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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES. PHASE III

Quarterly Progress Report, January—March 1978

By
T. F. Yen

Work Performed Under Contract No. EX-76-C-01-2031

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

January - March 1978

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DEPARTMENT OF ENERGY

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Abstract

The solubility limits of Synthoil and PAMCO asphaltenes have been measured as a function of Hildebrand solubility parameters and hydrogen bonding. Solvents with moderate hydrogen bonding capacity such as dioxane, ethyl benzoate and dibutyl phthalate were found to be most effective in dissolving asphaltenes over the widest range of solubility parameters.

VPO molecular weight studies of coal liquid derived carbenes, as a function of concentration in the solvent THF, indicate that these fractions are more strongly self-associated than the corresponding asphaltenes, and generally afford high infinite dilution number average molecular weights: Synthoil, 861; HRI H-Coal, 1156; Cat. Inc. SRC, 1228; PAMCO SRC, 1054.

The variable ESR temperature dependence of the spin intensity for a Synthoil asphaltene-I_2 charge transfer followed a 1/T (Curie-Weiss) dependence over the temperature range from 25^o to -114^oC suggesting that independent, non-interacting donor and acceptor doublets were formed.

Weight percent OH values, determined from 'H NMR analysis of silylated asphaltenes, were found to provide a reasonably linear correlation with the absorbance of the monomeric OH infrared stretching bands of the asphaltenes. The correlation found at C=25 g/l, path 1 mm in $CDCl_3$ is:

$$\text{Wt.\% OH} = 7.7\ A_{3590\ \text{cm}^{-1}}$$

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 liquefaction 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.

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(16) Characterization of asphaltenes by the n-d-M method.

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

(18) 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 Synthoil asphaltene, carbene and carboid fractions were obtained as a function of solubility parameters (1, 2). We have now extended this work to include the study of hydrogen bonding effects. A series of pure solvents, classified as poor, moderate, and strong hydrogen bonding solvents (3) (Table I) was used to obtain a solubility spectrum of Synthoil asphaltene as a function of solubility parameter and hydrogen bonding capacity (Fig. 2) Complete solubility occurs at the lowest solubility parameter for the strong hydrogen bonding solvents. The solvents with moderate hydrogen bonding capacity are effective over the widest range. Poor hydrogen bonding solvents are least effective.

In addition to the solubility of PAMCO SRC asphaltene, benzene insolubles (carbene and carboid) were studied as a function of solvent solubility parameter and hydrogen bonding. The solubility spectra of the above PAMCO fractions are shown

Fig. 1. Milestone Chart

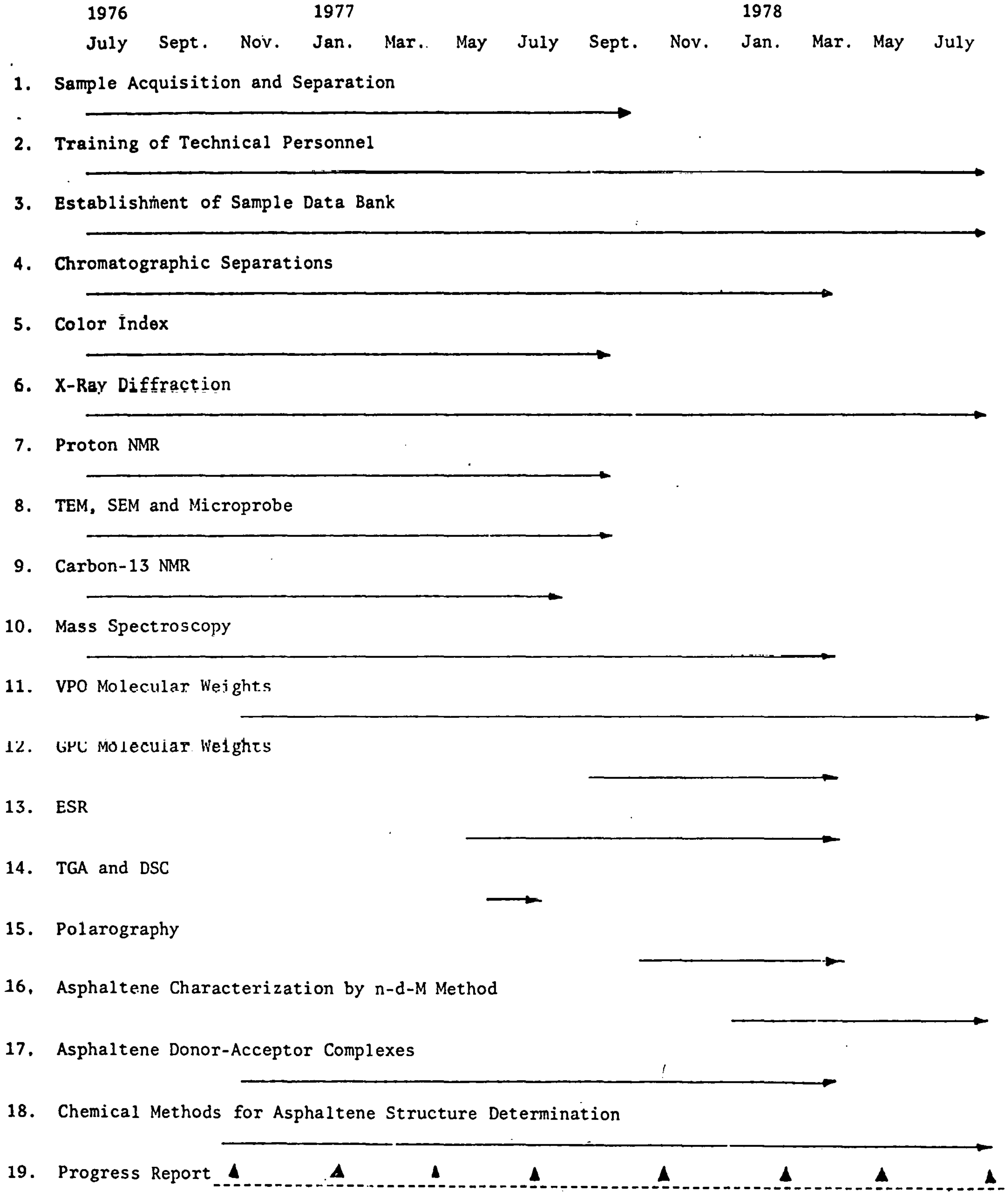

Table I. List of Pure Solvents

Solvent	Solubility Parameter	Hydrogen Bonding
cyclohexane	8.2	P
toluene	8.9	P
chlorobenzene	9.5	P
o-dichlorobenzene	10.0	P
nitroethane	11.1	P
nitromethane	12.7	P
diethyl ether	7.4	M
ethyl benzoate	8.2	M
dibutyl phthalate	9.3	M
dioxane	9.9	M
furfural	11.2	M
dimethylformamide	12.1	M
diethylamine	8.0	S
piperidine	8.7	S
propionic acid	9.9	S
pentanol	10.9	S
butanol	11.4	S
propanol	11.9	S
ethanol	12.7	S
methanol	14.5	S

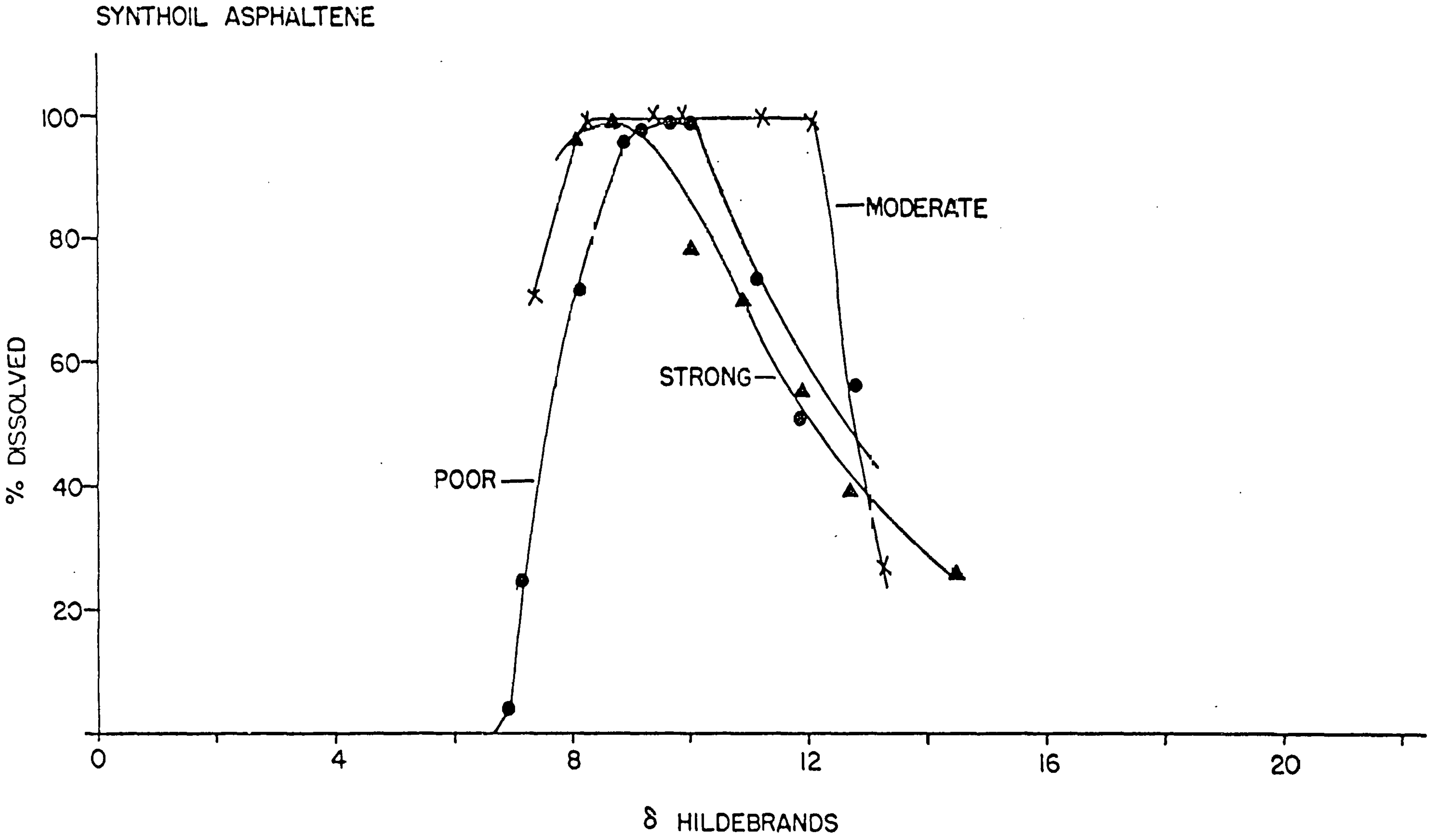

Fig. 2. Effect of Hydrogen Bonding on Dissolution of Synthoil Asphaltene in Pure Solvents

for mixed solvent systems (Table II) in Fig. 3. The effect of hydrogen bonding on dissolution of PAMCO asphaltene and benzene insolubles, in pure solvents, is presented in Figs. 4 and 5. Again it may be seen that the solvents with moderate hydrogen bonding capability are the most effective in dissolving these coal liquid fractions.

