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HYDROGEN BONDING IN ASPHALTENES AND COAL

~~Final Report~~

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DISCLAIMER

Objective and Scope of Work

The objective of this program is to investigate and to determine the nature of hydrogen bonding and other molecular interactions that occur in asphaltene and coal liquids, and to seek possible correlations between the interactions and the viscosity. The asphaltene components of samples of centrifuged liquid product, CLP, and solvent-refined coal, SRC, supplied by the Pittsburgh Energy Research Center, are isolated by solvent fractionation. The compositions of the asphaltenes are obtained by elemental analysis and the molecular weights by vapor pressure osmometry. The acid/neutral and base components of the asphaltenes are separated and again elemental analysis and molecular weights are obtained. The magnetic resonance, infrared and calorimetric methods are used to determine the strength of hydrogen-bond and other molecular interactions in the fractions isolated. Investigations on the toluene-insoluble and heavy-oil fractions are also carried out. In addition, extensive proton magnetic resonance, near-infrared and calorimetric studies are carried out for o-phenylphenol and quinoline, which serve as model compounds for the aromatic phenols and the heteronuclear aromatic base nitrogens, respectively, found in coal liquefaction products.

Contract EY-76-S-02-0063 on Hydrogen Bonding in Asphaltenes and Coal was awarded to Duquesne University for the period Oct., 1975-Sept., 1977. The Energy Research Development Administration was reorganized in the fall of 1977 as a part of the newly created Department of Energy, and the present contract at Duquesne University received no fund extension from Oct., 1977 to March 31, 1978. This is the final report, giving a summary of activities under the Contract for the entire period.

List of Publications

1. Hydrogen Bonding Study of Quinoline and Coal-Derived Asphaltene Components with o-Phenylphenol by Proton Magnetic Resonance, S.R. Taylor, L.G. Galya, B.J. Brown and N.C. Li, Spectroscopy Letters, 9, 733-741 (1976).

2. Enthalpies of Hydrogen Bonding Reactions Involving the Acid and Base Components of a Coal-Derived Asphaltene, A.G. Dietz, C. Blaha, and N.C. Li, J. Chem. Thermodynamics, 9, 783-787 (1977).

3. Nature of Hydrogen Bonding in Coal-Derived Asphaltene, S.R. Taylor and N.C. Li, Fuel, 57, 117-121 (1978).

4. Calorimetric Study of Quinoline Interaction with o-Phenylphenol and Coal-Derived Asphaltenes, K.C. Tewari, L.G. Galya, K.M. Egan, and N.C. Li, Fuel, in press.

5. Characterization of Coal Liquid Fractions. Molar Enthalpies of Quinoline Interaction with Coal-Derived Asphaltenes and Heavy Oils, K.C. Tewari, K.M. Egan and N.C. Li, Fuel, in press.

Summary of Activities

Table 1 lists the CLP samples which we have obtained from the Pittsburgh Energy Research Center, together with the number-average molecular weights of the asphaltene (A), acid/neutral asphaltene (AA), and base asphaltene (BA) fractions isolated from the CLP samples. Runs FB 44-56, 44-99, and 50-17 were prepared from West Virginia Ireland Mine bituminous coal, while runs FB 53-1, 53-59, and 57-42 were prepared from Kentucky hvAb, Homestead Mine coal, all at 27.6 MPa (4000 psi) pressure of hydrogen and 723 K reactor temperature. Table 1, column 2, " + " indicates that for the given run the reactor was packed with Harshaw 0402 T CoMo catalyst pellets, while " - " indicates that the reactor was charged with glass beads. Isolation of asphaltenes from the CLP samples and their further separation into AA and BA components were carried out in the manner previously described[1,2]. Molecular weights were determined by vapor pressure osmometry at 1-5 g/l in benzene solvent for fractions isolated from FB 44 and FB 50, and at 12-20 g/l in toluene solvent for FB 53 and FB 57.

Additional data on two CLP samples have been given to us by Dr. B.C. Bockrath, and are listed in Table 2. CLP FB 53, batches 1 and 59, and FB 57, batch 42, were obtained after 4, 236, and 168 hours, respectively, on runs made at 4000 psi hydrogen pressure and 723K reactor temperature.

Table 3 lists representative yields of toluene-insolubles (TI), asphaltenes (A) and heavy-oil (HO) from the various CLP samples. Table 4 lists the elemental analysis of fractions of liquid products, normalized on a moisture-ash-free-basis.

