

ASPHALT PAVING TECHNOLOGY 1980

Proceedings
Association of Asphalt Paving
Technologists
Technical Sessions

Index of Proceedings
1975-1980

Louisville, Kentucky
February 18, 19 and 20, 1980

Volume 49

ASPHALTENES, WHERE ARE YOU?

M. M. BODUSZYNSKI,¹ J. F. McKAY,² and D. R. LATHAM³

INTRODUCTION

Asphaltenes play a fundamental role in determining the mechanical and rheological properties of asphalts. Such important asphalt properties as temperature susceptibility or sol-gel transition phenomena depend on the quantity and nature of asphaltenes. Ironically, asphaltenes are the least characterized and the most controversial asphalt component, even though a great deal of effort has been devoted to investigation of their composition.

A typical asphalt separation procedure (1) is based on solubility in a normal alkane followed by adsorption chromatography of the soluble portion. This procedure separates asphalt into asphaltenes, resins, and oils. The fractions are usually characterized by two major properties: polarity and average molecular weight. Polarity of asphalt components is due to the presence of heteroatoms (N, S, O) and condensed aromatic rings and is arbitrarily defined by relative adsorptive strength or by solubility. Average molecular weight value is most often determined by vapor pressure osmometry and is affected by intermolecular associations that lead to erroneously high values.

Significant errors in the average molecular-weight measurements have resulted in major distortions of the concept of asphaltene structure. Asphaltenes are commonly viewed as the most polar and the highest molecular weight fraction of asphalt. To better understand the chemical nature of asphaltenes, more detailed studies of asphalt composition are needed.

The purpose of this study is to investigate the chemical composition of a petroleum asphalt (vacuum residue) and the mechanism of asphaltene precipitation. The emphasis of this work is on chemically defined compound types and their molecular weight distribution. Previous studies (2, 3, 4) have shown that precipitation of asphaltenes does not generate a chemically defined component of asphalt. It has also been shown that the composition of asphaltenes is to a great extent dependent on the chemical composition of the asphalt and the type of solvent used for precipitation. In this work, a chemical method of separation based on reactivity was used. The separation procedure includes chromatography on anion and cation resins to separate asphalt components capable of hydrogen bonding (acids and bases), followed by coordination chromatography on ferric chloride-Attapulgus clay to obtain a neutral Lewis base and a hydrocarbon fraction

¹Visiting Research Scientist, Chemistry Department, University of Wyoming, Laramie, Wyoming.

²Chemistry Research Associate, Laramie Energy Technology Center, Department of Energy, Laramie, Wyoming.

³Chemistry Research, Laramie Energy Technology Center, Department of Energy, Laramie, Wyoming.

Due to lack of time on the program this paper was read by title only.

which is further separated by adsorption chromatography on silica gel into saturate and aromatic hydrocarbons. Fractions were characterized with regard to chemical functionality and molecular-weight distribution. The results were compared with those on fractions obtained by solvent precipitation and adsorption chromatography using Corbett's separation procedure (5). The comparison was made to establish the mechanism of asphaltene precipitation.

In this paper we attempt to answer questions: (1) are the asphaltenes the highest molecular weight components of asphalt and (2) why do they precipitate?

EXPERIMENTAL

Origin and Preparation of the Asphalt

The straight-reduced asphalt (>675 C vacuum residue) was obtained from a medium sulfur (1.7 wt percent), waxy petroleum of 29° API gravity, supplied to Poland from the Soviet Union. Crude petroleum was first distilled through a lab-scale column to remove gasoline (atmospheric distillation) and gas-oil (vacuum distillation) fractions boiling below 365 C. The residue boiling above 365 C was then distilled in a wiped-wall vacuum distillation still to generate two distillation cuts and a >675 C heavy residue (asphalt). Temperature during distillation did not exceed 300 C, and thermal exposure was minimized by a very short residence time in the heated zone. No decomposition was detected during the distillation.

Chemical Method of Separation

The asphalt was separated into five fractions: acids, bases, neutral Lewis bases, aromatic hydrocarbons, and saturate hydrocarbons. The acid and base fractions were isolated using chromatography on anion exchange and cation exchange resins, respectively. The neutral Lewis bases fraction was isolated by complexation with ferric chloride adsorbed on Attapulugus clay. The remaining hydrocarbons were separated on silica gel into saturate and aromatic fractions. The separation scheme is shown in Figure 1.

Reagents and Apparatus.—Amberlite IRA-904 anion resin and Amberlyst 15 cation resin were obtained from Rohm & Haas. Both resins were prepared using the procedure previously published (6). Attapulugus clay (LVM 50/80 mesh) was coated with reagent grade ferric chloride hexahydrate according to the procedure previously published (6). Silica gel (grade 62) was used as received.

Cyclohexane, toluene, and methylene chloride were flash distilled. Isopropylamine (99 percent), normal heptane and dichloroethane, and methanol (HPLC grade) were used as received. The separations were made in glass columns 2.5 cm i.d. by 50 cm long. The system was equipped with a pump for solvent delivery. The rotary vacuum evaporator and nitrogen gas sweep evaporator at about 60 C were used for solvent removal from fractions.

Potentiometric Titration

The base fraction and subfractions were titrated potentiometrically with perchloric acid in acetic anhydride-benzene solution. Bases having a half-neutralization potential (HNP) of 350 mV or less were classified as strong bases, and those with an HNP greater than 350 mV were classified as weak bases.

Esterification Reaction

The acid fraction was dissolved in methylene chloride and was esterified using diazomethane to determine the amount of carboxylic acids present (8).

RESULTS AND DISCUSSION

Separation of the Asphalt into Compound-Class Fractions

One separation procedure used in this study is a chemical method of separation based on reactivity, which separates the asphalt into five compound-class fractions: acids, bases, neutral Lewis bases, aromatic hydrocarbons, and saturate hydrocarbons. This procedure defines acids and bases in terms of their ability to associate with the functional group of the anion $[-N(CH_3)_3OH]$ or the cation $[-SO_3H]$ resin, respectively. Due to the presence of polyfunctional compounds in the asphalt as well as to the ability of some functional groups to associate with either resin, the separation sequence influences the composition of the acid and base fractions. The compounds isolated in the coordination chromatography step are separated due to the ability to form charge-transfer complexes with ferric chloride and are defined as neutral Lewis bases. The fractions isolated from the asphalt as acids, bases, and neutral Lewis bases comprise polar compounds capable of association through hydrogen bonding. The fraction that was unreactive with both ion-exchange resins and ferric chloride-Attapulugus clay is nonpolar and is defined as hydrocarbons, although it still contains small amounts of heteroatoms. This fraction was further separated into aromatic and saturate hydrocarbons. The advantage of this separation procedure is that it provides fractions of concentrated functionalities and thus facilitates their identification.

The results of the separation and properties of the fractions are shown in Table 1. Three polar fractions (acids, bases, and neutral Lewis bases) represent approximately two-thirds of the total asphalt. These fractions comprise compounds high in heteroatoms. The saturate and aromatic hydrocarbon fractions contain small amounts of heteroatoms. These fractions comprise compound-types which are either unreactive with ion-exchange resins and ferric chloride or are sterically hindered and thus are defined as nonpolar.

The emphasis of this study is on polar fractions of the asphalt rather than hydrocarbon fractions because the polar fractions comprise compounds capable of association.

