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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES PHASE III

Quarterly Progress Report, October—December 1977

By
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University of Southern California
Los Angeles, California

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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES

Phase III

Quarterly Progress Report for the Period
October - December 1977

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Abstract

The 100% solubility limits for Synthoil coal liquid solvent fractions fall within the range: 9-12 hildebrands for asphaltene, and 10-11 hildebrands for carbene; the carboid was found to be essentially completely dissolved only in pyridine, δ = 10.6 hildebrands.

VPO molecular weight studies indicate that association of asphaltenes is a function of solvent polarity. Association increases along the series: benzene > chloroform > tetrahydrofuran, but infinite dilution number average molecular weight values are in close agreement for any asphaltene in these three solvents.

GPC weight average molecular weight values for the asphaltenes obtained from the five demonstration processes under study are found to range from 531-615.

Electron spin resonance studies of asphaltenes in solution, and temperature dependence studies of solid asphaltenes, and asphaltene charge transfer complexes with TCNE provided no evidence for charge transfer interactions leading to increased signal intensities.

Polarographic analyses of coal liquid solvent fractions provided evidence which suggests larger and more aromatic systems are present along the series: carboid > carbene > asphaltene > resin > oil.

Silylation and methylation of asphaltene silica gel chromatographic fractions provided data on the percentages of hydroxylic oxygen, and basic nitrogen present in each fraction.

OBJECTIVE AND SCOPE OF WORK

It is the objective of this project to isolate the asphaltene fractions from coal liquids from a number of liquefaction processes. These asphaltene fractions may be further separated by both gradient elution through column chromatography, and molecular size distribution through gel permeation chromatography.

Those coal-derived asphaltene fractions will be investigated by various chemical and physical methods for characterization of their structures. After the parameters are obtained, these parameters will be correlated with the refining, and conversion variables which control a given type of liquefation process. The effects of asphaltene in catalysis, ash or metal removal, desulfurization and denitrification will also be correlated. It is anticipated that understanding the role of asphaltene in liquefaction processes will enable engineers to both improve existing processes, and to make recommendations for operational changes in planned liquefaction units in the U.S.

The objective of Phase III is to continue the characterization of coal asphaltenes and other coal liquid fractions by the use of physical, instrumental and chemical methods. The structural parameters obtained will be used to postulate hypothetical average structures for coal liquid fractions.

SUMMARY OF PROGRESS TO DATE

During this quarter the following tasks have been undertaken and/or completed:

(1) Solvent separations.
(2) Training of new technical personnel is underway.
(3) Establishment of sample data bank.
(4) Chromatography of asphaltenes is being carried out.
(5-15) Characterization of coal liquid fractions by various physical and instrumental methods is continuing.

(16) Asphaltene donor-acceptor complexes are being studied by a variety of techniques.

(17) Characterization of asphaltenes by chemical methods is being carried out.

These tasks are listed in the milestone chart in Fig. 1. Detailed discussion of technical progress is found in the next section.

Detailed Discussion of Technical Progress

(1) Sample Acquisition and Separation

Work Accomplished:

(a) Solvent Separation of Coal Liquids

Coal liquid samples were solvent fractionated by the standard method in order to obtain stockpiles of the various solvent fractions.

(b) Solubility Parameters of Coal Liquid Fractions

Solvent fractionation has long been used to separate the fractions of the coal liquefaction product. In an attempt to more clearly define the coal liquid fractions, the solubility limits of the asphaltene and carbene fractions were obtained as a function of solubility parameters (1). We have now extended this work to include the carboid fraction. The results of the solubility experiments are shown in Fig. 2. Solubility limits for the asphaltene are between 9 and 12 hildebrands. Solubility limits for carbene are between 10 and 11 hildebrands. The carboid solubility peaks at ~11 hildebrands. It is 97% soluble in pyridine, δ = 10.62 hildebrands.

Hema was found to polymerize in several runs during solubility tests on the carboid, making reproducible results difficult to obtain. Polymerization usually occurred for solubility parameters of 11 and 12 hildebrands. The carboid, having a high concentration of unpaired spin centers, probably acts as a polymerization catalyst. Therefore, to obtain the solubility of the carboid in this region, pure solvents were used. They are listed in Table I.

Fig. 1. Milestone Chart

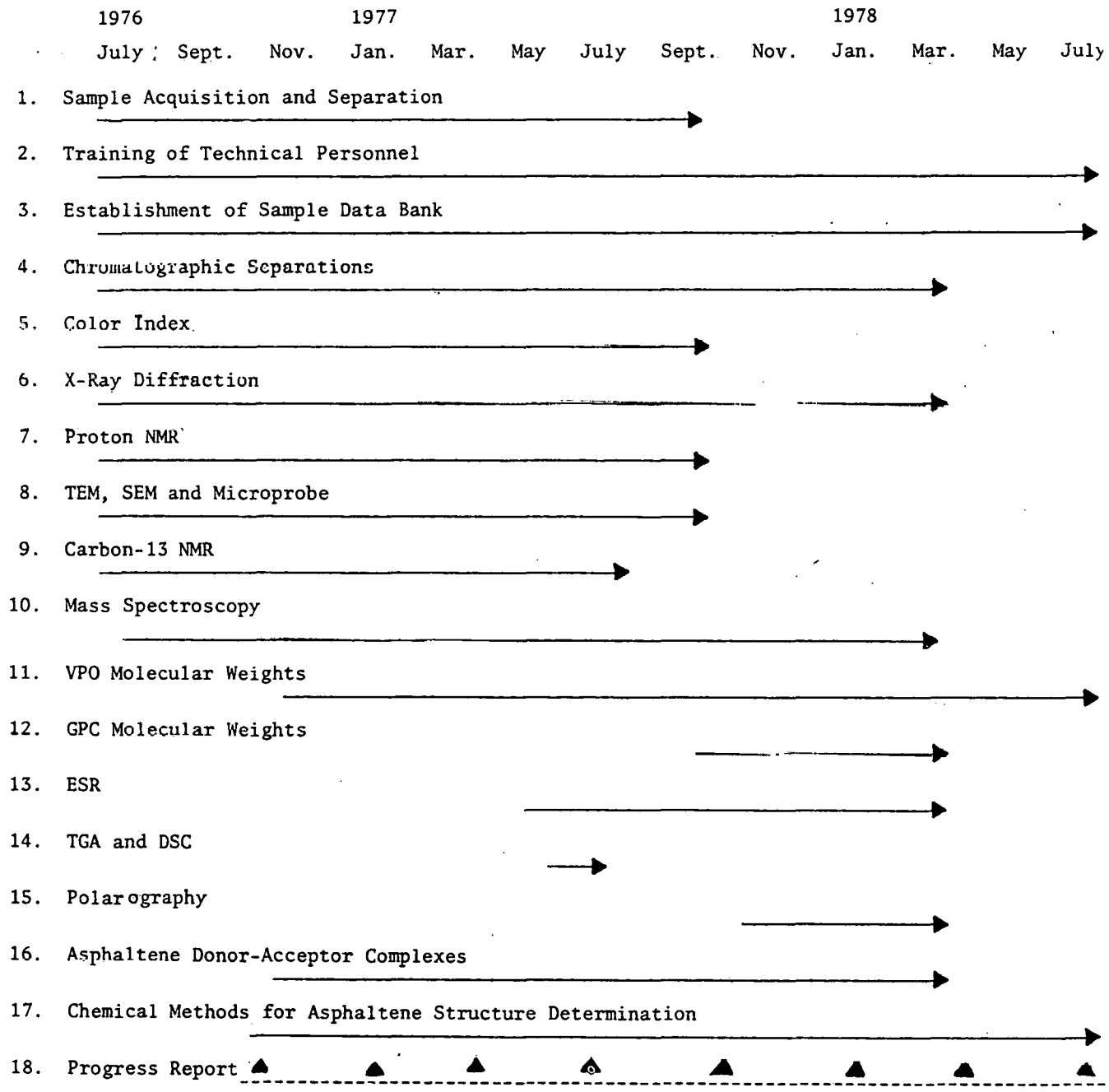


FIG.2 Solubility of Synthoil Coal Liquid Fractions Vs. Hildebrand Solubility Parameter δm

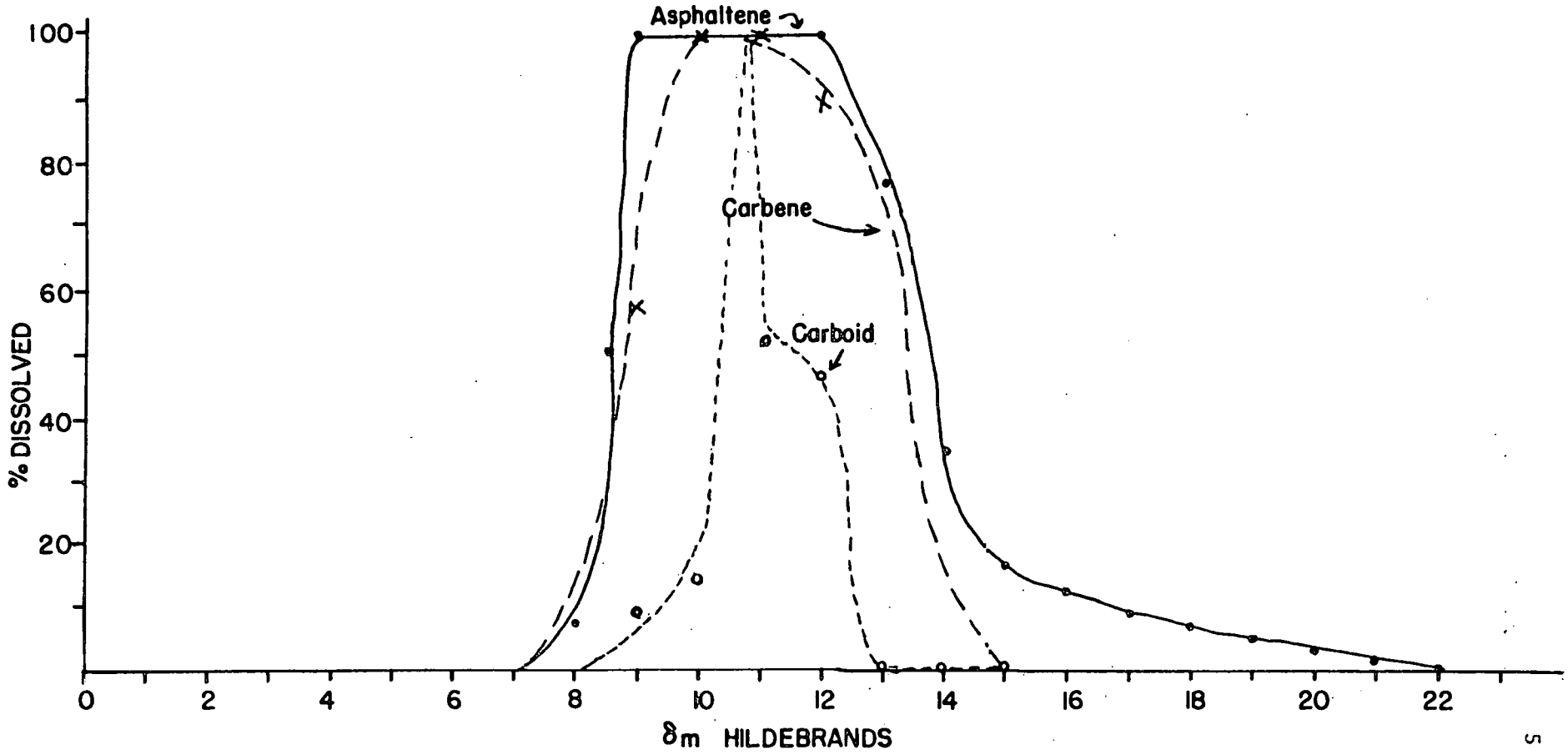


Table I. Hildebrand Values, δ , of Solvents

Solvent	δ
Pentane	7.02
Cyclohexane	8.19
Benzene	9.16
CS_2	9.92
Pyridine	10.62
Isobutyl Alcohol	11.24
Benzyl Alcohol	12.05
HEMA*	12.45
Water	23.50

*2-Hydroxyethyl Methacrylate.

