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The Gel Permeation Chromatography of Asphalt and the Characterization of Its Fractions in Terms of Molecular and Unit Sheet Weights

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Abstract

Asphalt obtained from a refinery in Montreal was dissolved in toluene then fractionated in a preparative gel permeation chromatograph (prep.-GPC). Twenty-three fractions differing widely in molecular weights were collected and characterized by analytical GPC, viscometry, vapor pressure osmometry (VPO), element analyses, infrared spectroscopy (IR), and nuclear magnetic resonance spectroscopy (NMR). Similar studies were also carried out, for comparison purposes, on aliphatic and aromatic hydrocarbons to elucidate structure information on the different asphalt fractions.

The GPC chromatograms of the fractions generally revealed narrow distributions indicating that their separation into different component groups has been reasonably well achieved. The number-average molecular weights $\bar{M}_n$ of the fractions, as computed from their GPC chromatograms making use of the calibration curve prepared with polystyrene, polyoxypropylene glycol, and polyoxyethylene glycol, did not correspond to those obtained by the VPO technique. To overcome the problem, an alternate approach was developed whereby a number of calibration curves were tested for the asphalt fractions, and the one which yielded the $\bar{M}_n$ values closest to those found by VPO method was

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retained for the present study. $\bar{M}_w$ values could then be computed and related with $[\eta]$ to calculate the Mark-Houwink constants K and a.

Aliphatic hydrocarbons were found to obey the "Benoit theory" according to which the elution volume of solutes is controlled exclusively by their hydrodynamic volumes. Aromatic hydrocarbons, however, were found to diverge considerably from this theory. The asphalt fractions were found to deviate somewhat from the Benoit theory but the extent to which this occurred was less than that observed with pure aromatic hydrocarbons.

The GPC, IR, NMR, and elements analyses results show that the aromaticity and the naphthenic carbon content of the fractions 5 to 9 in the intermediate molecular weight range are small while the paraffinic carbon content is maximum. Their unit sheet weight is 900 and is independent of their molecular weight. These appear to be made up of a number of unit sheets linked together rather than a single large pericondensed ring system.

INTRODUCTION

The composition of asphalts and the nature of their various components has been the subject of considerable research during the past few decades. The characterization of asphalts by techniques, such as viscometry (*1–4*), rheological studies (*5–10*), nuclear magnetic resonance spectroscopy (NMR) (*11–25*), infrared spectroscopy (IR) (*12*, *25–34*), gel permeation chromatography (GPC) (*22*, *35–50*), mass spectrometry (*51–56*), x-ray diffraction (*57*, *58*), electron scanning resonance (ESR) (*18*, *59–63*), ultracentrifugation (*4*, *64*, *65*), electron microscopy (*4*, *66*, *67*), inverse gas–liquid chromatography (*68–75*), and liquid–solid chromatography (*76–79*), has brought to light an abundance of relevant information regarding some of their basic characteristics.

Viscometric data (*1–4*) and the rheological studies (*5–10*) have shown that there is association of asphaltenes in the solution. Their viscosity behavior resembles very much that of a low molecular weight material associated through relatively weak bonds into aggregates which are stable only at low shear rates. An increase in the shear rate reduces the viscosity, indicating that the degree of association in asphaltene solutions is reduced. The phenomenon of aggregation was likewise noted during the characterization of asphaltenes by vapor pressure osmometry (VPO) (*16*, *36*, *47*) when different molecular weights were obtained on changing the solvent. This was attributed to varying extents of associations because of the different polarities of the solvents used. A comparison of molecular weights of asphaltenes obtained by VPO or by viscosity measurements made under high shear rates (*4*) with those obtained by the ultracentrifugation method revealed that ultracentrifugation (*4*), where the asphaltenes are not subjected to serious agitation, yielded higher molecular weights due to their possible aggregation.

The concept of aggregation in asphaltenes was studied by Dickie and Yen (*36*) who made use of other techniques, such as x-ray diffraction, mass spectrometry, VPO, and GPC, for characterization purposes. According to these authors, the microstructure of asphaltic materials in their elementary form consists of three entities: micelles, particles, and unit sheets. Micelles are described as being composed of smaller associated entities called particles which in turn are said to be made up of yet smaller unit sheets. The unit sheets are thought to be held together by intermolecular forces.

NMR studies on asphalts by Dickson et al. (*20*, *22*) showed that the weight of unit sheets in petroleum residues may be calculated from the NMR data. Earlier studies on IR absorption (*26*) had pointed out the presence of aromatic and paraffinic groups in asphalts. Altgelt and Hirsch (*23*), who studied Venezuelan asphalt, proposed an extensive scheme of structure relationships with which they calculated the percentage of aromatic, naphthenic, and paraffinic carbons, the number of ring systems per molecule, their average size, their compactness, and substitutions in them. Haley (*24*, *47*) and Dickinson (*25*) studied both blown and unblown Kuwait asphalts by GPC, VPO, and NMR. The measurements with the VPO instrument were made in various solvent mixtures and the results showed the different abilities of each solvent to break up intermolecular associations. This once again suggested that the asphaltene molecules consist of a number of unit sheets linked together rather than a single large pericondensed ring system. These authors have proposed a structural model around the aromatic, naphthenic, and linear chains in the asphalts, the different modes of bond formation having been computed by using simultaneous equations.

Studies based on x-ray diffraction by Yen and Erdman (*57*) revealed that the asphalt structure consists of stacks of about five condensed aromatic sheets surrounded by saturated cyclic and paraffinic substituents. Electron microscopic studies (*4*) showed that asphaltene clusters of varying size, with clustering more pronounced in those fractions which showed the highest molecular weights, occurred in the ultracentrifuge. The electron scanning resonance data of Tynan and Yen (*60*) suggest that association can take place either by π-π interaction or by coordination through heteroatoms in the sheets. Inverse gas–liquid chromatographic (Iglc) studies by

Petersen et al. (*68–75*) reveal that aggregate surfaces interact with many Iglc test compounds having chemical functional groups similar to those believed to be present in asphalts.

In spite of this abundance of valuable information available on asphalts in the literature, individual characterization of all asphalts must be carried out prior to their use because, depending upon their origin, their composition will vary considerably as will their rheological properties. Studies made on asphalt samples produced in large part in the Montreal refineries were carried out by Huot and Blanchard (*49*). These authors reported that the distribution of molecular weights of parent asphalts changed when these are subjected to thermal treatments. In order to study the effects of the thermal treatments on the changes which take place in the GPC molecular weight distribution of its various fractions, a parent asphalt was passed through a preparative type GPC from which 23 fractions of differing molecular weights were collected. Each fraction was characterized by analytical GPC, VPO, NMR, and IR spectroscopy. The principal results of these studies are related in the present text.

