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# Probing Size Exclusion Mechanisms of Complex Hydrocarbon Mixtures: The Effect of Altering Eluent Compositions

Stephanie Paul-Dauphin, Fatma Karaca,<sup>†</sup> Trevor J. Morgan, Marcos Millan-Agorio, Alan A. Herod,<sup>\*</sup> and Rafael Kandiyoti

Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.

Received July 16, 2007. Revised Manuscript Received September 3, 2007

This paper describes the application of size exclusion chromatography (SEC) to petroleum residue samples that are incompletely soluble in 1-methyl-2-pyrrolidinone (NMP). The limitations arising from the use of tetrahydrofuran, pure chloroform, and pure NMP have been reviewed. The SEC of polycyclic aromatic hydrocarbons (PAHs) in pure chloroform was observed to give longer elution times with increasing molecular mass, the opposite of the expected trend. Because the smallest molecules of coal tars are known to be PAHs, SEC can only be of use in investigating the larger molecules of unknown mass if the elution behavior of the smaller standard PAH relates to the calibration using polymers. The work relies on the observation that the NMP/chloroform mixtures dissolved both the heavier fractions of a coal tar pitch and the whole of a petroleum asphaltene, completely at the low concentrations needed for SEC. The first tests of the new SEC calibration have been carried out using a Mixed-E column and pure NMP, pure chloroform, and mixtures of these solvents as eluents. Most of the work was carried out at an NMP-to-chloroform volume ratio of 5:1. These initial results show elution times of polystyrene standards and PAH on a Mixed-E column using mixtures of NMP and chloroform as well as these solvent separately. The elution behavior of a vacuum residue in three different eluents is presented. The excluded peak observed in chromatograms of a vacuum residue and an asphaltene became more intense when using the mixed solvent compared to SEC using pure NMP as eluent. Synchronous UV–fluorescence spectra confirmed that petroleum derived components with the largest chromophores are insoluble in NMP but soluble in chloroform and observable by UV–fluorescence spectroscopy. The data suggest that the fraction insoluble in NMP was of larger aromatic cluster size and presumably attached to very large aliphatic groups that rendered the material insoluble in NMP but soluble in both chloroform and the mixed solvent.

## 1. Introduction

Size exclusion chromatography (SEC) is one of the techniques commonly used to characterize complex hydrocarbon mixtures which cannot be completely analyzed by GC or GC-MS. In the absence of methods able to access the entire mass range of the samples, SEC allows estimating, rather than determining, mass ranges of samples above the GC range, about 300–350 u for aromatic compounds and about 500 u for aliphatic compounds. Methods of calibration and developments in applying this technique to complex hydrocarbon mixtures have been described in some detail.<sup>1–7</sup>

Tetrahydrofuran (THF) was the solvent most frequently used as eluent in SEC.<sup>8–10</sup> However, THF does not dissolve coal-derived pitch samples completely; blockages of guard columns were observed, indicating material precipitating out of solution.<sup>11–13</sup> Failures of the size mechanism in THF eluent were identified in the fractionation of pitch<sup>14</sup> by planar chromatography and the preparative SEC fractionation of Athabasca bitumen,<sup>15</sup> and its use in SEC was abandoned.

Lafleur and Nakagawa<sup>16</sup> were the first to use 1-methyl-2-pyrrolidinone (NMP) as eluent for SEC. NMP dissolved the

<sup>\*</sup> Author for correspondence: e-mail, a.herod@imperial.ac.uk.

<sup>†</sup> Present address: Marmara University, Engineering Faculty, Department of Chemical Engineering, Kadikoy-Istanbul, Turkey.