(2) Characterization of Coal Liquid Fractions by Physical Methods

Work Accomplished:

(a) VPO Investigation of Asphaltene Molecular Weight

The VPO molecular weights of coal-derived asphaltenes vs. concentration in chloroform have been determined and are shown in Figures 3 to 7 and Table II. The results show that association of asphaltene also takes place in chloroform over the concentration range of 5-60 gm/l. In the dilute concentration range of 5-36 gm/l all of the asphaltenes afford positive linear correlations between concentration and molecular weight and the correlation coefficients are reasonably significant. The slopes of the linear correlation lines in chloroform are greater than those in THF, but smaller than those in benzene. This is because the chloroform is more polar than benzene, but less polar than THF and the association in chloroform is in between. However, the molecular weight values obtained by extrapolating the plots to infinite dilution are in very good agreement. This suggests that the coal-derived asphaltene dissociation tends to go to completion in all three solvents at infinite dilution.

Asphaltene Self-Association Model

The equilibrium constants of coal-derived asphaltenes in chloroform have been calculated based on the two parameter model derived last quarter (12) and are shown in Figures 3 to 7 and Table III. The results show that this two parameter model is also efficient in describing the self-association of asphaltenes in chloroform.

Comparing the equilibrium constants K_1 and K of these five different asphaltenes in benzene and chloroform, it is found that Synthoil and PAMCO

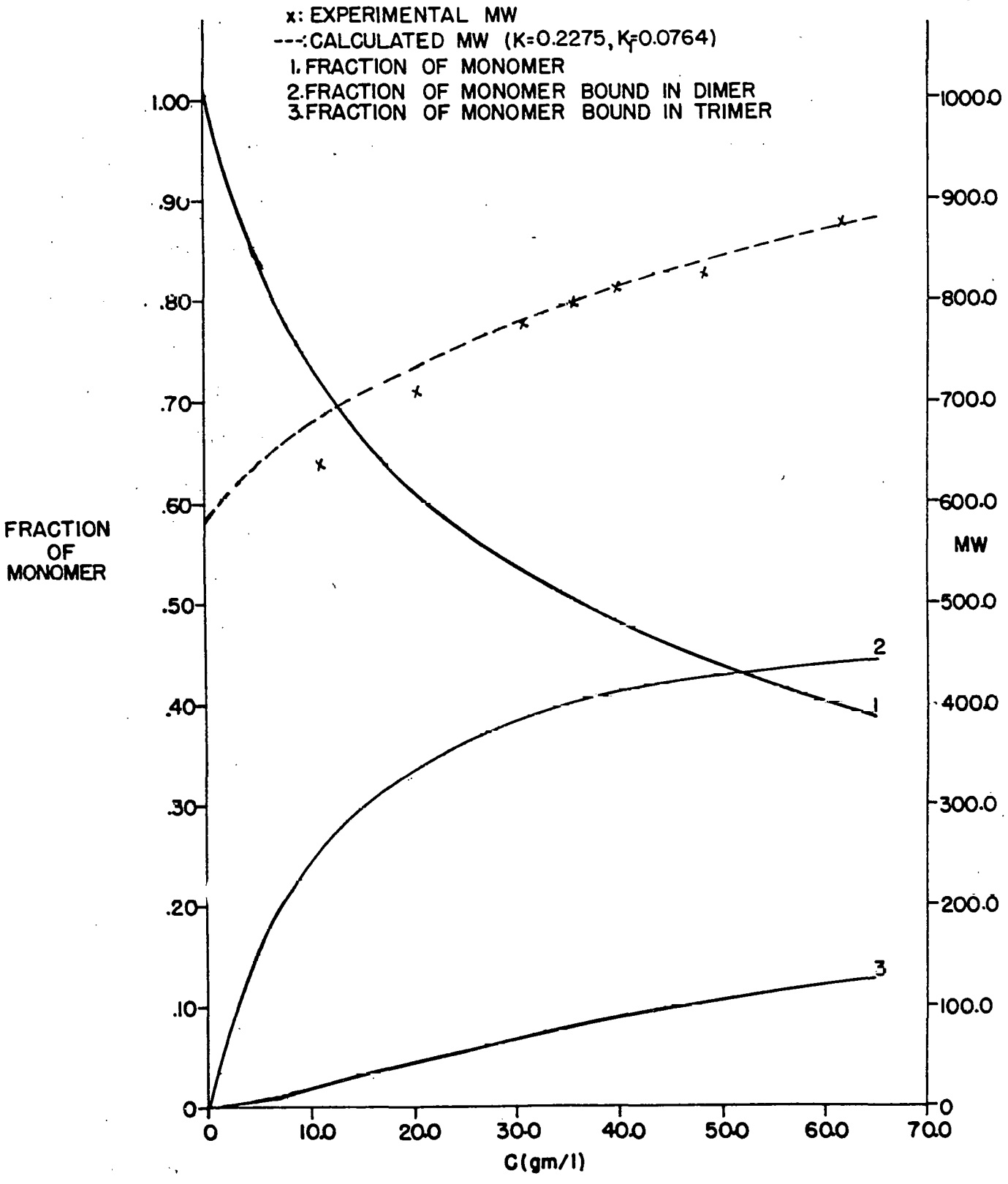


FIG. 3 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION SYNTHOIL ASPHALTENE IN CHLOROFORM

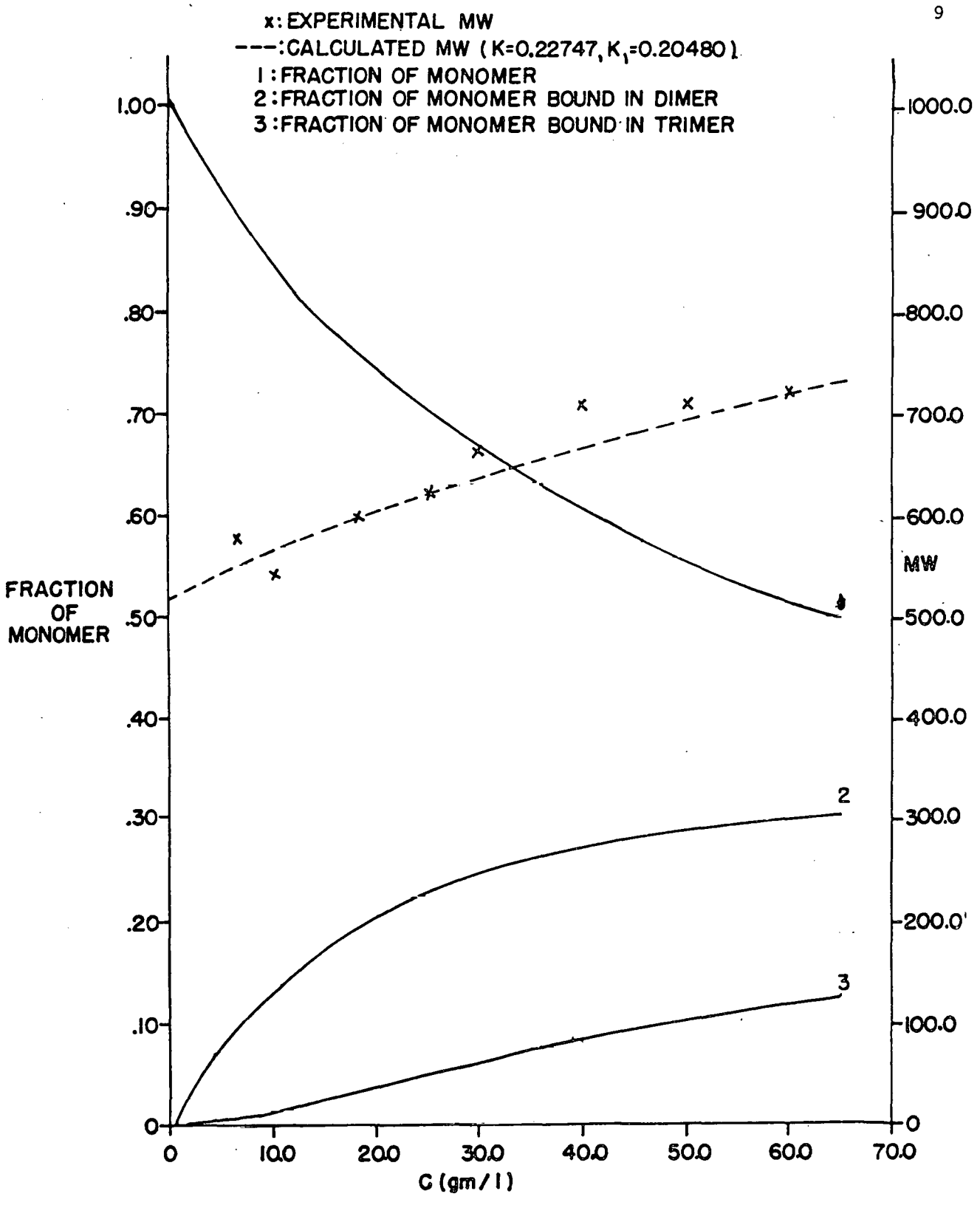


FIG. 4 FRACTIONS OF MONOMER AND VPO MW VS. CONCENTRATION HRI ASPHALTENE IN CHLOROFORM

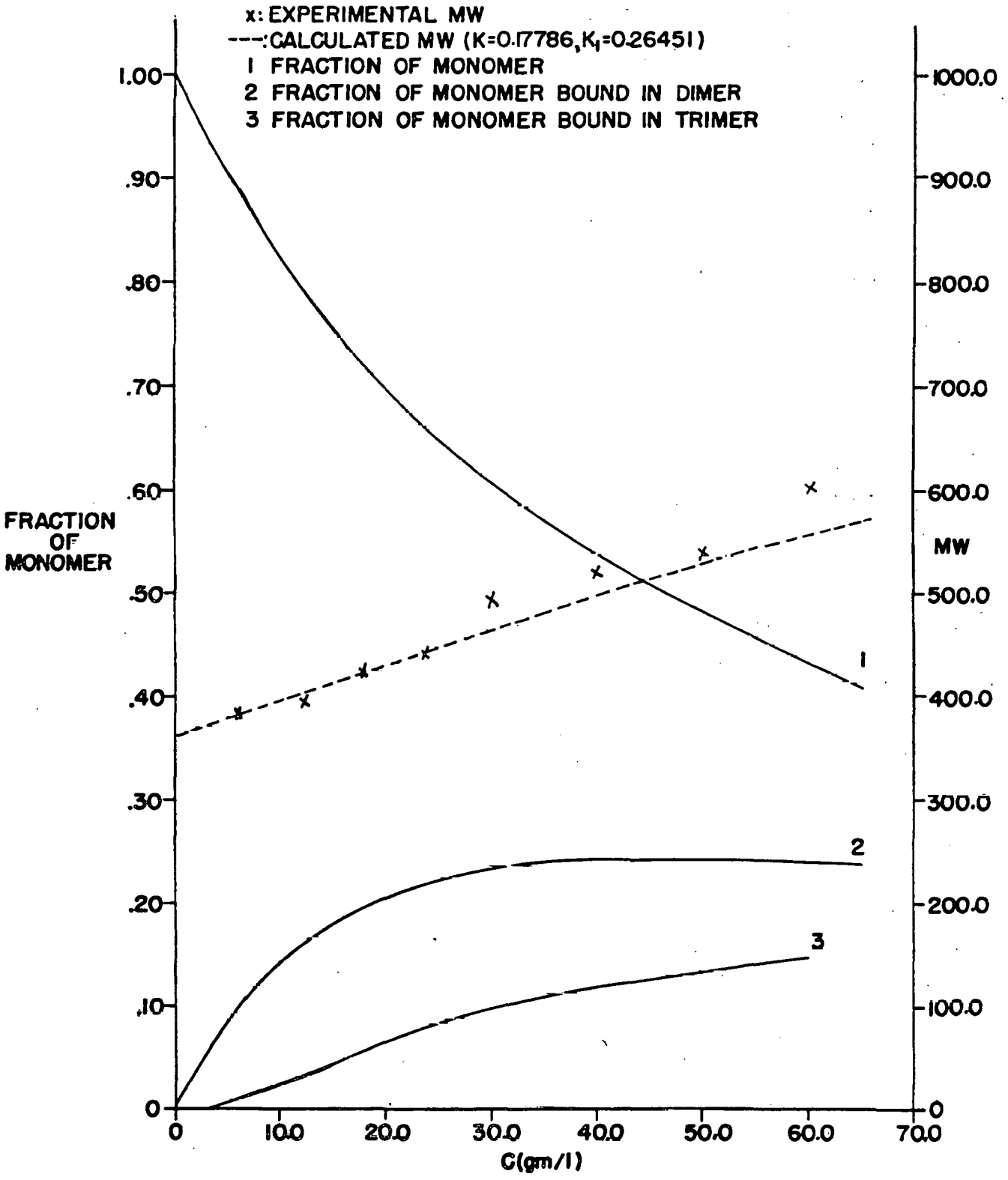


FIG. 5 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION FMC-COED ASPHALTENE IN CHLOROFORM