EXPERIMENTAL

Thirty grams of an asphalt sample originating from a petroleum refinery in Montreal (Quebec) were dissolved in toluene (1% wt. solution) and fractionated on a Waters Associates ANA-prep. GPC. The separating system consisted of two 1.2 m long by 6.5 cm outside-diameter polystyrene-gel filled columns having, by the Waters method, maximum rated porosities of 100 and 350 Å, respectively. The fractionation was carried out by automatic repetitive injections of the sample solutions, 100 ml being injected each time. Each injection yielded 23 fractions of 140 ml each and required about 3 hr. The whole fractionation process lasted for upwards of 4 days.

Analytical GPC

The various asphalt fractions obtained by prep.-GPC were analyzed with a Waters Associates, model 200, analytical GPC equipped with five polystyrene-gel-filled columns each, 1.2 m long and connected in series. Each column had, by the Waters method, maximum rated porosities of 60, 100, 10^3, 5×10^3, and 10^5 Å, respectively. The flow of solvent (THF purged with nitrogen) was maintained at 1 ml/min while the concentration of the polymer sample was limited to 1/4 of 1% in order to avoid "concentration effects" on the peak positions in the chromatograms. The calibration of the instrument was performed with narrow distribution samples of polystyrene (PS), polypropylene glycol (POPG), polyoxyethylene glycol (POEG), and hydrocarbons (both aliphatic and aromatic) of known molecular weights.

Vapor Pressure Osmometry (VPO) Analyses

Number-average molecular weights $\overline{M}_n$ of the asphalt fractions were determined with a vapor-pressure osmometer (Mechrolab's Model 301A) operated at 37°C with benzene as solvent. The instrument constant, 400 ohms/liter/mole, was determined with organic compounds of known molecular weights, notably naphthalene, anthracene, and benzil.

Viscosity Calculations

Calculation of the intrinsic viscosity of a given polymer or asphalt fraction was carried out by making use of the flow-time measurement data obtained with Ubbelohde suspending-type viscometers at 25°C for five different sample concentrations involving tetrahydrofuran as the solvent. Knowing the flow-time of the solvent, the computation of the intrinsic viscosity $[\eta]$, is carried out with

$$[\eta] = \left\{\frac{\text{flow time (sec) of the solution}}{\text{flow time (sec) of the solvent}} - 1\right\} \Big/ c \qquad (1)$$

when $c \to 0$.

NMR Analyses

The NMR spectra of asphalt fractions dissolved in carbon tetrachloride were obtained at 25°C with a Varian Associates model HA-90 (90 MHz) instrument and at 75°C with 220 MHz spectrometer at sweep width of 10 Hz/cm. Tetramethylsilane (TMS) was used as the internal standard.

IR Analyses

The IR spectra of the asphalt fractions were recorded on a Beckman-12 spectrophotometer from their solutions using cells of 0.05 mm thickness equipped with KBr windows and from pellets in which KBr acted as the support for the solid asphalt fractions.

RESULTS AND DISCUSSION

In Table 1 are shown the weights associated with each of the 23 fractions separated from the parent asphalt by means of the Waters Associates ANA-prep. GPC operated at 25 °C with benzene as the solvent. One notes that a major portion of the asphalt is associated with Fractions 3 to 14. Twenty of the 23 fractions (4 to 23) were dissolved in THF and characterized on a Waters Associates model 200 analytical GPC; Fractions 1 to 3 could not be dissolved completely in THF and thus could not be passed through the analytical GPC. In Fig. 1 are shown the results of the raw GPC

TABLE 1

Weight, GPC Elution Volume, Intrinsic Viscosity $[\eta]$, Number Average and Weight-Average Molecular Weights of Various Asphalt Fractions.

Fraction no.	Weight (g)	Elution volume V_e in 5 ml counts	$[\eta]$ (dl/g)	$\bar{M}_n$[a] (GPC)	$\bar{M}_n$ (VPO)	M_n[b] (GPC)	$\bar{M}_w$[b] (GPC)
1	0.090	—	—	—	—	—	—
2	0.184	—	—	—	—	—	—
3	0.592	—	—	—	—	—	—
4	1.213	30.6	0.059	4650	2460	2950	4040
5	1.372	31.5	0.062	3225	2220	2160	2950
6	1.786	33.0	0.055	1930	1520	1510	1930
7	2.290	33.7	0.048	1310	1090	1120	1290
8	2.560	34.5	0.039	1000	900	900	1030
9	2.507	35.0	0.035	800	770	780	860
10	2.063	35.7	0.032	650	720	680	710
11	1.394	36.3	0.032	510	630	620	650
12	0.921	37.1	0.032	390	550	570	590
13	0.813	37.6	0.028	340	550	550	590
14	0.634	38.0	0.033	300	490	550	650
15	0.501	38.5	0.033	270	580	540	650
16	0.424	39.2	0.029	220	510	490	500
17	0.368	Broad distribution	—	—	—	—	—
18	0.285	″ ″	—	—	—	—	—
19	0.249	″ ″	—	—	—	—	—
20	0.192	″ ″	—	—	—	—	—
21	0.187	″ ″	—	—	—	—	—
22	0.123	″ ″	—	—	—	—	—
23	0.184	″ ″	—	—	—	—	—
Total	20.932						

[a] Values obtained with calibration curve for polymer standards.

[b] Values obtained with calibration curve for asphalt fractions.

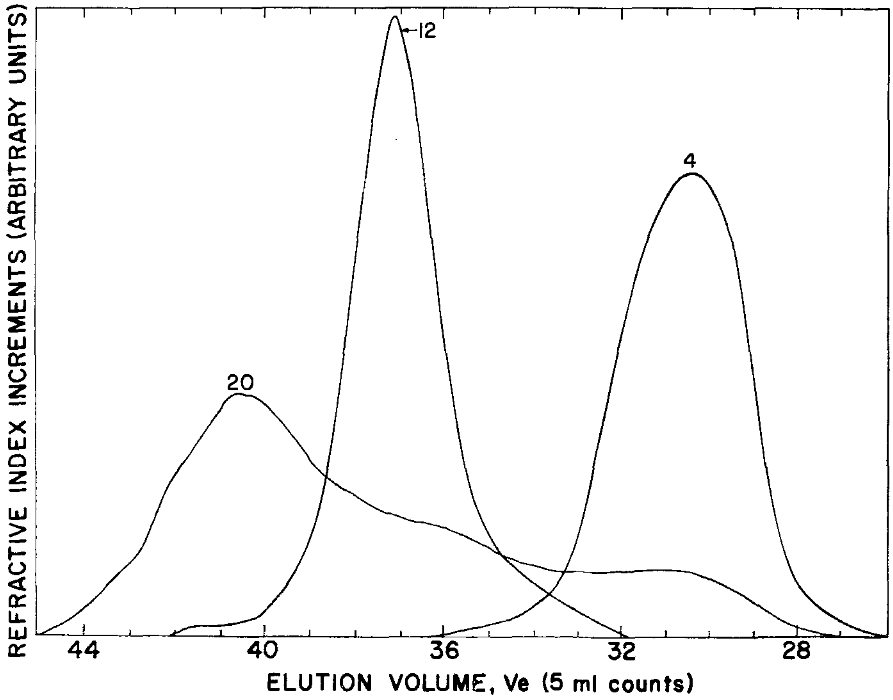


FIG. 1. GPC molecular weight distributions of asphalt fractions 4, 12, and 20.