The fact that solvents of moderate hydrogen bonding capacity are most effective in dissolving high molecular weight coal liquid solvent fractions may be rationalized by assuming that more than one type of solvent-solute interaction is important. That is, strong hydrogen bonding solvents may interact largely with specific sites, and solvents with poor hydrogen bonding capability may interact mainly through physical types of forces. However, moderate hydrogen bonding solvents may operate via both of these types of interactions.

(2) Characterization of Coal Liquid Fractions by Physical Methods

Work Accomplished:

(a) VPO Investigation of Coal Liquid Molecular Weights and Association

The VPO molecular weights of coal-derived asphaltenes are shown in Figures 6 to 10. The results show that the association of asphaltene takes place in THF over the concentration range of S-60 g/l. however, it is the least among the three solvents used so far (benzene, chloroform and THF). This is because THF is more polar than benzene and chloroform.

The VPO molecular weights of coal-derived carbenes vs. concentration in THF have also been determined in this quarter and are shown in Table III. Since some of the carbenes were in short supply, only two molecular weights at two different concentrations, have been taken and used for correlation and extrapolation for HRI and PAMCO SRC carbenes. These should be repeated with more

Table II. List of Solvents-Mixed

$$\delta m = \gamma_1 \delta_1 + \gamma_2 \delta_2$$

γ = volume fraction

δ = solubility parameter

Solvent	Solubility Parameter	Hydrogen Bonding
2-methylpentane	7.0	P
cyclohexane	8.2	P
cylcohexanol	9.9	M
HEMA*	12.5	scalc●
water	23.4	S

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*2-Hydroxyethyl methacrylate

●Sum of group contributions to hydrogen bonding capability

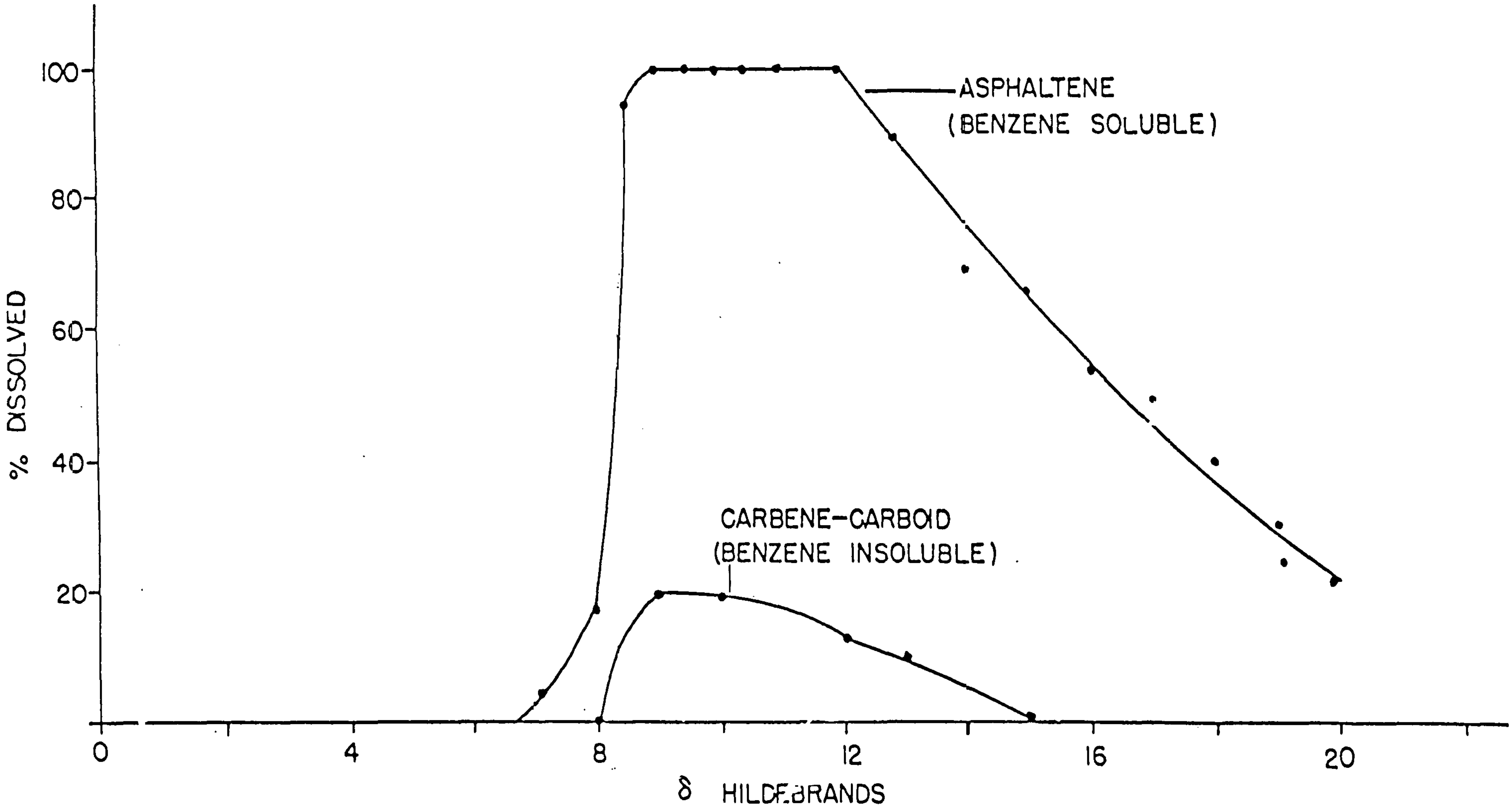

Fig. 3. Dissolution of PAMCO Benzene Soluble and Benzene Insoluble Fractions in Mixed Solvent Systems

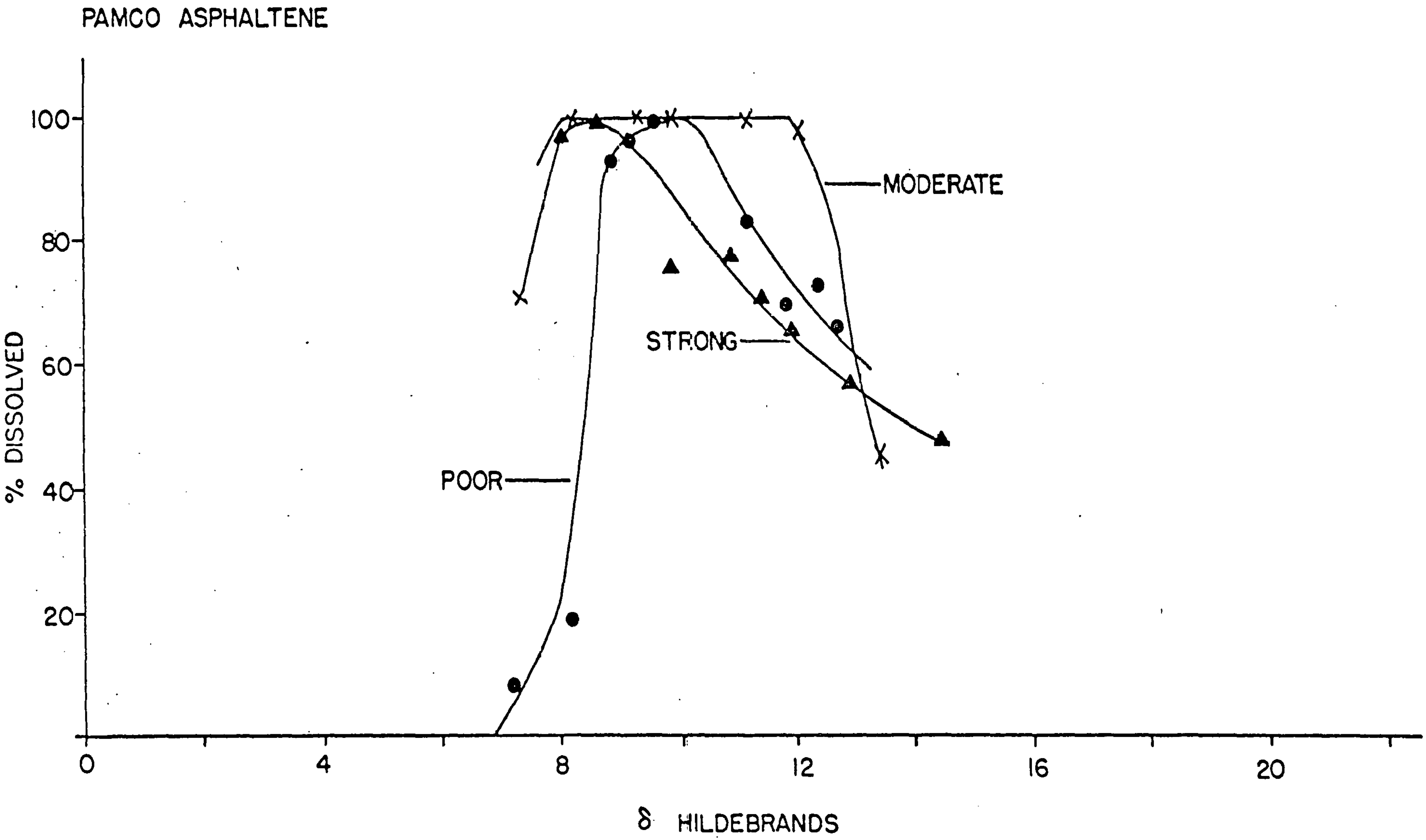

Fig. 4. Effect of Hydrogen Bonding on Dissolution of PAMCO Asphaltene in Pure Solvents