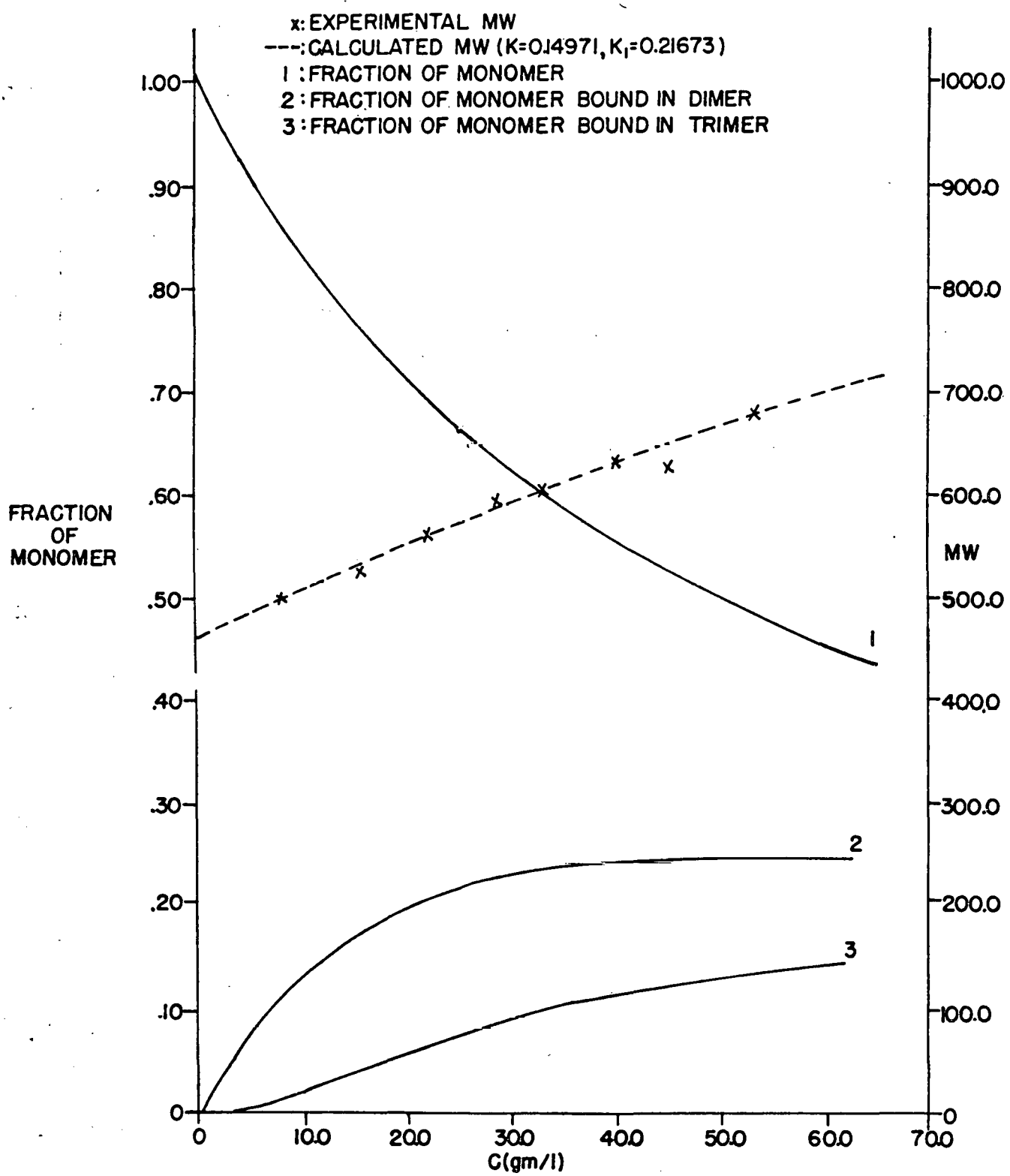


FIG. 6 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION CAT. INC. ASPHALTENE IN CHLOROFORM

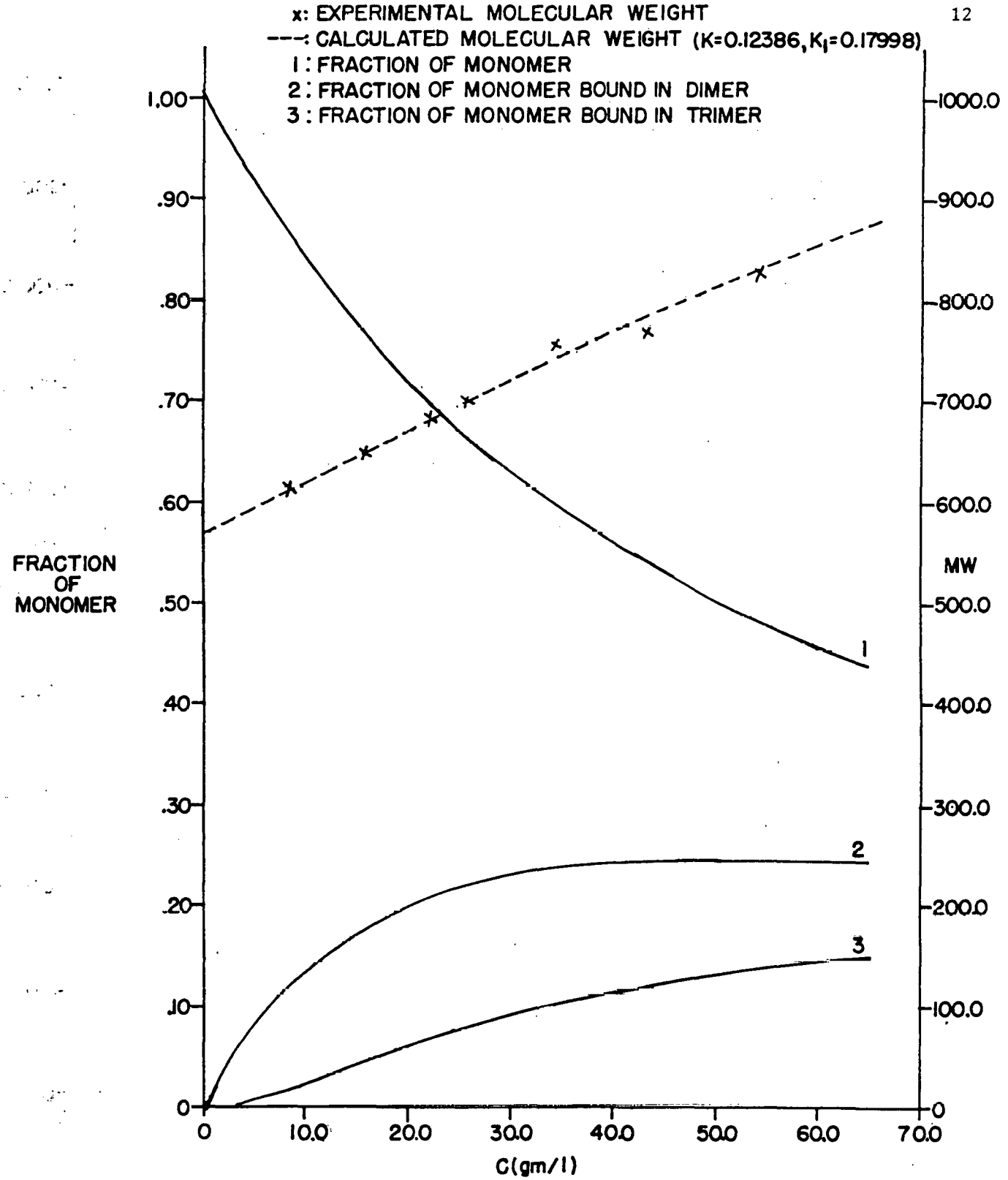


FIG. 7 FRACTIONS OF MONOMERS AND VPO MW VS CONCENTRATION PAMCO ASPHALTENE IN CHLOROFORM

Table II.. Molecular Weight of Asphaltenes vs. Concentration* in Benzene, THF and Chloroform

Asphaltene	Solvent	Least Squares Equation	Corr. Coeff.	Av. MW*** at Zero Conc.	% Dev.***
		MW = 2.85 + 0.96 C + 568 + 17.5	0.83		
Synthoil	THF**	MW = 2.42 ± 0.10 C + 562 ± 2.2	0.99	(561)	(1.0)
	Benzene	MW = 11.1 ± 0.60 C + 552 ± 10.4	0.995	567	3.2
	Chloroform	MW = 5.9 ± 0.30 C + 585 ± 8.8	0.988		
HRI H-Coal	THF	MW = 3.02 ± 0.36 C + 471 ± 6.0	0.95	(492)	(4.3)
	Benzene	MW = 6.27 ± 0.30 C + 513 ± 7.6	0.99	502	6.2
	Chloroform	MW = 4.31 ± 0.56 C + 523 ± 11.0	0.91		
FMC-COED	THF	MW = 0.16 ± 0.10 C + 382 ± 1.9	0.89	(375)	(1.9)
	Benzene	MW = 5.61 ± 0.26 C + 368 ± 4.5	0.99	370	2.9
	Chloroform	MW = 3.38 ± 0.21 C + 359 ± 3.6	0.987		
Cat.Inc.SRC	THF	MW = 1.11 ± 0.38 C + 486 ± 7.6	0.77	(483)	(0.5)
	Benzene	MW = 4.74 + 0.58 C + 481 + 12.1	0.95	477	2.5
	Chloroform	MW = 4.36 + 0.19 C + 465 + 3.8	0.99		
PAMCO SRC	THF	MW = 1.83 + 0.16 C + 502 + 3.3	0.96	(533)	(5.6)
	Benzene	MW = 7.26 + 0.51 C + 563 + 10.1	0.98	545	7.8
	Chloroform	MW = 5.35 + 0.26 C + 569 + 4.9	0.99		

*Conc. g/l.
**Results from two asphaltene samples prepared independently.
***Values in parentheses are obtained from benzene and THF only.

Table III. Calculated Equilibrium Constants and Standard Deviations of Coal-Derived Asphaltenes.

