-size molecules detected by SEC indicated broad agreement for masses up to about 5000 u. However, if the excluded peak of SEC corresponds to the higher mass range up to *m/z* 40,000, then it is likely that these molecules are adopting three-dimensional conformations. Data from the hydrocracking of heavy oils was used to confirm some of the outlined findings.

Keywords: UV-fluorescence spectrometry; MALDI-mass spectrometry; Size exclusion chromatography

1. Introduction

This paper presents recent work on molecular mass distributions of heavy oil fractions. The work is based on observations by size exclusion chromatography (SEC), with 1-methyl-2-pyrrolidinone (NMP) as eluent [1–3] and MALDI-mass spectrometry [4]. A detailed discussion of the SEC concerning the bimodal chromatograms and their significance has been given [3] and will not be repeated here. Other workers using SEC with NMP solvent [1,5,6] to examine aromatic systems have also seen bimodal distributions; in our work, concentration of solutions in the SEC columns were of the order of $5 \times 10^{-3}\%$ by weight [3] and the presence of aggregates of molecules has been discounted [7]. Problems suffered by SEC using other solvents have been summarised [8]; the use of refractive index detection requires much higher sample loadings than used in our work because that detector is less sensitive than detection by UV-absorbance, leading to overloading of the excluded region when using NMP [5,9].

As molecular mass determinations by SEC are dependent on calibration by specific polymers, attempts have been made to evaluate the relationship between molecular masses and the structures of various polymers used as molecular mass standards [3]. Determinations of molecular masses by MALDI-mass spectrometry have been used to provide data independent of the calibration of SEC [10] with polymers. By using standard molecules and samples from narrow-time fractions of pitch collected from preparative scale SEC, agreement has been found between polystyrene and polymethylmethacrylate calibrations of SEC (using NMP as eluent) and MALDI-MS at up to about 3000 u [11]. A continuum of molecular mass values up to at least *m/z* 100,000 has been observed by MALDI-MS, for a sample of the pyridine-insoluble fraction of a coal tar pitch [10]. The molecular mass range of petroleum asphaltenes continues to be a controversial

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issue and a summary of the current position has been given [12]; a problem with mass range determinations based on mass spectrometry is that the upper limit of mass is difficult to determine and may be limited by the ionisation method. Our work [3,4] has aimed to match determinations of mass ranges by independent techniques—SEC and MALDI-MS, and has achieved this for the small molecules of pitch and petroleum residues.

In the characterisation of complex hydrocarbon liquids, both MALDI and SEC show bimodal distributions of molecular mass. In SEC, all fractions from coal- and petroleum-liquid samples showed the presence of early eluting (apparently large molecular mass) material excluded from column porosity. A discernible valley of zero intensity may be observed between the two peaks. The later eluting peak is considered to correspond to material resolved by the column porosity. These observations are consistent with a shift in molecular conformation, of essentially planar molecules folding over to give molecular sizes disproportionately large with respect to their molecular masses. This is thought to happen somewhere above 6–10,000 u. In MALDI spectra of the same samples, the transition is not as clear-cut, although the observed mass ranges are not as extensive as the apparent mass ranges observed in SEC. We will return to these points with new data presented below.

The detailed characterisation of complex hydrocarbon mixtures is generally assisted by fractionation into narrower ranges of molecular masses [13], where size exclusion chromatograms of fractions of a coal tar pitch and a petroleum residue separated by planar chromatography shifted to increasingly greater molecular mass distributions as the strength and polarity of the solvent was increased. The same shifts to higher molecular mass were not observed when analysing similar fractions of pitch from TLC using SEC in THF solvent [14]. The solvent sequence from pentane, to toluene, acetonitrile and to pyridine is typical of solvents used in such work. The proportion of excluded material is generally observed to increase with increasing solvent polarity [13]. Synchronous UV-fluorescence spectra of these fractions have also been observed to shift to higher wavelengths with increasing strength and polarity of the solvent. However, fluorescence intensities (and quantum yields) decline rapidly as the masses of sample molecules examined increase [15].

Petroleum derived fractions mobile in pentane and toluene were found by SEC to be of larger molecular size when comparing petroleum residue and coal-derived samples. Internally, consistent data have been obtained with different SEC columns [13,16,17]. The work showed smaller molecular masses for the later eluting (second) peak of the coal tar pitch chromatogram, compared to the analogous (second) peak of the petroleum residue. However, the excluded peak was generally greater as a proportion of the whole fraction for coal liquids compared with petroleum residues. As would be expected, UV-fluorescence spectroscopy indicated that aromatic ring systems found in the coal tar pitch derived fractions were larger than those found in petroleum derived heavy oils.