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majority of the coal-derived liquids studied completely<sup>1,2,11–13,17–26</sup> and nearly always produced bimodal chromatograms for samples that were not distillates. Distillate samples produced monomodal distributions showing that the relatively small molecules fractionated by distillation behaved in the SEC system as small molecules.<sup>25</sup>

Further extensive work described elsewhere<sup>1–3,7,20,23</sup> using standard compounds and fractions from different chromatographic methods indicated that the calibration of SEC (with NMP as the eluent) using polystyrene (PS) and poly(methyl methacrylate) (PMMA) molecular mass standards gave valid estimations of molecular mass for coal tar pitch (up to approximately 3000 u) and the polycyclic aromatic hydrocarbon (PAH) standards available. The widest departures from the PS–PMMA line were recorded for polysaccharide polymer standards, indicating that oxygenated compounds would be expected to elute earlier than PAH when using NMP as the eluent.<sup>2,23</sup>

However, NMP does not dissolve aliphatic materials. We have observed that nearly half of some *petroleum* derived asphaltenes do not dissolve in NMP.<sup>4</sup> The wider use of SEC thus requires the use of a more selective solvent (or solvent mixture combination) that would wholly dissolve both petroleum and coal derived samples, including petroleum asphaltenes and distillation residues.

In addition to requiring the elaborate calibration procedures just described, SEC is also open to a degree of interpretation. Whether the material with large molecular masses observed in SEC might consist of aggregates of smaller polar molecules has been repeatedly debated. One line of approach originated from the inability of field-ionization<sup>27</sup> mass spectrometers and earlier laser desorption instruments<sup>28,29</sup> lacking sensitivity to materials above the 1000–1200 u range. It was proposed that molecules *not* detected by these instruments did not exist. Despite persisting problems regarding resolution at the higher masses, however, modern LD-MS and MALDI instruments are able to show, with high levels of reproducibility, the presence of material at masses as high as 100 000 u.<sup>5,30,31</sup>

Evidence for molecular aggregation in SEC using the eluent NMP was thought to have been found when experiments showed that peaks observed as excluded from the column porosity shifted to longer elution times (i.e., to smaller apparent molecular masses), when LiBr was dissolved in the eluent. These observations were interpreted in terms of larger molecules being disaggregated by the action of the additive to the eluent. The shifts were attributed to the dissipation of ionic binding forces, causing disaggregation of polar clusters, which would otherwise have appeared at retention times appropriate to larger molecular masses.<sup>32,33</sup> Other salts such as tetrabutylammoniumacetate (TBAA) were claimed<sup>34,35</sup> to disaggregate clusters. However, examination of the action of LiBr and other salts on nonpolar samples and coal-derived liquid fractions<sup>17,22,24</sup> indicated that the addition of salts directly to the SEC eluent had an adverse effect on the size exclusion mechanism. In this debate, the point at issue was *not* whether heavy hydrocarbon molecules may aggregate at all (which they clearly do at high concentrations) but whether molecules of complex heavy hydrocarbon samples might aggregate at concentrations encountered within the column and detector of an SEC system.

A method based on ultraviolet fluorescence depolarization<sup>36,37</sup> to estimate average molecular masses of petroleum asphaltenes was unable to detect average molecular masses above 1000 u; it was suggested that larger molecules did not exist in petroleum asphaltenes and that the identification of higher molecular masses in these samples arose from the aggregation of polar molecules. However, the sensitivity of UV–fluorescence based methods diminishes sharply with increasing molecular mass and disappears almost completely above about 3200 u, for both coal and petroleum derived samples.<sup>11,12,38–40</sup> The large molecular mass materials eluting early in SEC do not fluoresce.<sup>40</sup> Similar conclusions have been reached in two other laboratories.<sup>41,42</sup>

The absence of aggregation related effects at very low concentrations in SEC with NMP as eluent may be *inferred*, by experiments such as recovering eluted material and re-injecting into the same instrument, to test whether the sample appears at the same elution time. While providing a degree of confidence, such experiments do not constitute proof. Ultimately, *demonstrating the absence* of a particular phenomenon seems a difficult task. Conversely, the proposition that material with larger molecular masses than say 1000 u consists of aggregates requires a measure of verification that has not, to date, been forthcoming.