molecular weight distributions of asphalt Fractions 4, 12, and 20. These show the quality of the separation obtained on the styrogel filled columns that were used. One notes that good separation into fractions is achieved primarily in the case of relatively higher molecular weight asphalt fractions (4 and 12) since the GPC molecular weight distribution of the low molecular weight Fraction 20 is indeed very broad! In Table 1 are also shown the elution volumes recorded for the 20 fractions on the analytical GPC. It may be observed that for Fractions 17 to 23 the distributions tended to be very broad. On the basis of the assumption that peak heights in GPC chromatograms correspond directly to the concentration of the asphalt species, irrespective of their molecular weights, the peak heights of the raw GPC curves of all samples were normalized and based on these heights, the normalized curves were drawn to see if their sum at different elution volumes corresponds to the same heights as in the parent asphalt. This is shown in Fig. 2 in which one sees that in the high molecular weight

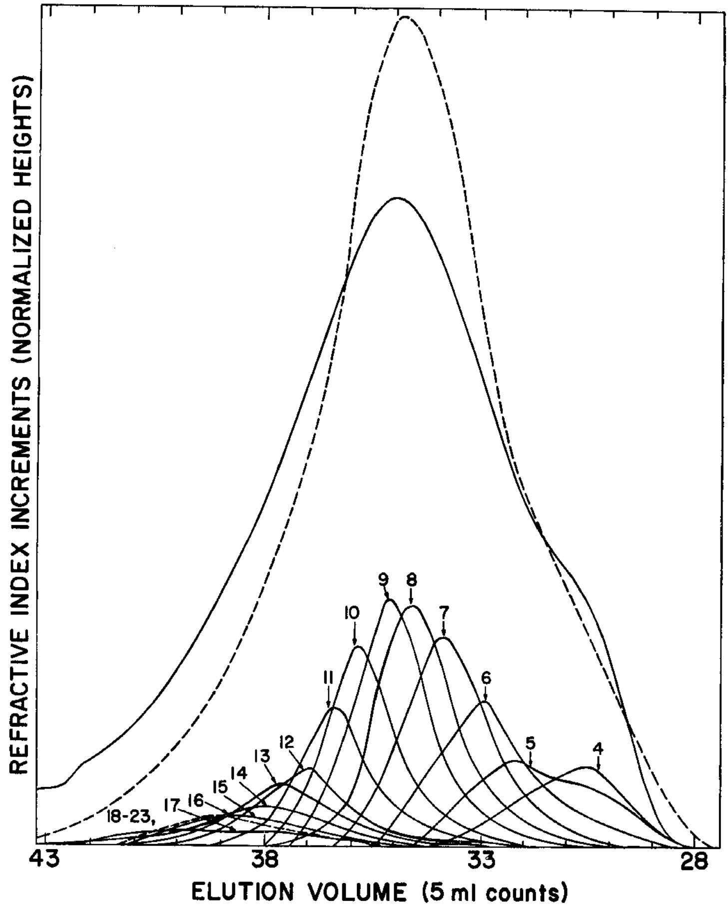


Fig. 2. Normalized GPC distributions of the parent asphalt and of its various fractions.

region there is practically no deviation at all; however, in the lower molecular weight region, the deviation is significant. It would appear that the fractions elute at slightly earlier counts than they do when present together in the parent bitumen. It is possible that the origin of this discrepancy lies simply in the corrections needed to remedy for axial dispersion of both the asphalt fractions and the parent substance in the columns.

In Table 1 are also shown the intrinsic viscosities $[\eta]$ and the $\overline{M}_n$ (VPO)'s of the asphalt fractions. In order to compute the Mark-Houwink constants K and a, where K and a are related to $[\eta]$ and the molecular weight M as follows: $\eta = KM^a$, besides $[\eta]$ one requires the values of $\overline{M}_w$. These can be calculated from the GPC curves of the asphalt fractions, if the calibration curve prepared with polymer standards is applicable to asphalts as well. In Fig. 3 is shown a plot of log $\overline{M}_w$ vs elution volume prepared using PS, POEG, and POPG standards. The following relations were used for the computations of $\overline{M}_w$ and $\overline{M}_n$:

$$\overline{M}_w = (\Sigma h_i M_i)/\Sigma h_i \quad \text{and} \quad \overline{M}_n = \Sigma h_i/\Sigma(h_i/M_i) \tag{2}$$

In Eq. (2), h_i is the peak height at a given elution volume V_{e_i}, and M_i is the corresponding molecular weight. One notes from Table 1 that the $\overline{M}_n$ values calculated with the calibration curve obtained with polymer standards do not agree with those obtained with the VPO technique, indicating that this curve cannot be used for the computations of $\overline{M}_w$ values of different fractions. In order to overcome this problem, an alternate approach was developed. A number of calibration curves (log $\overline{M}_w$ vs V_e) were tested for asphalt fractions and the one which yielded $\overline{M}_n$ values closest to those found by the VPO method was retained for the present study. By making use of this calibration curve, $\overline{M}_w$ values were calculated using Eq. (2). The results are presented in Table 1.

In Fig. 4 are shown log-log plots of $[\eta]$ vs $\overline{M}_w$ for some asphalt fractions. From the slopes of the linear lines, the value of a was found to be 0.5 and that for K was 1.22×10^{-3} dl/g. These values are of the same order of magnitude as that for polymers in general. A value of 0.5 for a further suggests that at 25°C THF is a θ-solvent for asphalts.

Universal GPC Calibration Curve for the Asphalt Fractions

Earlier studies on the parameters involved in the separation of polymers on GPC columns revealed that the molecular weight of the individual polymer was the most significant one. Later on, Benoit (*80*, *81*), who worked on both linear and branched polymers, suggested that it was not