Process	Monomer MW**	Solvent	K_1	K	Standard Deviation	% Dev.
Synthoil Asphaltene	567	Benzene	0.0762	0.0671	13.7	2.4
		Chloroform	0.0764	0.2275	23.5	4.1
HRI Asphaltene	502	Benzene	0.118	0.0866	9.0	1.8
		Chloroform	0.2048	0.2275	27,7	5.5
FMC-COED Asphaltene	370	Benzene	0.210	0,0813	20,7	5,6
		Chloroform	0.2645	0,1779	29,0	7,8
Cat. Inc. SRC Asphaltene	477	Benzene	0.225	0.109	12.2	2.6
		Chloroform	0.2157	0.1497	10.2	2.1
*PAMCO SRC Asphaltene	545	Benzene	0.061	0.0971	18.6	3.4
		Chloroform	0.180	0.1239	12.7	2.3

*Isolated from vacuum distilled bottom product.
**Molecular Weights at infinite dilution.

SRC asphaltenes have stronger association between molecules while FMC-COED and Cat. Inc. SRC asphaltenes have less. The equilibrium constants in chloroform are generally larger that in benzene since the association is more significant in less polar solvent benzene.

In the future we will measure VPO molecular weights as a function of concentration for all five asphaltenes in different temperatures and the association model will also be tested.

(b) GPC Molecular Weights

Gel permeation chromatography (GPC) was carried out on coal derived asphaltenes isolated from the coal liquids of the five demonstration processes under study. The Waters Associates HPLC system described previously was used (3). Molecular weight distributions, and weight-average molecular weights of the asphaltenes were determined by a standard method (4). The GPC system was calibrated with known standards (the GPC correlation curve is shown in Fig. 8, and the standard compounds presented in Table IV). In the present preliminary work a constant response factor was assumed for the UV detector. The GPC chromatograms for the asphaltenes are given in Fig. 9, and the weight average molecular weights, determined by the GPC method, are presented in Table V. The GPC chromatograms are fairly uniform with each asphaltene affording a high molecular weight shoulder, and either a low molecular weight shoulder or tailing probably due to adsorption. The $\overline{M}_w$ values range from 531 – 615, and are reasonably close to the $\overline{M}_n$ values found for the same asphaltenes by the VPO method. In the next quarter we will test these preliminary results by using a gravimetric method in which fractions are trapped, weighed, and then molecular weights determined independently by either VPO or mass spectroscopy.

FIG.8 GPC CORRELATION CURVE – MW VS. ELUTION VOLUME

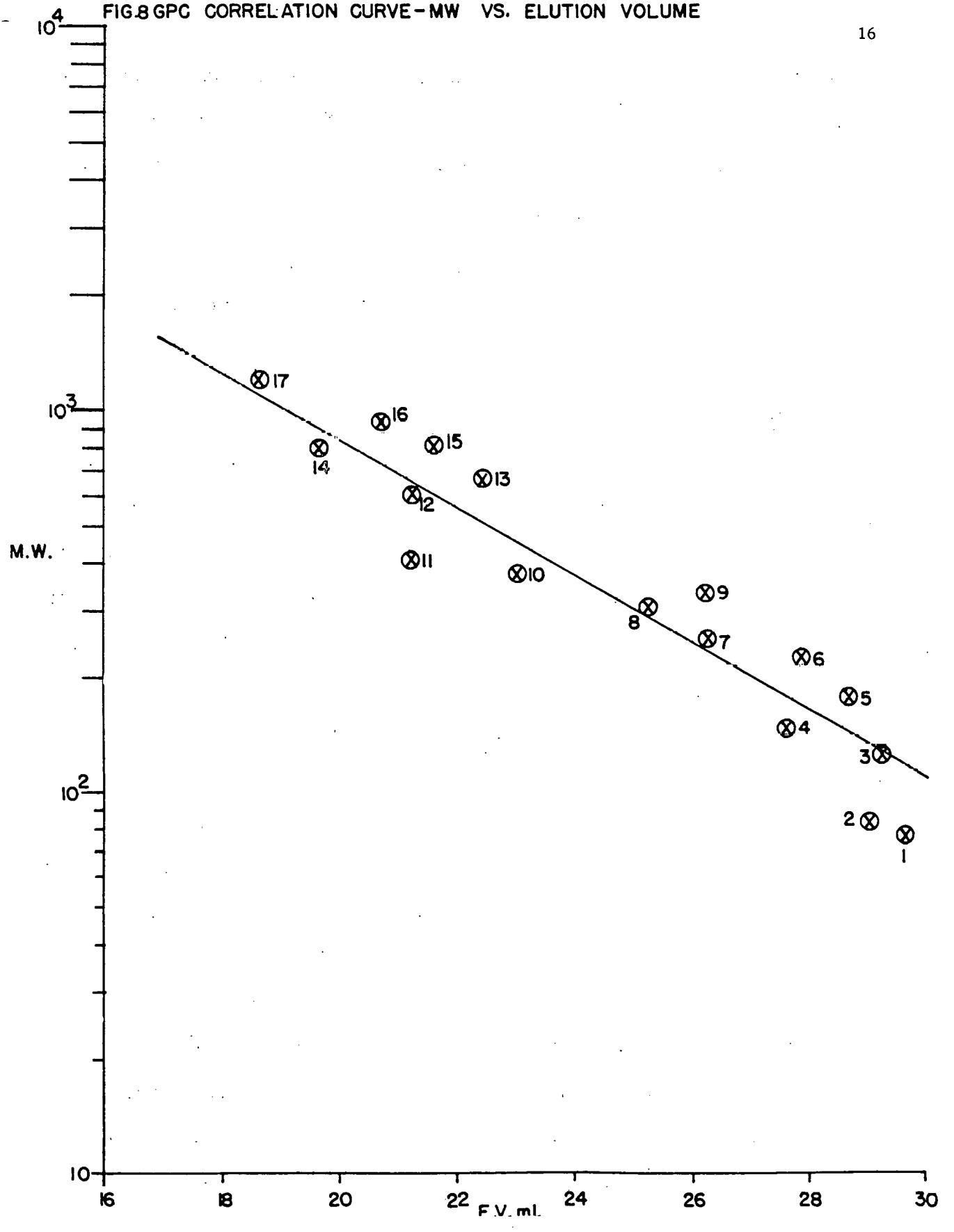


Table IV. Standard Compounds Used to Obtain GPC Correlation Curve*

	Standards	M.W.
1.	Benzene	78
2.	Cyclohexane	84
3.	Naphthalene	128
4.	Pentamethylbenzene	148
5.	Anthracene	178
6.	Benzanthracene	228
7.	9-phenylanthracene	254
8.	1,1'-Bi (acenaphthenylidene)	304
9.	9,10-Diphenylanthracene	330
10.	1,2,8,9-Dibenzpentacene	378
11.	Squalene	411
12.	Pressure Chemical Standard	600
13.	tetra-meso-4 methylphenylporphin	670
14.	Polypropylene glycol	800
15.	tetra-meso-2-naphthylporphin	818
16.	tetra-meso-biphenylporphin	918
17.	Polypropylene glycol	1200

*Columns used: Waters Associates μ-Styragel: 1 x 500Å, 2 x 100Å (each 7.8mm, 30cm length).

FIG. 9 GPC CHROMATOGRAMS OF ASPHALTENES

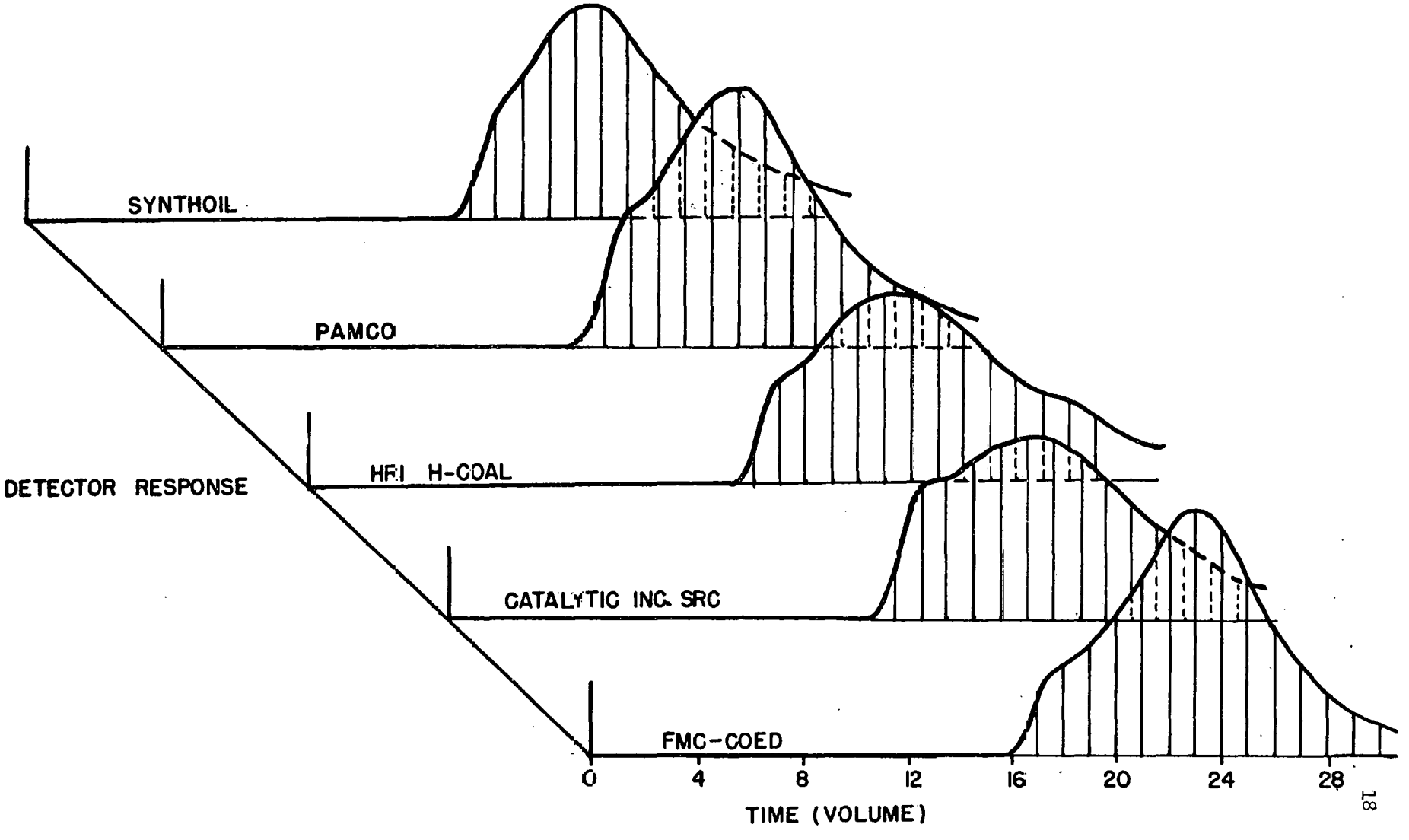


Table V. Weight Average Molecular Weight Determination of Asphaltenes by GPC Method

	FMC-COED	Cat. Inc. SRC	HRI	PAMCO	Synthoil
Molecular Weight from GPC*	531	597	549	592	615
Standard Deviation	11.17	9.0	11.99	7.55	29.65
% Deviation	2.1	1.5	2.1	1.3	4.8
Standard error of mean	5.6	4.5	4.9	3.8	14.8

*Columns used: μ-Styragel from Waters Associates : 1 x 500Å, 2 x 100Å (each 7.8mm ID, 20cm length). Data read off from U.V. spectrum.

(c) Electron Spin Resonance of Asphaltenes

In the last Quarterly Report (2) we discussed the experimental procedure for determining ESR data, and gave g-value, intensity, and line width data for coal liquid solvent fractions and asphaltene derived products in solution at room temperature. During the present Quarter we measured asphaltene spin intensities in benzene and pyridine solutions as a function of substrate concentration. We also studied the variation in sample intensities with temperature for a series of asphaltenes, and asphaltene derived products.

Previously it was suggested that coal-derived asphaltene association could be explained on the basis of a hydrogen bonding donor-acceptor model (5 - 6). However, because published reports support charge transfer complexation in petroleum asphaltenes (7 - 8), we decided to study coal-derived asphaltene to see if any evidence could be found to support this type of association mechanism. ESR studies were carried out on Synthoil asphaltene dissolved in benzene and pyridine, and also on solid samples of this aphaltene and its chromatographically separated components.