Each asphaltene and heavy oil fraction isolated from CLP samples FB 53 and FB 57, was examined by high resolution proton magnetic resonance at 220 MHz. The spectra were taken as carbon disulfide solutions with tetramethylsilane (TMS) as an internal reference. The proton distribution and structural parameters such as aromaticity, f_a, the degree of substitution on aromatic rings, σ, the average length of alkyl substituents on the aromatic rings, $\frac{H_o}{H_\alpha} + 1$,

and hydrogen/carbon ratio for the hypothetical unsubstituted aromatic nuclei H_a/C_a, using Brown and Ladner equations, are given in Table 5.

We have developed a calorimetric method for the simultaneous evaluation of equilibrium constant, K, and molar enthalpy, $\Delta H°$, for 1:1 adduct formation of quinoline (Qu) with fractions of coal liquid products[4,5]. The thermodynamic parameters obtained for the interaction between quinoline and the asphaltene and heavy-oil fractions obtained from CLP FB 53-1, 53-59 and 57-42 are summarized in Table 6. These samples are all prepared from the same feed coal, Kentucky hvAb, from Homestead Mine.

For asphaltenes which were isolated from FB 50, batch 17, in which West Virginia bituminous coal from Ireland Mine was used as feed stock, we reported[5] ΔH for Qu-AA interactions in benzene to be -4.08 kcal mol^{-1}. The molar enthalpy was measured for a small quantity of AA added to 200 cm^3 of a benzene solution containing 0.1M Qu. However, K was not determined, so that the enthalpy change is actually for an unknown amount of complex formed. Assuming K = 18 (Table 6) one calculates that under the experimental conditions in ref. 5, 90% of the complex is formed, instead of 100%. The corrected $\Delta H°$ is therefore (-4.08 x 0.9) = -3.7 kcal mol^{-1}. This value for Qu-AA in benzene, where AA is obtained from West Virginia bituminous coal, is in good agreement with the value (Table 6), -3.52 + 0.01 for Qu-AA, where the acid asphaltene is obtained from Kentucky hvAb coal.

For FB 50 batch 17, we also determined[5] ΔH for BA-OPP (OPP= o-phenylphenol) in benzene to be -4.17 kcal mol^{-1}. The value of ΔH for AA-OPP in benzene is calculated[5] to be -0.40 kcal mol^{-1}. It must be mentioned that, since the degree of reaction (equilibrium constant of complex formation) is not known quantitatively, these values represent upper bounds. However, it is safe to say that there is a much higher enthalpy of interaction of OPP with the base asphaltene (ΔH = -4 kcal mol^{-1}) than with the acid component (ΔH =

-0.4 kcal mol^{-1}). If we consider OPP as the hydrogen donor, then BA functions as a much better hydrogen acceptor than AA.

Since asphaltenes are really mixtures, we have investigated molecular interaction between pure compounds which serve as models for AA and BA. The values of $\Delta H°$ for OPP-Qu systems are in line with the calorimetric results for similar systems reported by Arnett et al.[7] The values of K and $\Delta H°$, Table 6, are larger in solvent CS_2 than CCl_4 as has been observed for phenol[8] hydrogen-bonded complexes in these solvents. The solvent effect is apparent and could be attributed largely to competing equilibria between the solutes and solvent rather than to some bulk dielectric constant of the solvent. The specific interaction between CCl_4 and pyridine[9] is well recognized. Using Arnett's pure base method, we reported a value of -7.17 kcal mol^{-1} for the total interaction of OPP with Qu and -1.76 kcal mol^{-1} for the non-hydrogen bonding model donor o-phenylanisole (OPA) with Qu, assuming CCl_4 as inert model solvent. If we consider that the extent of π-interaction in the OPP-Qu system is approximately the same as in the OPA-Qu system, then $\Delta H°$ (hydrogen-bonding) for OPP-Qu is calculated to be $(-7.17 - (-1.76)) = -5.41$ kcal mol^{-1}. These values lead to an estimate of 3:1 for the relative contribution of hydrogen-bond to π-interaction in the total enthalpy change for the OPP-Qu system. For the two pure model compounds, therefore, hydrogen bonding is more important than π-interaction.

Several comments are in order concerning comparison of the fractions isolated from FB 53-1, 53-59, and 57-42. Since the observed large increase in viscosity during the run FB 53 (Table 2) may be attributed largely to partial deactivation of the catalyst bed as runtime increases, a comparison of batches 1 and 59 of run FB 53, therefore, would be between the products made with greater and lesser degree of catalytic reactions, respectively. Furthermore, because of Yavorsky's observation[3] that for a short-residence-time pre-

heater and reactor, (FB53), the viscosity of the product oil and the concentration of sulfur in it increase far more rapidly during the run than for a long-residence-time preheater (FB 57), a comparison of FB-53 and FB-57 would reflect more than just the presence and absence of catalyst in the reactor.