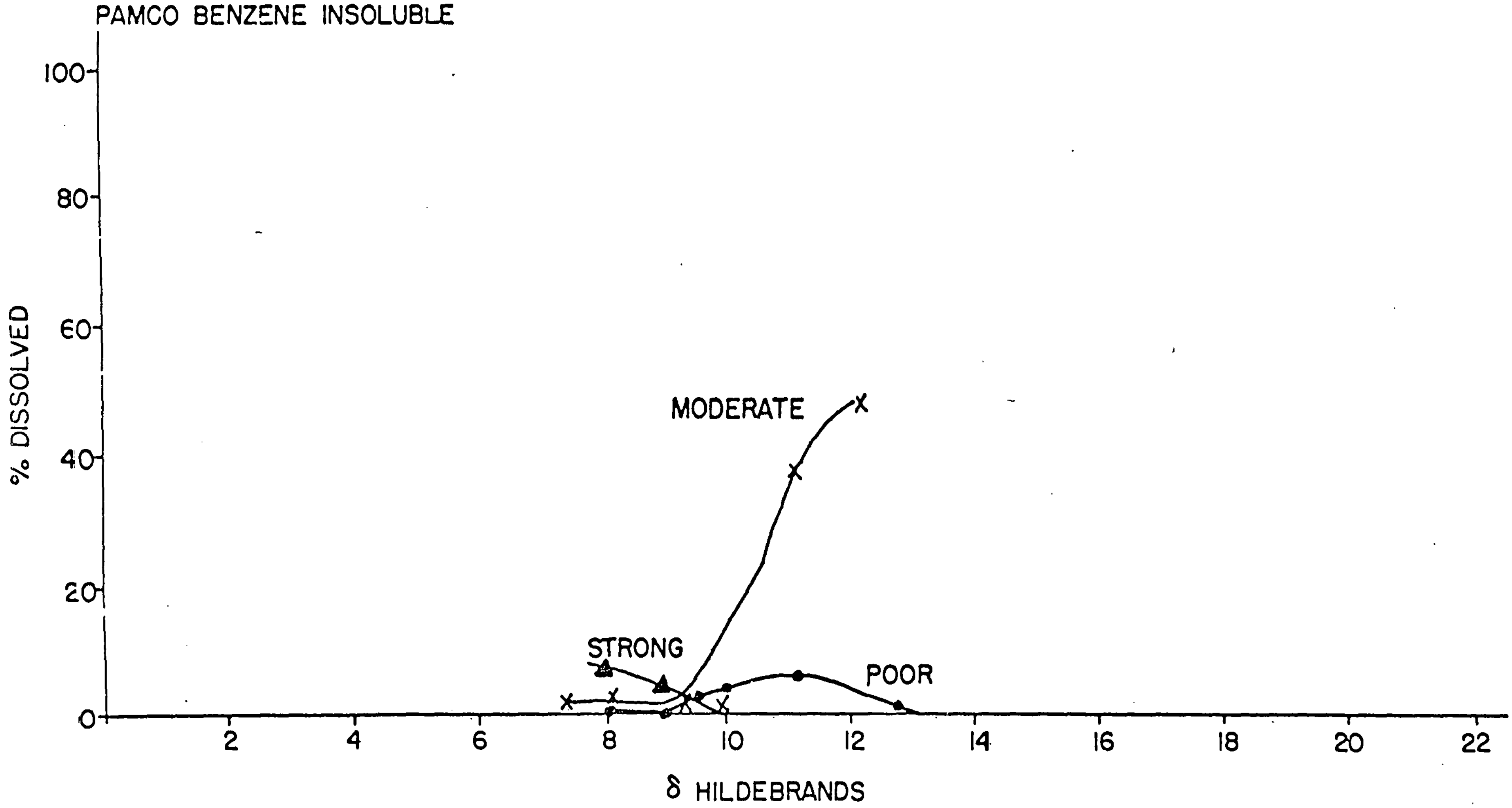

Fig. 5. Effect of Hydrogen Bonding on Dissolution of PAMCO Benzene Insolubles in Pure Solvents