The dependence of the ESR signal intensity vs. the concentration of asphaltene in benzene solution is presented in Fig. 10 . Despite the scatter in the experimental points, no discernible trend is evident. One point, determined in the solvent pyridine, is also presented. A second series of measurements was made on solid samples of Synthoil asphaltene and its chromatographically separated components, and on a Synthoil asphaltene - TCNE charge transfer complex. The temperature dependence of the signal intensity was studied. The results are presented in Figs. 11 - 12 .

The association of Synthoil asphaltenes in benzene has been studied by VPO. The associated asphaltenes are believed to approach complete dissociation

FIG.10 ESR SPIN INTENSITY OF SYNTHOIL ASPHALTENE VS CONCENTRATION IN BENZENE SOLUTION

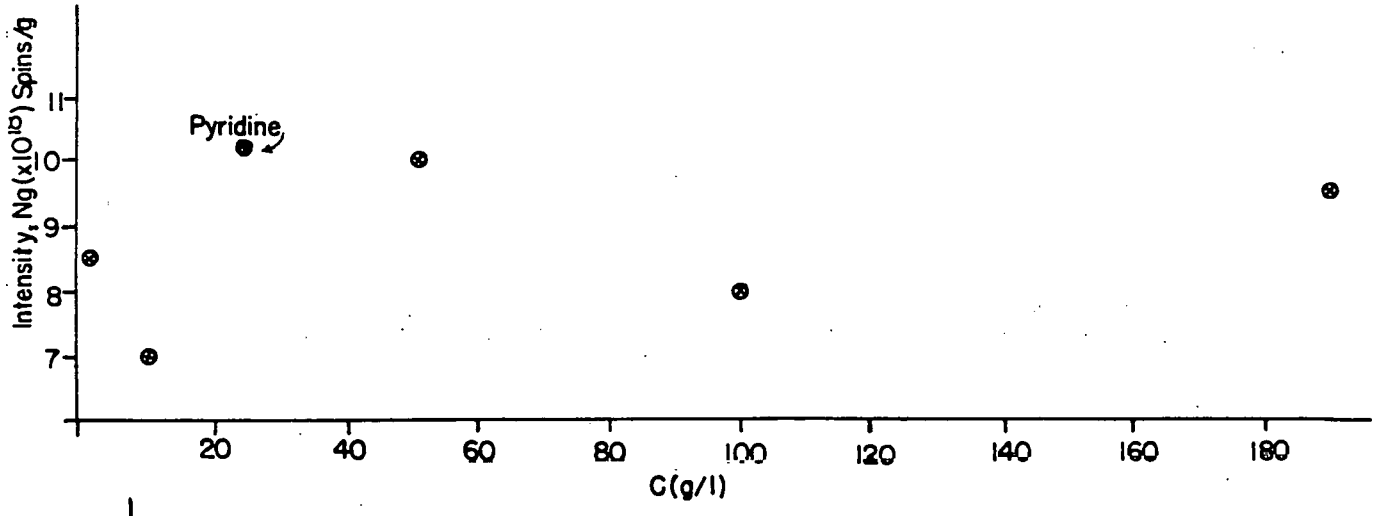


FIG 11 VARIABLE ESR TEMPERATURE DATA FOR SYNTHOIL ASPHALTENE (Et_2O ELUTED CHROMATOGRAPHY FRACTION)-TCNE CHARGE TRANSFER COMPLEX

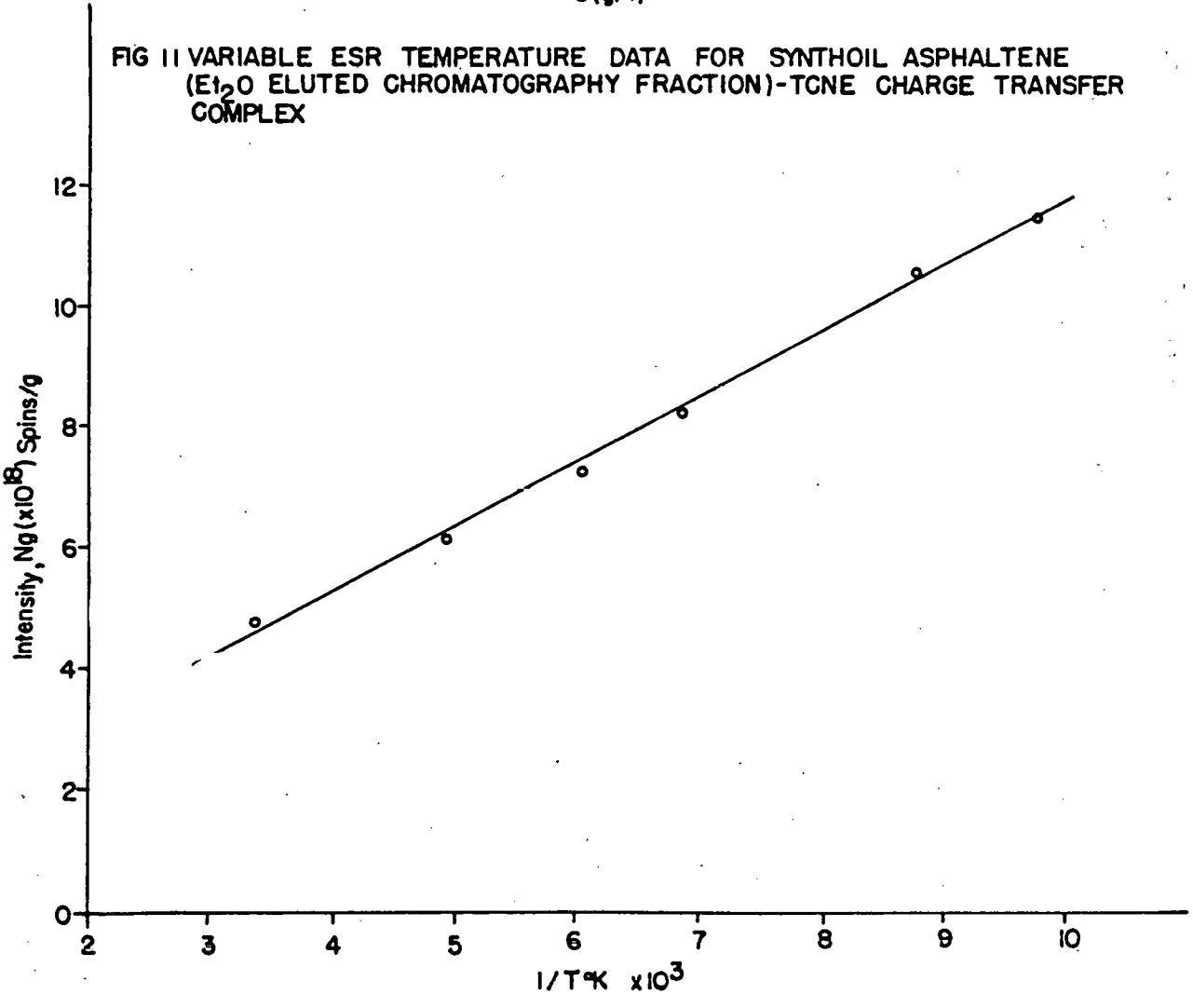
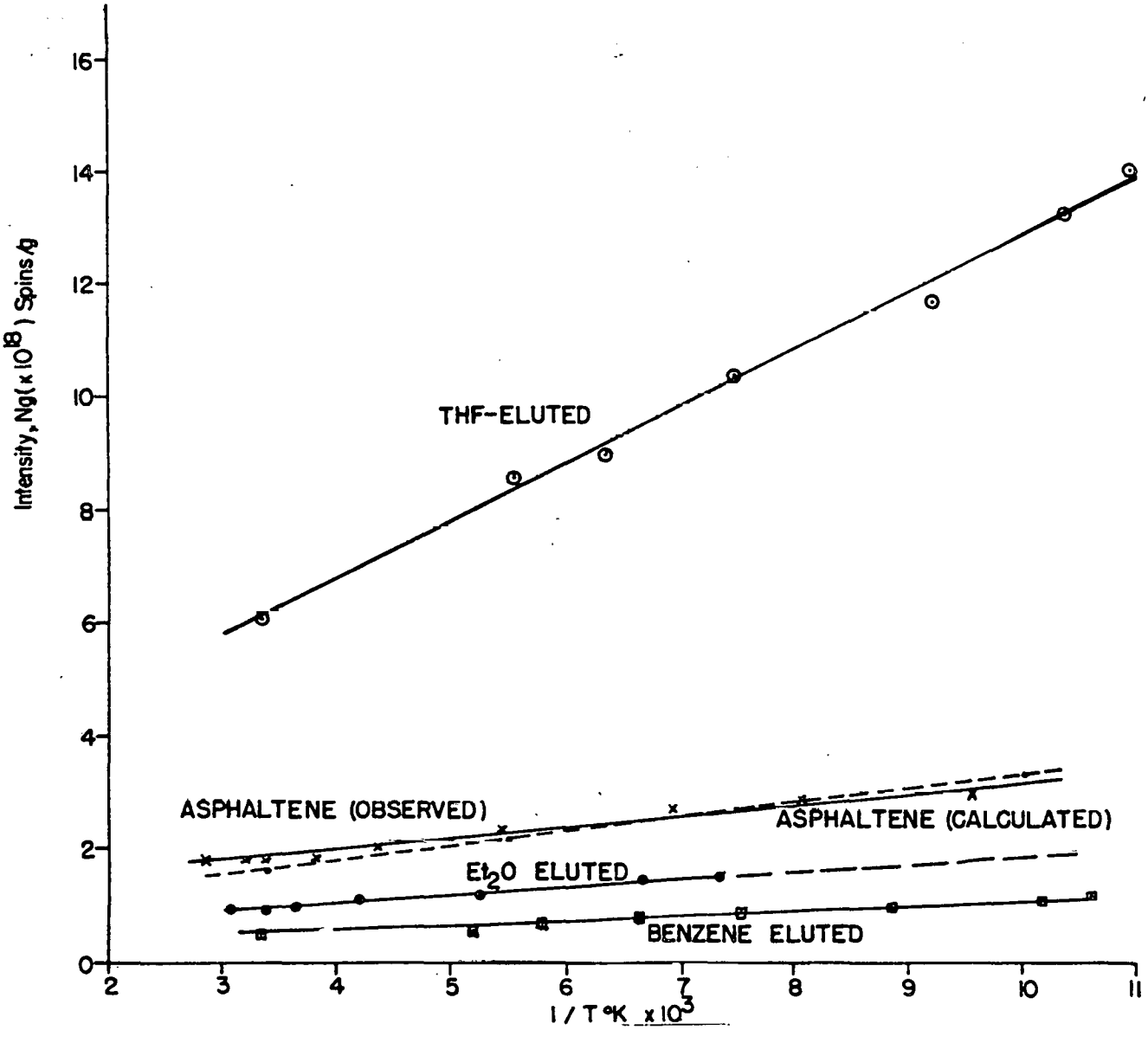


FIG. 12 VARIABLE ESR TEMPERATURE DATA FOR SYNTHOIL ASPHALTENE AND SYNTHOIL ASPHALTENE CHROMATOGRAPHY FRACTIONS



as their concentrations approach infinite dilution (2,6). At a concentration of 1 g/l the asphaltene is believed to be present almost completely as the monomer. At $\approx$ 20 g/l the monomer fraction is about 0.5, and above this concentration higher oligomers predominate. In some cases charge transfer complexes may be formed which have a triplet state which lies not far above the ground state (9). If this were the case such association complexes might have triplet states which were sufficiently populated at room temperature so that these complexes would show increased spin intensity. The fact that we observed no increase in spin intensity with concentration rules out the possibility, but does not rule out the possibility of complex formation in which the paramagnetic triplet state is energetically too high to be populated at room temperature.