From Table 3 it is evident that the effect of catalyst (FB 53-1) is to decrease the yields of asphaltenes and toluene-insolubles with a corresponding increase in the yield of pentane-soluble heavy oil. The degree of coal conversion is greatest with the catalyst-packed reactor bed, and decreases as the runtime increases. Comparison of FB 53-59 and FB 57-42 indicates that a longer residence-time preheater and reactor may favor conversion and decrease the viscosity of the oil. It is interesting to note that the atomic O/C and S/C ratios decrease linearly with increase in the yield of HO fraction.

From Table 4, the average molecular weight, percentage of heteroatoms (O,N,S) and atomic C/H ratio for the three fractions isolated from a given CLP decrease in the order: TI > A >HO. The presence of active catalyst (comparison of FB 53-1 with 53-59), serves to decrease the average molecular weight, percentage of heteroatoms (S and O), percentage of toluene-insolubles and asphaltene, and to increase the atomic C/H ratio of both the TI and A fractions. These factors could be related to the effects of preasphaltene and asphaltene on the viscosity of the product oil.[10,11]

From Table 5 it is interesting to note that all three heavy oil fractions show a larger fraction of the hydrogens bound to aliphatic carbons, β or further from the aromatic rings, H_o. Process severity seems to have no effect on aromaticity, f_a, and the aromatic/benzylic hydrogen ratio. This is in agreement with the constant atomic C/H ratio for the three HO fractions observed in Table 4. We infer, therefore, that the three HO fractions are similar in molecular and structural buildup.

Asphaltene fractions show larger aromaticities, larger percent of aromatic hydrogen and smaller aliphatic branches as compared to the heavy oil fractions.

The effect of catalyst on asphaltene fraction seems to increase the aromatic/benzylic (H_a/H_α) ratio, aromaticity and atomic C/H ratio (Table 4). The use of long-residence-time preheater (FB57-42) results in similar effects as the use of catalyst (FB53-1), but to a lesser extent. We may, therefore, consider that asphaltenes contain labile benzylic hydrogens that are removed with the conversion of asphaltenes to oil.

Coal liquid fractions are complex mixtures of substituted heterocyclic aromatics and there are varying degrees of aromatic π-π , charge-transfer, H bonding and dipole-dipole interactions. The observed values of K and $\Delta H°$, therefore, correspond to the total interaction involving these equilibria. Although there is large variation in the $\Delta H°$ values, Table 6, the computed K values for the interaction of quinoline with the three asphaltene fractions or with heavy oil fractions, (from FB 53-1, 53-59 and 57-42) within experimental errors, are the same. This leads us to believe that enthalpy change is a more important measure of the strength of molecular interactions in these systems.

Since the severity of process, as mentioned earlier, has no effect on the aromaticities, aromatic/benzylic hydrogen ratio and atomic C/H ratio of the three isolated heavy oil fractions (Table 4), the observed variation of $\Delta H°$ for Qu-HO systems, could be viewed on the basis of varying degree of hydrogen-bond interactions involving largely aromatic phenols which serve as hydrogen donors to quinoline. A linear relation exists between $\Delta H°$ values and the oxygen content per mole of HO (Table 4). Although a contribution involving acidic NH as hydrogen donor can not be totally ignored, we consider that since phenol is a stronger acid, (pK_a of phenol and pyrrol at 20°C are 9.89 and ~15, respectively), it is most likely to contribute more to hydrogen-bond formation with quinoline.

The aromaticity and other structural parameters of the asphaltene fraction, to some extent, are affected by the process severity. The values of $\Delta H°$ in Qu-A systems, would possibly involve varying degrees of contributions from hydrogen-bonding and other molecular interactions. However, we have found that the observed $\Delta H°$ values increase in order of decreased aromaticity and increased oxygen content per mole, of the asphaltene fraction. We suggest that the observed large increase of $\Delta H°$ value could also largely be attributed to the hydrogen-bonding effect involving phenolic hydrogens.

Characterization of the asphaltenes and their acid and base components with thin layer chromatography showed the acid components (especially the pentane soluble fraction of the acid component) to contain acidic phenols while none were observed for the base component. PMR (60 MHz) spectra of the acid components in CS_2 showed a broad resonance at 5 ppm downfield from TMS that was assigned to the acidic (OH/NH) protons. Upon addition of a drop of D_2O, this resonance was replaced by a sharp HDO resonance at 5.4 ppm indicating complete exchange. No such deuterium exchangeable resonance was observed with the base component from FB44-56 or FB 50-17.