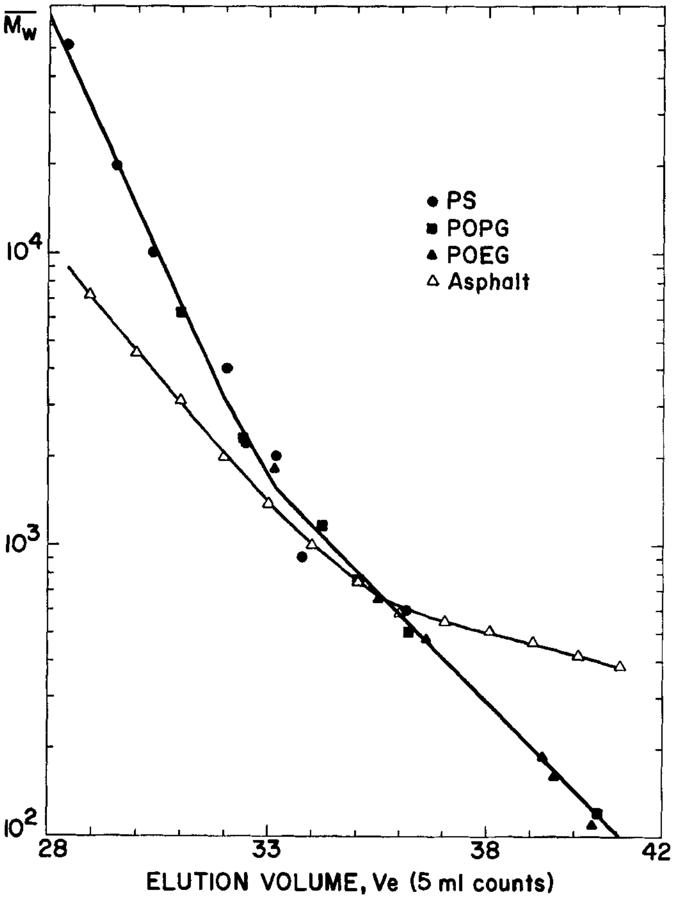


FIG. 3. GPC calibration curve, log $\bar{M}_w$ vs elution volume V_e, prepared with polystyrene standards and polymers of propylene and ethylene glycol.

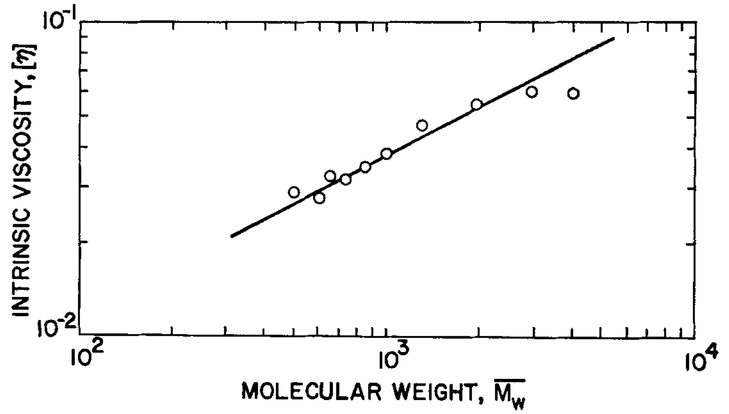


FIG. 4. Log-log plot showing the variation of $[\eta]$ with $\bar{M}_w$ for various asphalt fractions.

the molecular weight alone but rather the hydrodynamic volume ($[\eta]M$) of the species which is the controlling parameter in their separation on GPC columns. Thus, if a plot of log $[\eta]\overline{M}$ vs elution volume were made with a given set of polymers, a linear or curved line should be obtained (depending on the range of molecular weights used) on which polymers originating from other monomers should fit as well. This is often referred to as the "Benoit Universal Calibration Curve." Many groups have confirmed this finding and more recently Belenkii et al. (*82*, *83*) showed it to be applicable even to polymers of very low molecular weight.

With a view to verifying the validity of this curve for asphalt fractions, a universal calibration curve was prepared with PS, POEG, and POPG samples, based on the data given in Table 2. The $[\eta]M$ vs V_e data in Table 2 for the asphalt fractions were then plotted on the same graph in an attempt to fit the calibration curve. Although the higher molecular weight fractions do indeed fall on the curve (Fig. 5), the lower molecular weight fractions deviate from it. In order to identify the nature of the lower molecular weight asphalts which deviate from the universal calibration curve, $[\eta]M$ vs V_e data for both aliphatic and aromatic hydrocarbons, taken from Table 2, were plotted on the same graph. All of the aliphatic hydrocarbons respect the hydrodynamic volume vs elution volume relationship; however, the aromatic hydrocarbons obviously do not obey this concept. It seems therefore that aromatics constitute an important

TABLE 2

Molecular Weights $\bar{M}_w$, Elution Volumes V_e, Intrinsic Viscosity $[\eta]$, and the Products of $[\eta]$. $\bar{M}_w$ for Polystyrene, Polyoxypropylene Glycols, Polyoxethylene Glycols, Aromatics, Aliphatic Hydrocarbons, and Asphalt Fractions

Product or fraction no.	$\bar{M}_w$	V_e	$[\eta]$	$[\eta]\bar{M}_w$
Polystyrenes (PS)				
PS 51,000	51,000	28.4	0.308	15,700
PS 19,800	19,800	29.5	0.174	3,450
PS 10,300	10,300	30.4	0.103	1,060
PS 10,000	10,000	30.3	0.105	1,050
PS 4,800	4,800	32.2	0.064	307
PS 4,000	4,000	32.1	0.058	232
PS 2,200	2,200	32.5	0.047	104
PS 2,030	2,030	33.2	0.044	89
PS 900	900	33.7	0.043	38
PS 600	600	36.2	0.032	19
Polyoxypropylene Glycols (POPG)				
POPG 4,025	6,250	30.9	0.092	575
POPG 2,025	2,310	32.5	0.060	139
POPG 1,025	1,300	34.3	0.038	49
POPG 750	750	35.1	0.036	27
POPG 425	460	36.2	0.025	12
Propylene glycol	76	40.6	0.019	1.4
Polyoxyethylene Glycols (POEG)				
POEG 600	656	35.6	0.038	25
POEG 400	467	36.6	0.031	14
Tetraethylene glycol	194	39.3	0.023	4.4
Triethylene glycol	160	39.6	0.021	3.4
Diethylene glycol	106	40.4	0.019	2
Aliphatic Hydrocarbons				
Hexatriacontane	507	35.2	0.046	24
Dotriacontane	451	35.6	0.039	18
Octasosane	395	36.2	0.032	13
Tetracosane	339	36.7	0.030	10
Octadecane	255	37.9	0.023	6

(continued)

TABLE 2 (continued)

Product or fraction no.	$\bar{M}_w$	V_e	$[\eta]$	$[\eta]\bar{M}_w$
		Aromatics		
Benzene	78	44.6	0.003	0.2
Naphthalene	128	44.3	0.012	1.5
Anthracene	178	43.8	0.017	3.1
Chrysene	228	43.2	0.027	6.1
Dibenz-[a-h] anthracene	278	42.3	0.026	7.4
Triphenyl methane	244	40.6	0.018	4.5
		Asphalt Fractions		
4	4,040	30.6	0.059	238
5	2,950	31.5	0.062	183
6	1,930	33.0	0.055	106
7	1,290	33.8	0.048	62
8	1,030	34.5	0.039	40
9	860	35.0	0.035	30
10	710	35.7	0.032	23
11	650	36.3	0.032	21
12	590	37.1	0.032	19
13	590	37.6	0.028	17
14	650	38.0	0.033	21
15	650	38.5	0.033	21
16	500	39.2	0.029	15

part in the lower molecular weight asphalt fractions as was confirmed from the results of NMR spectra which are discussed later.