In the solid state Synthoil asphaltene is believed to be associated in stacked clusters containing $\approx$ 4 aromatic sheets per cluster (2). Such systems, if they were formed by charge transfer association might be expected to show ESR intensity - temperature dependence curves containing both 1/T (Curie-Weiss doublet) and exponential (singlet-triplet) components (7 - 8). The results presented in Figs. 11 and 12 indicate no exponential component down to 95^{o}K for either Synthoil asphaltene, or for a charge transfer complex formed between a basic Synthoil asphaltene fraction and the acceptor TCNE. This suggests that coal derived asphaltene complexes contain little or no triplet states with energies low enough to be populated at our experimental temperatures. These findings do not preclude the possibility of weak charge transfer complexes being formed, but they suggest that the ESR method of confirming the presence of such complexes may not be applicable in such cases.

An alternative procedure, previously employed by Retcofsky et al. (10), involves determining the temperature variation of the ESR intensities of

asphaltenes and some of the separated components of the asphaltenes. They found, for their acid/neutral and base components, that the weighted averages of these two components reproduces the temperature dependence of the total asphaltene before separation. We carried out the same type of study on our silica gel chromatography fractions, Fig. 12 , and also found that the weighted averages of the benzene, diethyl ether, and THF eluted fractions reproduces the temperature dependence of the total asphaltene before separation. This suggests that charge transfer interactions if present, may not be major binding forces between asphaltene components.

(d) Polarography

Polarography has been used for the determination of aromaticity type in coals and SRC coal liquefaction products (11). Crude estimates of reducible aromatic species in SRC solvent elution chromatography fractions have been made. The concentration of polycondensed aromatic structures produced in an SRC process was found to increase as a function of temperature and time.

Polarographic analyses were carried out in this quarter on Synthoil solvent fractions, Synthoil asphaltene chromatography fractions, and asphaltenes obtained from the other coal liquefaction products under study.

The current-potential curves were recorded with a Princeton Appled Research (PAR) Model 174A Polarographic Analyzer. The mode of operation employed was current-sampled DC polarography (Tast polarography). In this mode of operation the current is measured for a very short period of time (16.7 ms) just before the drop is dislodged by a drop timer. The use of slow scan rates and fairly rapid drop times produces a curve having the change in current from one step to the next so small as to produce a smooth curve. A comparison between ordinary DC polarography and current-sampled DC polarography is shown for the substrate anthracene in Fig. 13.

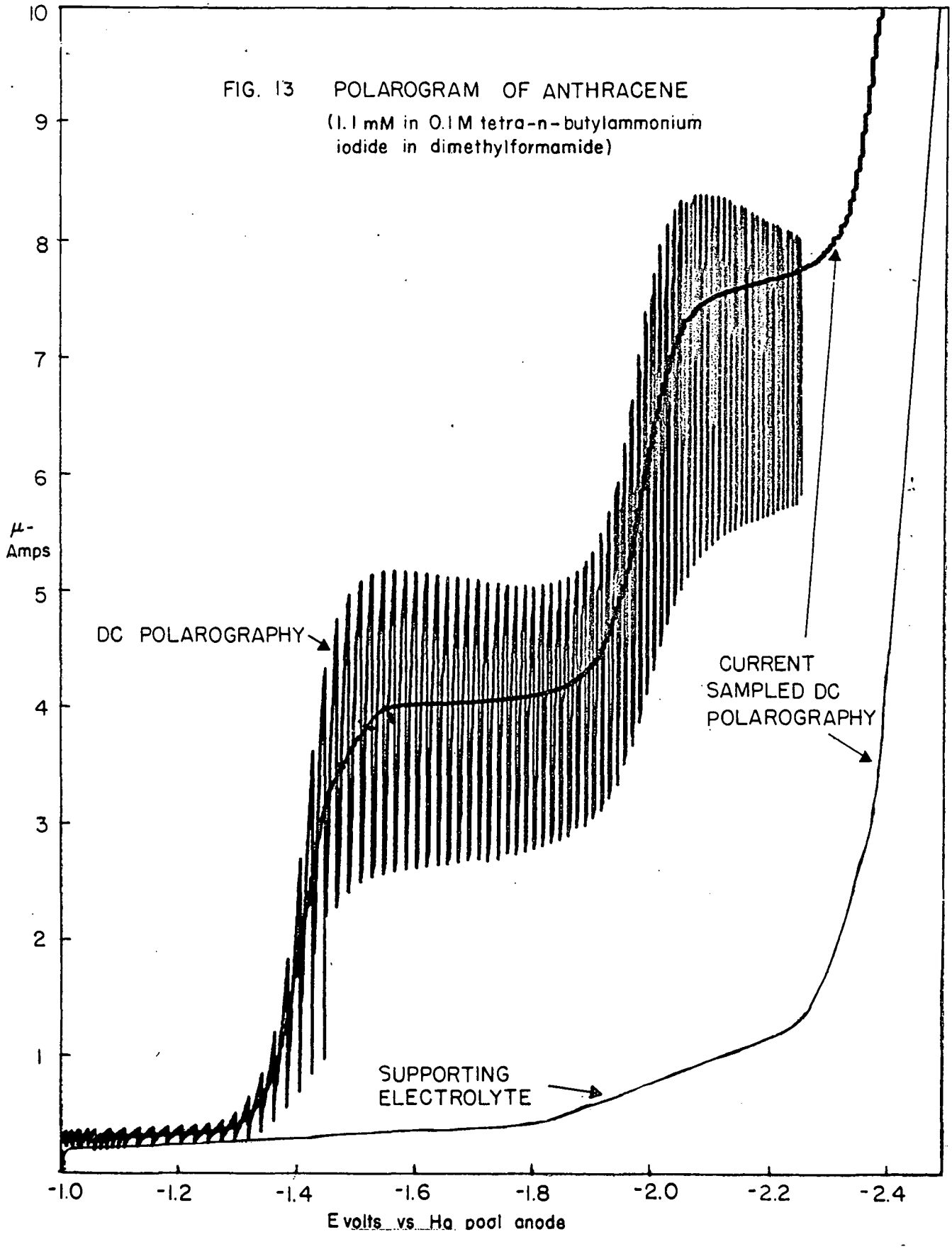


FIG. 13 POLAROGRAM OF ANTHRACENE
(1.1 mM in 0.1 M tetra-n-butylammonium iodide in dimethylformamide)

All potentials were measured with reference to an internal mercury pool anode in 0.1M tetra-n-butylammonium iodide in dimethylforamide (which is - 0.55V vs. a standard calomel electrode). The H_g pool cell was thermostated at 25.0 $\pm$ 0.5°C. The decomposition potential of the supporting electrolyte solution is approximately -2.40 volts versus the Hg pool anode. Solutions of the coal liquid solvent and chromatography fractions were run at standard concentrations of 5 x 10^{-4}M in deoxygenated supporting electrolyte solutions under an inert gas.

The Ilkovic equation is generally used to describe the relationship between the diffusion current and the concentration of the reducible species when polarographic measurements are carried out with a dropping mercury electrode (12):

$$i_d = knD^{1/2}C\ m^{2/3}t^{1/6}$$

where i_d = diffusion current in μamps

k = 607

n = number of electrons/molecule taking part in the process

D = diffusion coefficient in cm^2/sec

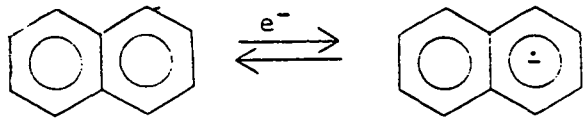
C = concentration of active substance in m mole/l

m = mercury flow rate in mg/sec

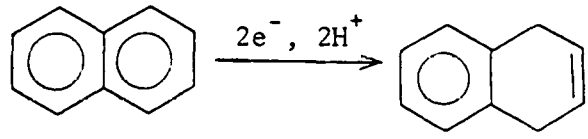
t = mercury drop time in sec

When m and t are measured, or held constant, and D values are approximately equal then the quantity i_d/C (diffusion constant) may be assumed to be proportional to the number of electrons per molecule involved in the reduction.

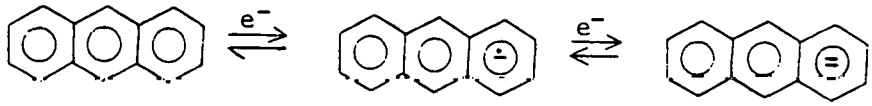
In solvents of low protonating power, such as DMF, the radical anion formed by the addition of an electron to many aromatic hydrocarbons may become long lived enough to diffuse away from the mercury drop without undergoing addition of a second electron. At more negative potentials, however, two electrons may be added, For example, in DMF, naphthalene is reduced in a single one electron wave,



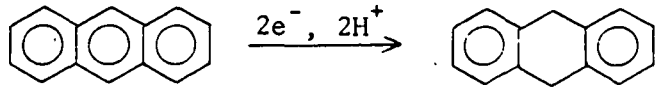
however, in protic media naphthalene shows a single wave corresponding to a two-electron reduction:



Anthracene affords two one electron waves in aprotic media:



but only one two electron wave in protic media (13):



Hoijtink (14) has explained results in protic media on the basis of the following mechanism: (S = substrate = aromatic hydrocarbon)

$$S + e^- \rightleftharpoons S^{\cdot -} \xrightarrow[H_2O]{k} SH \cdot \xrightarrow[fast]{e^-} SH^- \xrightarrow{H^+} SH_2$$

The half-wave potentials for a number of polycyclic aromatic compounds are shown in Fig. 14 . The polarograms of Synthoil coal liquid solvent fractions are presented in Fig. 15 . The maximum half-wave potentials and diffusion constants of coal liquid solvent fractions and asphaltenes are given in Table VI.

The results may be interpreted in a qualitative way only because of the complexity of the materials under study. Half-wave potentials of aromatic hydrocarbons are known to be related to the energy of the lowest vacant molecular orbital (15). This MO parameter is crudely related to the number and structural configuration of the individual aromatic rings which make up the con-

FIG. 14 Halfwave Potentials ($E_{1/2}$) of Aromatic Compounds (In 0.1M tetra-n-butylammonium iodide – DMF)