Previous work on petroleum asphaltenes and distillation residues in this laboratory has attempted to define molecular mass ranges using SEC and by MALDI-mass spectrometry [4,18]. There was broad agreement between results from the two methods regarding the mass range of the late eluting peak in SEC for unfractionated residues and heptane insolubles and these mass ranges were similar to those found by fluorescence depolarisation [19]. The remaining problem is that the mass range of the excluded peak of SEC is undefined. Since this material does not fluoresce, determination of its mass range is of some importance for the number and weight average masses of residues and asphaltenes. In examining petroleum-derived fractions, the insolubility of alkanes in NMP presents a severe limitation, which is less important in the case of (more aromatic) coal-derived liquids. However, the NMP soluble material is the aromatic component of residues and asphaltenes [6] free from aliphatics and not composed of aggregates when in dilute solution in NMP [7].

As observed previously, fractionation allows the less abundant high mass fractions to be observed more clearly. This simply means that material that is more abundant tends to mask the detection of distinct but less abundant material. Thus, SEC chromatograms of whole (i.e. unfractionated) samples have been observed to show narrower molecular size distributions compared to, say, heptane-insoluble fractions alone [4,18]. Mass ranges by MALDI-MS also reflected the masking effect of the more abundant low mass fraction. Spectra of the whole samples have been observed to extend up to m/z 5000 while for the heptane-insoluble fraction of the same material, spectra were observed to extend up to m/z 10,000 [4,18]. The need for isolation of the heavy ends is demonstrated by this work since the less abundant higher mass material may go effectively undetected in the presence of the more abundant, lower mass material.

We have recently shown that fluorescence quantum yields decline sharply for material with molecular masses of 2000–3000 u. Heptane-insoluble fractions of petroleum residues contain a proportion of material that does not normally fluoresce despite having strong UV absorbance, suggesting the presence of complex structures able to lose the energy of UV absorbance by pathways other than fluorescence [15]. Certainly, no material eluting under the excluded peak of SEC chromatograms in petroleum derived asphaltene fractions can be observed by UV-fluorescence spectrometry [19]. Molecular mass estimates based on UV-fluorescence depolarisation therefore appear incapable of observing material in this mass range, and above.

Taken together, observed mass ranges from MALDI-MS tend to broadly agree with the mass ranges estimated from SEC for the retained (second) peaks, within a factor of approximately two. Major questions remain, however, regarding the molecular masses, structures and conformations of material excluded from the SEC column porosity. Previous indications from the use of colloidal silica samples with controlled particle size [3] suggest that the excluded material could be three-dimensional. Similarly, we have observed samples of fullerenes to appear at ‘apparent’ molecular masses commensurate with their molecular diameter rather than their mass [3].

Recent MALDI-MS based work [10] to characterise a pyridine-insoluble fraction of a coal tar pitch has given a continuous, albeit bimodal mass range up to about *m/z* 100,000. Material excluded from column porosity in SEC represents a much broader mass range when compared with the molecular masses of polystyrene standards eluting at the same times. It is likely the high mass lobe of the MALDI-spectrum (also see below) actually corresponds to the material excluded from column porosity in SEC. One likely mechanism for molecules to appear (elute) as much larger (earlier) than they really are would be by the adoption of folded conformations or three-dimensional structures. The aim of the present work was to extend recent work by MALDI-MS to the characterisation of heavy oils. The observed consequences of catalytic hydrocracking reactions on the molecular mass distributions of these materials will be briefly examined.

2. Experimental

2.1. Samples

Several petroleum vacuum residues have been examined following fractionation by solvent solubility in heptane. They include a Petrox refinery (near Concepcion, Chile) vacuum residue, “sample 1” and “sample 2” (proprietary vacuum residue samples) from earlier work [17], vacuum bottoms A, B and C (proprietary samples from a refinery in Holland), a Forties residue as well as a Maya heptane insoluble asphaltene (a gift from Dr. J. Ancheyta). Solvent solubility was used to fractionate the samples, to avoid loss of the largest molecules onto the silica, as was observed to occur during planar chromatography and column chromatography [20].

2.2. Size exclusion chromatography

Two 300 mm long, 7.5 mm i.d. polystyrene/polydivinylbenzene packed columns (Polymer Laboratories, UK), labelled as Mixed-A (20 μm particles) and Mixed-D (5 μm particles) have been used. Operating conditions of the system have been previously described in detail [3,21–26]. The Mixed-D column was operated at 80 °C with a Perkin-Elmer LC 250 isocratic pump, with eluent NMP pumped at 0.5 ml min^{-1}. The larger porosity Mixed-A column was operated at room temperature with the same NMP flow rate (0.5 ml min^{-1}).