Similar observations were made by Grubisic and Gallot (*84*) through GPC analyses which showed that for samples with identical molecular weights, those samples of aromatic origin had higher elution volumes than did the corresponding samples of aliphatic origin. This may be explained on the basis of an adsorption phenomenon affecting the aromatics in the GPC columns. This adsorption is dependent on the structure of the aromatics, the nature of the groups attached to them, and the polarity of the medium used for the separation (*2*, *85–89*).

Based on the results of GPC analyses where it has been shown that the asphalt fractions fit the universal calibration curve, it can be concluded that asphalts behave much like polymers. The deviations from the uni-

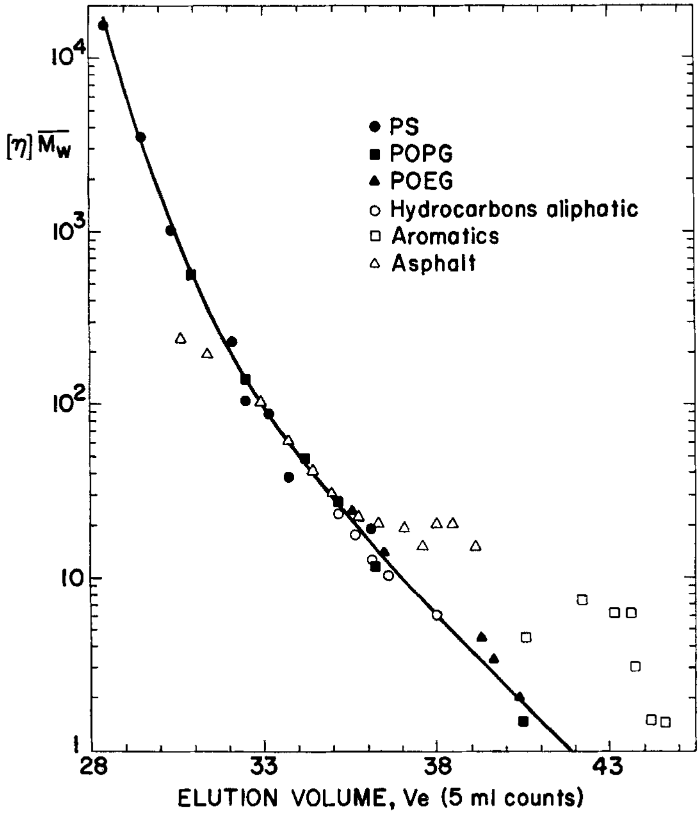


FIG. 5. Plot of log $[\eta]\ \bar{M}_w$ vs elution volume V_e for polystyrene, polyoxypropylene glycols, polyoxyethylene glycols, asphalt fractions, aliphatic hydrocarbons, and aromatics.

versal curve, observed for the lower molecular weight asphalt fractions, may also take place in oligomeric polymer materials due to the aromatic constituents in them. The concept of asphalts behaving like polymers is also seen from the plots of log $[\eta]$ vs log $\overline{M}_w$ (Fig. 4) shown earlier, where the variation is linear. This concept is in good agreement with that reported in the literature (*2*, *4*, *23–26*, *36*, *47*, *57*) where it is suggested that asphalts have a linear structure made up of numerous "units sheets" rather than single large pericondensed aromatic ring systems.

The structural differences of the various asphalts as indicated by the GPC data may further be confirmed by other techniques, e.g., element analyses, IR and NMR spectroscopy. These techniques were used and the results obtained are discussed below.

Element Analyses

In Table 3 are presented the results of the element analyses carried out at the "Organic Microanalyses" laboratory in Montreal. Although the proportion of different elements is not identical, these do not show significant trends except that the C/H atomic ratio is minimum for the intermediate asphalt fractions. Thus it is not possible to hold the element composition of each fraction responsible for the deviation observed with Benoit universal calibration curve. However, the atomic ratios C/H, O/H,

TABLE 3

Element Analyses and Their Atomic Ratios for Various Fractions of the Parent Asphalt

No.	C (%)	H (%)	N (%)	O (%)	S (%)	C/H (atomic ratio)	O/H (atomic ratio)	$\frac{O+S+N}{H}$ (atomic ratio)
4	81.03	8.72	0.65	7.04	3.14	0.774	0.050	0.067
5	83.06	10.37	1.19	2.10	2.74	0.667	0.013	0.029
6	87.18	11.20	1.01	0.60	0.00	0.648	0.003	0.006
7	81.99	11.04	0.59	4.24	2.14	0.618	0.024	0.034
8	83.33	11.44	1.79	1.64	1.80	0.607	0.009	0.025
9	82.42	10.51	0.30	3.71	2.39	0.653	0.022	0.031
10	83.34	10.26	1.77	2.18	2.45	0.677	0.013	0.033
11	81.67	10.38	0.76	4.41	2.78	0.655	0.026	0.040
12	83.11	9.79	1.44	2.11	3.55	0.707	0.013	0.035
13	82.41	9.30	0.67	4.90	2.72	0.738	0.033	0.047
15	82.34	9.94	1.43	2.64	2.96	0.690	0.017	0.036

and (O + S + N)/H calculated for each fraction and presented in Table 3 are of considerable significance in the computation of structural parameters and will be used in combination with the NMR data later on.

IR Analyses

In Fig. 6 are shown the IR spectra of asphalt Fractions 5, 9, and 15. These show important peaks at the following wave numbers (cm^{-1}): 3400 (ν_{as} OH and NH), 3060 (ν_{C-H} ar), 2960 (ν_{as} CH_3), 2920 (ν_{as} CH_2), 2850 (ν_{as} CH_3, ν_{as} CH_2), 1735 (δ_{C-O-C} carboxylic), 1610 ($\delta_{C=C}$ arom), 1460 (δ_{as} CH_3, δ_{as} CH_2), 1380 (δ_{as} CH_3), 1300 (C–N, R–NO_2, SO_2 stretching), 1050–1200 (ν_{C-O} ethers) and 700–900 (δ_{C-H} out of plane). The assignment of the different peaks agrees well with that reported in the literature (*26*, *28*, *32*, *90*). It should be noted that the relative intensities of the different peaks shown in Fig. 6 for the three asphalt fractions studied are