The OPP-OH PMR resonance undergoes downfield shift on addition of base components from FB44-56 and from FB50-17. Both base components cause a downfield shift linearly dependent upon concentration, an effect which may be ascribed to hydrogen bonding. Decreased temperature causes a greater observed downfield shift, also indicative of hydrogen-bonded interactions. Owing to excessive line broadening of the OPP-OH resonance in the presence of either base component, it was not possible to calculate equilibrium constants from these data. Neither the acid component nor the original asphaltenes cause this observed downfield shift.

Figure 1 shows the near-infrared spectra of the acid component and base component of FB44-56 in CS_2. While a weak OH absorption at 1.42 μm can be seen

for the acid component, the base component has no absorption band in this region. Figure 2 shows the n.i.r. spectrum of the pentane-soluble fraction of the acid asphaltene derived from CLP FB50-17. The OH absorption at 1.42μm in Figure 2 is clearly seen and the implications of this observation will be discussed below.

The first overtone stretching vibration of the OPP hydroxyl group occurs at 1.44 μm in CS_2 in the near infrared region. Upon addition of the base component of either CLP FB 44-56 or FB 50-17 to a 0.014M solution of OPP in CS_2, the absorbance due to the free OH group is reduced and is a linear function of the base component concentration. In agreement with our PMR results, neither of the acid components nor the original asphaltenes cause a decrease in the OPP absorbance at 1.44 μ. Figure 3 shows these results graphically. These observations provide direct evidence for the interaction of the OPP hydroxyl group with the base components.

Ultimately, one would like to study the interactions of the base asphaltene components directly with the acid asphaltene components. However, direct observation of the OH stretching vibration for the acid component is extremely difficult in the near infrared region. From Figure 1, it is seen that although the peak height at 1.42 μm is only 0.07, [A=1.53)-(A-1.46)], the absorbance at the peak is already 1.53, whereas for the pentane-soluble fraction, the peak height is actually equal to the absorbance (Fig. 2). While the observation of downfield shifts in the PMR spectrum of the acid component upon the addition of the base component has been reported,[1] quantitative data have been obtained only through the use of model compounds. Using the pentane-soluble fraction of the acid component, we have observed the change in its absorbance at 1.42 μm in CS_2 as a function of base component (FB50-17) concentration. It can be seen in Figure 4 that addition of the base asphaltene component causes the observed absorbance to decrease linearly as a function of concentration. This constitutes direct observation of complex formation between the acidic phenols separated

from the acid asphaltene component with the base asphaltene component.

It is instructive to examine the elemental analyses and molecular weights given in Table 4 for FB 44-56 and FB 50-17. In particular, one should note the similarity of results, the largest difference being the molecular weights of the two base components. While the molecular weights of the two base components are number average values, we feel that the difference for the base components is significant. It may be that the use of the catalyst (FB44-56) leads to greater degradation of the compounds which make up the base components although more evidence will be necessary to support this conclusion.

Our n.i.r. results for the interaction of base components of 44-56 and 50-17 with OPP are enlightening. The results show the direct interaction of the base components with the hydroxyl group of OPP; furthermore, it was possible to observe quantitative differences in the extent of interactions for the two base components. As shown in Fig. 3, the base component derived from CLP FB44-56 (prepared with the catalyst) is more effective in reducing the free OPP-OH absorbance than the base component derived from CLP FB50-17 (prepared with glass beads in place of the catalyst). Although, in part of Fig. 3, absorbance is plotted against moles of base component added, these data have also been plotted as grams of N added and weight of base component added, with the same overall result. Apparently, the hydrogen-bond-acceptor nature of the base component can be influenced by reaction conditions. Since this study involved only two CLP samples, we are continuing to investigate the generality of these observations.

These results implicate steric hindrance of the nitrogen in the base components as being responsible for the observed difference in the hydrogen-bond acceptor strengths of the two base components. While both base components interact very nearly equally with the small HCl molecule in the separation scheme, the base component from CLP FB50-17 does not form hydrogen-bond as effectively as the base component from FB44-56 with the larger OPP molecule. The base com-

ponent from FB50-17 also has a higher molecular weight, therefore, its nitrogen may be more hindered, giving rise to the observed difference.