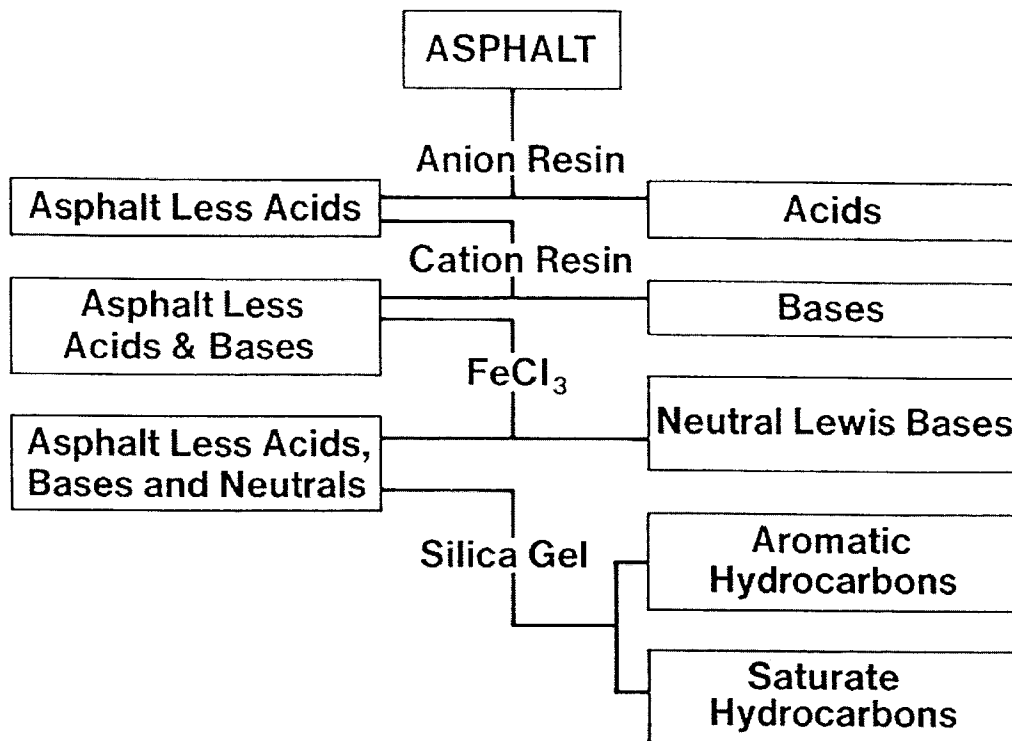


Fig. 1. Chemical Method of Asphalt Separation.

Separation of Acid and Base Fractions.—A sample of asphalt (17 g) was dissolved in cyclohexane (100 ml) and charged into the first of the two anion resin columns arranged in series (each column had been wet packed in cyclohexane with approximately 200 g of Amberlite IRA-904 resin) followed by the series of two cation resin columns (each column had been wet packed in cyclohexane with approximately 230 g of Amberlyst 15 resin). The unreactive material was eluted from the resins with cyclohexane (2000 ml) using the pump at 2 ml/min flow rate. After this step, anion and cation resin columns were disconnected, and material retained on each of the resins was recovered. Compounds hydrogen bonded to the anion resin (acids) were recovered by elution with 2000 ml of the mixture of methylene chloride (50 percent), toluene (25 percent), and methanol (25 percent) saturated with carbon dioxide. Compounds hydrogen bonded to the cation resin (bases) were recovered by elution with 2000 ml of the mixture of methylene chloride (40 percent), toluene (25 percent), methanol (25 percent), and isopropylamine (10 percent). Recovery of the material was 98.5 wt percent.

Separation of Neutral Lewis Base Fraction.—The coordination chromatography system consisted of two columns. The first column was wet-packed with cyclohexane and 170 g of Attapulugus clay coated with ferric chloride. The second column was wet-packed with 200 g of Amberlite IRA-904 anion resin. The system was equipped with a pump for solvent delivery. A sample of acid- and base-free asphalt (3 g) dissolved in

cyclohexane was charged into the first column. Elution of nonreactive material (hydrocarbon fraction) was accomplished using cyclohexane (1500 ml) at approximately 3 ml/min flow rate.

The neutral Lewis bases-ferric chloride complexes were eluted with dichloroethane (fraction 1) followed by a mixture of methylene chloride (50 percent), toluene (25 percent), and methanol (25 percent) (fraction 2). Both fractions were passed through the anion resin column where complexes were broken. The ferric chloride salt was retained on the resin, and neutral Lewis bases were recovered in the eluate as two fractions. Solvents were removed, and the fractions were redissolved in benzene and passed over the anion resin to remove the remaining ferric chloride. Recovery of the material for this step was 98.1 wt percent.

Separation of the Hydrocarbon Fraction.—The hydrocarbon fraction obtained after removal of acids, bases, and neutral Lewis bases from the asphalt was further separated on silica gel. A sample of hydrocarbon fraction (400 mg) was dissolved in heptane and charged into the silica gel (80 g) column. The saturate fraction was eluted with normal heptane (400 ml) at approximately 3 ml/min flow rate. Aromatic hydrocarbons were eluted as three fractions using (1) heptane (400 ml), (2) 400 ml of a mixture of heptane (85 percent) plus toluene (15 percent), and (3) 500 ml of a mixture of methylene chloride (80 percent) plus methanol (20 percent). The three fractions were then combined to give a total aromatic hydrocarbon fraction. Solvents were removed in the previously described manner. Recovery of the material in this separation step was 99.1 wt percent.

Separation by Corbett's Procedure

The asphalt was separated into five fractions: asphaltenes, saturates, naphthene-aromatics, polar aromatics-1, and polar aromatics-2 using Corbett's procedure (5) as shown in Figure 2. The separation of the asphalt into asphaltenes and maltenes using normal heptane is a physical method of separation based on solubility. This separation step was followed by chromatography of the soluble portion (maltenes) on alumina to produce four generic fractions using solvents of increasing elution strength. Chromatography was performed in a glass column (Altex) 2.5 cm i.d. and 50 cm long, equipped with a solvent-delivery pump. Recovery of the material was 99.0 wt percent.

Elemental Analyses

Elemental analyses of the asphalt and the fractions were conducted by commercial laboratories. Carbon, hydrogen, and sulfur were determined gravimetrically as carbon dioxide, water, and barium sulfate, respectively. Nitrogen was determined by a micro-Kjeldahl method.

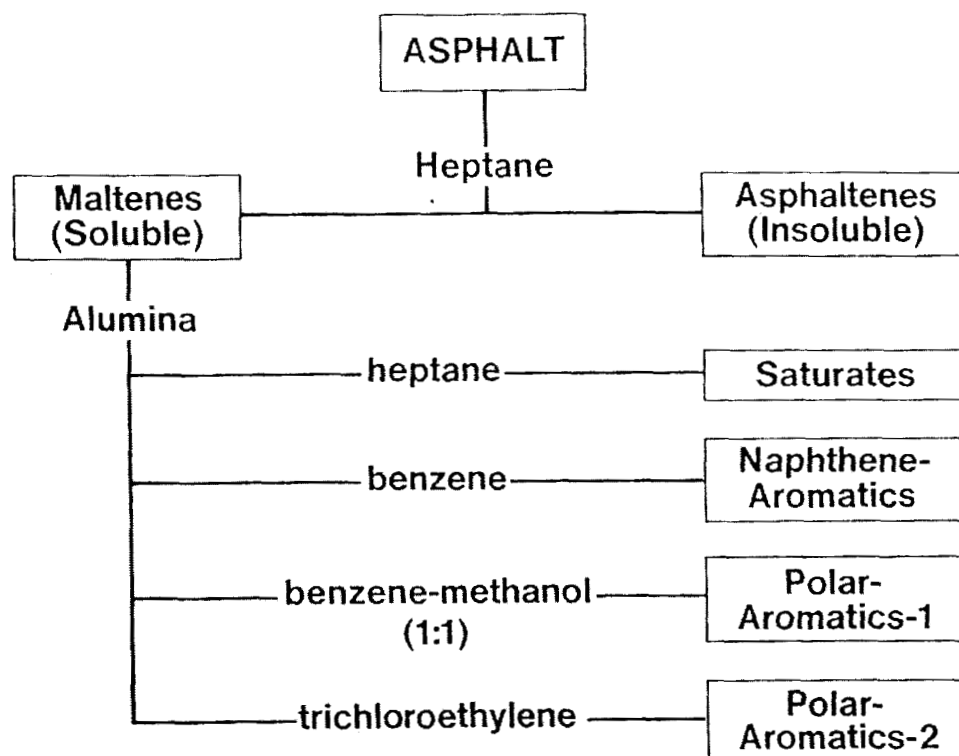


Fig. 2. Separation of Asphalt by Corbett's Procedure.