All this emphatically *does not* mean that we know all that we need to know about SEC, let alone on the structures and mass distributions of asphaltenes. Molecular mass and structural information regarding the nature of material giving signal under the excluded peak is lacking. Similarly, further work is needed to ascertain a safe upper limit of molecular masses identifiable

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by SEC. Another obvious problem concerns the nature of the solvent NMP. Although coal liquids appear to dissolve completely in NMP, petroleum asphaltenes are only partly soluble in this solvent. Others have used chloroform,<sup>43</sup> but the calibration using PS standards was not adequate to predict molecular masses of PAH standards.

We have recently observed that NMP/chloroform mixtures of 5:1, 6:1, and 7:1 ratios (v/v) were able to dissolve completely several samples of petroleum asphaltenes at the low concentrations needed for SEC. It was decided to try chloroform/NMP mixtures as eluent in SEC. This paper presents initial results from this work, investigating the relationship between PS standards and PAH on a Mixed-E column used with mixtures of the two solvents. In addition, we have compared the elution behavior of a vacuum residue in three solvents, chloroform, NMP, and an NMP/chloroform mixture, at a ratio of 5:1, and a Maya asphaltene in the mixed solvent.

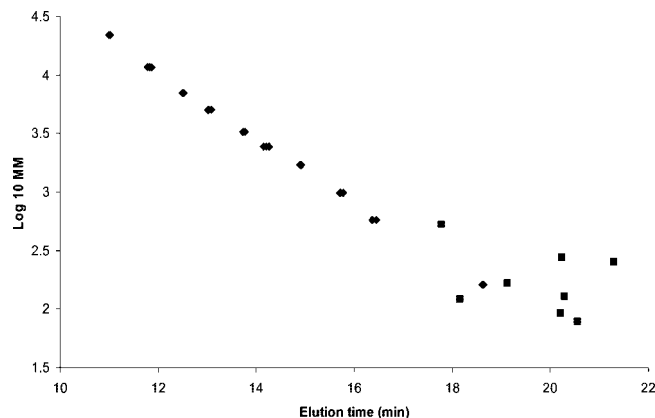
## 2. Experimental Section

**2.1. SEC.** The Mixed-E column used in this work (Polymer Laboratories, Church Stretton, U.K.) has been used with several other solvents. THF was used initially,<sup>14</sup> followed by NMP<sup>17</sup> including NMP with 10 mM LiBr and more recently with chloroform and the mixed solvent NMP/chloroform at the volume ratios 5:1, 6:1, and 7:1 as well as with pure NMP. The column was 300 mm long by 75 mm o.d., packed with 3  $\mu$ m particles of PS/polydivinylbenzene. It shows a linear calibration between elution volume and  $\log_{10}$  molecular mass (MM) accommodating PS molecular mass standards from mass 580 to 20 000 u in toluene solution.

Different temperatures and flow rates have been used with the various solvents. The conditions for THF were room temperature and a flow of 0.5 mL/min. The initial work using NMP required that the column was heated to 85 °C with a flow rate of 0.45 mL/min because of the relatively high viscosity of NMP and the limit on back-pressure of the pump. After several years out of use, the column was re-used with NMP and a different pump and found to be able to operate at room temperature with a flow rate of 0.5 mL/min; these same conditions have been used in the present work. When used with either chloroform or the mixed (5:1, 6:1, and 7:1 by volume NMP/chloroform) solvents, the operating conditions were room temperature and a flow of 0.5 mL/min. The same column had been used with heptane as eluent to investigate aliphatics by SEC.<sup>44</sup>

Detection of PSs and PAH in the eluent was by UV absorbance using wavelengths of 254 nm for THF and 267 for NMP and PSs but 300 nm for PAH, 254 nm in chloroform, and 278 in NMP/chloroform. A major problem is that NMP is opaque below about 270 nm so that PSs can only be detected in the presence of a significant absorbance by the solvent. An alternative detection method, evaporative light scattering (ELS) from Polymer Laboratories, has been used in some cases. The evaporation and nebulizer temperatures were set close to the boiling point of NMP, 202 °C, to obtain satisfactory results.