In Figure 3, OPP is used as a model for the acid components of these asphaltenes. The direct observation of interaction between the acid and base components has proved to be extremely difficult due to the small OH absorbance in the n.i.r. spectrum and to the broadness[1,12] of the OH resonance in the PMR spectrum. On the other hand, we have shown that the pentane-soluble fraction of the acid component gives rise to an easily measured and observed OH absorbance in the n.i.r. region and that one can quantitatively measure the interactions of the phenolic hydroxyl groups in this fraction with the base components of asphaltenes. We feel that these results warrent the use of this pentane-soluble fraction of the acid component for studying the chemical structure and reactivity of the acid component.

Some Studies With Solvent-Refined Coal, SRC

From a solvent-refined-coal conversion product, obtained from a mixture of No. 9 and No. 14 seams of Kentucky coal, we have isolated the toluene-insoluble fraction, asphaltene, and heavy oil. The asphaltene was further separated into acid/neutral and base components by precipitation of the base component as a hydrochloride salt from a toluene solution with dry HCl gas. The base HCl adduct was then freed of HCl by the addition of a dilute (0.05 N) NaOH solution. The base and acid/neutral components were obtained in a weight ratio of 56/44. The molecular weights, obtained by vapor pressure osmometry, are 643, 674, 440, and 300 for the asphaltene, base asphaltene component, acid/neutral asphaltene component, and heavy oil, respectively.

The base asphaltene component causes a noticeable decrease in the o-phenylphenol (OPP)-OH asborance at 1.44 μ in CS_2, while the whole asphaltene and the acid/neutral asphaltene component cause only slight decrease, as shown in Figure 4. This is in agreement with the result obtained by Taylor and Li[2] for

asphaltene and its components isolated from CLP samples. The observation provides direct evidence for the interaction of the OPP hydroxyl groups with the base asphaltene component. Additional evidence for this interaction is the much greater broadening of the OPP-OH nmr signal as well as a larger extent of down-field shift of the OPP-OH nmr signal resulted from the addition of the base asphaltene component to a solution of OPP in CS_2, as compared with the addition of the acid/neutral asphaltene component.

We have measured viscosity changes on the addition of whole asphaltene, base asphaltene, and acid/neutral asphaltene to a solution of heavy oil in benzene, at 293.5K. The result is given in Fig. 5. It is seen that the acid/neutral asphaltene component exerts a smaller effect on viscosity change when compared to the addition of base asphaltene or whole asphaltene.

Although Fig. 5 is obtained for asphaltenes isolated from SRC, preliminary data on the AA and BA fractions from CLP FB53-59 show the same effect on viscosity of a solution of heavy oil in benzene. In the previous section of this report, we report that for CLP FB 50-17, there is a much higher enthalpy of interaction of OPP with the base (ΔH= -4 kcal mol^{-1}) than with the acid component (ΔH= -0.4kcal mol^{-1}), and that therefore BA functions as a much better hydrogen acceptor than AA toward OPP as the hydrogen donor. If we consider OPP as a model compound representative of the aromatic phenols in heavy oil, then the enthalpy data suggest that hydrogen bonding between heavy oil and base asphaltene has something to do with the striking effect of BA (as compared with AA) on the viscosity of heavy oil in benzene. Since the asphaltenes and heavy oils from SRC behave in a similar manner as those from CLP samples, it is reasonable to suggest that hydrogen bonding between heavy oil and base asphaltene, from both SRC and CLP samples, may be important in determining the viscosity of the solutions.

Bockrath et. al. [13] report that when solutions of acid/neutral and base

asphaltene fractions (from CLP FB 44-15 and 99) are mixed, the viscosity is larger than expected, and they attribute this effect to "complex formation, presumably due to hydrogen bonding between the acidic and basis components". They also found that BA (from FB 44-15 and 99) has a larger effect on increasing the viscosity of oil than does AA, and they correlate this with gel permeation studies[14] which show that BA is composed predominantly of molecules larger than those of AA.

In our SRC samples, the molecular weights of BA and AA are 670 and 440, respectively, so that there may also be a correlation between viscosity and molecular size; in addition to the correlation between hydrogen bonding and viscosity.

Table 1 Molecular Weights of Asphaltenes for CLP Samples

Run	Catalyst	Mass % A	Weight ratio AA/BA	M W A	M W AA	M W BA
FB44-56	+	15.2	42/58	530	380	600
FB44-99	+	20.2	39/61	530	380	600
FB50-17	-	18.4	45/55	510	390	680
FB53-1	+	19.0	48/52	680	570	960
FB53-59	+	33.3	53/47	740	620	950
FB57-42	-	28.4	47/53	530	430	680

Table 2 Residence times* and viscosities of CLP samples

CLP	Preheater residence time (minutes)	Reactor residence time (minutes)	Viscosity SSF at 82°C
FB 53-1 (Co-Mo Catalyst)	11	3	25.1
FB 53-59 (Co-Mo Catalyst)	11	3	>700**
FB 57-42 (Glass Pellets)	17	6	122-133***

*Residence time of coal slurry feed in preheater and reactor was calculated from cold-model studies.