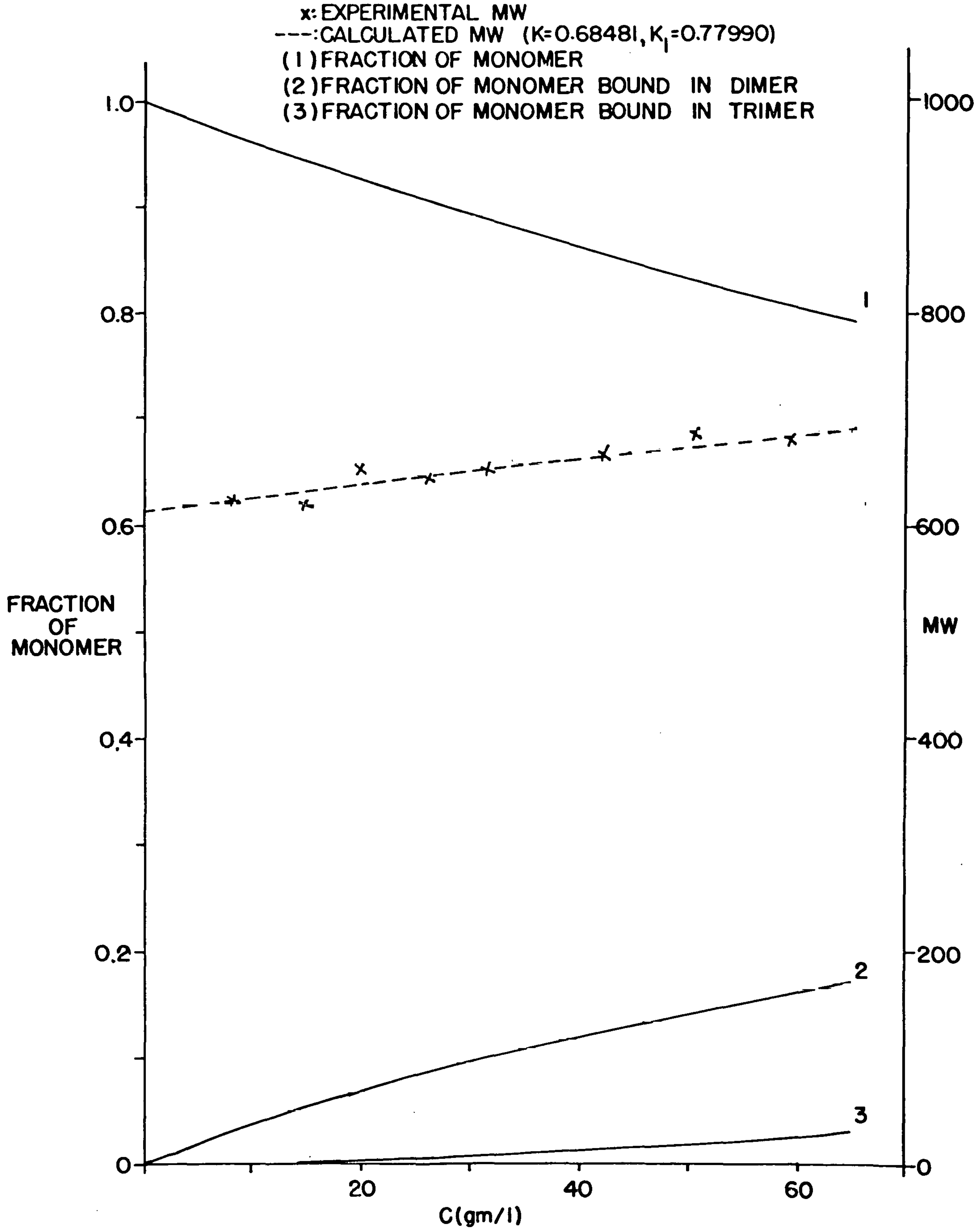

FIG: 6. FRACTIONS OF MONOMER AND VPO MW VS. CONCENTRATION SYNTHOIL ASPHALTENE IN THF

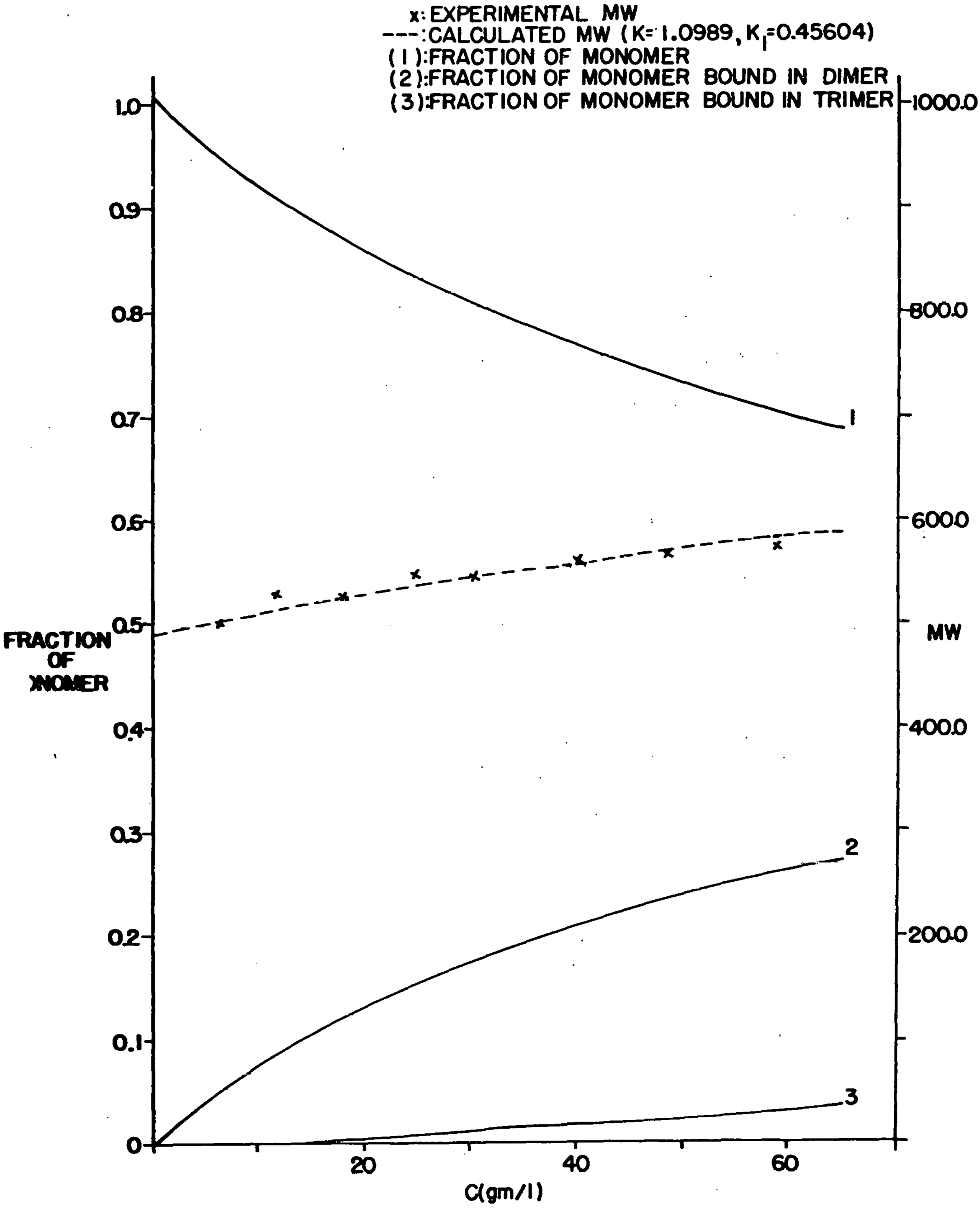

FIG. 7 FRACTIONS OF MONOMER AND VPO MW VS. CONCENTRATION HRI ASPHALTENE IN THF

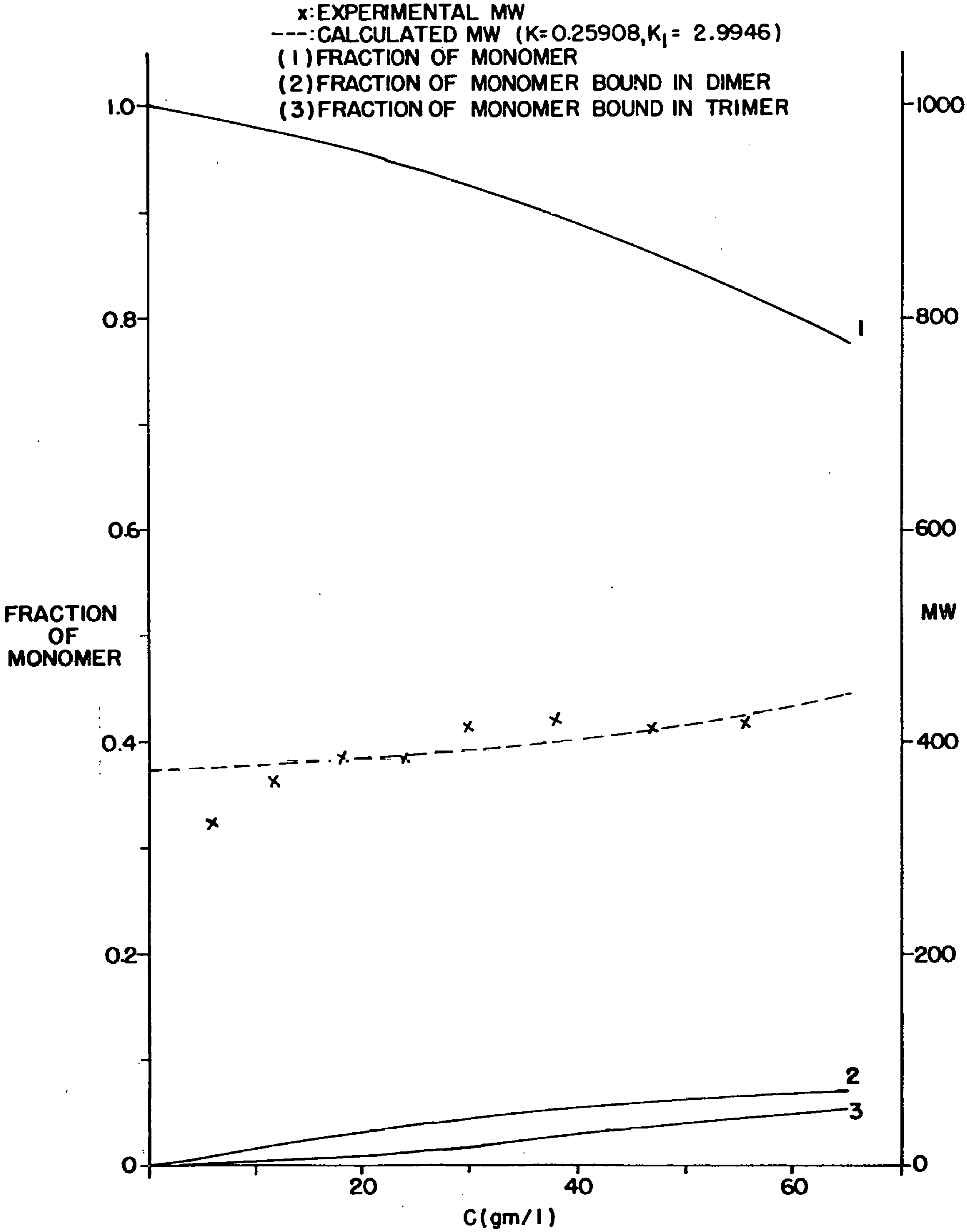

FIG. 8 FRACTIONS OF MONOMER AND VPO MW VS. CONCENTRATION FMC COED ASPHALTENE IN THF

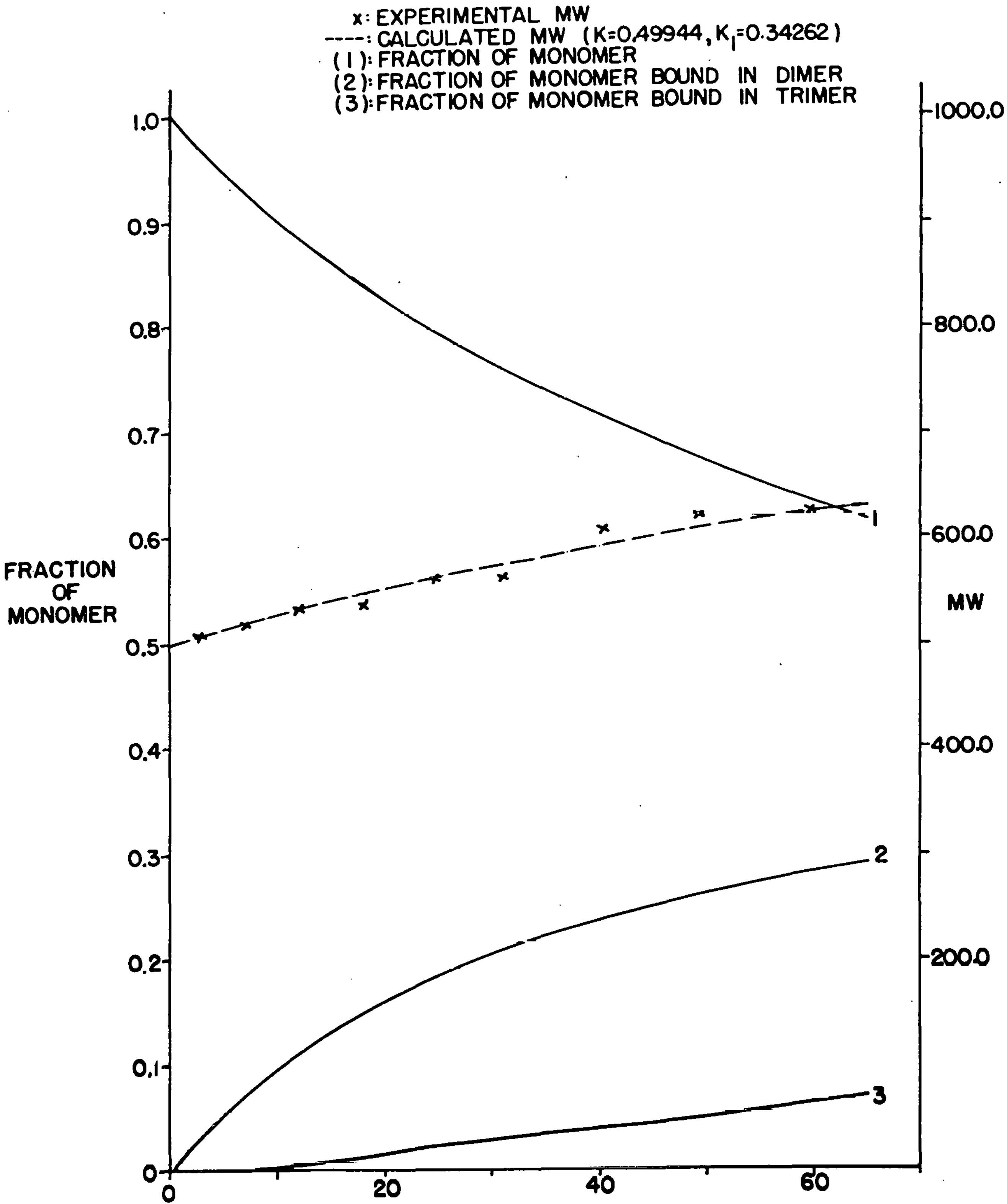

FIG. 9 FRACTIONS OF MONOMER AND VPO MW VS. CONCENTRATION CAT. INC. ASPHALTENE IN THF

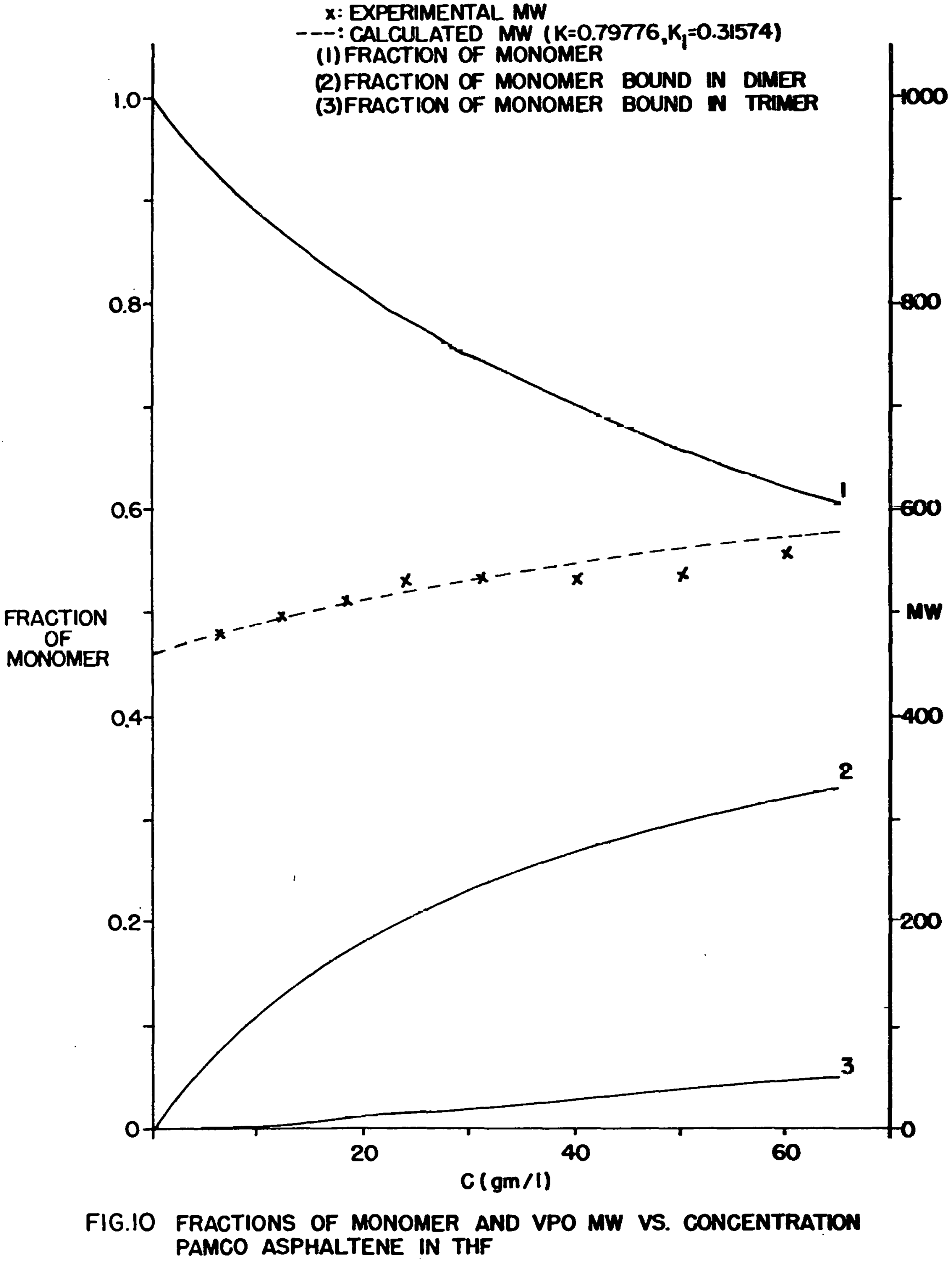

FIG.10 FRACTIONS OF MONOMER AND VPO MW VS. CONCENTRATION PAMCO ASPHALTENE IN THF

Table III Molecular Weight of Carbenes vs. Concentration* in THF

	Least Squares Equation	Corr. Coeff.	Av. MN at Zero Conc.
Synthoil Carbene	$MW = 5.97 \pm 0.28\,C + 861 \pm 6.45$	0.989	861.
HRI Carbene	$MW = 24.63 \pm 0.52\,C + 1156 \pm 10.43$***	0.999	1156.
FMC-COED Carbene	$MW = 1.37 \pm 0.21\,C + 323 \pm 4.82$	0.94	323.
Cat. Inc. SRC Carbene	$MW = 4.08 \pm 0.47\,C + 1228 \pm 9.11$	0.97	1228.
PAMCO SRC** Carbene	$MW = 6.31 \pm 0.47\,C + 1054 \pm 10.05$***	0.99	1054.

---

*Conc. g/l.

**Vacuum distillation residue.

***Only two points used, should be repeated.

points in the next quarter. Despite this, the results show that association of carbene also takes place in THF over the concentration range of 10-36 g/l and the correlation between concentration and molecular weight is linear. The slopes of the correlation lines of carbenes in THF are usually greater than those of asphaltenes in THF. This indicates that the self-association of carbene is generally stronger than that of asphaltene.

Asphaltene Self-Association Model

The equilibrium constants of coal-derived asphaltenes in THF have been calculated based on the two parameter model derived before (1) and are shown in Figures 6 to 10 and Table IV. The results show that this two parameter model is also efficient in describing the self-association of asphaltenes in THF.