SEC has the ability to be coupled on-line to a variety of detectors. A Perkin-Elmer LC 290 variable wavelength UV-absorbance detector and an Applied Biosystems diode array detector set at 280, 300, 350 and 370 nm were used routinely. An evaporative light scattering detector (Polymer Laboratories ELS 1000) has normally been used in series. This was particularly useful during calibration with PMMA standards and other work with samples with no or weak UV-absorption. On the other hand, UV-detection is useful for observing lower boiling aromatics that normally evaporate with the eluent during the ELS thermospray stage. Previous attempts to evaluate the utility of UV-fluorescence spectrometers have found no sensitivity to sample concentration above molecular masses of about 3000 u [27,28]. The ELS and UV-absorbance detectors have similar sensitivity to sample whereas refractive index detectors are less sensitive by a factor 10, necessitating overloading of the excluded region in order to generate enough signal [9,29].

2.3. UV-fluorescence spectroscopy

The procedure has been described elsewhere [30]. The Perkin-Elmer LS50 luminescence spectrometer scanned at 240 nm min^{-1} with a slit width of 25 nm; synchronous spectra were acquired at a constant wavelength difference of 20 nm. A quartz cell with 1 cm path length was used. The spectrometer featured automatic correction for changes in source intensity as a function of wavelength. Emission, excitation and synchronous spectra of the samples were obtained in NMP; only synchronous spectra are shown. Solutions were diluted with NMP to avoid self-absorption effects: dilution was increased until the fluorescence signal intensity began to decrease. However, it was necessary to examine the fluorescence from heptane-insoluble fractions in relatively concentrated solutions because the fluorescence quantum yields were rather low; in these cases, sample was added until the fluorescence signal was significantly greater than the background fluorescence.

2.4. Mass spectrometry

A Bruker Daltonics Reflex IV MALDI-TOF mass spectrometer was used for LD-MS and MALDI-MS. Various matrices were investigated including sinapinic acid, graphite, mercaptobenzothiazole (MBTA), trichloroacetic acid (TCAA), dihydroxybenzoic acid (DHB). A HIMAS detector operating in the linear mode was used generally to investigate the higher molecular mass region. Parameters – extraction voltage and detector voltage – were altered to attempt to detect the very high mass materials of the vacuum residue without either losing the smaller mass ions or overloading the detector, while increasing laser power to 90% of maximum. In addition, delays in applying the extraction voltage were used, of 200, 400 or 600 ns to enhance the relative intensities of high-mass ions while losing the faster ions from smaller molecules. Calibrations with a set of standards with masses between 6 and 18 kDa were run for every extraction voltage.

2.5. Hydrocracking experiments

The microbomb reactor and the procedure followed to run experiments in the presence of a solvent have been described elsewhere [31]. Briefly, 200 mg of sample were mixed with 1 g of tetralin and 100 mg of catalyst in the microbomb reactor. It was then pressurised with hydrogen and placed in a fluidised sand bath heater where it reached the operation temperature and pressure, 440 °C and 190 bar, respectively. Subsequent modifications to the experimental procedure were made in order to avoid the use of solvent [32]. Hydrocracking runs were 2 h long and the products were recovered and analysed. SEC chromatograms of the feed and hydrocracking products were run in a Mixed-A column under conditions as described above.

3. Results and discussion

3.1. Size exclusion chromatography

Fig. 1a compares SEC chromatograms of the unfractionated Forties residue and three vacuum residues: Petrox, 'sample 1' and 'sample 2' acquired using NMP as eluent in the Mixed-D column with detection by UV-absorbance at 350 nm. Fig. 1b presents analogous chromatograms for vacuum bottoms samples A, B and C obtained using the Mixed-A column with detection by UV-absorption at 350 nm. In both sets of chromatograms, these unfractionated samples showed very little material excluded from column porosity, eluting at short elution times. The chromatograms were similar to those of the heptane-soluble fractions (not shown) that comprise the bulk of the samples.

The main (second) peak eluted after 16 min on the Mixed-D column (Fig. 1a) and after 19 min on Mixed-A column (Fig. 1b). In both sets of chromatograms, a region of near zero intensity of several minutes was observable between the two peaks. The polystyrene masses corresponding to the leading edges of the main peaks at 16.5 min (Mixed-D) and 19 min (Mixed-A) were 2200 and 4300 u, respectively. The masses at peak intensity for these samples correspond to a polystyrene mass of about 400 u at 18.5 min for the Mixed-D column and about 180–100 u at 21.5–22 min for the Mixed-A column. The calibration of the larger pore diameter Mixed-A column was not expected to be accurate at low mass. The Mixed-D column is expected to resolve the low mass range (100–1000 u) more accurately; the calibration is considered to be more reliable and is in approximate agreement with recent measurements on asphaltenes using atmospheric pressure chemical ionisation mass spectrometry [12] and surface tension measurements [33].