**Too viscous for measurement.

***Viscosity of batches 41 to 43.

Table 3 Representative yields of tolerence-insolubles, asphaltenes, and heavy oil from CLP samples

CLP	Toluene - insol. (TI), %	asphaltene (A) %	Heavy Oil (HO) %
FB 44-56	6.2	15.2	78.6
FB 50-17	6.7	18.1	75.2
FB 53-1	5.6	19.0	75.4
FB 53-59	10.4	33.3	56.3
FB 57-42	9.3	28.4	62.3

Table 4 Elemental analysis of fractions of liquid products (maf)

Source	Fraction	C	H	O	N	S	Cl	Atomic C/H ratio	MW
44-56	A	87.65	5.65	3.95	1.96	0.81		1.29	530
	AA	87.3	6.05	3.4	0.85	1.02	a	1.20	380
	BA	88.3	6.15	2.9	2.16	0.32	0.27	1.20	600
	(HCl-free)								
50-17	A	86.2	5.95	3.6	1.34	0.93		1.21	510
	AA	87.5	6.2	3.4	0.83	1.03	1.06	1.18	390
	BA	87.45	5.85	3.15	2.49	0.84	0.20	1.25	680
	(HCl-free)								
53-1	TI	83.44	4.80	6.11	2.28	2.29	0.38	1.45	
	A	88.17	5.90	3.10	1.95	0.77	0.11	1.25	680
	HO	88.18	8.70	1.72	0.87	0.39	0.14	0.84	240
53-59	TI	71.79	4.41	11.48	2.05	9.86	0.41	1.36	
	A	85.83	6.46	4.42	2.02	0.88	0.39	1.11	740
	HO	86.28	8.61	3.17	1.05	0.73	0.16	0.84	290
57-42	TI	77.17	4.83	8.40	2.55	6.89	0.16	1.33	
	A	86.30	6.44	4.19	2.02	0.95	0.10	1.12	530
	AA	85.45	6.73	4.68	1.21	0.77	1.16	1.06	430
	BA	86.04	6.09	3.45	3.03	1.15	0.24	1.18	680
	(HCl-free)								
	HO	86.76	8.48	2.88	1.13	0.64	0.11	0.85	260

Table 5

Proton distribution and structural parameters of asphaltenes and heavy oils

Samples	Fraction	Area percent, PMR spectra Aromatic H_a	Benzylic* H_α	Aliphatic* H_o	Aromatic/Benzylic H_a/H_α	f_a	σ	$H_o/H_\alpha + 1$	$\frac{H_a}{C_a}$
FB53-1	HO	23.7	31.1	45.2	0.76	0.55	0.41	2.45	0.87
FB53-59	HO	23.8	31.9	44.3	0.75	0.54	0.43	2.39	0.93
FB57-42	HO	25.8	32.9	41.3	0.78	0.56	0.42	2.26	0.93
FB53-1	A	38.8	30.3	30.9	1.28	0.75	0.32	2.02	0.61
FB53-59	A	32.6	34.5	32.9	0.94	0.70	0.40	1.95	0.70
FB57-42	A	36.5	33.5	30.0	1.09	0.72	0.36	1.90	0.72

*Separation point between H_α and H_o chosen at 1.94 ppm

Table 6 Summary of Thermodynamic parameters

Source	System	K^{-1} Mole dm^{-3}	$-\Delta H^{o}$ Kcal $mole^{-1}$	$-\Delta S^{o}$ e.u.
	OPP + Qu in CCl_4	0.1607	6.64 ± 0.01	18.7
	OPP + Qu in CS_2	0.096	7.50 ± 0.02	20.5
FB 53-1	Qu + A in C_6H_6	0.0515	3.58 ± 0.03	6.1
	Qu + HO in C_6H_6	0.0323	1.01 ± 0.01	-3.4
FB 53-59	Qu + A in C_6H_6	0.0585	6.22 ± 0.03	15.2
	Qu + HO in C_6H_6	0.0352	1.98 ± 0.02	0.0
FB 57-42	Qu + A in C_6H_6	0.0532	4.04 ± 0.05	7.7
	Qu + AA in C_6H_6	0.0549	3.52 ± 0.01	6.0
	Qu + BA in C_6H_6	0.0543	2.81 ± 0.01	3.6
	Qu + HO in C_6H_6	0.0328	1.79 ± 0.03	-0.8

Legends of Figures

Figure 1 NIR spectra in CS_2 (absorbance, A, vs. wave length, μm) of (a) the acid component, 2.8 mg/ml, and (b) base component, 3.1 mg/ml, of asphaltene from CLP FB 44-56.