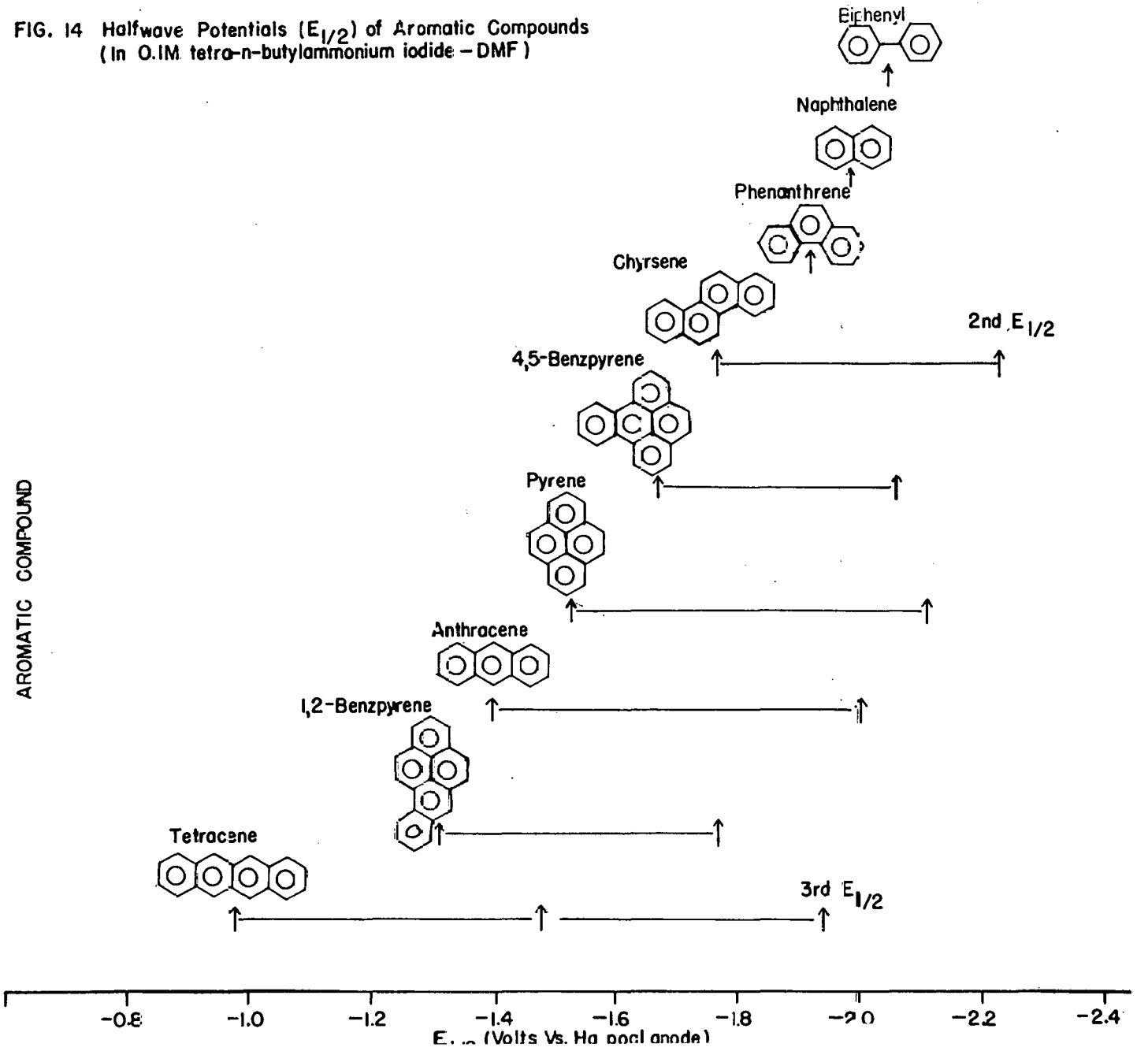


FIG. 15 Polargrams of Synthoil Coal Liquid Fractions

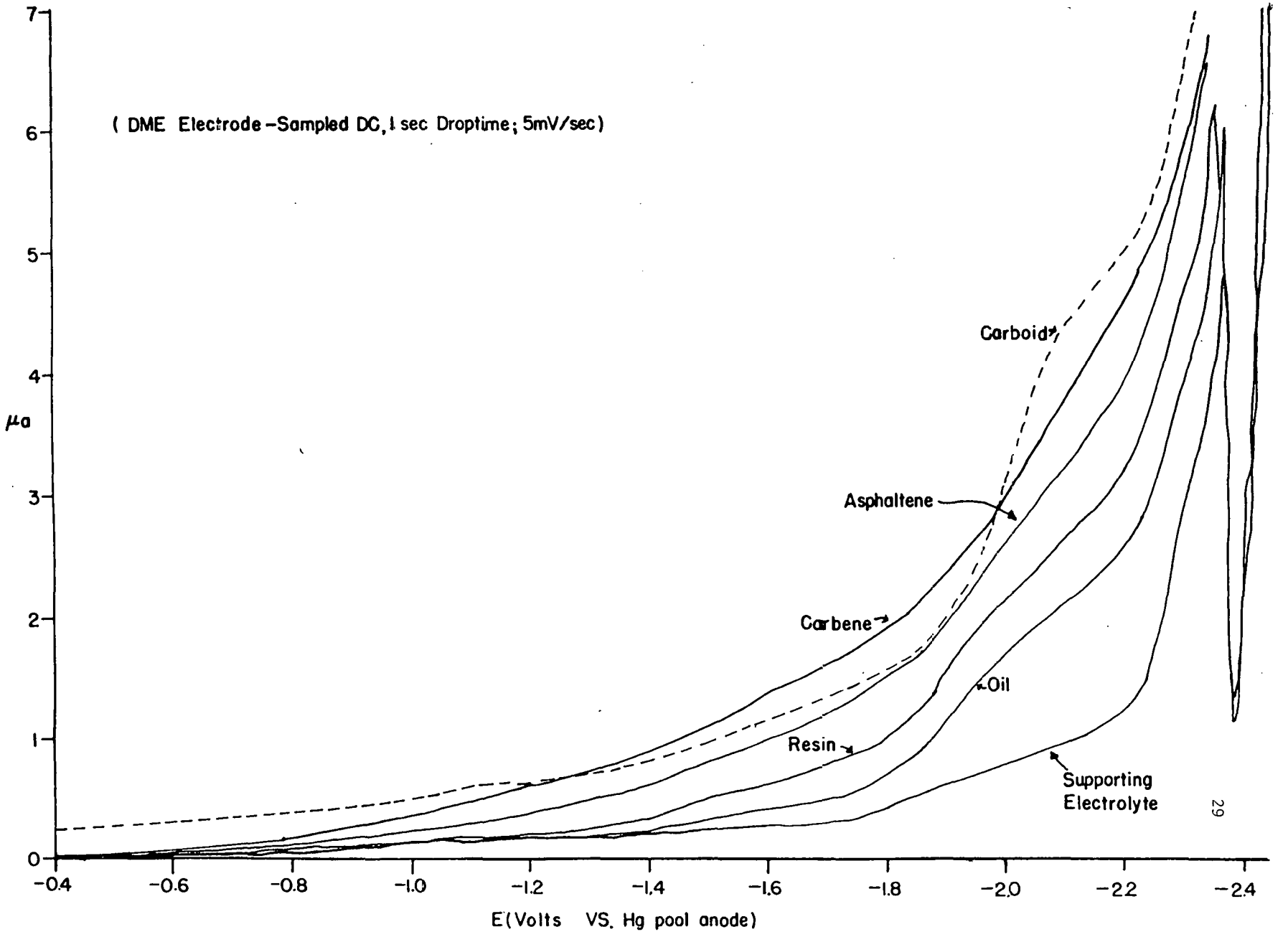


Table VI. Half-Wave Potentials and Diffusion Constants of Coal Liquid Solvent Fractions and Asphaltenes

Sample	$-E_{1/2}$ Max. (volts)	$\frac{i_d}{C}$*
Synthoil Oil	2.0	2.6
Synthoil Resin	1.9	3.9
Synthoil Asphaltene	2.0	5.4
Synthoil Carbene	2.0	6.7
Synthoil Carboid	2.0	7.8
FMC COED Asphaltene	2.0	2.6
Synthoil Asphaltene	2.0	5.4
HRI Asphaltene	2.0	5.8
PAMCO SRC Asphaltene	2.0	6.4
Cat. Inc. SRC Asphaltene	2.0	6.4
Synthoil Asphaltene	2.0	5.4
Benzene Eluted**	2.0	6.8
Diethyl Ether Eluted	2.0	4.6
THF Eluted	2.0	5.8

*At -2.20 V. i_d/C for Naphthalene = 2.1.

**Silica Gel Chromatography Fractions.

densed polycyclic aromatic ring system. Benzene, the $E_{1/2}$ of which is estimated to be ≃ -3.0 V, cannot be reduced because this voltage is greater that that of any supporting electrolyte solution presently known. Small, 2-3 ring systems such as phenanthrene, naphthalene and biphenyl are reduced in the range -1.92 to -2.05 V. Anthracene and larger condensed ring systems undergo initial reduction in the range of -1.0 to -1.77 V. Inspection of Fig.15 and Table VI reveals most of the reduction for coal liquid fractions occurs above -1.8 V. Almost all of the major half-wave reduction waves take place at about -2.0 volts. This trend becomes less pronounced as one proceeds along the series: oil > resin > asphaltene > carbene > carboid. The total reduction per average molecule, as measured by i_d/C, also increases along the same series. The oil fraction which has an i_d/C value approximately equal to that of naphthalene (2.6) also undergoes almost all reduction around -2.0 V. (Substitution of aromatic rings by alkyl groups is known to raise the $E_{1/2}$ (16)). The asphaltene fractions show relatively more reduction below -1.8 V, indicative of the presence of larger ring systems. They also afford i_d/C in the range 5.4-6.4 (except FMC-COED, i_d/C = 2.6) which suggests addition of ≃ 2-3 electrons per molecule. This trend suggest larger aromatic ring systems and molecules which have more than one aromatic ring system. For example, the average hypothetical Synthoil asphaltene molecule could contain two 3-ring aromatic systems condensed within the naphthenic system or possible some 2-ring + 4 ring systems (2). These trends, more reduction at lower $E_{1/2}$, and higher i_d/C values, are seen to increase in going to the carbene and carboid fractions which have been shown to be comprised of larger and more aromatic systems (2 , 17 , 18).

(3) Chemical Methods for Asphaltene Structure Determination

Work Accomplished:

Chemical methods which may be useful in the structure elucidation of asphaltene include: hydroxyl oxygen determination by silylation, basic nitrogen determination by methylation with methyl iodide, reduction with potassium and an alcohol or alkyl halide, and mild oxidation with suitable oxidizing agents.

(a) Silylation of Hydroxyl Groups

In previous Quarterly Reports (2, 18-20) we described the procedure and results for the silylation of asphaltenes, and other coal liquid derived products. During the present quarter we repeated the silylation of the synthoil asphaltene silica gel chromatography fractions in order to test the reliability of the silylation procedure. The results, presented in Table VII, are seen to be fairly reproducible. The average deviation is ± 9%.

The benzene eluted fraction is seen to have the lowest percentage of oxygen, 2.71, but the highest percent OH/O_{total}, 57. The diethyl ether, and THF eluted fractions have larger percentages of oxygen, 6.50 and 7.38, but lower percent OH/O values of 32 and 34 respectively. These results confirm the qualitative results presented previously which were determined by IR spectroscopy (19). The basic components of coal asphaltenes contain substantial amounts of hydroxyl groups in addition to ether oxygen and basic nitrogen. In the next quarter we plan to silylate acid/neutral and basic asphaltene fractions obtained by HCl precipitation in order to compare these materials with our chromatography fractions.

Table VII Analysis of Silylated Synthoil Asphaltene Silica Gel Chromatography Fractions

Asphaltene	% Si in Silylated Asphaltene	% OH in Silylated Asphaltene[a]	% O in Starting Asphaltene[b]	% OH/O_{total} in Starting Asphaltene	% OH/O_{total} Average
Starting	3.02	2.00	3.93	51	47 ± 4
	2.82	1.74		44	
Benzene Eluted (46)[c]	2.20	1.33	2.71	49	57 ± 8
	2.8	1.72		64	
Diethyl Ether (37)[c]	3.0	1.86	6.50	29	32 ± 3
	3.6	2.26		35	
THF Eluted (17)[c]	3.8	2.40	7.38[d]	33	34 ± 2
	4.1	2.62		36	

[a]Using method of S. Friedman, C. Zahn, M. Kaufman, and I. Wender, Fuel, 40, 38 (1961).

[b]By difference.

[c]Weight percent of starting asphaltene.

[d]Direct Determination.

(b) Methylation of Basic Nitrogen Groups

In previous Quarterly Reports we described the procedure for methylation of basic nitrogen containing asphaltenes (18) and reported preliminary results (18, 20, 2). During the present Quarter some methylations of Synthoil asphaltene, and asphaltene-derived silica gel chromatography fractions were repeated in order to check the precision of the methylation procedure. The results are shown in Table VIII.

The methylation of starting asphaltene is seen to be fairly reproducible in terms of percentages of benzene soluble and insoluble fraction, and %N and atomic I/N ratios of the benzene insoluble fraction. The general premise that no iodine should appear in the benzene soluble fraction, since alkylated asphaltene iodide should precipitate from solution, is violated. It is likely that our simple procedure does not remove all CH_3I decomposition products containing iodine from the benzene soluble fraction. However, we still assume that the nitrogen found in this fraction is not methylated, and, therefore, non-basic nitrogen. The nitrogen found in the benzene insoluble fraction is assumed to be basic nitrogen to the extent that the atomic I/N ratios indicate, i.e., about 0.66 of the nitrogen in this fraction is methylated and therefore basic. The conclusions which can be reached from these premises are:

(1) Asphaltene nitrogen is about 64% non-basic.