**2.2. Samples.** PS standards were obtained from Polymer Laboratories; the various PAHs and fullerites were from Aldrich, Gillingham, U.K. The solvents were from BDH, Poole, U.K. (THF and chloroform as HPLC grade), and Rathburn Chemicals Ltd., Walkerburn, Scotland, U.K. (NMP, peptide synthesis grade). Vacuum residue C used previously<sup>30,40</sup> was investigated as a test of the method with the eluents NMP (NMP soluble fraction), 5:1 mixed solvent (whole sample), and chloroform (whole sample). An asphaltene prepared from Maya crude as the heptane insoluble



**Figure 1.**  $\log_{10}$  MM vs elution time for PS standards (diamonds) and PAH (squares) eluted in THF from a Mixed-E column from the data of ref.<sup>14</sup> not previously shown in this form.

fraction<sup>30,40</sup> was a gift from Dr. Ancheyta from the Mexican Petroleum Institute.

**2.3. UV-Fluorescence Spectroscopy.** The procedure has been described elsewhere.<sup>38</sup> The Perkin-Elmer LS50 luminescence spectrometer was set with a slit width of 25 nm, to scan at 240 nm  $\text{min}^{-1}$ ; 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 sample of vacuum residue C were obtained in NMP and chloroform; 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.

## 3. Results and Discussion

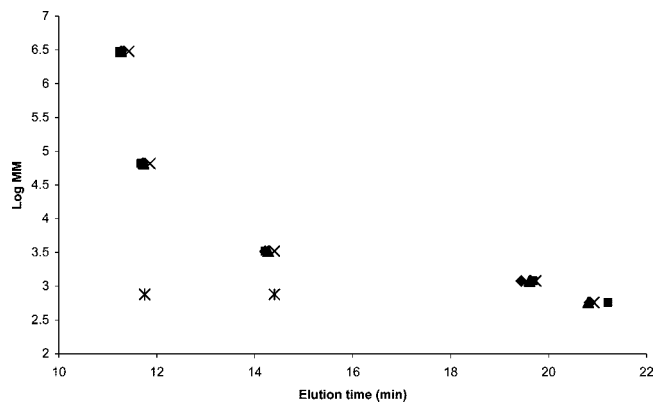
Figure 1 presents the calibration line for the Mixed-E column, obtained using THF as eluent. A set of PAH compounds and PS samples were used as molecular mass standards. These data were taken from previous work<sup>14</sup> and show that the sequence of PS molecular mass standards gave a linear relation between  $\log_{10}$  MM and elution time. However, elution times for the PAH compounds were significantly different from the molecular mass values suggested by this calibration and for some PAHs were the opposite to the expected trend. The observations (i) that THF did not dissolve coal tar pitch completely and (ii) that there was an evident discrepancy between the PS calibration and elution times of known PAH compounds led to abandoning THF as eluent for SEC altogether.

Clearly, the molecular mass range of coal liquids is not known with any degree of precision. It seemed reasonable, therefore, to consider the calibration of the SEC column as adequate, provided the molecular masses of known PAH compounds could be estimated with reasonable consistency by a calibration using polymer standards of known molecular mass. Accordingly, the SEC columns (Mixed-D and Mixed-A from Polymer Laboratories) were calibrated, using sets of PS, PMMA, and polysaccharide molecular mass standards, as well as PAH compounds, and several polymers of different types (molecular masses) and polydispersities. This campaign was carried out using pure NMP as eluent. The calibrations have been shown elsewhere<sup>1-3,7,23</sup> and indicated that the elution times of the majority of the standards could be estimated within one or two minutes of their measured elution times using the PS-PMMA calibration. The discrepancies with oxygenated samples have been discussed above and were taken as the worst departure from the PS-PMMA line. The difference at about 12.5 min elution time

