

## HP-GPC ANALYSIS OF ASPHALT FRACTIONS IN THE STUDY OF MOLECULAR SELF-ASSEMBLY IN ASPHALT

P. W. Jennings, J. A. S. Pribanic, J. A. Smith, T. M. Mendes  
Department of Chemistry and Biochemistry  
Gaines Hall, Montana State University  
Bozeman, MT 59717-0340

**Keywords:** asphalt; intermolecular interactions; asphalt fractions

### INTRODUCTION

The nature of intermolecular interactions in asphalt cement remains incompletely understood, although the body of evidence continues to grow. Several types of interactions are possible. In a number of papers, the theory has been propounded that micelles, formed by the stacking of flat aromatic molecules via pi-pi interactions, are important constituents of asphalt cements [1]. J. C. Petersen, on the other hand, has concentrated efforts on the study of functional groups containing oxygen, nitrogen and sulfur because some of these functional groups could interact through polar forces [2]. Less attention has been paid to possible van der Waals interactions except in cases in which long unsubstituted aliphatic chains (waxes) crystallize within the asphalt [3]. Nevertheless, all of these interactions could contribute to the formation of an intermolecular network, the characteristics of which may determine the behavior of the asphalt cement.

Because of the complexity of asphalt, such interactions are difficult to study. High Performance Gel Permeation Chromatography (HP-GPC) has been used to demonstrate the tendency of self-assembled units to form in whole asphalts and some fractions [4,5]. Molecules in many common asphalts show a distinct tendency to self-assemble; a few asphalts show little if any such character. The latter asphalts are likely to be thermally sensitive, that is, to be subject to early thermal cracking and/or permanent deformation [6]. In experiments in which the polarity of the eluting solvent was changed, it appeared that both polar and non-polar interactions are much more important in those asphalts which exhibit self-assembly than in those which do not [7].

In efforts to clarify the chemical nature of asphalt cements, two important fractionations of asphalt have been performed by Western Research Institute (WRI) under auspices of the Strategic Highway Research Program (SHRP). Preliminary work on the HP-GPC analysis of two fractions from Ion Exchange Chromatographic separations was described previously [5]. Further work on these and other fractions will be the subject of this paper.

### EXPERIMENTAL PROCEDURES

Two fractions from preparative size exclusion chromatographic (SEC) separations of each of eight asphalts were supplied by WRI. This molecular size separation uses toluene as solvent. The separation is based on a transition from non-fluorescence to fluorescence of the eluting substances. The non-fluorescent fraction,

labelled SEC I, is thought to consist of associated entities whereas the fluorescent fraction (SEC II) is composed of individual molecules [8] or perhaps small associated units.

Using ion exchange chromatography (IEC), WRI obtained five fractions from each of the same eight asphalts. These are strong acid, strong base, weak acid, weak base and neutral materials [9].

Both SEC and IEC fractions were used as received and subjected to HP-GPC analyses as previously described [5]. Tetrahydrofuran (THF) was used as solvent.

## RESULTS AND DISCUSSION

### *A Note about the Solvent*

Tetrahydrofuran is a common solvent for HP-GPC analysis of asphalts and their fractions. At the low sample concentrations used (0.5% w/v), THF disrupts most intermolecular associations present in the neat asphalt. However, the strongest associative bonds, both polar and non-polar, apparently do survive in THF solution. Thus, we suggest that THF is the solvent of choice for indicating the *tendency* of molecules in an asphalt to form strong associations by any mechanism (polar and/or non-polar). This is particularly important because we theorize that the extent to which the molecules in an asphalt form an intermolecular network consisting of both polar and non-polar interactions contributes to the ultimate performance of the asphalt.

### The SEC Fractions

The SEC I and II fractions from each of eight asphalts were analyzed by HP-GPC in THF. In Figure 1, the chromatograms which were detected by 340 nm absorption for SEC I and II fractions are superimposed on that of the parent asphalt for two asphalts, representing the range of results observed.

In all cases studied, SEC I is more aromatic<sup>(1)</sup> and has more large molecular size (LMS) material<sup>(2)</sup> than the corresponding whole asphalt, whereas SEC II is much less aromatic and shows no evidence in the LMS region for intermolecular association. However, there are significant differences among asphalts. For example, in THF, asphalt A shows strong evidence for intermolecular association in the whole asphalt and in SEC I, but asphalt G contains little, if any, self-assembled material in the whole asphalt and the least amount in SEC I of all asphalts tested (Figure 2). Furthermore, the percentages of LMS material in the whole asphalts bear a nearly linear relationship to the percentages of LMS in their respective SEC I fractions ( $r^2=0.89$ ).