Fig. 2 presents size exclusion chromatograms for the heptane-insoluble fractions of the samples in Fig. 1. These diagrams clearly show how the fractionation process has been effective in concentrating the larger molecular mass material excluded from column porosity. Furthermore, the later eluting (second) SEC peak was shifted to shorter elution times (larger molecular size) by approximately 2 min in the two sets of data. These heptane insolubles were equivalent to less than one or two percent by weight of the vacuum residues at the most.

Fig. 3 presents the SEC chromatograms of the Maya asphaltene and a heptane-soluble fraction; the asphaltene corresponded to about 11.3% by weight of the original crude [34] while the heptane-soluble fraction corresponded to about 1.3% of the asphaltene [15]. The heptane-soluble fraction contained a smaller proportion of excluded material than the

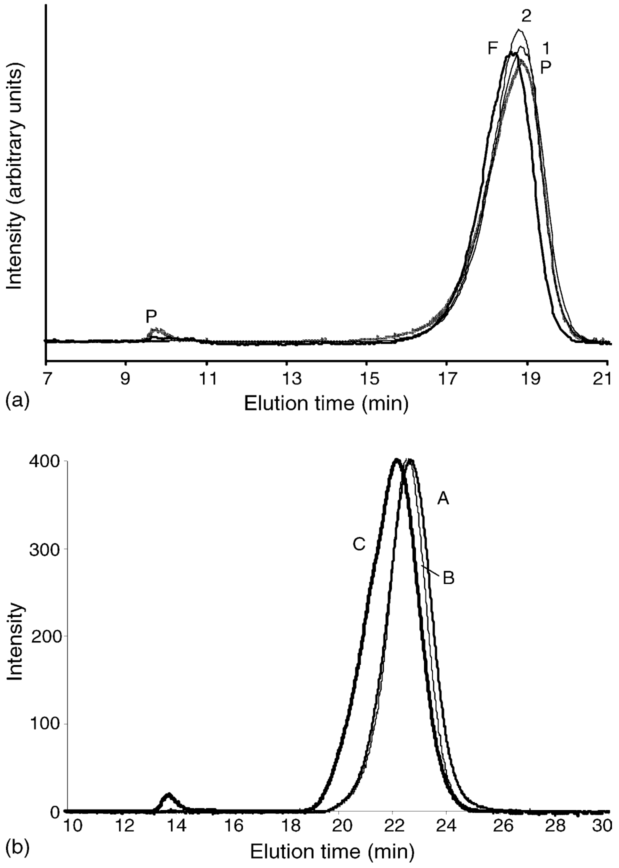

Fig. 1. (a) SEC chromatograms on Mixed-D of Petrox, Forties, vacuum residues samples "1" and "2"; detection by UV-A at 350 nm. (b) SEC chromatograms on Mixed-A of vacuum bottoms A, B and C; detection by UV-A at 350 nm.