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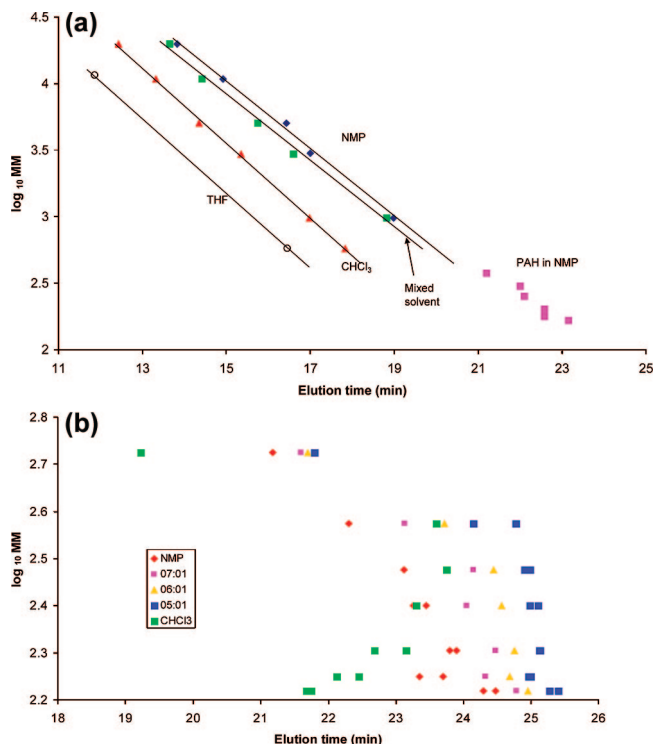
**Figure 2.** Log<sub>10</sub> MM vs elution time for PS standards eluted from the Mixed-E column using NMP (diamonds and crosses) and NMP with 10 mM LiBr (squares and triangles) with results in duplicate and also showing the elution times of fullerite in the two eluents (stars, with the later-eluting one in NMP plus LiBr).

consisted of the PS-PMMA line showing 15000 u, while the PSAC line showed about 6500 u, differing by a factor of less than 2.5.

The present work aims to widen the range of samples that can be characterized using the same SEC system. The first tests of the new calibration have been carried out using a Mixed-E column and pure NMP, pure chloroform, and specific mixtures of these solvents as eluents. Figure 2 presents parts of a previous calibration work<sup>17</sup> not hitherto shown, using NMP with and without LiBr as eluent and PSs as calibrant. The data show four SEC runs with a PS mixture (molecular masses  $3.04 \times 10^6$ , 66 000, 3300, 1200, and 580 u) including two runs with LiBr and indicated that LiBr had no effect on the elution times of the PSs. The elution times of a fullerene mixture were affected by LiBr. In NMP alone, the fullerenes showed a peak at an elution time of 11.75 min, while in NMP with LiBr dissolved, the fullerenes showed a peak at an elution time of 14.4 min. The SEC chromatograms of fractions of a naphthalene pitch were similarly affected, with shifts to longer elution times. Similarly, the effect of LiBr on coal liquids was to delay their elution,<sup>17</sup> giving the appearance that the molecules had been “disaggregated”, but showing in reality that LiBr ruined the size exclusion mechanism for aromatics by introducing surface interactions.

Figure 3a shows calibration data (log<sub>10</sub> MM vs elution time) for PS standards with (i) pure chloroform, (ii) pure NMP, and (iii) a 5:1 mixture of NMP/chloroform as eluents. The figure also shows the elution times of PAH compounds in NMP only. Calibration data for 6:1 and 7:1 NMP/chloroform mixtures lie in the same region of the figure as the NMP and 5:1 mixture and are not shown. The THF calibration line using PSs of Figure 1 is included for comparison.