Molecular Weight Measurements

Molecular weight distributions and average molecular weights of the asphalt and derived fractions were determined by field ionization mass spectrometry (FIMS) at SRI International (7). Samples were 95 percent or more volatile under conditions of analysis. Average molecular weights were also determined in a commercial laboratory using vapor pressure osmometry (VPO) in benzene and methylene chloride solutions at concentrations of 2 to 20 g/l. Results obtained at three different concentrations were then extrapolated to infinite dilution to determine the average molecular weight.

Infrared Analyses

Infrared spectra were obtained on a Perkin-Elmer Model 621 grating spectrophotometer. Two analytical procedures were used. Quantitative infrared spectra in methylene chloride were obtained using the procedure developed by McKay et al. (8, 9). Five major compound types were identified: carboxylic acids, phenols, pyrroles, amides, and pyridines. These compound types are high-molecular-weight homologs of the parent species.

The quantitative method using differential infrared spectrometry developed by Petersen (10) was also used for determination of carboxylic acids, phenols, pyrroles, and 2-quinolones.

Table 1. Properties of the Asphalt and Compound-Type Fractions

Fraction	Weight Percent of Asphalt	Weight Percent					Average Molecular Weight		
		Carbon	Hydrogen	Sulfur	Nitrogen	Oxygen*	(VPO)**	(VPO)***	(FIMS)
Total asphalt	100	84.91	10.03	3.35	0.90	0.81	1448	1550	1048
Acids	21	83.76	8.53	3.81	1.46	2.44	2310	2277	973
Bases	19	81.78	9.81	3.69	1.73	2.99	1702	1459	1106
Neutral Lewis bases	29	83.76	9.98	2.66	0.48	3.12	1490	1459	1067
Aromatic hydrocarbons	24	85.19	9.78	2.61	0.14	2.28	1084	1207	1102
Saturate hydrocarbons	7	85.47	13.06	0.48	0.04	0.95	1030	950	1157

*By difference
 **In benzene
 ***In methylene chloride

Characterization of the Acids.—Infrared spectroscopy was the primary tool used for the analysis of functionalities present in the acid fraction. Two methods were used. The method of McKay et al. (8) enabled identification of four major compound-types: carboxylic acids, phenols, pyrroles, and amides. The spectrum of the total acid fraction is shown in Figure 3. The characteristic free phenol band centers at about 3590 cm^{-1} . The band resulting from intramolecular hydrogen bonding in phenol is at about 3540 cm^{-1} . The band at about 3460 cm^{-1} is assigned to pyrrolic N-H. Identification of the carbonyl types requires information based on the separation procedure and/or chemical reactions. The small shoulder at approximately 1725 cm^{-1} may indicate very small amounts of carboxylic

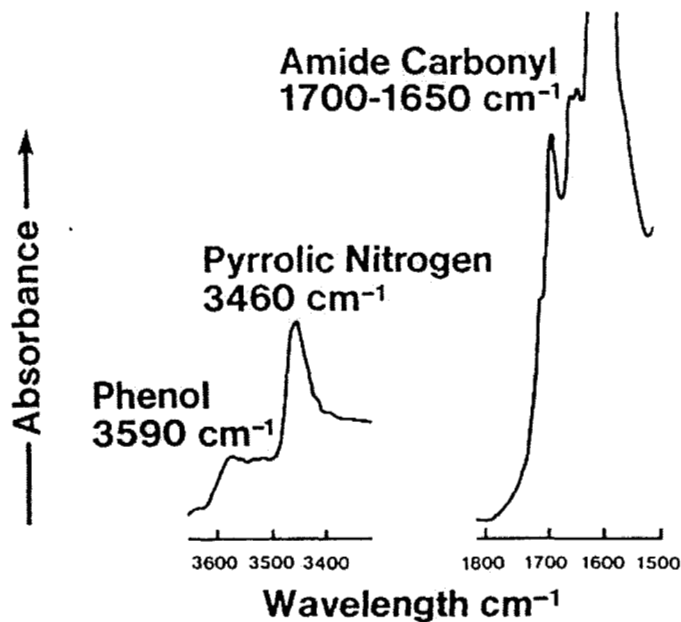


Fig. 3. Infrared Spectrum of Acid Fraction.

acids. Esterification reaction showed less than 1 wt percent of carboxylic acids in the acid fraction. Bands between 1700 and 1650 cm^{-1} are assigned to carbonyl absorption of amides and possibly other unidentified carbonyl compounds.

The quantitative method of Petersen (10) is based on differential infrared spectrometry combined with chemical reactions such as base hydrolysis and silylation and enables estimates of amounts of the compound types. Differential spectra were examined in pyrrolic N-H, phenolic O-H, and carbonyl regions. The results shown in Table 2 indicate that the asphalt acid fraction consists predominantly of pyrroles and phenols. Small amounts of amides of the 2-quinolone type and a very small amount of carboxylic acids were also found. High heteroatom content in the acid fraction implies that more than one functional group per molecule may be present. A simple calculation using the data in Table 1 (elemental analyses and an FIMS average molecular weight) shows that the average asphalt acid molecule contains 1.2 sulfur atoms, 1.0 nitrogen atom, and approximately 0.5 oxygen

Table 2. Differential Infrared Analysis of the Acid Fraction

Compound type	Concentration (moles/liter)
Carboxylic acids	0.01
2 - Quinolones	0.05
Pyrroles	0.66
Phenols	0.31

atom. Oxygen- and nitrogen-containing groups found in the acid fraction are generally polar and capable of participating in strong intermolecular associations through hydrogen bonding. The sulfur-containing groups were not investigated in this study because they have nondefinitive or weak bands and cannot be analyzed by infrared spectrometry alone. However, high sulfur content (3.81 wt percent) in the acid fraction implies that such compound types as thiophenes and sulfides may be present. These compound types are, however, not very polar and probably do not contribute significantly to intermolecular associations.

The acid fraction exhibits the lowest H/C ratio among the fractions, indicating high aromaticity. Presence of condensed aromatic ring systems in molecules comprising this fraction may also contribute to intermolecular associations. The FIMS molecular-weight envelopes of the asphalt fractions (Figure 4) represent distributions of parent ions. The results show that all compound-class fractions exhibit the same molecular-weight range from approximately 400 to 1800. However, the average mass value of acids (973) is low compared with the mass values of the other four fractions (1106, 1067, 1102, and 1157 in Figure 4). This may be because polar compounds