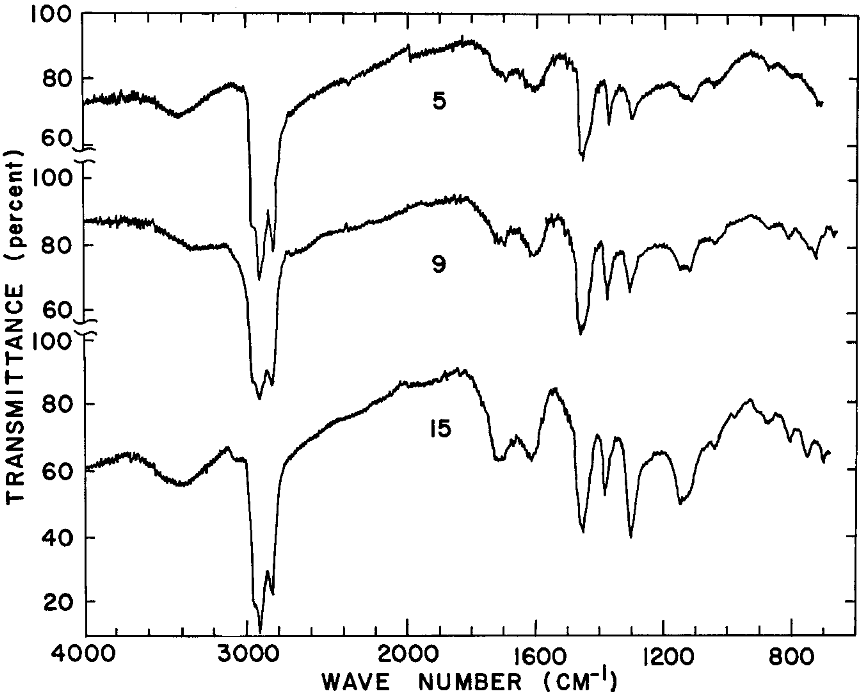


FIG. 6. IR spectra of asphalt fractions 5, 9, and 15.

TABLE 4

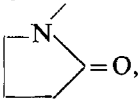
IR Relative Intensities Measured at Different Wave Numbers for Various Asphalt Fractions Using 10% Solutions in Each Case

Wave number (cm^{-1})

No.	2920	2850	2920 + 2850	1700	1610	1460	1380	1380/ 1460	1300	1150
5	0.44	0.43	0.87	0.02	0.01	0.16	0.06	0.38	0.04	0.11
6	0.52	0.50	1.02	0.02	—	0.18	0.07	0.39	0.04	0.05
7	0.52	0.48	1.00	0.02	—	0.17	0.07	0.41	0.02	0.11
8	0.44	0.47	0.91	0.01	—	0.18	0.07	0.39	—	0.06
9	0.47	0.45	0.92	0.02	—	0.17	0.07	0.41	0.04	0.13
10	0.37	0.42	0.79	0.02	—	0.17	0.07	0.41	0.05	0.07
11	0.33	0.36	0.69	0.02	0.01	0.16	0.07	0.44	0.07	0.15
12	0.30	0.35	0.65	0.03	0.02	0.17	0.07	0.41	0.02	0.08
13	0.25	0.31	0.56	0.03	0.02	0.17	0.07	0.41	0.09	0.15
14	0.21	0.25	0.46	0.04	0.02	0.14	0.06	0.43	0.12	0.09
15	0.18	0.23	0.41	0.05	0.03	0.14	0.05	0.36	0.13	0.16

not the same. To observe the changes that take place in the proportions of the various functional groups associated with the different asphalt fractions, quantitative studies were carried out by recording IR spectra of 10% asphalt solutions in dichloromethane and analyzing the relative intensities of the different peaks. The results are presented in Table 4. The intensity of the peak at 3060 cm^{-1}, attributed to aromatic protons (*32*), was not included in the table because its value is below the magnitude of the percent error of the instrument ($\pm 5.0\%$). The results of the analyses presented in Table 4 suggest that as the molecular weight of the asphalt fractions decreases (Fractions 5 to 15):

(a) The ratio 1380/1460 ($\delta_{CH_3}/\delta_{CH_3} + \delta_{CH_2}$) remains constant within ± 0.04 of 0.40 and δ_{CH_2} decreases. Thus the total paraffinic content (sum of the stretching vibrations of CH_3 and CH_2 (ν 2920 + ν 2850 cm^{-1}) or bending vibrations ($\delta_{CH_3} + \delta_{CH_2}$)) decreases.

(b) The intensity of the peak around 1700 cm^{-1} attributed to C–O stretching vibrations (*91*) in compounds with groups such as Ar-CHO, Ar-COOH, -CO-NH$_2$, -CO-NH-X,  6-membered cyclic imide, R-CO-SR, R-CO-S-Ar, and R-O-CO-N increases. Using the assignment of Helm and Petersen (*30*) for the 1700 cm^{-1} peak, it would seem that the number of carboxylic acid groups increases.

(c) The aromaticity, calculated by the intensity of the 1610 cm^{-1} peak ($\delta_{C=C}$ arom), increases.

(d) The intensity of the peak at 1300 cm^{-1} (asym stretching of SO_2, C–N stretching, and C–O stretching of esters) and 1150 cm^{-1} (C–O–C asym stretching of esters, C–CN asym stretching, sym SO_2 stretching) shows no regular trends, primarily, it is believed, because these represent cumulative stretching vibrations due to three different groups, the proportion of each being different depending upon the molecular weight of the particular asphalt fraction.

Based on the results of the element analyses and the IR studies presented earlier, it is possible to draw a qualitative picture of the constitution of the various fractions; however, in order to elucidate the structure of asphalt in a more precise manner it is by far preferable to use NMR spectroscopy in conjunction with element analysis and IR studies. Brown and Ladner (*12*), during their studies on coal-like materials by element analyses, NMR and IR spectroscopy, developed equations to compute certain structural parameters for coals, e.g., aromaticity (fa), degree of substitution (σ), and H_{ar}/C_{ar}, the atomic hydrogen to carbon ratio of the hypothetical unsubstituted aromatic material. Haley (*47*), who studied asphalts and asphaltene fractions, extended the approach of Brown and Ladner (*12*) and derived equations leading to the computation of unit sheet weight of asphaltene fractions. An approach similar to that of Haley (*47*) has been used in this work and is discussed below.

NMR Analyses and Calculation of Structural Parameters

In Fig. 7 is shown a 220 MHz NMR spectrum of bitumen Fraction 13, recorded at 75°C in carbon tetrachloride as solvent and TMS as internal standard. The highlights of this spectrum are as follows:

(1) 9.0 to 9.5 τ methyl ($-CH_3$) or H_γ protons.
(2) 8.0 to 9.0 τ methylene ($-CH_2$) or H_β protons.
(3) 7.0 to 8.0 τ methine (–CH) or H_α protons.
(4) 2.0 to 3.6 τ aromatic protons H_{ar}.

These assignments agree well with those proposed by Williams (*11*), Ramsey et al. (*19*), Dickson et al. (*20*, *22*), and Haley (*24*). A few samples

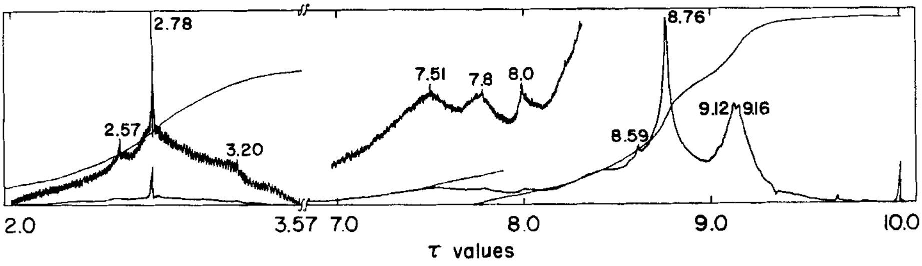


FIG. 7. A 220 MHz NMR spectrum of asphalt fraction 13 in carbon tetrachloride as solvent at 75 °C and TMS as internal standard.

were also recorded at room temperature (25 °C) in CCl_4 as solvent with a 90 MHz instrument. The results of the analyses by 90 and 220 MHz instruments were the same.