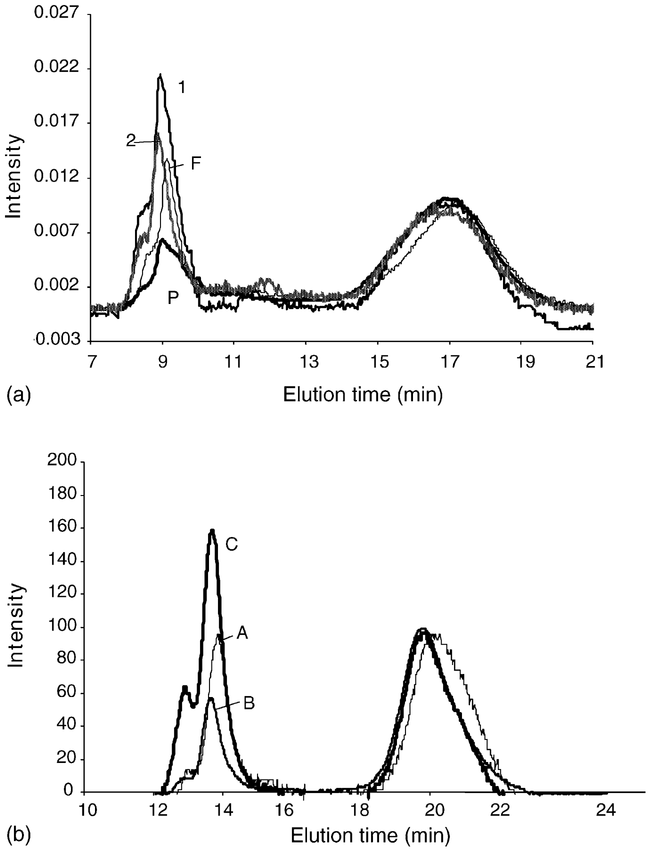

Fig. 2. (a) SEC chromatograms on Mixed-D of heptane insolubles of Petrox, Forties, samples 1 and 2; detection by UV-A at 350 nm. (b) SEC chromatograms on Mixed-A of heptane insolubles of vacuum bottoms A, B and C; detection by UV-A at 350 nm.

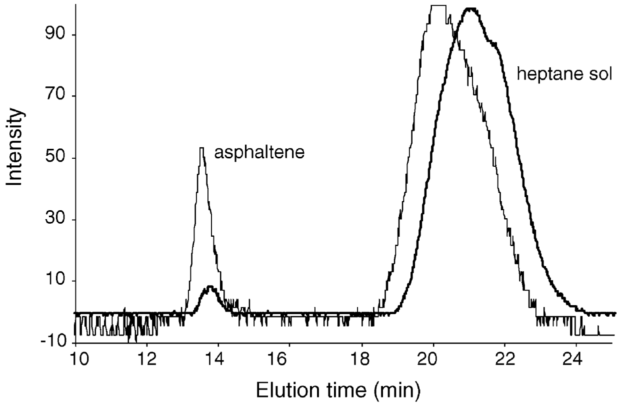

Fig. 3. SEC chromatograms of Maya asphaltene and a heptane-soluble fraction, Mixed-A.

whole asphaltene and the retained peak shifted to longer elution times than for the asphaltene. These differences parallel the differences observed between the vacuum residues of Fig. 1 and their heptane-insoluble fractions of Fig. 2.

We have shown elsewhere [3,7] that, at the sample concentrations used during SEC (in solution in NMP), the excluded peak cannot have been caused by aggregation of smaller polar molecules. Furthermore, material showing up under the excluded peak shows no significant fluorescence [15]. These data indicate the structures to be complex.

We have shown previously [3] that molecules such as fullerenes and solid particles with known spherical shapes elute in the excluded region (not as indicated by the mass) but with a relation between particle diameter and elution time that is entirely independent of particle density. This appears to be a unique property of SEC in NMP solvent; in SEC of Athabasca bitumen in THF [35], the material seen as excluded in NMP eluted with the bulk of the sample in THF and was not detected. The molecular masses of material excluded from column porosity, arrived at by SEC using the present calibration methods [3], usually appear to be larger than those detected by MALDI-mass spectrometry, at times by an order of magnitude or more. One likely explanation for the discrepancy between SEC and MALDI-MS may be linked to changing molecular conformations, as molecular masses increase beyond the range indicated by the resolved (second) peak. It is thought that initially two-dimensional molecules may bend and fold over as they increase in molecular mass. If molecular shape alters in this way, the molecule would behave as if it were far larger than its molecular mass would suggest. Evidence of three-dimensional structure, observed in the XRD pattern of a hard-dried pyridine-insoluble fraction (of a coal tar pitch) would tend to support this view [36].

Comparison of the elution times of the excluded material with those of spherical standards [3] indicates effective diameters for the excluded materials in Fig. 2a of 1–10 nm, for Fig. 2b from 1 to 8 nm and for the Maya asphaltene of not more than 1 nm. Diameters measured for spherical colloidal particles of crude oils [37] have shown similar values that did not reduce to less than 1 nm on dilution; extreme dilution may be expected to complete the disaggregation of asphaltenes in benzene. In our work [38], the presence of relatively large molecules is confirmed and the significance of their presence is that large molecules will be able to act as centres for aggregation in solvents less powerful than NMP where they are not in true solution.

SEC chromatograms with UV-absorbance and UV-fluorescence detection of the heptane-insoluble fractions of vacuum bottoms samples A and B are shown in Fig. 4. Other similar examples have been shown previously [15] for the Maya asphaltene and the heptane insolubles of vacuum bottoms B and the Forties residue. These data indicate that the excluded materials of the heptane insolubles have no significant fluorescence and may be classed as complex molecular structures; only the relatively small molecules in the fractions show fluorescence.