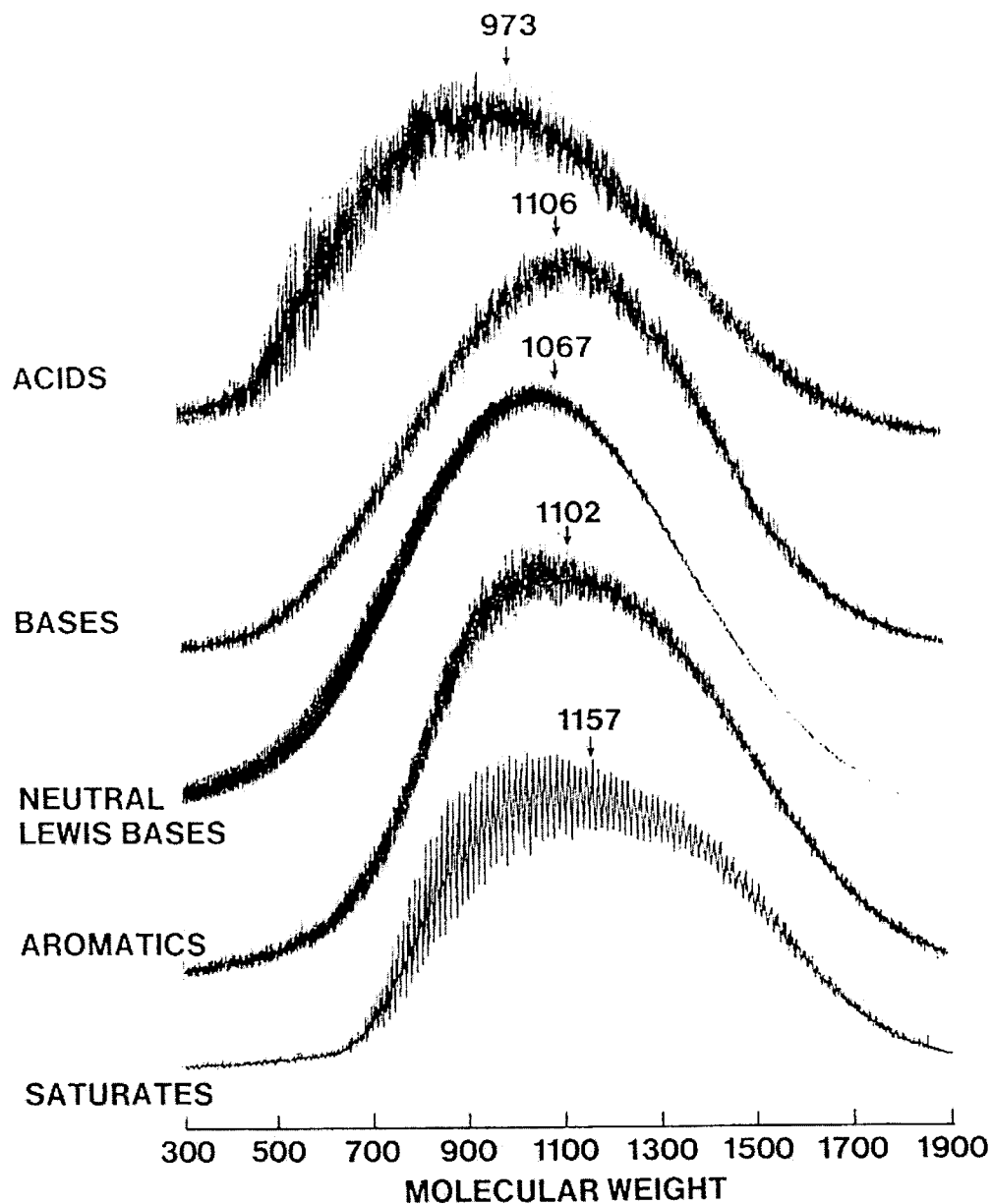


Fig. 4. Molecular Weight Envelopes of the Compound-Class Fractions.

of the acid fraction exist in a strongly associated state, making them less volatile during the distillation and causing them to concentrate in the heavy residuum (asphalt). The VPO apparent average molecular weight of the acid fraction (2310 and 2277 in Table 1) is much higher than that determined by FIMS. This implies that VPO measurements were appreciably affected by intermolecular associations.

Characterization of the Bases.—The total base fraction was separated on basic alumina into four subfractions to facilitate characterization. Identification and quantitative estimates of compound types in the asphalt bases were made primarily using infrared spectrometry and potentiometric

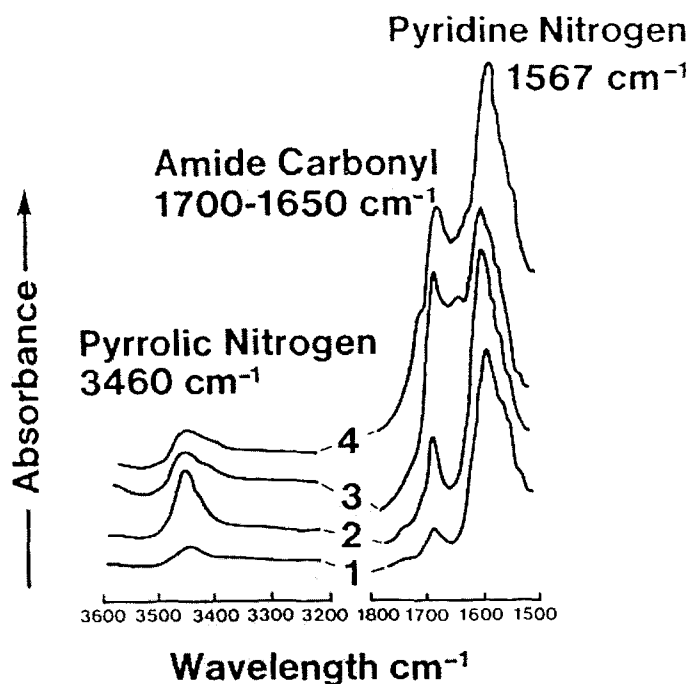


Fig. 5. Infrared Spectra of Base Subfractions.

titration. The procedure of McKay et al. (9) was used for infrared analysis of the bases. Infrared spectra of the four subfractions are shown in Figure 5. The spectra show unresolved absorption bands at 1567 cm^{-1} that are characteristic of pyridines, carbonyl absorption between 1700 cm^{-1} and 1650 cm^{-1} assigned to amides, and the absorption of pyrrolic nitrogen compounds at 3460 cm^{-1} . The spectrum of subfraction 1 shows that this fraction consists primarily of pyridines and very small amounts of amides and pyrroles. Amounts of amides and pyrroles increase with the increase in the subfraction number. Quantitative estimates of the compound types in the bases were not made by infrared spectrometry because the functional group absorption of strong bases, presumably pyridines, could not be measured because of overlap with aromatic bands.

The distribution of strong, weak, and nontitratable nitrogen was determined by potentiometric titration. The results shown in Table 3 are in general agreement with the infrared analyses. Subfraction 1 consists primarily of strong bases, presumably pyridines. Compounds showing amide

Table 3. Potentiometric Titrations of the Base Subfractions

Sub-fraction	Wt Percent of Total Bases	Total Nitrogen Wt Percent	Wt Percent of Nitrogen in:		
			Strong Bases	Weak Bases	Nontitratable
1	35.9	1.14	0.83	0.00	0.31
2	17.3	1.39	0.51	0.47	0.41
3	32.2	1.48	0.37	0.67	0.44
4	2.4		Insufficient amount of sample		
Recovery	87.8				

infrared bands in subfractions 2 and 3 are present as weak bases. Amounts of nontitratable nitrogen increased from subfraction 1 through 3. This untitratable nitrogen may be in pyrrole compounds or in compounds containing two nitrogen atoms. As with the acid fraction, the sulfur-containing groups were not investigated. High sulfur content (3.69 wt percent) in the base fraction shows that polyfunctional molecules are present. The three major compound types identified in the asphalt bases (pyridines, amides, and pyrroles) are polar and are capable of hydrogen bonding with other polar molecules.

The FIMS molecular-weight envelope of the base fraction (Figure 4) shows that compounds comprising this fraction have molecular-weight range from approximately 400 to 1800. The FIMS average molecular weight of bases (1106) is lower than that determined by VPO (1702 and 1459 in Table 1). This implies that VPO measurements for the base fraction were affected by intermolecular associations.