In Table 5 are presented the data obtained from the NMR analyses in terms of α, β, γ, and aromatic protons and presented in the form of ratios [H_α/H_T, H_β/H_T, H_γ/H_T, $(H_\beta + H_\gamma)/H_T$, H_γ/H_β and H_{ar}/H_T, where H_T is the total number of protons]. It is interesting to note that, in the linear chain, H_α increases, H_β decreases, and H_γ remains more or less constant as the molecular weight decreases. Furthermore, the paraffinic content (presented here as $H_0^* = (H_\beta + H_\gamma)/H_T$) decreases with decreasing molecular weight with H_γ/H_β remaining within 0.38 ± 0.06 and the aromaticity H_{ar}/H_T increasing with decreasing molecular weight. These two observations agree well with the IR spectroscopic data. The presence of high aromatic content in the lower molecular weight asphalt fractions was also pointed out by the GPC data. One would normally imagine that the proportion of aromatics should decrease with decreasing molecular weight of the asphalt fraction but such is not the case.

Based on the results obtained by GPC, element analyses, IR and NMR spectroscopy, the structural parameters of Brown and Ladner (*12*) and Haley (*47*) may be computed to evaluate the unit sheet weight of each asphalt fraction and relate it to its $\bar{M}_w$ value. These parameters, however, are based on the assumption that (a) more than three rings are pericondensed and (b) no aromatic rings are joined by single bonds. If one assumes that these hypothesis are valid for the present system, the different parameters may be defined as follows:

$$\text{Aromaticity } (f_a) = \frac{\dfrac{C}{H} - \dfrac{H_\alpha^*}{x} - \dfrac{H_0^*}{y}}{C/H} \qquad (3)$$

TABLE 5

The Proportions of α, β, γ, and Aromatic Protons in the Various Asphalt Fractions as Computed from Their NMR Spectra

No.	$H_\alpha^* = H_\alpha/H_T \times 10^2$	$H_\beta/H_T \times 10^2$	$H_\gamma/H_T \times 10^2$	$H_0^* = (H_\beta + H_\gamma)/H_T \times 10^2$	H_γ/H_β	$H_{ar}^* = H_{ar}/H_T \times 10^2$
4	6.6	67.3	23.2	90.5	0.34	2.8
5	9.0	65.9	20.4	86.3	0.31	4.7
6	8.0	65.3	22.7	88.0	0.35	4.0
7	4.8	69.6	22.7	92.3	0.33	2.9
8	6.6	69.8	20.8	90.6	0.30	2.8
9	8.6	67.4	21.7	89.1	0.32	2.3
10	9.7	59.7	25.0	84.7	0.42	5.6
11	14.6	57.1	22.6	79.7	0.40	5.7
12	16.4	54.4	21.5	75.9	0.40	7.7
13	16.6	51.5	22.7	74.2	0.44	9.2
14	21.8	50.2	21.4	71.6	0.43	6.6
15	17.8	48.5	20.2	68.7	0.42	13.5
16	22.2	46.5	16.5	63.0	0.35	14.8
17	19.7	43.5	15.1	58.6	0.35	21.7
18	24.4	42.6	14.8	57.4	0.35	18.2
19	22.1	46.6	13.7	60.3	0.29	17.6
20	19.6	45.8	11.1	56.9	0.24	23.5
21	14.8	50.4	14.8	65.2	0.29	20.0

where $H_\alpha^* = H_\alpha/H_T$ and $H_0^* = (H_\beta + H_\gamma)/H_T$. x is the atomic ratio of hydrogen to α-carbon substituents in the nonaromatic system and y is the atomic ratio of hydrogen to unattached groups in the same system (*12*).

Brown and Ladner (*12*) assumed that $x = y = 2$ for coal-like materials. Ramsey et al. (*19*) and Dickson et al. (*20*), who studied asphalts, also used values of 2.0 for x and y. Haley (*47*), in his studies on asphalts, however, suggested a value of $x = 1.92$. Making use of this value, he was able to link unit sheet weight to molecular weights. In the present study, a value of $x = y = 1.85$ was used for the computation of unit sheet weights. The origin of this value lies in Eq. (4), proposed by Brown and Ladner (*12*) to determine the ratio of aromatic protons to aromatic carbons:

$$\frac{H_{ar}}{C_{ar}} = \frac{\dfrac{H_\alpha^*}{x} + H_{ar}^* + \dfrac{O}{H}}{\dfrac{C}{H} - \dfrac{H_\alpha^*}{x} - \dfrac{H_0^*}{y}} \tag{4}$$

where $H_{ar}^* = H_{ar}/H_T$.

Keeping in mind that H_{ar}/C_{ar} never exceeds a value of 1, various values ranging from 1.8 to 2.0 were assigned to x and y, and it was found that $x = y = 1.85$ yielded the ratio H_{ar}/C_{ar} always less than 1 and the unit sheet weights were always less than $\bar{M}_n$ found by the VPO method. The other equations needed to compute the unit sheet weights and other relevant information about the asphalt fractions, as proposed by Haley (*47*), are as follows:

$$\text{Degree of substitution} = \frac{\dfrac{H_\alpha^*}{x} + \dfrac{O + S + N}{H}}{\dfrac{H_\alpha^*}{x} + \dfrac{O + S + N}{H} + H_{ar}^*} \tag{5}$$

Number of aromatic carbons C_{ar}:

$$\frac{H_{ar}}{C_{ar}} = \frac{1 + \sqrt{C_{ar} - 11}}{C_{ar}} \tag{6}$$

Naphthenic carbons:

$$\%C_{naph} = 54.3\left(\frac{H_\gamma}{H_\beta} + 0.100\right) \tag{7}$$

Paraffinic carbons:

$$\%C_{par} = 100 - (\%C_{naph} + \%C_{ar}) \tag{8}$$

Total number of carbons C_T:

$$C_T = C_{ar}/f_a \tag{9}$$

Unit sheet weight:

$$\text{U.S.W.} = \frac{C_T \times 12 \times 100}{C_T\,(\%)} \tag{10}$$

Based on the results of element analyses, NMR data, and VPO molecular weights and making use of Eqs. (3) to (10), in Table 6 are presented some of the structural parameters of asphalt Fractions 4 to 15. In all of the asphalt fractions, it is the paraffinic carbon (C_{par}) content which is the highest, constituting 40 to 65% of the total carbon. This is followed by naphthenic carbon (C_{naph}) whose proportion ranges between 20 and 30% and finally aromatic carbon (C_{ar}) which varies between 10 and 30%. Although the extent of the different carbon contents varies, the degree of substitution σ remains constant within ± 0.09 of 0.64. The variation of certain other structural parameters may best be illustrated graphically as is shown in Fig. 8 where are listed the $\%C_{naph}$, $\%C_{par}$, and f_a as a function of $\overline{M}_w$. It is of interest to note that while the aromaticity f_a and $\%C_{naph}$ pass through a minimum for intermediate molecular weight asphalts, the $\%C_{par}$ attains a maximum for these molecular weights. This may explain why the asphalt fractions with intermediate molecular weights having low aromatic but high paraffinic contents obey the Benoit universal GPC curve (see Fig. 5) whereas those with high or low molecular weights having higher aromatic but low paraffinic content do not fall on this calibration curve. Similar observations were recorded with aliphatic and aromatic hydrocarbons where the former followed the universal curve and the latter did not.