The observed position of the various PS calibration lines in Figure 3a followed the order of increasing viscosity of the eluents. Comparison of Figures 1 and 3 indicates that THF eluted the PS standards earlier than chloroform. From THF (viscosity at 25 °C, 0.456 mPa·s) to pure chloroform (viscosity at 25 °C, 0.537 mPa·s) and to pure NMP (viscosity at 25 °C, 1.66 mPa·s), the calibration graphs were observed to shift to later elution times but remained approximately parallel. The viscosity values are from the literature,<sup>45–47</sup> but it is not clear if viscosity has an



**Figure 3.** Log<sub>10</sub> MM vs elution time for PS standards and PAH standards eluted from the Mixed-E column using chloroform, NMP, and a mixture of NMP and chloroform (5:1). (a) PSs in chloroform, NMP, and 5:1 NMP/chloroform and PAH in NMP only, also showing the relative position of the THF calibration line of Figure 1. (b) PAH chloroform only, NMP only, and NMP/chloroform mixtures (shown as 5:1, 6:1, and 7:1 volume ratios), colors as shown on the figure.

effect on the elution times of the standards by SEC. The calibration graphs for PSs in the mixed solvents were found to lie closer to the line for pure NMP as eluent; they appear to be almost indistinguishable within experimental error but clearly shift a little towards the calibration line for chloroform alone. A similar comparison of calibration curves has been made<sup>48</sup> for PS-divinylbenzene columns using *N,N*-dimethylformamide (DMF) or THF as eluents with PS and poly(ethylene glycol) (PEG) standards; PS and PEG in DMF and PEG in THF eluted over similar times, but PS in DMF eluted much later, up to 20 min under the conditions used. The difference in behavior of the PS in DMF was attributed to adsorption of PS on the column packing, while hydrogen bonding of the PEG to DMF (and PS to THF) was presumed to increase their elution volumes by enhancing their molecular volumes.

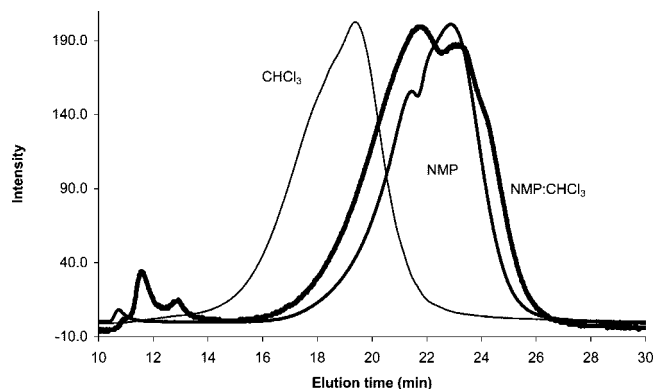
We next consider the elution of the PAH and other standards and how they relate to the polymer calibration. Figure 1 with SEC data using THF as eluent shows that the PAH elutes with quite different characteristics than the PSs. Data for the elution of PAH compounds using pure NMP as eluent are shown in Figure 3a and in greater detail in Figure 3b for the other eluents, chloroform, and the mixed solvents. The data in NMP alone serve to define the trends seen in NMP with other mixed-bed columns reported previously.<sup>1–3,23</sup> The small PAH molecules elute slightly later than indicated by the PS calibration, as seen in Figure 3a. The data for PAH eluting in chloroform alone clearly make up a line with the slope going the “wrong way”, with elution times *lengthening* as molecular masses *increase*.

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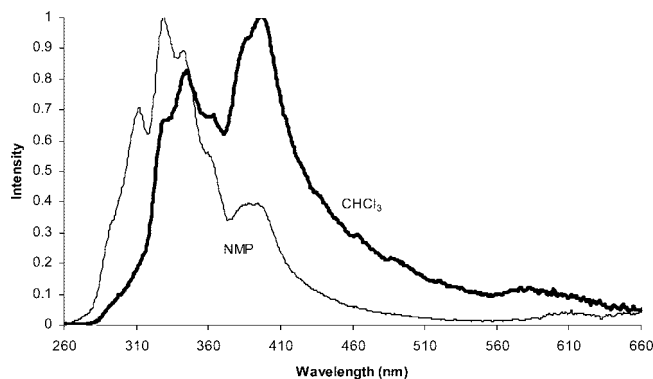
**Figure 4.** SEC on the Mixed-E column of vacuum residue C using chloroform, NMP and 5:1 NMP:chloroform as eluents, detection at 278 nm UV absorbance.