Comparing the equilibrium constants K_1 and K of these five different asphaltenes in benzene, chloroform and THF, it is found that Synthoil and PAMCO SRC asphaltenes have stronger association between molecules while FMC-COED and Cat. Inc. SRC asphaltenes have less. This suggests that more energy may be needed in upgrading heavy fractions of coal liquid from Synthoil and PAMCO SRC than those from FMC-COED and Cat. Inc. SRC.

The equilibrium constants in THF are generally larger than in benzene and chloroform, since THF is more polar and tends to dissociate the asphaltene molecules as they are dissolved.

Figure 11 is a combination of experimental and calculated molecular weights of Synthoil asphaltene in benzene, chloroform and THF. It is observed that in benzene the association is more significant and the variation of MW vs. concentration is higher than in the other two solvents, chloroform and THF. However, the dissociation tends to go to completion in all three solvents at infinite dilution. From the calculated MW, it is also noted that in dilute concentration all asphaltenes afford linear correlations between concentration

Table IV.

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
		THF DMF	0.7799	0.6848	9.5	1.7
HRI Asphaltene	502	Benzene	0.118	0.0866	9.0	1.8
		Chloroform	0.2048	0.2275	27.7	5.5
		THF DMF	0.4560	1.0989	8.1	1.6
FMC-COED Asphaltene	370	Benzene	0.210	0.0813	20.7	5.6
		Chloroform	0.2645	0.1779	29.0	7.8
		THF DMF	2.9946	0.2591	25.5	6.9
Cat. Inc. SRC Asphaltene	477	Benzene	0.225	0.109	12.2	2.6
		Chloroform	0.2151	0.1497	10.2	2.1
		THF DMF	0.3426	0.4994	10.4	2.2
*PAMCO SRC Asphaltene	545	Benzene	0.061	0.0971	18.6	3.4
		Chloroform	0.180	0.1239	12.7	2.3
		THF DMF	0.3157	0.7978	16.5	3.0

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*Isolated from vacuum distilled bottom product

**Molecular Weights at infinite dilution

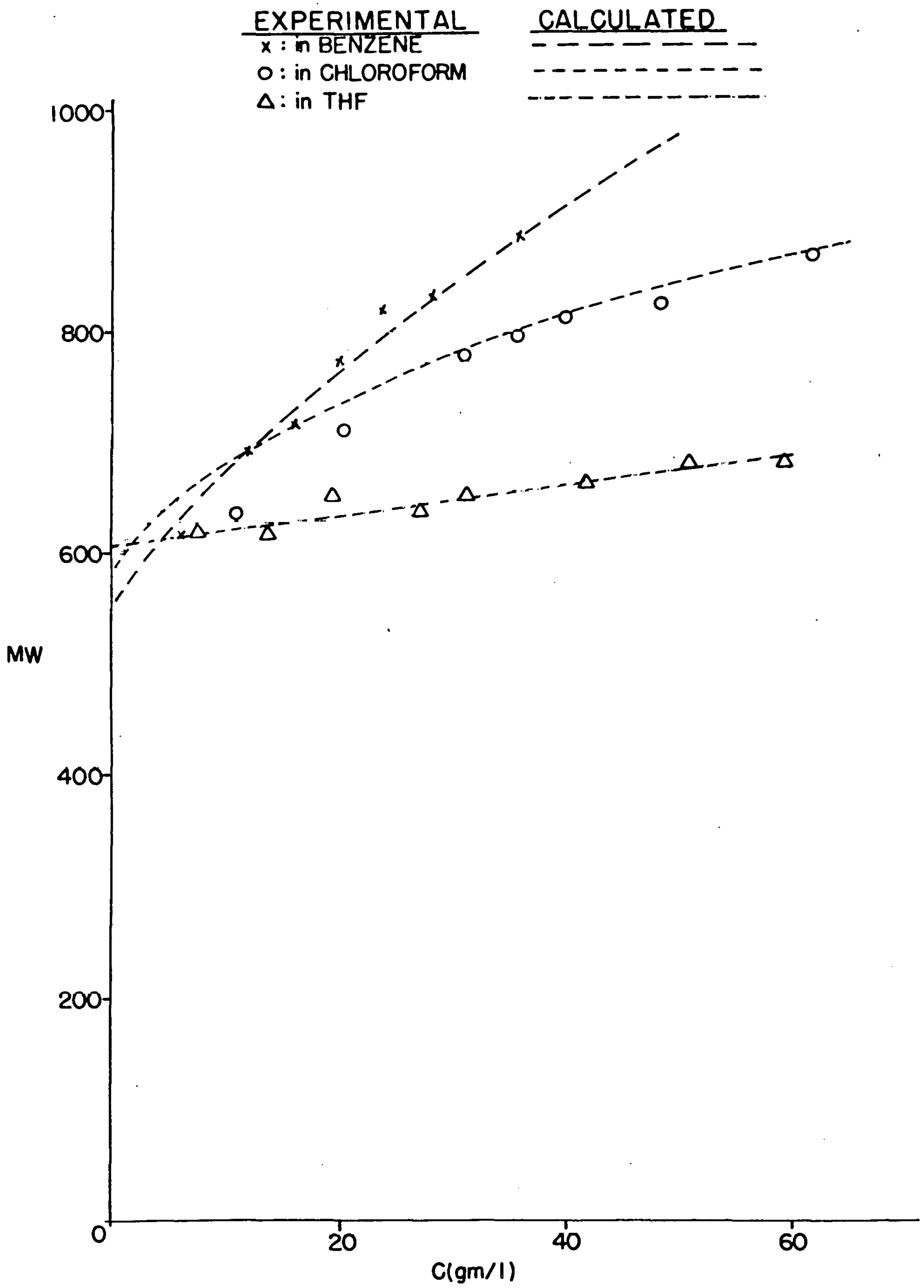


FIG.11 MW OF SYNTHOIL ASPHALTENE VS CONCENTRATION IN DIFFERENT SOLVENT

and molecular weight and this agrees with the assumption drawn before (4) that molecular weights vs. concentration may be reasonably approximated as linear in dilute solution for coal-derived asphaltenes.