Characterization of the Neutral Lewis Bases.—Compound types in this fraction form complexes with ferric chloride. Based on nitrogen content and FIMS average molecular weight of the total neutral Lewis bases fraction (Table 1), every third molecule contains one nitrogen atom. We believe that appreciable amounts of polynuclear aromatics may be present in this fraction. Condensed polynuclear aromatic hydrocarbons are known to be excellent π -electron donors and thus would be expected in the neutral Lewis bases fraction.

Table 4. Separation of the Neutral Lewis Bases on Basic Alumina

Subfraction	Weight percent of	
	Fraction 1	Fraction 2
1	46.0	9.1
2	13.1	4.6
3	31.1	67.3
Recovery	90.3	81.0

The two neutral Lewis base fractions were further separated on basic alumina into three subfractions to facilitate characterization by infrared spectroscopy. The results of the separation are shown in Table 4. Infrared spectra of the three subfractions derived from each main fraction of neutral Lewis bases are shown in Figures 6 and 7. The most predominant functional group bands in the spectra are carbonyl absorption of amides between 1700 cm^{-1} and 1650 cm^{-1} and pyrrolic N-H absorption at 3460 cm^{-1} . Subfractions 3 of both the neutral Lewis base fractions show small bands at 3590 cm^{-1} that may be due to the phenol O-H absorption. Infrared analyses of the neutral Lewis bases show that amides and pyrroles are predominant compound types and imply that appreciable amounts of condensed polynuclear aromatic hydrocarbons are also present in this fraction.

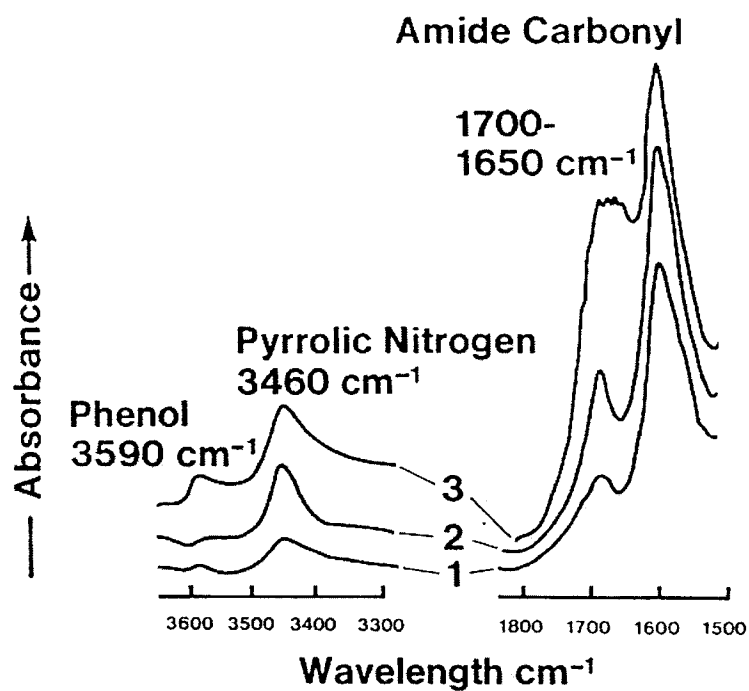


Fig. 6. Infrared Spectra of Neutral Lewis Base Subfractions (of Fraction 1).

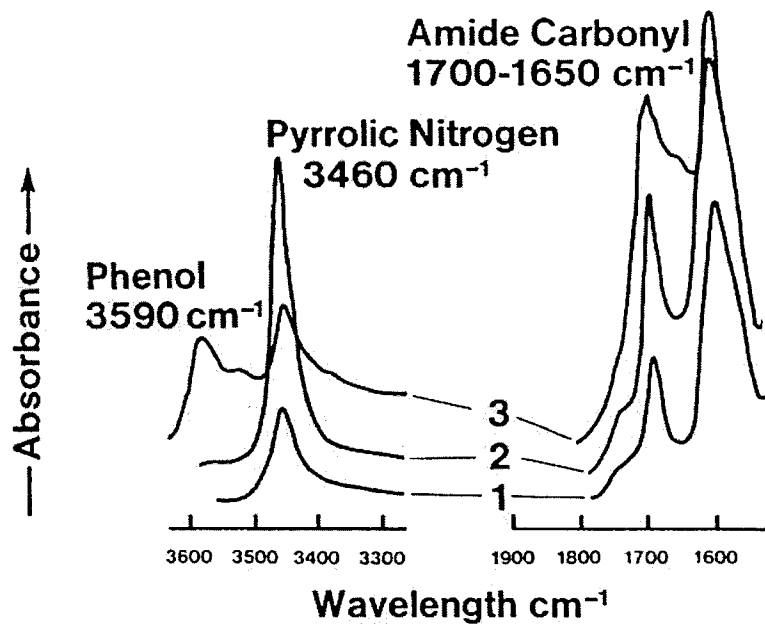


Fig. 7. Infrared Spectra of Neutral Lewis Base Subfractions (of Fraction 2).

The FIMS measurements (Figure 4) show that the neutral Lewis base fraction exhibits molecular weight range from approximately 400 to 1800, with the average molecular-weight value being 1067. The VPO apparent average molecular weight of this fraction (1490 and 1459 in Table 1) is higher than that determined by FIMS, thus indicating the effect of intermolecular associations on VPO measurements.

Compound-Type Composition of the Asphalt

The results of the chemical separation study show that asphalt consists of polar and polarizable compound types capable of hydrogen bonding. The following compound types were found in the asphalt: pyrroles, phenols, pyridines, amides including 2-quinolones, and carboxylic acids. These compound types are known to be responsible for molecular interactions resulting in intermolecular associations. High percentages of heteroatoms (N, S, O) in the acid, base, and neutral Lewis base fractions suggest considerable concentrations of mixed heteroatom types. The presence of polynuclear aromatic ring systems can also contribute to intermolecular associations observed in these fractions.

An important result regarding molecular weights of the asphalt fractions was obtained using field ionization mass spectrometry. FIMS shows that all fractions of the asphalt have the same molecular-weight distributions of approximately 400 to 1800, with the average value being about 1000 (Figure 4). The significant effect of intermolecular associations of compounds comprising the acid, base, and neutral Lewis bases fractions on average molecular-weight measurements by VPO was observed (Table 1).

The Concept of Asphaltene Composition and Formation

Because major compound types responsible for intermolecular associations of asphalt components have been identified and have been found to have the same molecular-weight distribution, with the average molecular-weight value being about 1000, the question arises: where are the asphaltenes commonly viewed to have molecular weight of 5,000 to 50,000? To answer this question, the asphalt was subjected to a separation by Corbett's procedure (Figure 2) that produces an asphaltene fraction. Results were compared with those for fractions produced by chemical separation.

The first separation step of this procedure is based on the solubility in normal heptane and separates the asphalt into asphaltenes (insoluble) and maltenes (soluble). The emphasis in this study is on asphaltenes rather than on maltenes. The results of the separation and the properties of the fractions are shown in Table 5.