3.2. MALDI-mass spectrometry

The progress in the development of MALDI- and LD-MS to coal liquids has been described in some detail [10,11]. For the pyridine-insoluble fraction of a coal tar pitch, this work has extended mass ranges from less than *m/z* 500 to about *m/z* 10,000, up to more than 100,000 u. The rationale for this work was that conditions of ionisation should be selected such that both small molecules up to *m/z* 4000 or so as well as the very

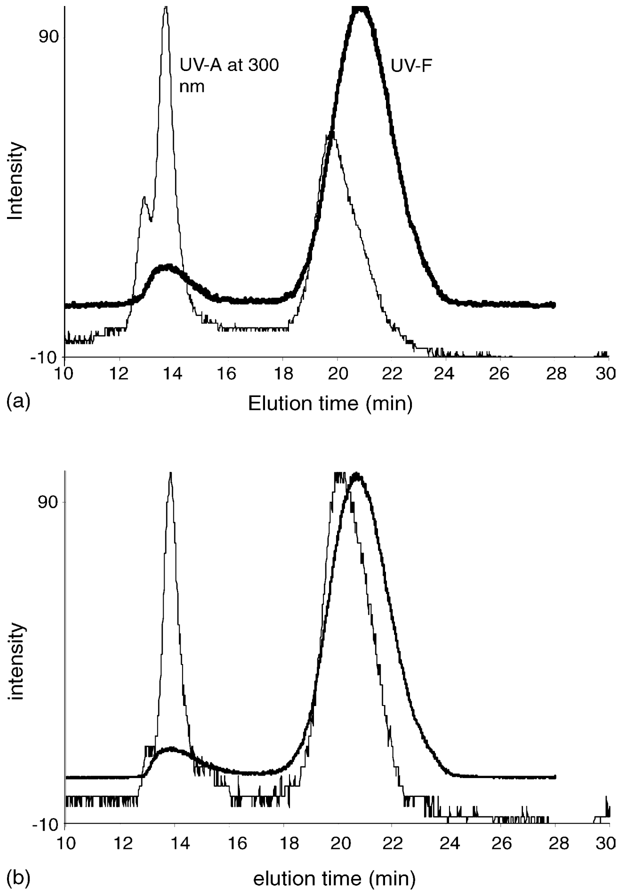

Fig. 4. (a) UV-A at 300 nm and UV-F (bold line) SEC of heptane insols of Vac Bottoms C, Mixed-A. (b) UV-A at 300 nm and UV-F (bold line) SEC of heptane insols of Vac Bottoms A, Mixed-A.

large molecules eluting from SEC in the excluded region, would appear in the mass spectrum without causing the detector to overload and produce spurious effects. Accordingly, the intensity of each spectrum (of the total 100 summed) was maintained at less than 100 intensity units [10].

In the present work, with the mass spectrometer, similar methods were applied during tests on the Maya petroleum asphaltene. Preliminary results indicated the presence of ions of low intensity up to *m*/*z* 40,000 or so. Further work is needed to confirm the mass range and to extend it to other residue samples. Fig. 5 shows a mass spectrum obtained during tests with the Maya asphaltene. The instrument parameters were selected to give a high laser power (90% of maximum). The HIMASS detector voltage was reduced from the usual 10 to 5 kV, in order to operate without causing the detector system to overload, due to high-intensity ions from small molecules. The laser desorption mass spectrum in Fig. 5 shows a bimodal distribution of ions from less than *m*/*z* 1000 to about *m*/*z* 40,000. Low mass molecules are liable to have evaporated in the ion source vacuum before ionisation and therefore the ions of mass less than *m*/*z* 1000 may be missing from the spectrum.

3.3. Catalytic hydrocracking of heavy oils

Previous work in this laboratory undertook to examine the catalytic hydrocracking of coal-liquids and the Petrox residue. Reactions were carried out under 190 bar hydrogen pressure in the presence of tetralin as solvent [38,39]. In both of these studies, the first stage of the reaction was the destruction of the material excluded from the porosity of the SEC column, but deposition of the largest molecules of the samples onto the catalyst as a carbon-rich layer prevented making the assumption that all of the excluded material had been hydrocracked rather than laid down on the catalyst. The presence of tetralin further complicated the situation since polymerisation of the solvent added to the apparent product slate.