(2) About 50% of the asphaltene molecules which contain a basic nitrogen atom also contain a second non-basic nitrogen atom on the average.

The asphaltene derived silica gel chromatography fractions were also examined again. The benzene eluted fraction is seen to afford little or

Table VIII. Analysis of CH_3I Methylated Synthoil Asphaltene Silica Gel Chromatography Fractions

	Benzene Soluble Fraction				Benzene Insoluble Fraction			
Asphaltene	%	%I	%N	Atomic I/N	%	%I	%N	Atomic I/N
Starting (1.73)[a]	61	1.82	1.40	0.14	39	13.37	2.35	0.63
	52	2.90	1.29	0.25	48	13.35	2.14	0.68
Benzene Eluted (0.95)[a]	(100)	<0.3	1.14	0.03	(0)	-----	----	----
	(100)	<0.3	0.93	0.03	(0)	-----	----	----
Diethyl Ether Eluted (1.70)[a]	(0)	---	----	----	(100)	12.74	1.51	0.93
	24	0.34	1.59	0.02	76	15.59	2.04	0.84
THF Eluted[b] (3.06)[a]	21	<0.3	2.12	0.02	79	15.52	2.53	0.67
	35	1.78	2.22	0.09	65	14.36	2.74	0.58

[a]% Nitrogen in unreacted asphaltene.

[b]Methylation run in THF due to incomplete solubility of this material in benzene (only 72% soluble in benzene by Soxhlet extraction). THF is stripped from the product, which is then Soxhlet extracted to obtain benzene soluble/insoluble fractions.

no benzene insoluble materials on methylation, and almost no addition of methyl iodide (< 0.3% iodine on analysis) which supports the assertion that this chromatography fraction does not contain a significant amount of basic nitrogen containing asphaltene. The diethyl ether eluted fraction was methylated again using a different sample. The results indicate that the ether eluted asphaltene gives largely a single product which contains practically all basic nitrogen, I/N = 0.89 ± 0.05. The THF eluted fraction affords a benzene soluble fraction which contains very little basic nitrogen, I/N = 0.06 ± 0.04, and a benzene insoluble fraction which contains a substantial proportion of basic nitrogen, I/N = 0.63 ± 0.05.

(c) Oxidation

Synthoil asphaltene was oxidized by a mild, stepwise oxidation procedure as described in the last quarterly report (2). The highly oxidized product, which was esterified with BF_3/MeOH, was examined this Quarter by GC-MS analysis.

GC-MS analysis was carried out by the California Analytical Laboratories, Inc., Sacramento, California. They employed a Finnigan high performance system, equipped with the INCOS automated library search system for matching unknowns with library spectra. The column used was a 6 foot, 3% Dexsil, held at 50°C for 2 minutes, then programmed at 10°/minute to 260°C, then held for 15 minutes. The GC spectrum is shown in Fig. 16. The probable identification of the separated peaks by mass spectrometry is presented in Table IX.

The complexity of the observed benzene aromatic acid type products could be indicative of a high degree of aliphatic or alicyclic linkages between aromatic units. Alternatively, it may be that our oxidation con-

FIG. 16 GC OF ESTERIFIED $KMnO_4$ OXIDIZED SYNTHOIL ASPHALTENE

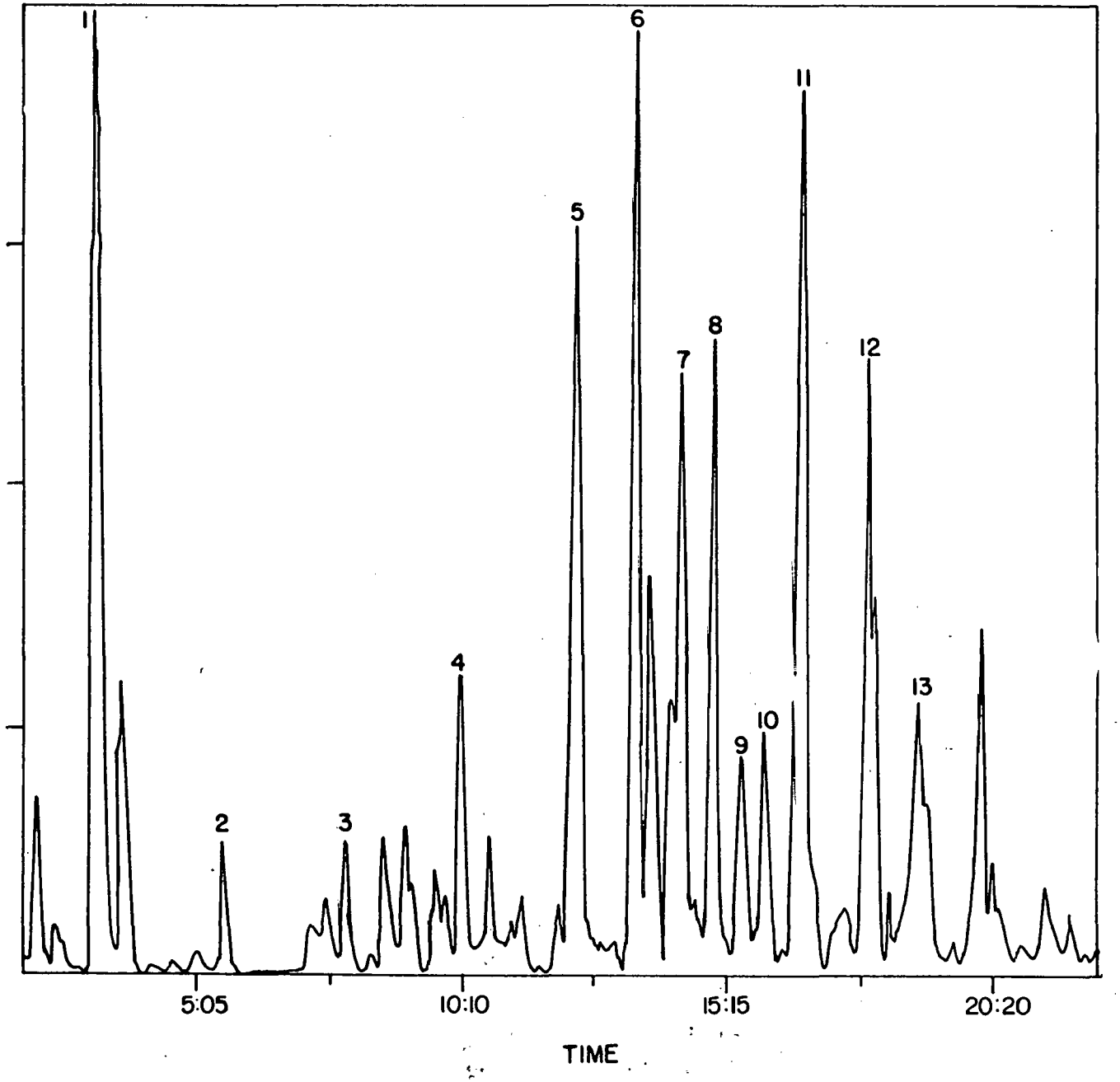


Table IX . Mass Spectrometric Identification of GC Separated Esterified $KMnO_4$ Oxidized Synthoil Asphaltene

Peak No.	Assignment[a]	Parent Peak
1	2-Acetylbut-1-ene	98
2	(C_3-benzene)	120
3	Methylbenzoate	136
4	Adipic Acid,-dimethyl ester	157
5	Phthalic anhydride	148
6	Dimethylphthalate	194
7	(Methylphthalic anhydride)	162
8	(Methyl dimethylphthalate)	208
9	(Methyl dimethylphthalate)	208
10	($C_6H_4(CH_2COOCH_3)_2$, $C_6H_2(CH_3)_2(COOCH_3)_2$)	222
11	(CH_3OCO-$C_6H_4(CO)_2O$)	206
12	($C_6H_4(COOCH_3)_3$)	252
13	($C_6H_3(CH_3)(COO\ CH_3)_3$)	266

[a]Compounds listed without parentheses were identified by comparison with spetra found in the INCOS library of spectra. Compounds in parentheses were tentatively indentified from parent peak and cracking pattern.

ditions are producing degradation of larger aromatic rings such as naphthalene, anthracene and phenanthrene. Therefore, in the next quarter we will oxidize some model aromatic compounds to ascertain the extent of aromatic ring degradation. We shall also examine fractions of less oxidized asphaltenes by GC-MS to see whether larger aromatic acids can be identified.

Conclusion

Solubility limits of Synthoil asphaltene, carbene and carboid fractions have been measured as a function of Hildebrand solubility parameters. The 100% solubility limits for asphaltene fall within the range 9-12 hildebrands, for carbene within the range 10-11 hildebrands, but the carboid was found to be essentially completely dissolved in only the solvent pyridine, $\delta = 10.62$ hildebrands.

Additional VPO molecular weight studies of asphaltenes, as a function of concentration, in the solvent chloroform indicate that association, intermediate between benzene and THF, occurs in this solvent. However, molecular weight values obtained by extrapolation to infinite dilution are in close agreement for all asphaltenes in all three solvents.

Gel permeation chromatography was carried out on the coal derived asphaltenes from the five demonstration processes under study. Molecular weight distributions, and weight-average molecular weights ($\bar{M}_w$) were determined. The $\bar{M}_w$ values are found within the range from 531-615, and are reasonably close to the number average molecular weights found previously for the same asphaltene by the VPO method.

Electron spin resonance spin intensity measurements have been carried out on asphaltenes in benzene solution. No change in spin intensity with concentration was observed which rules out the possibility of observable electron transfer taking place as a consequence of association in benzene.

ESR measurements on solid asphaltene, and solid asphaltene-TCNE charge transfer complexes were carried out down to -178°C to study the temperature dependence of the signal intensity. All ESR spin intensity-temperature dependence curves showed only Curie-Weiss (1/T) components. This suggests that coal derived asphaltene solid state clusters contain little or no triplet states with energies low enough to be populated at our experimentally observed temperatures.

ESR spin-intensity temperature dependence studies on silica gel separated asphaltene components were carried out. It was found that the weighted average temperature dependence of the benzene, diethyl ether, and THF eluted fractions reproduces the temperature dependence of the total asphaltene before separation. This suggests that charge transfer interactions, if present, may not be significant binding forces between coal derived asphaltene components.

Polarographic analyses were carried out on coal liquid solvent fractions, coal derived asphaltenes and chromatographically separated asphaltene components. Most of the reduction for coal liquid fractions takes place above -1.8V vs. Hg pool anode, and the major halfwave reduction waves for most fractions occur at $\simeq$-2.0 V. As one proceeds along the series: oil, resin, asphaltene, carbene, and carboid, one observes increasing total reduction per average molecule, as measured by i_d/C values, and an increasing percentage of reduction taking place at lower potentials. These trends suggest larger and more aromatic systems are present as one progresses down the series.

Silylation and methylation of asphaltene silica gel chromatographic fractions indicates that the neutral fraction, benzene eluted, which contains the lowest percentage of oxygen, 2.71, contains the highest percentage of OH/O_{total}, 57, and almost no basic nitrogen. The basic fractions, diethyl ether eluted and THF eluted, which contain 6.50% and 7.38% of oxygen respectively, have only 32% and 34% OH/O_{total} respectively. These latter fractions contain large percentages of basic nitrogen as measured by atomic I/N values of 0.89 and 0.63 respectively.

GC-MS analysis of oxidized synthoil asphaltene has shown large amounts of complex benzene carboxylic acid derivatives are produced in the oxidation. Further studies with model compounds will be required to determine whether these results are due to a high degree of aliphatic or alicyclic linkages between aromatic units, or degradation of larger aromatic ring systems under the experimental conditions.

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