However, there are some interesting details within this data. First, there is much less evidence for the presence of self-assembled entities in the LMS regions of

---

<sup>(1)</sup>The aromatic content of samples can be compared by summing the areas in mAU under the chromatographic curves at 230, 254, 280, 340, 380, 410 and 440 nm. This is called the total conjugated volume, CV<sub>1</sub>.

<sup>(2)</sup>Percentage of LMS is defined as the percentage of CV<sub>1</sub> appearing in the large molecular size region of the chromatogram, before 17 minutes elution time in this system.

SEC I fractions from Group 1<sup>(3)</sup> asphalts than in SEC I fractions from other Groups. Furthermore, these fractions begin to elute as much as two minutes earlier than their parent asphalts. This indicates that the process of SEC separation in toluene may force some intermolecular polar associations that a) are not present in the original asphalt and b) are quite stable. That such a change is induced by the SEC process is further evidenced by the fact that SEC I fractions from Group 1 asphalts are not completely soluble in THF, whereas the parent asphalts are easily soluble.

Second, when one observes the strong response in the LMS region for SEC I fractions, it would be easy to assume that all the LMS material in the whole asphalt is accounted for by the SEC I fraction. However, when the amount of LMS material explained by SEC I and II<sup>(4)</sup> is compared with that found by analysis of the whole asphalt, differences among the asphalts are observed (Table I). For example, for asphalts A, B and D, less LMS material is calculated from the SEC I and II fractions than is observed in the whole asphalt. Since the SEC preparation using toluene should encourage polar interactions while disrupting pi-pi bonds, the HP-GPC data may indicate that pi-pi interactions are somewhat more important than polar interactions in these three asphalts.

For asphalts C, F and K, the difference between calculated and observed LMS percentages is small (within experimental error). This may mean either a) that neither interactive mechanism is important, or b) that both interactions contribute about equally in the whole asphalt. Earlier studies with changes in solvent polarity indicate that the latter is true for asphalt K. For asphalts C and F, in which little intermolecular interaction is noted, it may be that both polar and non-polar associations contribute about equally to the low LMS content.

Asphalts G and M present a different picture in that the total LMS percentage in SEC I and II is higher than in the whole asphalt. This difference is substantial in asphalt M, less so in asphalt G. We suggest that the SEC separation of G in toluene encourages polar interactions not present in the whole asphalt, as mentioned earlier. In the whole asphalt, in fact, neither polar nor non-polar interactions seem to be important.

Asphalt M (Group 4)<sup>(5)</sup>, well known as an unusual material, does not change its reputation here. We suggest that, not only does the SEC separation encourage polar bonds not present in the whole asphalt, but also it disrupts non-polar interactions that are particularly strong in this asphalt. That is, toluene may actually invert the interactions prevalent in the neat asphalt. It should be noted that asphalt M is known as a highly compatible material from which little if any asphaltene can be precipitated by heptane. That is, heptane can not induce the separation of polar materials perhaps because they are so strongly solubilized by virtue of pi-pi interactions. This would be consistent with the HP-GPC results.

---

<sup>(3)</sup>Group 1 asphalts have narrow molecular size distribution, with little evidence for intermolecular association (i.e., little LMS shoulder area) in the HP-GPC chromatogram. These asphalts are often temperature sensitive and may crack early and/or rut in a pavement.

<sup>(4)</sup>Percent LMS whole asphalt, calc. = (% LMS SEC I)(wt % SEC I) + (% LMS SEC II)(wt % SEC II)/100.

<sup>(5)</sup>Asphalts in Group 4 possess narrower molecular size distributions than Group 2 asphalts, but the overall molecular size is quite large.

### The IEC Fractions

Among the fractions from Ion Exchange Chromatography – strong acids, strong bases, weak acids, weak bases and neutrals – the strong acids exhibit most intermolecular association in THF. These fractions are highly aromatic (Table II) and, because of the isolation procedure, should contain molecules with strongly acidic functional groups as well as those with a strong acid and one or more additional functional groups. Thus, the extensive intermolecular association is not surprising. Nevertheless, there are significant differences among the chromatograms of strong acid fractions from different asphalts (Figure 3). The chromatogram of strong acids from asphalt G (representing Group 1 asphalts), although showing evidence for considerable intermolecular interaction, also indicates that most of the materials are unassociated. This contrasts with the situation for strong acids from asphalt A (Group 2)<sup>(6)</sup>, which are seen to be predominantly in the LMS region and thus highly associated.

Strong base fractions are also quite aromatic (Table II). The molecules could also have more than one functional group (but not a strong acid since they have been removed). Their chromatograms indicate less self-assembly in the strong bases than in the corresponding strong acids and less self-assembly among Group 1 asphalts than others.