Since the degree of association in benzene is larger, the fraction of monomer in benzene should be less than in the other two solvents, and these results are shown in Figure 12. In benzene solution, as the concentration increases, the fraction of asphaltene, existing as a dimer reaches a maximum, and then decreases, and higher multimers become increasingly important. Since the association in chloroform and THF is less, more concentrated solutions are needed for dimer to reach maxima and are not shown on this graph. In highly concentrated solutions these larger multimers become dominant and start to precipitate. Evidence for association of monomer asphaltenes into 4-6 average layers in the solid state has been found by x-ray diffraction spectroscopy (5).

For the next quarter, the molecular weights of resin and and mixture of resin and asphaltene will be taken in THF and benzene in order to study the interaction between resin and asphaltene. Also, the molecular weights of asphaltenes at 65°C in benzene will be measured and the two parameter model will be tested.

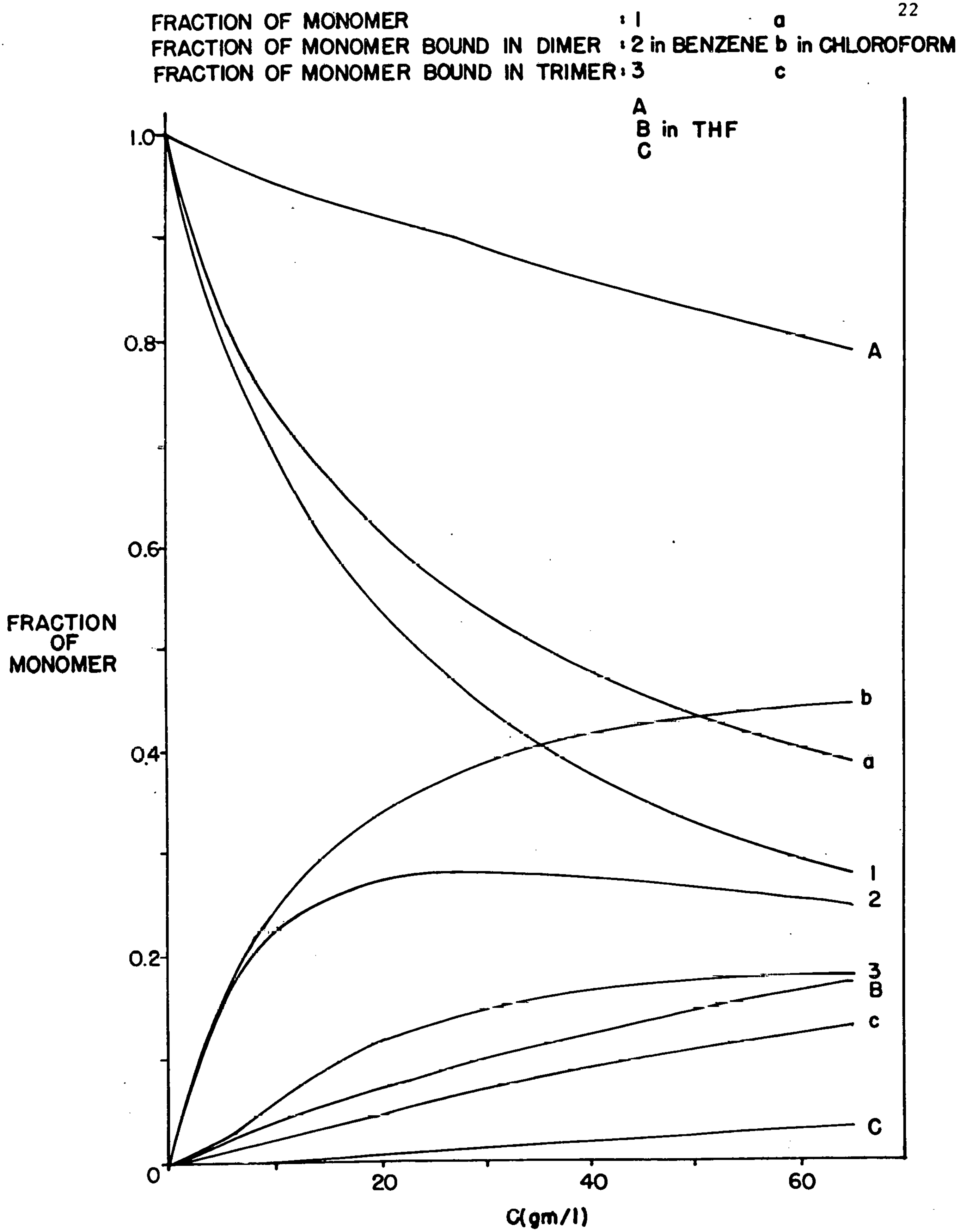


FIG.12 FRACTIONS OF MONOMER VS CONCENTRATION SYNTHOIL ASPHALTENE

(b) Electron Spin Resonance of Asphaltenes

In previous Quarterly Reports (1 , 2) we discussed the determination of ESR data, and the results obtained in a study of sample intensity variations as a function of temperature. The ESR spin intensity curves for Synthoil asphaltene, and Synthoil asphaltene chromatography fractions showed only $1/T$ (Curie-Weiss) temperature dependence. The same type of $1/T$ dependence was observed for a Synthoil asphaltene - TCNE charge transfer complex.

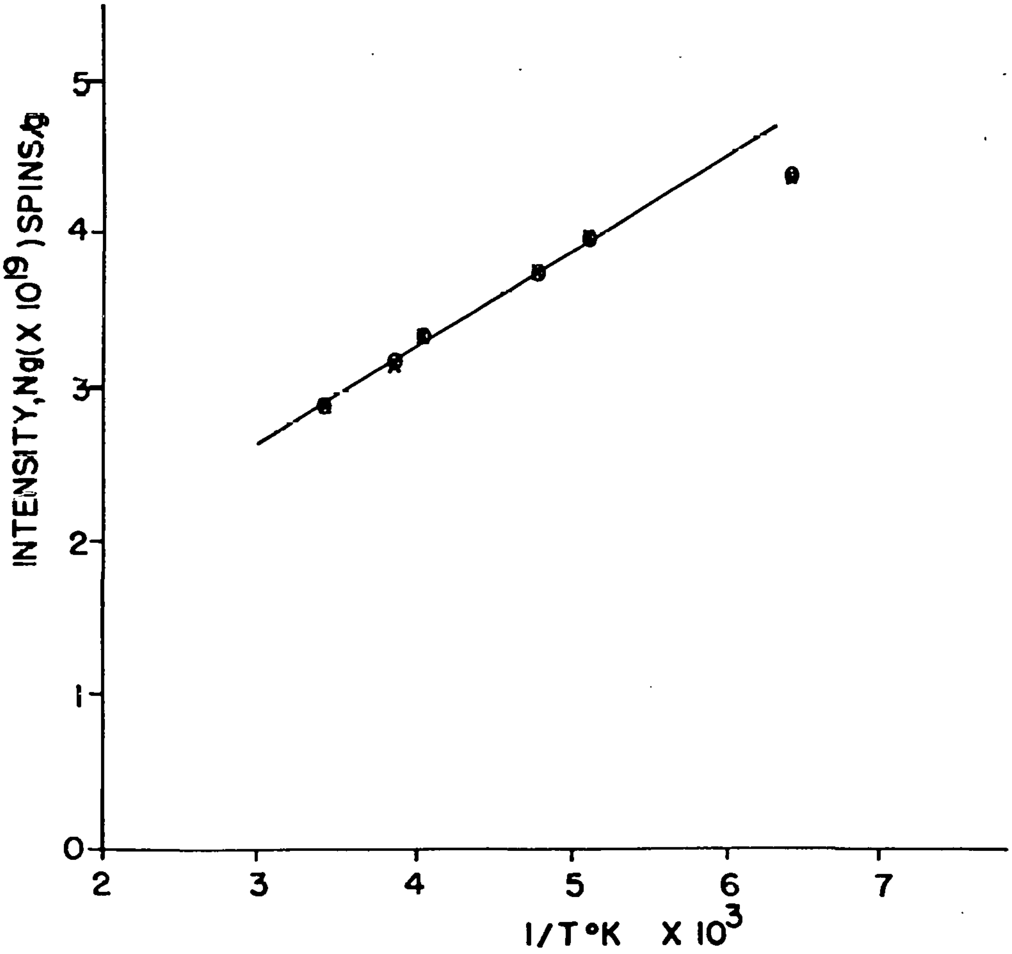
In the present Quarter we measured the variable ESR temperature dependence of the spin intensity for a Synthoil asphaltene - I_2 charge transfer complex. The results, shown in Fig. 13 , indicate that the signal intensity also follows a $1/T$ (Curie-Weiss) dependence. This result may be explained by assuming that the charge transfer complexation results in the formation of independent, non-interacting, donor and acceptor doublets.

(c) Characterization by n-d-M Method

The n-d-M method is an empirical method, and has long been used in petrochemical analysis for determining carbon distribution and ring content of olefin free petroleum portions boiling about the gasoline range (6). The n stands for refractive index, d, for density, and M for molecular weight. By utilizing these three parameters one may determine the percentage of carbon atoms in aromatic ring structures ($\%C_A$); in naphthenic ring structures ($\%C_N$), and in paraffinic structures ($\%C_P$). By applying this method the mean number of aromatic rings R_A, and the mean number of naphthenic rings R_N can also be estimated.