Data show that the asphaltene fraction has higher heteroatom content and a lower H/C ratio than the other asphalt fractions. A dramatic effect of intermolecular associations on VPO average molecular weight of asphaltenes is evidenced by comparison of VPO and FIMS data (4015 and 873, respectively). This effect diminishes with the decrease of polarity of the fractions—polar aromatic fractions still show considerable differences in

Table 5. Properties of Generic Fractions of the Asphalt

Fraction	Percent of Asphalt	Weight percent					Average Molecular Weight		
		Carbon	Hydrogen	Sulfur	Nitrogen	Oxygen*	(VPO)**	(VPO)***	(FIMS)
Asphaltenes	16	84.05	7.84	4.42	1.48	2.21	4015	4068	873
Polar aromatics-2	3	81.90	8.49	3.62	1.00	4.99	3075	-	1104
Polar aromatics-1	45	83.99	9.61	3.69	0.78	2.53	1405	1448	1020
Naphthene-aromatics	32	85.10	10.84	2.91	0.14	1.01	1062	1148	1234
Saturates	4	85.88	13.51	0.19	0.07	0.35	1036	-	1127

*By difference

**In benzene

***In methylene chloride.

average molecular weights determined by the two methods, while nonpolar saturates and naphthene-aromatics fractions show practically no differences. FIMS molecular-weight envelopes of the five generic fractions are shown in Figure 8. The spectra show that all fractions have the same molecular-weight range of approximately 400 to 1800. It has been shown earlier (Figure 4) that fractions produced by the chemical method of separation had also the same molecular-weight range. The average mass value of asphaltenes is 873—the lowest of all fractions. Thus, the results show that asphaltenes are not the highest molecular weight component of asphalt. On the contrary, asphaltenes comprise compounds of relatively low (compared with other asphalt fractions) molecular weight but very high polarity.

The quantitative differential infrared spectrometry method of Petersen (10) was used for determination of -OH, -NH, and carbonyl compounds in

Table 6. Differential Infrared Analysis of Asphaltenes

Compound type	Concentration (moles/liter)
Carboxylic acids	0.01
2 - Quinolones	0.02
Pyrrroles	0.27
Phenols	0.14

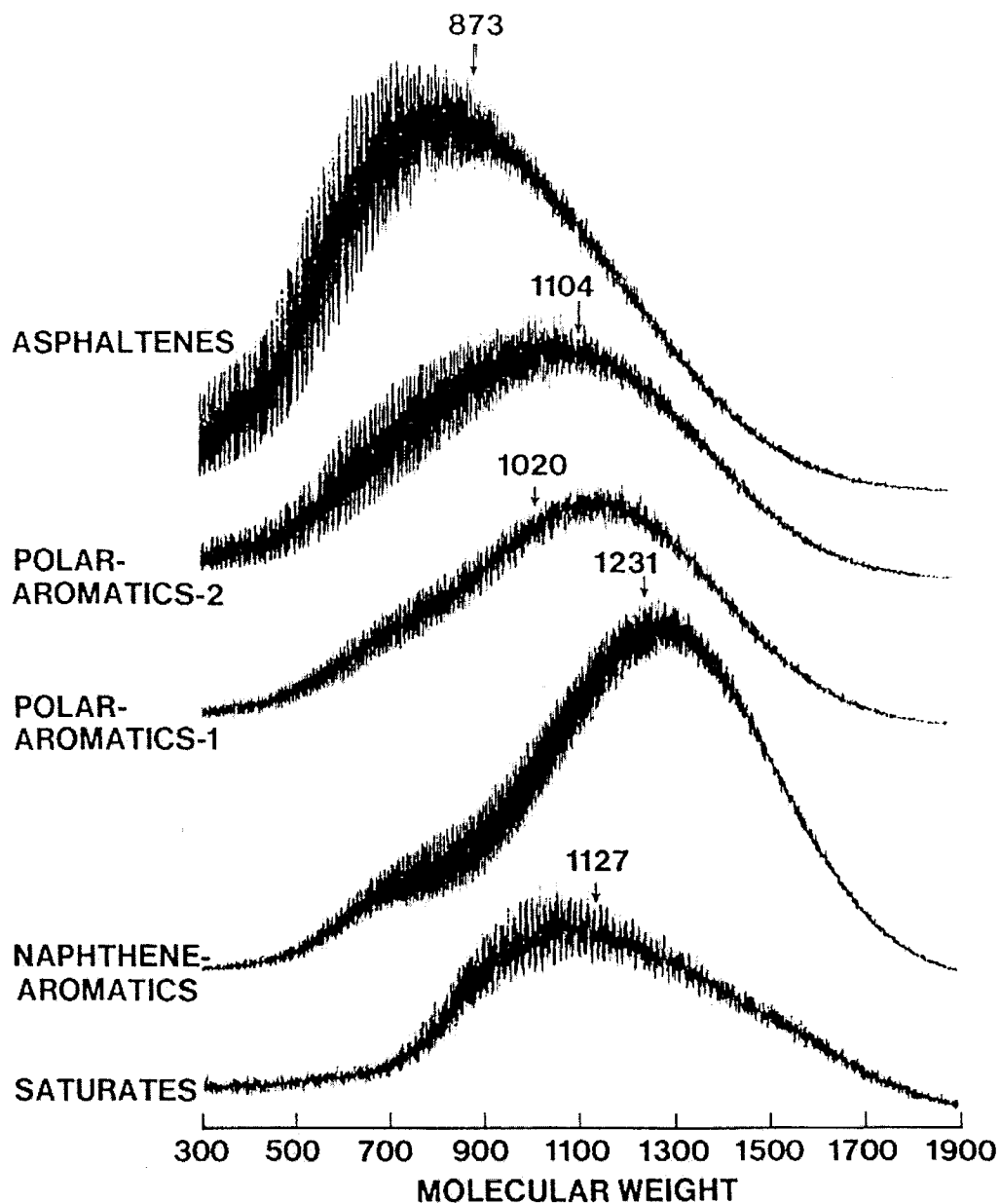


Fig. 8. Molecular Weight Envelopes of the Generic Fractions.

the asphaltenes. These compounds have functional groups which are responsible for strong intermolecular associations. The results of analysis are given in Table 6. The infrared analysis shows that pyrroles and phenols are the predominant compound types identified in the asphaltenes. Small amounts of carboxylic acids and 2-quinolones were also found. All these compound types, which were also identified in the acid fraction, are capable of hydrogen bonding (11-14). However, the amount of nitrogen-containing compound types identified in asphaltenes by infrared analysis does not account for total nitrogen present in this fraction (1.48 wt percent in Table 5). This implies that other unidentified nitrogen compound types

must be present. Most probably, pyridines found in the base fraction also contribute to asphaltene formation.

Here we answer the question, "Where are the asphaltenes?" Based on the fact that treatment of the acid- and base-free asphalt with normal heptane did not produce precipitate, we conclude that compounds comprising asphaltenes are in the acid and base fractions of the asphalt. Because the total amount of acids and bases in the asphalt is 40 wt percent (Table 1) and amount of asphaltenes is 16 wt percent (Table 5), only the most polar components of these fractions precipitate as asphaltenes.

Based on results obtained in this study the formation of asphaltenes can be explained as follows. Treatment of the asphalt with normal alkane (heptane) upsets the solubility equilibrium of a very complex mixture of asphalt components. The excess of the nonpolar solvent causes the most polar compound types present in the asphalt to become insoluble. These compound types are capable of strong intermolecular associations resulting in the formation of agglomerates which precipitate as asphaltenes. Both the formation and composition of the asphaltenes result from a solubility phenomenon of the physical separation procedure.

CONCLUSIONS

1. Asphalt consists of polar and polarizable compound types capable of association (pyrroles, phenols, amides including 2-quinolones, carboxylic acids, pyridines, and polynuclear aromatics) and nonpolar compound types (aromatic and saturate hydrocarbons).
2. All compound types present in the asphalt have about the same molecular-weight distribution, with the average molecular-weight value being about 1000.
3. Asphaltenes are agglomerates of polar and polarizable compounds formed due to the intermolecular associations, and their composition results from a solubility phenomenon of the separation procedure.
4. Compounds comprising asphaltenes are present in the acid and base fractions of the asphalt.
5. Asphaltenes such as classically viewed to be very high (5000 to 50,000) molecular-weight components of asphalt *do not exist* in the asphalt studied.