In Table 6 are also presented the ratios of H_{ar}/C_{ar} for the different asphalt fractions. These values may be used to compute the number of aromatic carbons (C_{ar}) which in turn, when combined with the aromaticity factor (f_a) and the help of Eq. (9), yields the total number of carbon (C_T). Table 6 shows that C_T decreases regularly with decreasing molecular weight of the asphalt fractions. Earlier, in Table 5, it was noted that the percent aromatic protons H_{ar}^* increased regularly with decreasing molecular weight. Combining these two results it can be concluded that as the molecular weight of the asphalt fraction decreases, it becomes richer in compounds carrying smaller numbers of condensed ring systems.

In Table 6 are also presented the unit sheet weights of the various asphalt fractions as computed with the equations derived by Brown and Ladner

TABLE 6

Structural Parameters for Various Asphalt Fractions

No.	f_a	σ	H_{ar}/C_{ar}	C_{naph} (%)	C_{par} (%)	C_{ar}	C_T	U.S.W.	$\bar{M}_w$	$\bar{M}_w$/U.S.W.
4	0.32	0.79	0.46	23.9	44.1	31.0	97	1430	4040	2.8
5	0.23	0.62	0.71	22.3	54.7	12.8	56	810	2950	3.6
6	0.20	0.57	0.67	24.4	55.6	14.5	78	1000	1930	1.9
7	0.15	0.67	0.85	23.3	61.7	8.8	58	860	1290	1.5
8	0.13	0.68	0.89	21.7	65.3	7.9	59	840	1030	1.2
9	0.19	0.77	0.73	22.8	58.2	12.0	63	920	860	0.9
10	0.25	0.60	0.73	28.2	46.8	12.2	49	710	710	1.0
11	0.22	0.68	—	27.1	50.9	—	—	—	—	—
12	0.29	0.62	0.86	27.1	43.9	8.5	29	420	590	1.4
13	0.33	0.60	0.87	29.3	37.7	8.4	25	360	590	1.6
15	0.32	0.49	—	28.0	39.8	4.5	14	200	650	3.2

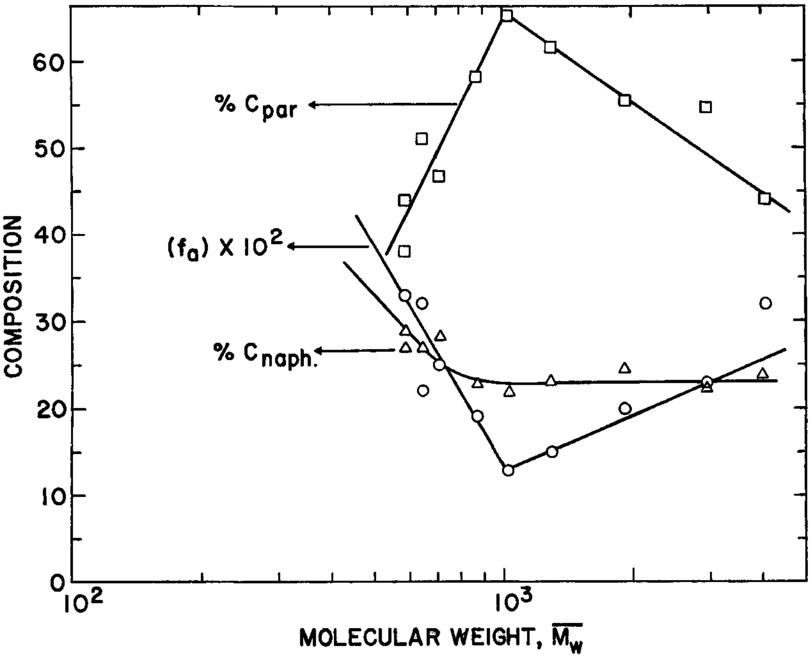


FIG. 8. Variation of f_a, $\%C_{naph}$, and $\%C_{par}$ as a function of $\bar{M}_w$ of the asphalt fractions.

(*12*) and Haley (*47*). These unit sheet weights are compared with the GPC weight-average molecular weights of the asphalt fractions. The unit sheet weight of asphalt Fractions 5 to 9 is of the order of 900. Only Fractions 4 and 10 deviate considerably from this value. These results agree well with those obtained by Dickson et al. (*20*, *22*) and Haley (*47*). Fractions 4 to 10 appear to be identical to the asphaltene fractions obtained by the precipitation of asphalt in isopentane. The other Fractions 12 to 15, having low values of unit sheet weights, are probably better compared to oils and resins.

The unit sheet weight of 900 for Fractions 5 to 9 is independent of the molecular weight of the fraction and thus would suggest that the asphalt fractions are built up of a number of unit sheets rather than a single large pericondensed ring system. A comparison of the unit sheet weight of an asphalt fraction with that of its weight-average molecular weight $\overline{M}_w$ (see Table 6), suggests that the number of unit sheets required to build an asphalt fraction may vary between 1 and 4. The formation of asphaltenes through the polymerization of a number of unit sheet weights is in agreement with results presented by Yen et al. (*57*) and Ferris et al. (*18*), who suggested that unit sheets were of the same dimension for all solvent fractionated asphaltenes and postulated a 16-ring structure of condensed aromatic sheets linked by saturated bridges.

It may be concluded from the above that:

(1) The set of GPC columns used for the fractionation of asphalt samples yields good separation only in the higher molecular weight region. To obtain better fractionation, additional column length would be required in series with the columns used or other more efficient separation materials would have to be loaded in the columns.

(2) Asphalt fractions behave much like polymers as illustrated by the $[\eta]$ vs $\overline{M}_w$ relationship and the fitting of $[\eta]M$ data on the Benoit's universal calibration curve.

(3) GPC, element analyses, IR, and NMR spectroscopy results show that aromaticity and naphthenic carbon content are small in the intermediate molecular weight asphalt fractions whereas paraffinic carbon content is maximum in the same fractions.

(4) The unit sheet weight of the intermediate Fractions 5 to 9 is 900 and independent of the molecular weight of the fraction. These are made up of a number of unit sheets rather than a single large pericondensed ring system.

Studies on the rheological properties of these asphalt fractions are in progress. Results will be published in due course.

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