The refractive indexes of coal-derived asphaltenes were determined as a function of concentration in dilute solutions. Several different solvents were used, and the index of refraction of each asphaltene was determined by extrapolation to 100% concentration (7). All the refractive indexes were measured at 25°C with a Bausch & Lomb Co., thermostated, refractometer. A few minutes were allowed to

FIG.13 VARIABLE ESR TEMPERATURE DATA FOR SYNTHOIL ASPHALTENE (Et_2O ELUTED CHROMATOGRAPHY FRACTION)-I_2 CHARGE TRANSFER COMPLEX



let the solution come to 25°C in the refractometer before measurements were made. The solvent systems included benzene, chloroform, dimethyl formamide (DMF) and tetrahydrofuran (THF). The concentrations of the solutions were 0.05, 0.1, 0.2 and 0.4% by weight.

The powder density of Synthoil asphaltene was measured by a helium displacement method. The densitometer used was based on the basic design proposed by Schumb (8) with same improvements, as shown in Fig. 14. The density was measured at room temperature and atmospheric pressure.

The refractive indexes of the four coal-derived asphaltenes obtained from different solutions, at 25°C,and the average values are shown in Table V. These data show that the extrapolated refractive indexes of each coal asphaltene, obtained from different solutions, are in reasonably close agreement. The coefficient of variance is around 1% in three cases and less than 3% for Synthoil asphaltene. The average refractive indexes are: Synthoil asphaltene, 1.6668; HRI, 1.6979; Cat. Inc., 1.7009; and PAMCO, 1.7282.

A preliminary value for the density of Synthoil asphaltene, obtained by the helium displacement method, is 1.1756 g/ml. This datum, together with the refractive index, and molecular weight, 561 g/mole (4), may be used to calculate the carbon distribution of Synthoil asphaltene according to the n-d-M method. The procedure is outlined in Table VI. The calculated carbon distribution of Synthoil asphaltene according to this method is: $\%C_A$, 74; $\%C_N$, 34; $\%C_P$, -8; the aromatic ring content R_A is 5, and the naphthenic ring content R_N is 5. The aromaticity f_a, obtained previously from an NMR study was 0.70 (9), which is close to the result obtained here. The hypothetical molecular structure of Synthoil asphaltene proposed previously (1) contained six aromatic rings and three naphthenic rings. The negative percentage of paraffinic carbon is not too unreasonable because the paraffinic content consists of only a few methyl groups.

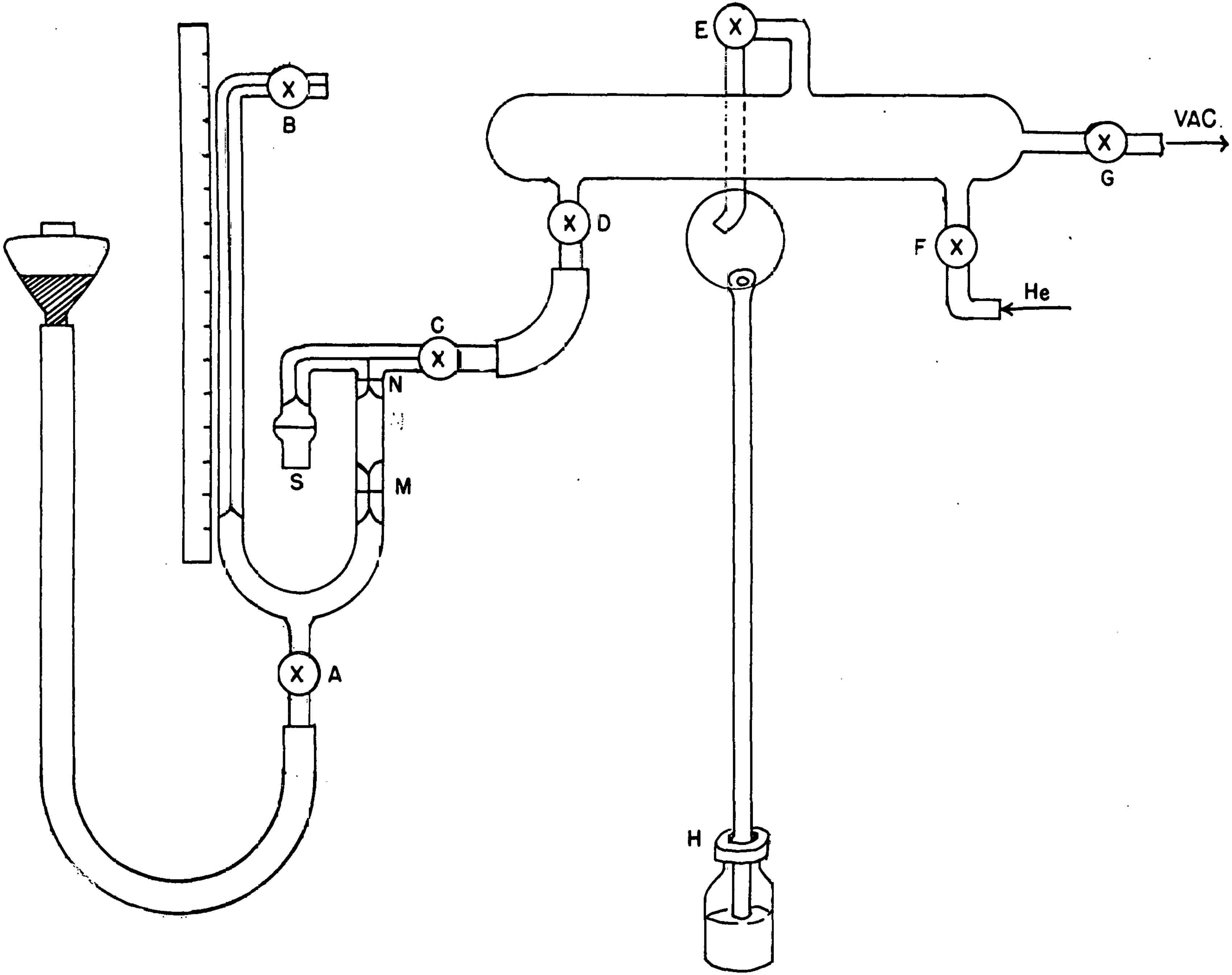


FIG. 14 HELIUM DENSITOMETER

Table V. Extrapolated Refractive Indexes of Coal-Derived Asphaltenes in Different Solvents

	Asphaltenes			
Solvent	Synthoil	HRI	Cat.Inc.	PAMCO
Benzene	1.7013	1.7008	——	——
Chloroform	——	1.7130	——	——
DMF	1.6144	1.6694	1.7052	1.7111
THF	1.6847	1.7084	1.6966	1.7452
Average	1.6668	1.6979	1.7009	1.7282
Standard Dev.	0.0461	0.0197	0.0061	0.0241
% Coeff. of Variance	±2.77	±1.16	0.36	1.40

Table VI. Structural Calculation Formulas Used in the n-d-M Method[a]

Calculate	$v = 2.501\ (n-1.4735) - (d-0.8487)$ $w = (d-0.8487) - 1.11\ (n-1.4735)$
$\%C_A$	$v > 0$ $\%C_A = 428v + 3660/M$ $v < 0$ $\%C_A = 575v + 3660/M$
$\%C_T$	$w > 0$ $\%C_T = 815.5w - 3S^b + 10150/M$ $w < 0$ $\%C_T = 1436w - 3S + 10750/M$
$\%C_N$ $\%C_P$	$\%C_N = \%C_R - \%C_A$ $\%C_P = 100 - C_R$
R_A	$v > 0$ $R_A = 0.437 + 0.055Mv$ $v < 0$ $R_A = 0.437 + 0.080Mv$
R_T	$w > 0$ $R_T = 1.352 + 0.146M\ (w-0.005S)$ $w < 0$ $R_T = 1.352 + 0.180M\ (w-0.005S)$
R_N	$R_N = R_T - R_A$

[a] Ref.

[b] S = % Sulfur

Therefore, one may assume that the negative valuc obtained (-8%) actually represents a result close to zero.

Additional measurements and calculations will be carried out in the next quarter to refine the accuracy and reproducibility of the n-d-M method for calculating structural parameters of coal-derived asphaltenes.

(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 (1, 2, 10-12), we described the procedure and results for the silylation of asphaltenes and other coal liquid derived products. During the present quarter we repeated the hydroxyl determination by use of proton NMR analyses. The results are presented in Table VII. Proton NMR analysis is believed to be a more useful and reliable method than the direct silicon analysis method developed by Friedman et al. (13). This is because chemical shifts can be used to assign observed bonds to alcoholic or hindered phenolic TMS derivatives (0-0.2 ppm) or simple phenols (0.18-0.4 ppm) (14). In addition, the presence of unreacted silylating reagents such as hexamethyldisilazane or hydrolysis products such as hexamethyldisiloxane, which absorb at 0 ppm, can be determined readily. Figure 15 shows the 'H NMR spectrum of the TMS derivative of Synthoil asphaltene in the trimethylsilyl ether absorption region. Relatively strong absorptions are observed in the region assigned to simple phenols (0.26-0.22 ppm), and smaller bands are observed in the region assigned to alcoholic or hindered phenolic absorption (0.12-0.07 ppm).