ACKNOWLEDGMENT

The authors express their sincere appreciation to Dr. J. C. Petersen of the LETC for his assistance in providing differential infrared spectrometry data and for valuable discussion of the results of this study. The authors also express their appreciation to Dr. S. E. Buttrill, Jr., of SRI International, for his assistance in providing field ionization mass spectrometry data. Acknowledgment is also given to S. A. Holmes of the LETC for performing potentiometric titrations.

The assistance of the Laramie Energy Technology Center for partial support of this research is gratefully acknowledged. M. Boduszynski expresses his sincere appreciation to the Council for International Exchange of Scholars for granting his scholarship.

LITERATURE CITED

1. F. S. Rostler, "Fractional Composition: Analytical and Functional Significance" in *Bituminous Materials: Asphalts, Tars, and Pitches* (Ed. A. J. Hoiberg), Vol. 2, Part 1, Chap. 6, p. 194. New York: Interscience Publishers, 1965.
2. M. Boduszynski, B. R. Chadha, and T. Szkuta-Pochopien, *Fuel*, Vol. 56 (1977), 432.
3. J. F. McKay, P. J. Amend, T. E. Cogswell, P. M. Harnsberger, R. B. Erikson and D. R. Latham, "Petroleum Asphaltene: Chemistry and Composition" in *Analytical Chemistry of Liquid Fuel Sources, Tar Sands, Oil Shale, Coal and Petroleum* (Ed. P. C. Uden, S. Siggia, and H. B. Jensen) Advances in Chemistry Series 170, Chap. 9, *American Chemical Society*, Washington D.C., 1978.
4. M. Boduszynski, Preprints Div. of Petrol. Chem., *American Chemical Society*, Vol. 24, No. 4 (1979), 935.
5. L. W. Corbett, *Analytical Chemistry*, Vol. 41 (1969), 576.
6. J. F. McKay, P. J. Amend, P. M. Harnsberger, T. E. Cogswell, and D. R. Latham, *Fuel*, (Part 1) submitted for publication.
7. G. A. St. John, S. E. Buttrill, Jr., and M. Anbar, "Field Ionization and Field Desorption Mass Spectrometry Applied to Coal Research" in *Organic Chemistry of Coal*, (Ed. J. W. Larsen) *American Chemical Society Symposium Series*, No. 71, 1978.
8. J. F. McKay, T. E. Cogswell, J. H. Weber, and D. R. Latham, *Fuel*, Vol. 54 (1975), 50.
9. J. F. McKay, J. H. Weber, and D. R. Latham, *Analytical Chemistry*, Vol. 48 (1976), 891.
10. J. C. Petersen, *Analytical Chemistry*, Vol. 47 (1975), 112; and private communication.
11. J. C. Petersen, *Fuel*, Vol. 46 (1967), 295.
12. J. C. Petersen, *J. Phys. Chem.*, Vol. 75 (1971), 1129.
13. J. C. Petersen, R. V. Barbour, S. M. Dorrence, F. A. Barbour, and R. V. Helm, *Analytical Chemistry*, Vol. 43 (1971), 1491.
14. R. V. Barbour and J. C. Petersen, *Analytical Chemistry*, Vol. 46 (1974), 273.

Discussion

MR. L. W. CORBETT (Written Discussion): This is an interesting treatise of a subject that has long escaped solution. If we assume that asphaltene per se are particles consisting of several molecules or units, it is conceivable that field ionization may cause dissociation into individual molecules as the energy involved should be enough to do this. Even though it is conceived that a solvent such as n-heptane can bring about association, the fact that a solvent is used does not explain why association occurs. The presence of high molecular weight fractions, reported to be 3000 or more, in natural crude oil as well as in residua has been reported by various techniques, such as the ultra-centrifuge, gel permeation, solution viscosity and vapor pressure

osmometry and by numerous investigators. Schooling teaches us that there is always a directional relationship between fraction boiling points and molecular weight, viscosity, density, critical temperature and even color. The basic petroleum separation step is distillation which causes successively higher boiling fractions to be distilled off while the higher boiling fractions are concentrated in the residuum. Thus by increasing the distillation cut-point, we are also increasing the average molecular weight of each of the fractions in the distillation residua. Even though molecular type is a factor in this relationship, I find it difficult to understand why asphaltenes do not show up in distillate or lower boiling fractions, since you claim that asphaltenes have on the average lower molecular weights than any of the other

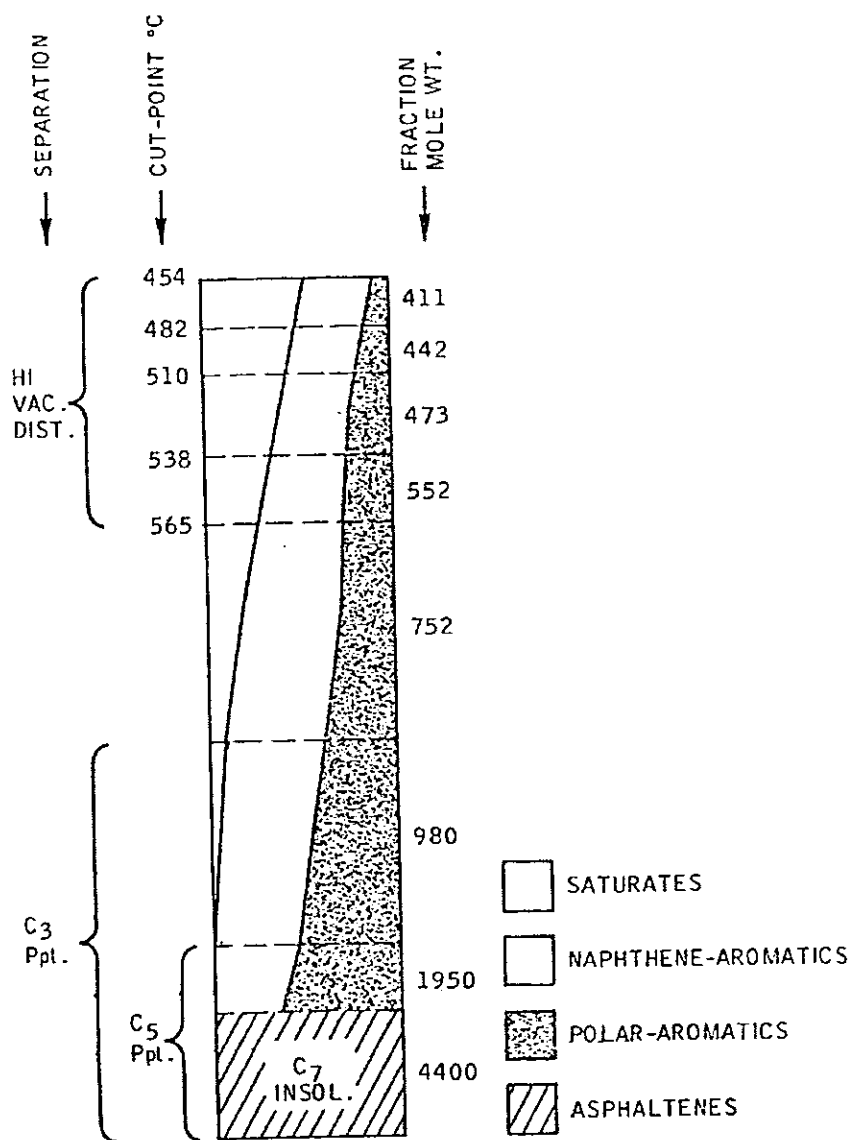


Fig. A. Distribution of Molecular Types and Sizes in a Residua Showing Effect of Separation Methods on a 191 Penetration Asphalt from Crude Type C.

type fractions. There are many published references that show asphaltenes to be always concentrated under either distillation or by solvent treatment. Asphalt technologists seldom put much faith in asphaltene molecular weight determination because of the disparity of results by the various methods. However, vapor pressure osmometry is commonly accepted for use on the non-asphaltene fractions. Figure A on page 140, serves to indicate the distribution of sizes and types found in most crude residua, subject to variations due to crude source. Thus if I may rephrase your title, "Asphaltenes, What Have You Done with Them?"