The weak acid and weak base fractions are quite aromatic but demonstrate little if any tendency toward self-assembly in THF, i.e., any intermolecular bonds are quite weak. Neutral fractions are the least aromatic of the IEC fractions and display no evidence for self-assembly in the LMS regions of their chromatograms.

It is expected that the process of IEC separation may destroy some intermolecular interactions because each contributor belongs in a separate category. Thus, the total LMS percentage for all the IEC fractions is expected to be significantly less than that obtained by HP-GPC analysis of the whole asphalt (Table III). For most asphalts, this is true. However, for asphalt G, there is no significant difference between these approaches, again suggesting that intermolecular interactions are not strong in this asphalt.

### SUMMARY AND CONCLUSIONS

Separation of asphalts into fractions has provided somewhat simpler samples by which to study intermolecular interactions in the asphalts. Separation by size exclusion chromatography (SEC) using toluene has yielded SEC I, composed of large species associated by polar bonds, and SEC II, consisting of essentially nonassociated molecules (as evidenced by HP-GPC analysis). Analyses of these fractions by HP-GPC in THF emphasize the aromatic character of SEC I (but not of SEC II), agree that SEC I contains highly associating components, but distinguishes among asphalts as to the extent, strength and source (polar or non-polar) of the interactions.

Other fractions derived from ion exchange chromatography were also analyzed by HP-GPC. These analyses confirm that components in the strong acids fraction, which are highly aromatic and may include molecules with more than one functional

---

<sup>(6)</sup>Group 2 asphalts include most common materials. They have broader molecular size distributions and show strong evidence for intermolecular interactions.

group, are extensively associated. However, the strong acids do not account for all of the associated entities in the asphalt. Thus, even though the other polar fractions appear by HP-GPC not to be associating when separated, they must contribute significantly to the self-assembled materials observed in the whole asphalt. However, the strength, and therefore the contribution to behavior, of intermolecular associations, differ among asphalts.

#### ACKNOWLEDGEMENTS

The support of the Strategic Highway Research Program is gratefully acknowledged.

We thank researchers at Western Research Institute, Laramie, Wyoming, for providing samples.

#### REFERENCES

- [1] Yen, T.F., "A Macrostructure of Petroleum Asphalt," PREPRINTS, Div. of Petrol. Chem., ACS, 35, (3)314 (1990).
- [2] Petersen, J.C., "Chemical Composition of Asphalt as Related to Asphalt Durability. State of the Art," and references cited therein, in Transportation Research Record, TRB, National Research Council, Washington, D.C., 1984.
- [3] Planche, J.-P., et al., "Relationships between Characterization of Asphalt Cements by Differential Scanning Calorimetry and their Physical Properties," PREPRINTS, Div. of Petrol Chem., ACS, 35, (3)330 (1990).
- [4] Brulé, B., et al., "Characterization of a Road Asphalt by Chromatographic Techniques (GPC and HPLC)," J. Liquid Chromatography, 2, 437 (1979).  
Brulé, B., et al., "Contributions of Gel Permeation Chromatography (GPC) to the Characterization of Asphalts," in Liquid Chromatography of Polymers and Related Materials II. Cazes and Delamore, Eds., Dekker, 1980.
- [5] Jennings, P.W., et al., "High Performance Gel Permeation Chromatography in the Characterization of Self-Assemblies in Asphalt," Fuel Sci. and Technol. Int., in press.
- [6] Jennings, P.W., et al., unpublished results.
- [7] Jennings, P.W., et al., "High Performance Gel Permeation Chromatography in the Characterization of Self-Assemblies in Asphalt. 2.," Proceedings, International Symposium on Chemistry of Bitumens, June, 1991, Rome, Italy.
- [8] Branthaver, J.F., et al., "Separation of SHRP Asphalts by Preparative Size Exclusion Chromatography," PREPRINTS, Div. of Petrol. Chem., ACS, 35, (3)407 (1990).
- [9] Branthaver, J.F., et al., "Separation of SHRP Asphalts by Ion Exchange Chromatography," PREPRINTS, Div. of Petrol. Chem., ACS, 35 (3)376 (1990).

Table I. Differences between % LMS observed in the whole asphalt and that calculated from amounts in SEC I and II.

Asphalt	a % LMS observed <sup>(1)</sup>	b % LMS calculated <sup>(2)</sup>	difference a - b
A	19.2	16.5	2.7
B	14.2	11.7	2.5
C	8.2	7.3	0.9
D	24.0	20.0	4.0
F	8.3	8.3	0.0
G	3.2	4.7	-1.5
K	19.5	18.6	0.9
M	20.1	24.2	-4.1

<sup>(1)</sup> Experimental error  $\pm 0.5$

<sup>(2)</sup> See footnote 4

Table II. Relative aromaticity of fractions from Ion Exchange Chromatography from HP-GPC Analysis.