Table VII. ^{1}H Analysis of Silylated Asphaltenes

Asphaltene	% H as OH[a]	At. OH/O total	Wt % O	Wt % OH
Synthoil	2.13	0.58	3.93	2.42
FMC-COED	4.03	0.59	7.11	4.46
PAMCO SRC	3.48	0.69	4.68	3.43
Cat. Inc. SRC	3.20	0.67	4.58	3.26
HRI H-Coal	2.18	0.41	4.96	2.18
Synthoil Chrom. Fractions				
Benzene Eluted	1.34	0.58	2.39	1.47
Et_2O Eluted	2.55	0.51	5.40	2.93
THF Eluted	1.08	0.18	5.97	1.15

[a] $$\% \text{ H as OH} = \frac{\frac{\text{TMS Area}}{9}}{\frac{\text{TMS Area}}{9} + (\text{Remaining H Area})}$$

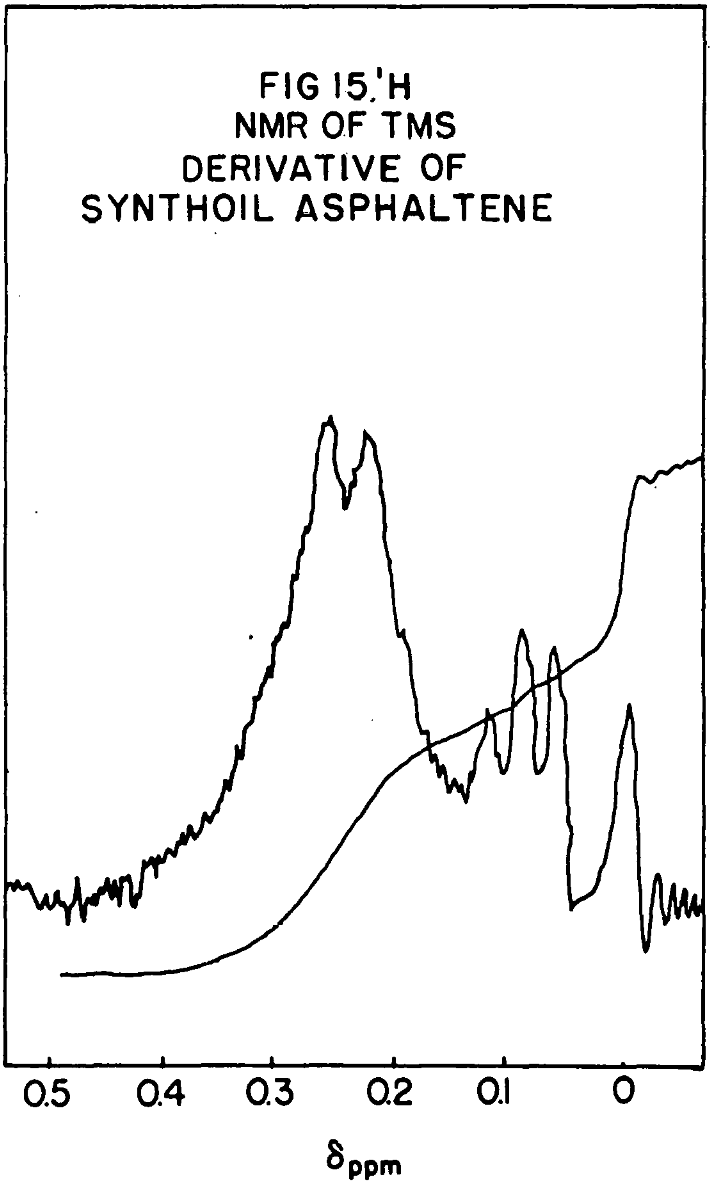
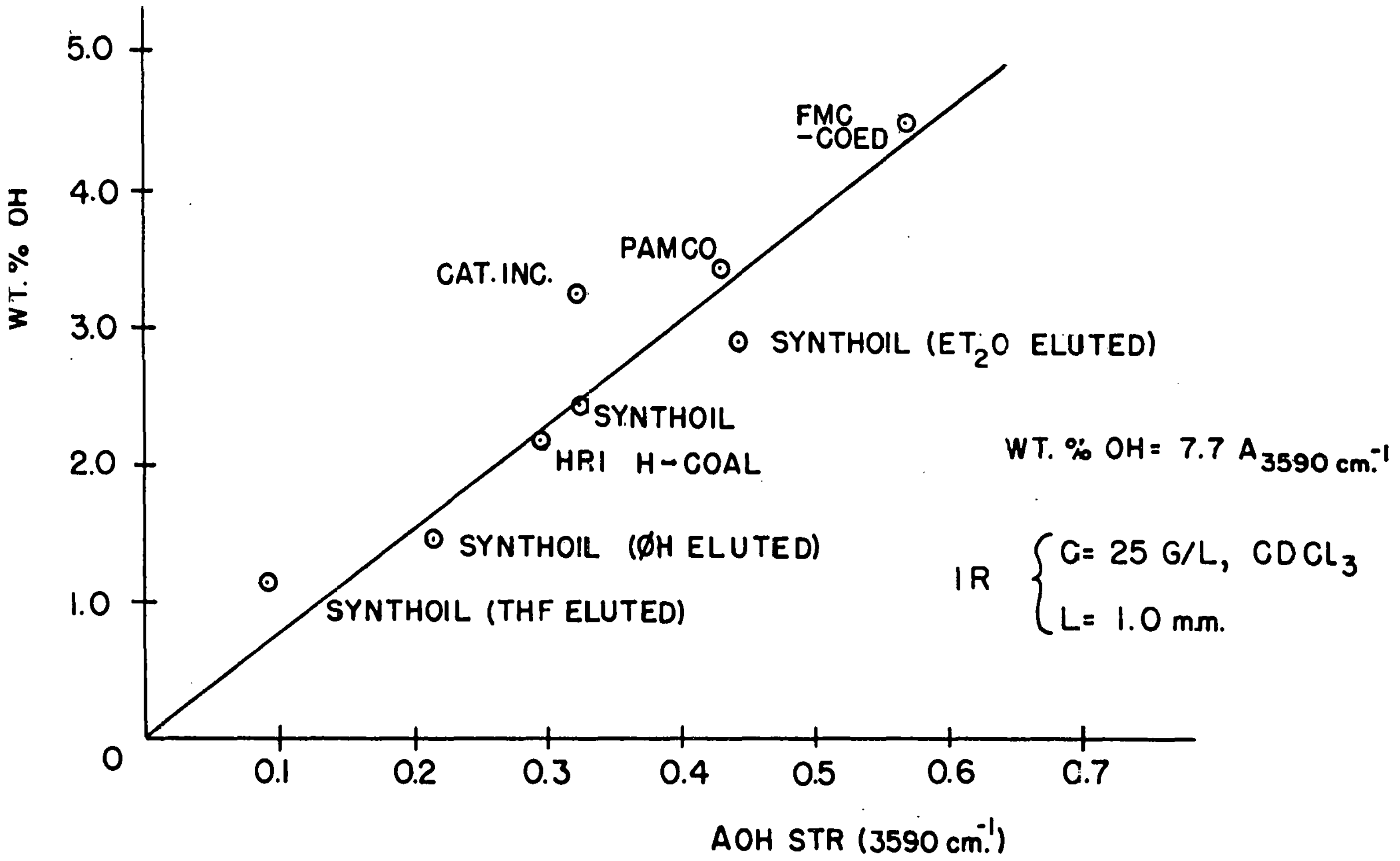


FIG 15. ^{1}H NMR OF TMS DERIVATIVE OF SYNTHOIL ASPHALTENE

The results reported in Table VII are qualitatively similar to those reported earlier, which were obtained from direct silicon analysis by use of the method of Friedman et al. The Cat. Inc. and PAMCO SRC asphaltenes both had distinctly lower atomic OH/O_{total} values of 0.67 and 0.69 (previously reported as 0.92 and 0.97). This discrepancy was probably caused by contamination of the silicon analysis samples with unreacted HMDS and/or hexamethyldisiloxane.

The weight percent OH values for the different asphaltene samples were plotted against the absorbance of the monomeric OH infrared stretching bands at 3590 cm^{-1}. The results (Figure 16) afford a reasonably linear correlation despite the fact that all the asphaltenes are not completely dissociated at 25 g/l concentration in $CDCl_3$. This type of correlation should be useful as a simple means of obtaining the %OH of asphaltenes and other types of coal liquefaction products.

FIG. 16 CORRELATION OF ASPHALTENE OH ABSORBANCE VS. WT. % OH FROM NMR ANALYSIS OF SILYLATED ASPHALTENES



Conclusion

The solubility limits of Synthoil and PAMCO asphaltenes have been measured as a function of Hildebrand solubility parameters and hydrogen bonding. Complete solubility occurs at the lowest solubility parameter for the strong hydrogen bonding solvents. The solvents with moderate hydrogen bonding capacity are effective over the widest range. Poor hydrogen bonding solvents are least effective. Moderate hydrogen bonding solvents may operate best because of combined interactions with specific sites, and general physical force type of interactions.

VPO molecular weight studies of coal liquid derived carbenes, as a function of concentration, in the solvent THF indicate that the self-association of carbene is generally stronger than that of similarly derived asphaltenes.

The variable ESR temperature dependence of the spin intensity for a Synthoil asphaltene-I_2 charge transfer complex was determined. The signal intensity followed a 1/T (Curie-Weiss) dependence in the range studied. This result may be explained by asssuming that the charge transfer complexation results in the formation of independent, non-interacting, donor and acceptor doublets.

Preliminary measurements of the index of refraction, and density of asphaltenes have been carried out. This data, along with the molecular weight values determined previously, have been used to calculate preliminary structural parameters for asphaltenes by use of the n-d-M method.

Weight percent-OH values, determined from ^1H NMR analysis of silylated asphaltene, afford a reasonably linear correlation with the absorbance of the monomeric OH infrared stretching band of asphaltenes and asphaltene derivative. This type of correlation should be useful as a simple means of obtaining the %OH of asphaltenes and other types of coal liquefaction products.

References

1. DOE-ERDA Report No. FE-2031-9, Sept. 1977.
2. DOE-ERDA Report No. FE-2031-10, Dec. 1977
3. H. Burrell, Polymer Handbook, Ind. Ed. Interscience, New York, 1975.
4. I. Schwager, W. C. Lee and T. F. Yen, Anal. Chem., 49, 2363 (1977).
5. DOE-ERDA Report No. FE-2031-4, June 1976.
6. K. Van Nes and H. A. Westen, "Aspects of the Constitution of Mineral Oils," Elsevier Publ. Co., New York, 1951.
7. O. Merz, Farbenchemiker, 2, 259 (1931).
8. W. C. Schumb and E.S.R. Rittner, J. Am. Chem. Soc., 65, 1692 (1943).
9. I. Schwager, P. A. Farmanian, and T. F. Yen, ACS Advances in Chem. Series, "Tar Sands and Oil Shale," 1978.
10. DOE-ERDA Report No. FE-2031-6, Dec. 1976.
11. DOE-ERDA Report No. FE-2031-7, Mar. 1977.
12. DOE-ERDA Report No. FE-2031-8, June 1977.
13. S. Friedman, L. Zahn, M. Kaufman, and I. Wender, Fuel, 40, 38 (1961).
14. F. K. Schweighardt, H. L. Retcofsky, S. Friedman, and M. Hough, Anal. Chem., 50, 368 (1978).