Fig. 6a shows the SEC chromatograms for the Petrox residue before and after hydrocracking for 120 min, using pillared clay catalysts [39], Cr montmorillonite calcined at 500 °C and a tin laponite as well as a standard NiMo on silica PBC 90D catalyst and no-catalyst. These chromatograms show both the destruction of the excluded peak and the shift of the retained peak to longer elution times (smaller molecules) for the pillared clays, the poorer behaviour of the standard NiMo catalyst and the polymerisation in the absence of catalyst. The SEC column was overloaded in this work such that the excluded material spread into the valley between the peaks; however, the trends on hydrocracking are unmistakeable. Also, since the solvent medium used in the experiments was tetralin, some products from the tetralin may be present; the tetralin products would not appear significant in Fig. 6a since they would have maximum UV absorbance in the region 254–270 nm, where the NMP eluent is opaque. Therefore, the trends shown in Fig. 6a may be taken as representing the behaviour of the petroleum residue rather than the tetralin products.

Problems derived from the use of tetralin have been overcome in more recent work where both coal liquids [31,32] and vacuum residues were hydrocracked in the absence of a

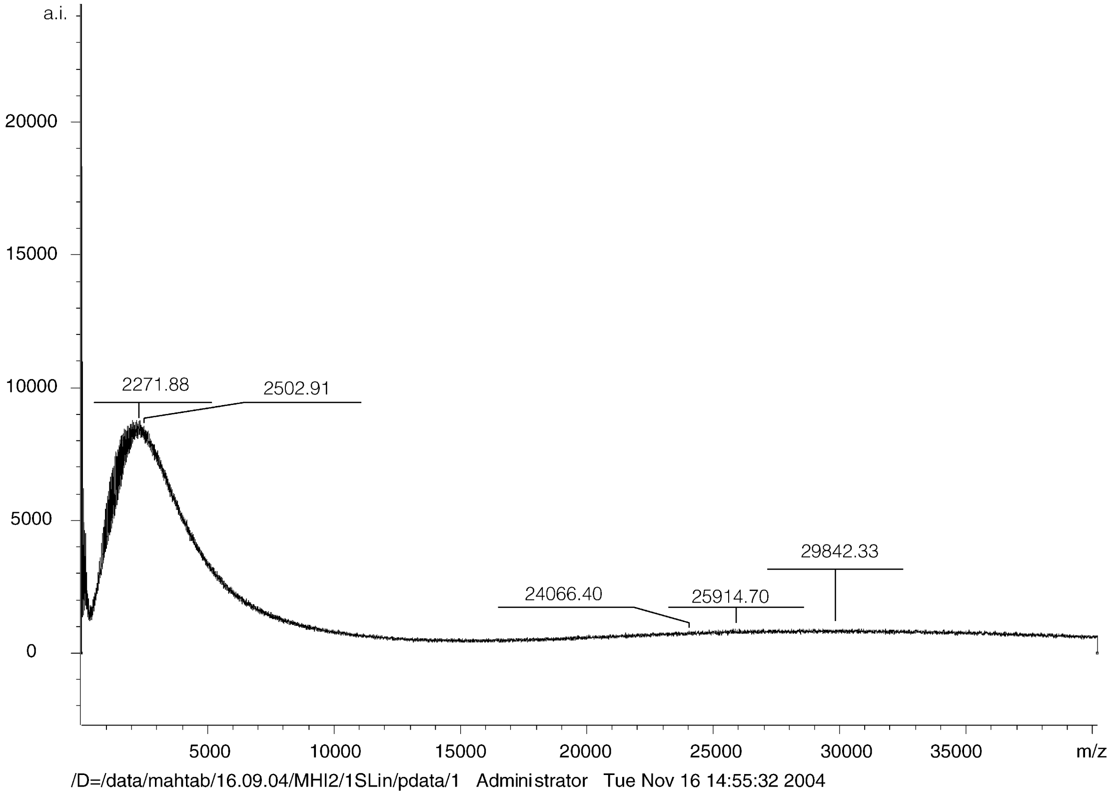

Fig. 5. LD-MS of Maya asphaltene.