These findings show that pure chloroform is unlikely to elute materials containing aromatic compounds in a satisfactory fashion. Clearly, this category includes coal liquids as well as the more aromatic parts of petroleum asphaltenes and distillation residues. Despite the previous, reasonably widespread use of chloroform as eluent in the SEC of petroleum derived fractions, the data presented in Figure 3b suggest the necessity for greater circumspection in selecting eluents for both heavier petroleum fractions as well as for coal liquids.

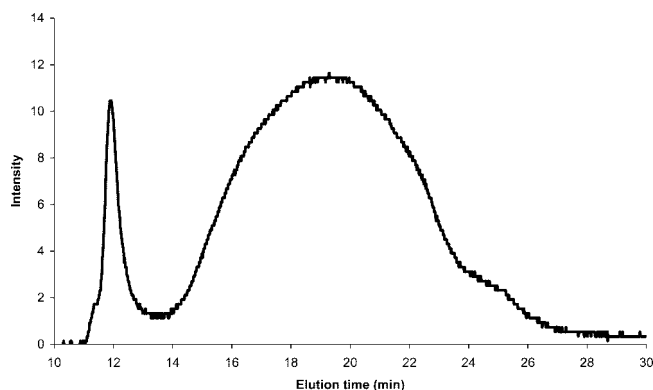
In Figure 3a,b, the PAH samples were observed to elute closest to the polymer calibration when pure NMP was used as eluent. To some extent this justifies the use of NMP in previous applications, with the emphasis then on coal liquids, as in the case of previous calibrations of the Mixed-D and Mixed-A columns. Indeed, experience to date suggests NMP to represent the best system for examining coal liquids. As already explained, however, NMP cannot dissolve petroleum asphaltenes completely. Despite the discrepancies observed in SEC, furthermore, chloroform is known to have the ability to dissolve petroleum asphaltenes completely. It seemed reasonable, therefore, to experiment with mixtures of the two solvents, to attempt preparing a mixture that would borrow the desirable characteristics of both solvents.

Accordingly we experimented with various mixtures of NMP and chloroform. The 5:1, 6:1, and 7:1 volume mixtures of NMP and chloroform all appeared able to dissolve asphaltenes completely. First, the elution behavior of PAH compounds using these mixtures was investigated. The data in Figure 3b show that the PAH eluted in the order of decreasing molecular mass, with increasing elution time. However, the shifts to longer elution times with decreasing molecular mass became smaller as the proportion of chloroform increased, such that for the 5:1 mixture, the elution time became almost constant (vertical line) as the molecular mass decreased. This may be considered the definition of the permeation limit, the latest elution time for any small molecule, as defined by the theoretical calibration curve for SEC.<sup>49</sup>

As an initial test of the method, a vacuum residue used in previous work,<sup>30,40</sup> Vacuum Residue C, was examined in the new eluent mixtures. The sample was first dissolved in NMP and passed through the column using pure NMP as eluent. The NMP soluble fraction was then submitted to SEC using pure chloroform as eluent. Finally, a sample of "vacuum residue C" was dissolved in the 5:1 NMP/chloroform mixture and analyzed



**Figure 5.** Synchronous UV-fluorescence spectra of vacuum residue C in chloroform and NMP.



**Figure 6.** SEC on Mixed-E of Maya asphaltene using NMP/chloroform (5:1) and detection at 278 nm UV absorbance.

by SEC using the 5:1 mixture as eluent. The chromatograms from these experiments are compared in Figure 4.

The effect of using the mixed solvent was to increase the proportion of excluded material compared with elution in NMP alone, while in pure chloroform, no excluded peak was observed. The chromatogram using the mixed solvent eluted the smallest size molecules of the residue later than did the NMP eluent, in agreement with the behavior of PAH in Figure 3b, while chloroform eluted most of the sample earlier than observed in NMP or the mixed solvent. The shift towards earlier elution times when chloroform is used as eluent is similar to the expected 2–3 min on the basis of the changes in the calibration lines for the different solvents as shown in Figure 3a.