Asphalt	Whole	SA <sup>(1)</sup>	SB <sup>(2)</sup>	CV <sub>t</sub> (x 10 <sup>5</sup> ) WA <sup>(3)</sup>	WB <sup>(4)</sup>	N <sup>(5)</sup>
A	22.6	34.9	30.1	33.0	27.5	14.7
B	26.9	43.5	36.7	35.2	33.4	15.8
C	23.9	40.9	30.5	35.6	29.7	14.2
D	20.6	30.7	25.6	28.3	19.7	11.8
F	27.6	40.2	35.1	35.6	34.4	16.9
G	24.8	35.0	29.7	31.8	26.8	16.6
K	24.6	33.7	28.7	28.3	30.5	14.9
M	23.5	38.3	28.9	31.6	28.3	13.8

CV<sub>t</sub> - total conjugated volume, see Footnote 1

<sup>(1)</sup> Strong acid

<sup>(3)</sup> Weak acid

<sup>(5)</sup> Neutral

<sup>(2)</sup> Strong base

<sup>(4)</sup> Weak base

Table III. Differences between % LMS observed in the whole asphalt and that calculated from amounts in the IEC fraction.

Asphalt	a		difference a - b
	% LMS observed <sup>(1)</sup>	% LMS calculated <sup>(2)</sup>	
A	19.2	13.4	5.8
B	14.2	9.9	4.3
C	8.2	1.3	6.9
D	24.0	16.8	7.2
F	8.3	6.0	2.3
G	3.2	3.8	-0.6
K	19.5	13.2	6.3
M	20.1	16.3	3.8

<sup>(1)</sup>  $\pm 0.5$

<sup>(2)</sup> from % LMS in all IEC fraction

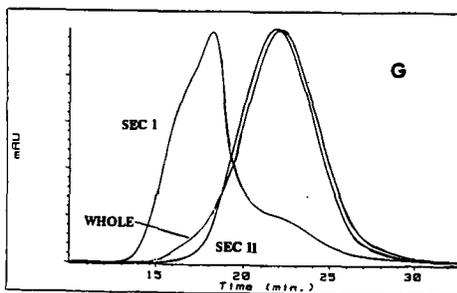
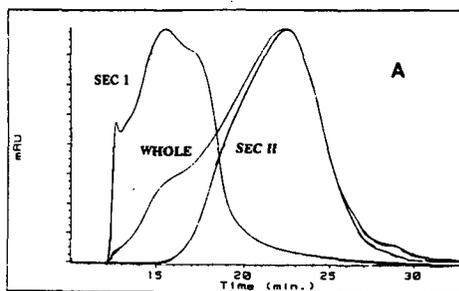


Figure 1. Chromatograms of SEC I, SEC II and whole asphalt for asphalts A and G. Chromatograms are normalized to same peak height for visual emphasis.

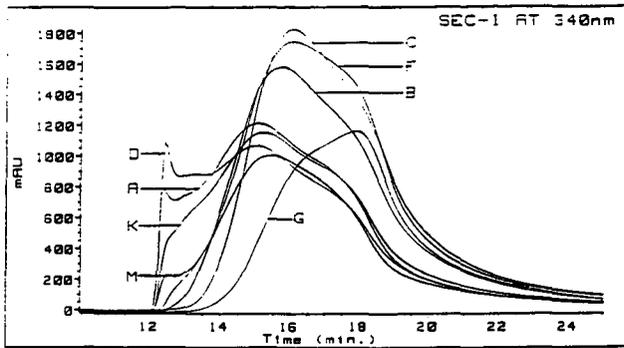


Figure 2. Chromatograms (340 nm) for SEC I fractions of eight asphalts.

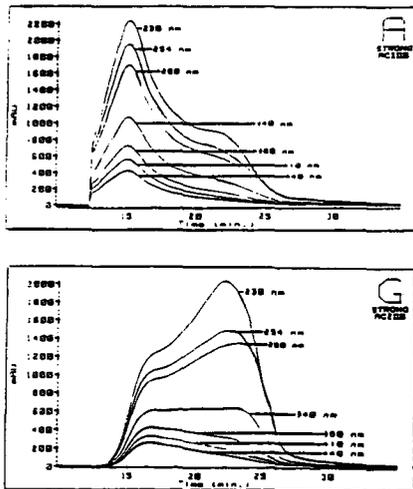


Figure 3. Chromatograms at seven wavelengths for strong acid fractions of asphalts A and G.