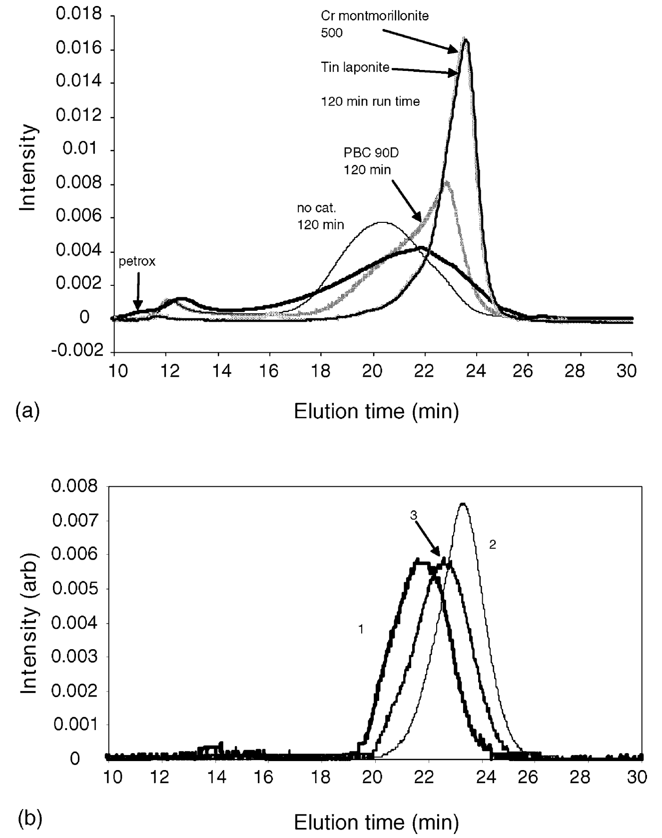

Fig. 6. (a) Hydrocracking of Petrox residue with various catalysts for 120 min; Mixed-E column at 300 nm UV-A. Data from Ref. [39]. (b) Hydrocracking of vacuum bottoms C (1), using fresh catalyst (2) and coated catalyst (3), Mixed-A column detection by UV-A at 300 nm.

solvent. The vacuum bottoms C were hydrocracked for 2 h at 440 °C in the presence of an aluminium montmorillonite as catalyst. The catalyst coated with carbonaceous deposits recovered from the first run was reused together with fresh feed in a hydrocracking experiment run under the same conditions. Although the vacuum bottoms C are heavier than the coal-derived liquids in terms of boiling point distributions, they were hydrocracked to a larger extent than the coal samples.

Fig. 6b shows the SEC chromatograms of the vacuum bottoms C and hydrocracking products recorded with the Mixed-A column. It can be seen that the small excluded peak eluting at about 14 min in the SEC of the feed was completely removed from the chromatogram of the hydrocracking products. Moreover, the retained peak shifted towards smaller masses relative to that of the feed in both runs. However, this shift of the retained peak is smaller in the run when an already coated catalyst is used. There are two factors that may contribute to the retained peak eluting at earlier times in the second run. Firstly, the catalyst deactivation is expected to be larger during the second use of the catalyst. Secondly, the deposition of heavy ends on the catalyst surface decreases when an already coated catalyst is employed, and therefore the amount of heavier materials in the liquid products tends to increase. Overall, these results show a clear reduction in molecular sizes after hydrocracking.

4. Summary and conclusions

The paper describes method development work aiming to characterise high mass materials in heavy oil fractions by size exclusion chromatography (SEC) using NMP as eluent and MALDI-mass spectrometry. Several petroleum vacuum residues and a Maya asphaltene have been examined.

In SEC using 1-methyl-2-pyrrolidinone as eluent, all samples showed bimodal distributions; however, only small quantities of material were excluded from column porosity. Material under the early eluting peak, excluded from column porosity corresponded to apparently very large molecular masses. The later eluting (second) peak corresponded to signal from a smaller range of masses and was relatively intense. The mass range of the second peak was from approximately 200 to 1500 u peaking at 400–500 u for residues. The excluded peak was separated from the main small molecule peak by a region of zero intensity.

The heptane-insoluble fractions of all samples concentrated the larger mass material, excluded from column porosity. The resolved (second) peak of this fraction corresponding to smaller molecules was observed to shift to earlier times than was found for the whole (unfractionated) sample. The mass range of this peak extended up to 5–7000 u with a peak at about 1200–1400 u based on polystyrene calibration data.

In UV-fluorescence spectrometry, the heptane-insoluble materials did not fluoresce strongly. Materials excluded from column porosity showed no fluorescence, indicating that UV-fluorescence based methods are unable to detect these high mass materials.

MALDI-mass spectra of the Maya asphaltene gave a bimodal, continuous mass range up to about *m/z* 40,000. The low mass range peak of the MALDI spectrum broadly corresponds to the lower mass (second) peak in SEC, for masses up to about 5000 u. However, the excluded peak in SEC appears to extend to far larger masses than those observed by MALDI-mass spectrometry. One likely explanation for the discrepancy between SEC and MALDI-mass spectrometry may be linked to changing molecular conformations in SEC, as molecular masses increase beyond the range indicated by the resolved (second) peak. Initially, two-dimensional molecules are thought to bend and fold over as they increase in molecular mass, behaving as far larger molecules, than their actual masses would suggest.

Hydrocracking evidence indicates that the excluded material rapidly breaks down to smaller masses while the size of the small molecules is also reduced.

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