The synchronous UV-fluorescence spectra in both NMP and chloroform are compared in Figure 5 and clearly indicate marked differences in chromophores detected in the two solvents: the largest aromatic systems appear insoluble in NMP but soluble in chloroform. Similar differences have been shown for a Kuwaiti asphaltene.<sup>4</sup> Ongoing work aims to investigate the structural differences as well as molecular masses of fractions of the sample soluble in NMP and in the various other mixtures with chloroform.

Figure 6 shows the SEC chromatogram of the Maya asphaltene on the Mixed-E column using the 5:1 NMP/chloroform mixture as eluent. Previous work with this asphaltene has been carried out with the Mixed-A column and with NMP as eluent.<sup>30,40</sup> In those chromatograms, the excluded peak was significantly lower in intensity than that detected in the Mixed-E column (Figure 6). The difference between the two sets of observations appears to be attributed to the improved solubility of the asphaltene in the mixed solvent. These data show that the fraction of the asphaltene insoluble in NMP but soluble in the mixed solvent was of large aromatic clusters but presumably

(49) Malawer, E. G. In *Handbook of Size Exclusion Chromatography*; Chi-san, W., Ed.; Chromatographic Science Series Vol. 69; Marcel Dekker Inc.: New York, 1995; Chapter 1.

attached to large aliphatic groups rendering the fraction insoluble in NMP alone. Similar findings come from the UV–fluorescence spectra mentioned above. More samples of asphaltenes and NMP insoluble fractions will be examined as the next part of the investigation to establish the method.

#### 4. Summary and Conclusions

This study applies SEC to petroleum residue samples that are partially insoluble in NMP by investigating the use of mixed solvents as eluent. The limitations arising from the use of THF and chloroform as eluents in the SEC of aromatic samples such as PAH standards and a petroleum vacuum residue have been shown. NMP is known to be incapable of completely dissolving vacuum residues and asphaltenes. It was observed that NMP/chloroform mixtures (5:1, 6:1, and 7:1 ratios, v/v) were able to dissolve both heavier fractions of a coal tar pitch and the whole of a petroleum asphaltene completely. The first tests of the new SEC calibration have been carried out using a Mixed-E column and pure NMP, pure chloroform, and mixtures of these solvents as eluents. All of these solvents produce acceptable calibration graphs between  $\log_{10}$  MM of PS standards and elution time, but these calibrations do not all relate adequately to the elution times of PAH standards.

The paper presents initial results from an investigation of elution times of PS standards and PAH on a Mixed-E column using mixtures of NMP and chloroform. We have also compared the elution behavior of a vacuum residue in three different

eluents: pure chloroform, pure NMP, and an NMP/chloroform mixture, at a ratio of 5:1. The NMP system appears best for PAH standards, but for petroleum residues, NMP mixed with some chloroform (7:1, 6:1, or 5:1 volume ratios) appears the most suitable compromise, being able to completely dissolve the petroleum residues.

The excluded peak observed in chromatograms of vacuum residue and asphaltene (and previously in all coal liquids studied) became more intense when using the mixed solvent compared with NMP alone. Synchronous UV–fluorescence spectra confirm that petroleum derived components with the largest chromophores are insoluble in NMP but soluble in chloroform and observable by UV–fluorescence spectroscopy. The data suggest that the fraction insoluble in NMP was of larger aromatic cluster size and presumably attached to very large aliphatic groups that rendered the material insoluble in NMP but soluble in both chloroform and the mixed solvent. More samples of asphaltenes and NMP insoluble fractions will be examined as the next part of the investigation to establish the method on a firm basis.

**Acknowledgment.** S.P.-D. would like to acknowledge the City and Guilds College at Imperial College London for financial support for her internship. We thank Dr. Jorge Ancheyta of the Mexican Petroleum Institute for the gift of an asphaltene sample from Maya crude.

EF700410E