DR. M. M. BODUSZYNSKI (Written Response): I would like to thank you for your interest in our paper. Indeed, we have shown in our paper that asphaltenes are agglomerates or particles, if you will, consisting of several molecules bonded due to intermolecular associations. The reason that the intermolecular associations do not result in the precipitation of asphaltenes from an asphalt is a delicately balanced mixture of compounds that depend upon each other for solubility. This means that compounds which form asphaltenes remain dispersed in an asphalt due to the "peptizing power" of maltenes. Treatment of an asphalt with n-heptane upsets the solubility equilibrium of a very complex mixture of asphalt components. The ratio of nonpolar to polar molecules is altered and the more polar compounds capable of forming strong intermolecular associations are less soluble and precipitate as asphaltenes.

In regard to your comment that high molecular weight fractions, reported to be 3000 or more, have been found in petroleum I would like to explain as follows. The fact that numerous investigators using various techniques have reported very high molecular weight values does not prove that these results represented true molecular weights. It is known that intermolecular associations lead to erroneously high molecular weight values obtained by such techniques as ultra-centrifugation, gel permeation chromatography, solution viscosity or vapor pressure osmometry. The evidence for a dramatic effect of associations upon average molecular weight measurements by VPO has been also provided in our paper.

Field ionization mass spectrometry (FIMS) is a relatively new technique for determining molecular weight. FIMS causes dissociation of associated molecules into individual molecules and thus provides a true molecular weight profile of the studied material.

We have observed, however, the effect of strong intermolecular associations upon volatility. The FIMS results of our studies on high vacuum residua and asphalts showed that the whole residuum or asphalt may be as high as 100 percent volatile under conditions of analysis while asphaltenes separated (precipitated) from those materials may be as low as 80 percent volatile. This suggests that asphaltenes in the total asphalt are better dispersed, less associated.

Now, I would like to answer your question of why asphaltenes do not show up in lower boiling fractions but are concentrated in the residuum. During the distillation of petroleum the average molecular weight of each of the fractions, including the residuum, increases. However, the given

boiling point is not directly proportional to the average molecular weight but is dependent on the chemical structure of the compounds present in the fraction. A simple example can illustrate this phenomenon. Dibenzopyrrole has molecular weight of 167 and a boiling point of 354.8 C while normal dodecane having almost the same molecular weight—170, has a boiling point of 209 C. Similarly phenol—94.1 molecular weight, and toluene—92.1 molecular weight, have boiling points 181.4 C and 110.6 C, respectively. This shows that polar compounds capable of associations are less volatile than nonpolar compounds of the same molecular weight. As we have shown in our paper, the major compound-types found in asphaltenes included: pyrroles, phenols, amides, carboxylic acids, and pyridines. These compound-types form association bonds. Thus, it is not surprising that these compound-types have low volatility and concentrate in the residuum although their molecular weight is lower than that of accompanying nonpolar compounds. The limited solubility of these compound-types can be explained in the same manner. More polar molecules are less soluble (miscible) in nonpolar n-alkane solvents.

I would like to comment on the Figure A enclosed in your discussion. It is known that aromaticity and polarity of petroleum fractions increase with increasing boiling point. Even though the concentration of naphthene-aromatics and in particular the polar-aromatics in your Figure A increases with the increasing distillation cut-point I find it difficult to understand why the boundary line between those two fractions stops at the point indicating the heptane-insoluble asphaltenes. If we assume that this line is extrapolated down to the bottom of the bar-graph we will see that the major part of the heptane-insoluble asphaltenes contains polar compound-types defined by you as polar-aromatics. That is exactly what we have found in our study. Asphaltenes are not chemically or structurally different from resins. Asphaltenes contain polar compound-types which are defined by the separation procedure as acids and bases. The intermolecular associations of those polar compound-types affect molecular weight measurements by vapor pressure osmometry. Thus, this is not surprising that the VPO average molecular weight values provided in your Figure A increase rapidly with increasing concentration of polar compounds. I would also expect that the boundary line between saturates and naphthene-aromatics could, in case of a waxy crude oil, be extrapolated down to the bottom of the bar graph. High molecular weight paraffins have been reported in literature to co-precipitate with asphaltenes, especially when pentane is used.

In conclusion I would like to explain that we have not done anything harmful, such as cracking, to the asphaltenes. We have only taken the advantage of the fact that asphaltenes are formed due to intermolecular associations. By using the separation on ion-exchange resins we were able to break down those association forces and to separate the compound-types comprising asphaltenes. Thus, we would rather have kept the title of our paper: "Asphaltenes, Where Are You?"

MR. R. L. DUNNING (Written Discussion): This paper is very significant as it places the concept of asphaltenes into an entirely new light. Rather

than being some high molecular weight collection of molecules which differ substantially from what we call maltenes, we find that they are really only one end of the spectrum of a continuum of molecular compounds of increased polarity and solubility parameter, which, at some point are no longer soluble in alkane solvents. Studies by Heithous (1), Kolbanovskaya (2), Altgelt and Harle (3) and others have discussed the importance of the relative solubility of the components of asphalt on the properties of asphalt.

Hillyer and Leonard (4) have studied the effect of weak solvents on concentrated solutions of resins and have observed an "excess viscosity" which is caused by the inability of the solvent to completely disperse agglomerates of polar resin molecules. The same process can be visualized to be occurring in asphalt when the breadth of the composition of the components of asphalt is so wide, that certain fractions tend to agglomerate, and possibly even phase out. The result would be an abnormally high viscosity and low ductility. We (5) have also discussed this concept in arriving at the composition parameters which we feel should be considered in selecting modifiers for recycled asphalt pavements.

This paper therefore emphasizes the need to concern ourselves with the internal solubility of the asphalt components in assessing the rheological behavior of asphalt and the change of those properties with time and with state of oxidation. Rather than concern ourselves with measuring the effect of various concentrations of sulfuric acid on asphalt or running chromatographic analyses, perhaps we should consider asphalt from the point of view of non-electrolytic solution chemistry, which concerns itself with the whys and wherefores of solutions.

Literature Cited

1. O. J. Heithous, Symposium on Fundamental Nature of Asphalt, American Chemical Society, Division of Petroleum Chemistry, New York, 11-16 Sept. 1960. Preprints pH023.
2. A. S. Kolbanovskaya, *Koloidnyi Zhurnal*, Vol. 30 (1968), p. 393.
3. K. H. Altgelt and O. L. Harle, *I & E.C. Product Research and Development*, Vol. 14 (1975), p. 240.
4. J. J. Hillyer and W. J. Leonard, "Solvents, Theory and Practice," (R. W. Tess, Ed.), Advances in Chemistry Series #124, American Chemical Society, Washington, D.C. (1973).
5. R. L. Dunning and R. L. Mendenhall, "Recycling of Bituminous Pavements," American Society for Testing and Materials Special Technical Publication 662, (L. E. Wood, Ed.) *American Society for Testing and Materials*, (1978), pp. 35-46.

DR. BODUSZYNSKI (Written Response): The authors thank Mr. R. L. Dunning for his kind comments on this paper. We agree with Mr. Dunning's opinion that asphalt composition and properties should be considered from the point of view of the internal solubility of the asphalt components. That is why we emphasized in the paper the need to concern ourselves with the intermolecular association of compounds comprising asphalt.