Figure 2 NIR spectra in CS_2 of the pentane-soluble fraction of the acid component (12 mg/ml) derived from CLP FB 50-17.

Figure 3 Variation in the OPP free-OH absorbance at 1.44μm as a function of the addition of asphaltene to a 0.014 M solution of OPP in CS_2. ▫, asphaltene from FB 50-17; △, acid component of asphaltene from FB 50-17; ., base component of asphaltene from FB 50-17; o, base component of asphaltene from FB 44-56. Curves for the asphaltene and acid component of asphaltene from FB 44-56 coincide with those for the asphaltene and acid component of asphaltene from FB 50-17.

Figure 4 Variation in the OH absorbance of the pentane-soluble fraction of the acid component derived from CLP FB 50-17 at 1.42μm in CS_2 as a function of the addition of the base component derived from CLP FB 50-17; conc. of pentant-soluble fraction-12 mg/ml.

Figure 5 Effect of asphaltenes (from SRC) on (OPP) - OH absorbance, 1.44μm in CS_2.

Figure 6 Effect of asphaltenes (from SRC) on viscosity of solutions of heavy oil (from SRC) in benzene, at 293.5 K.

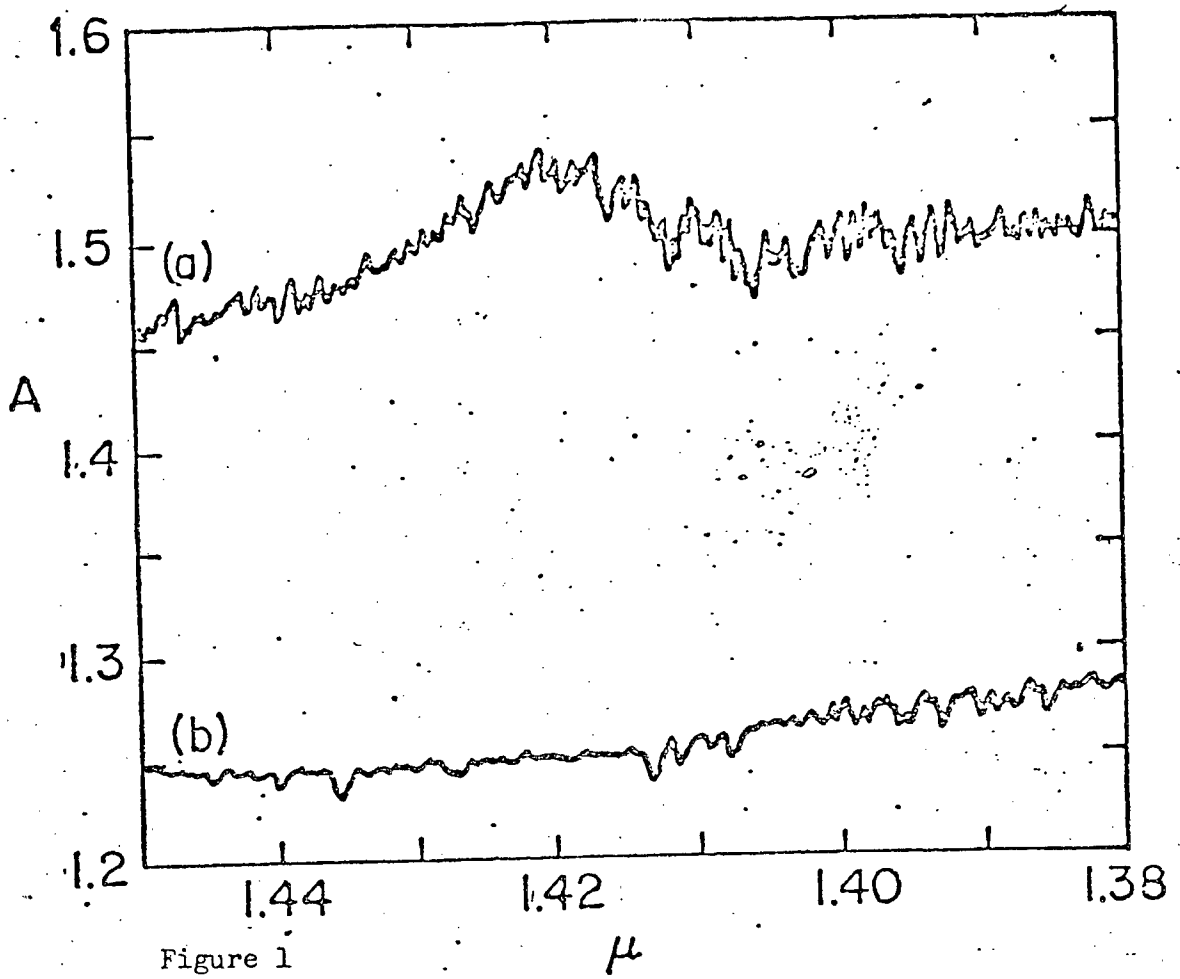

Figure 1

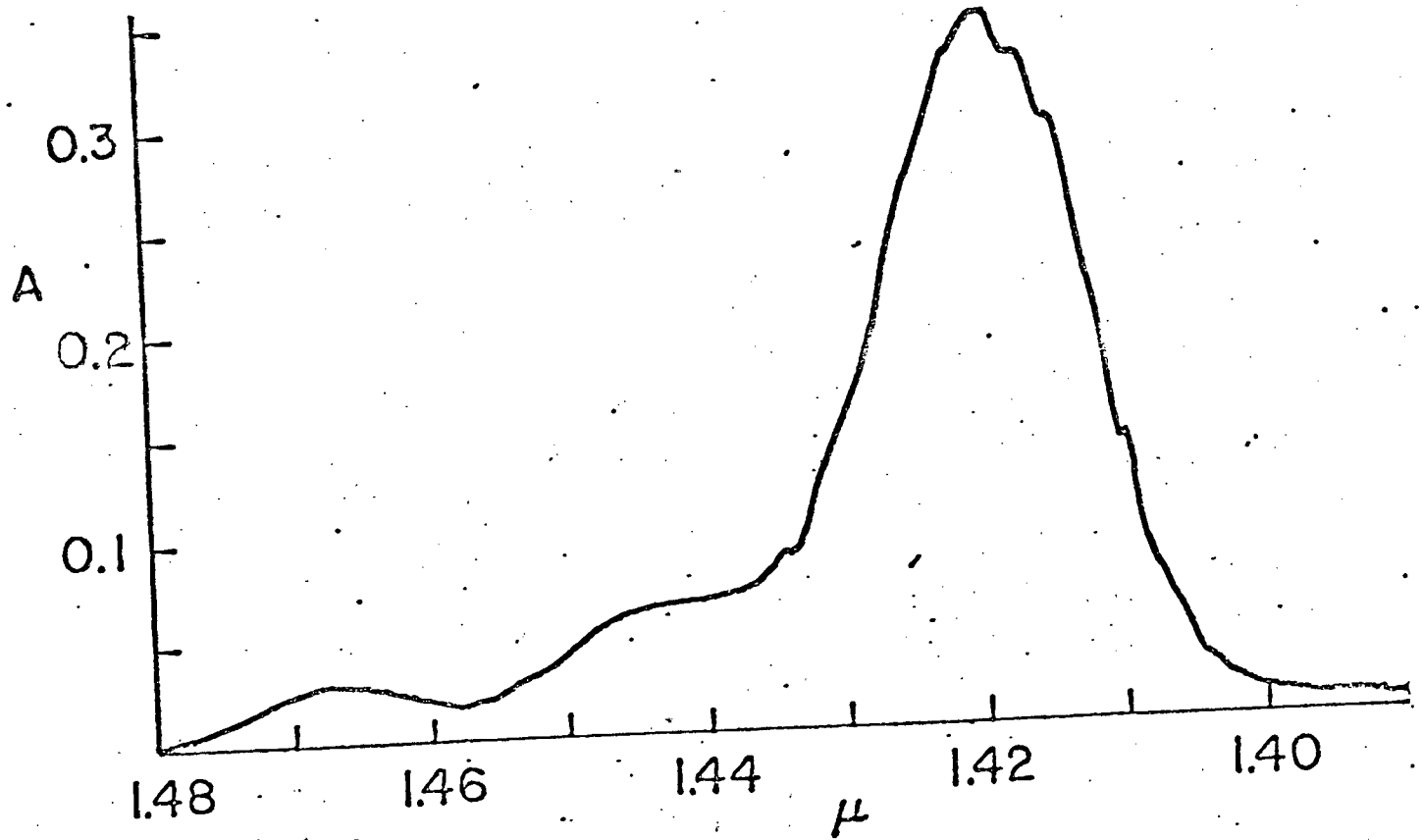

Figure 2

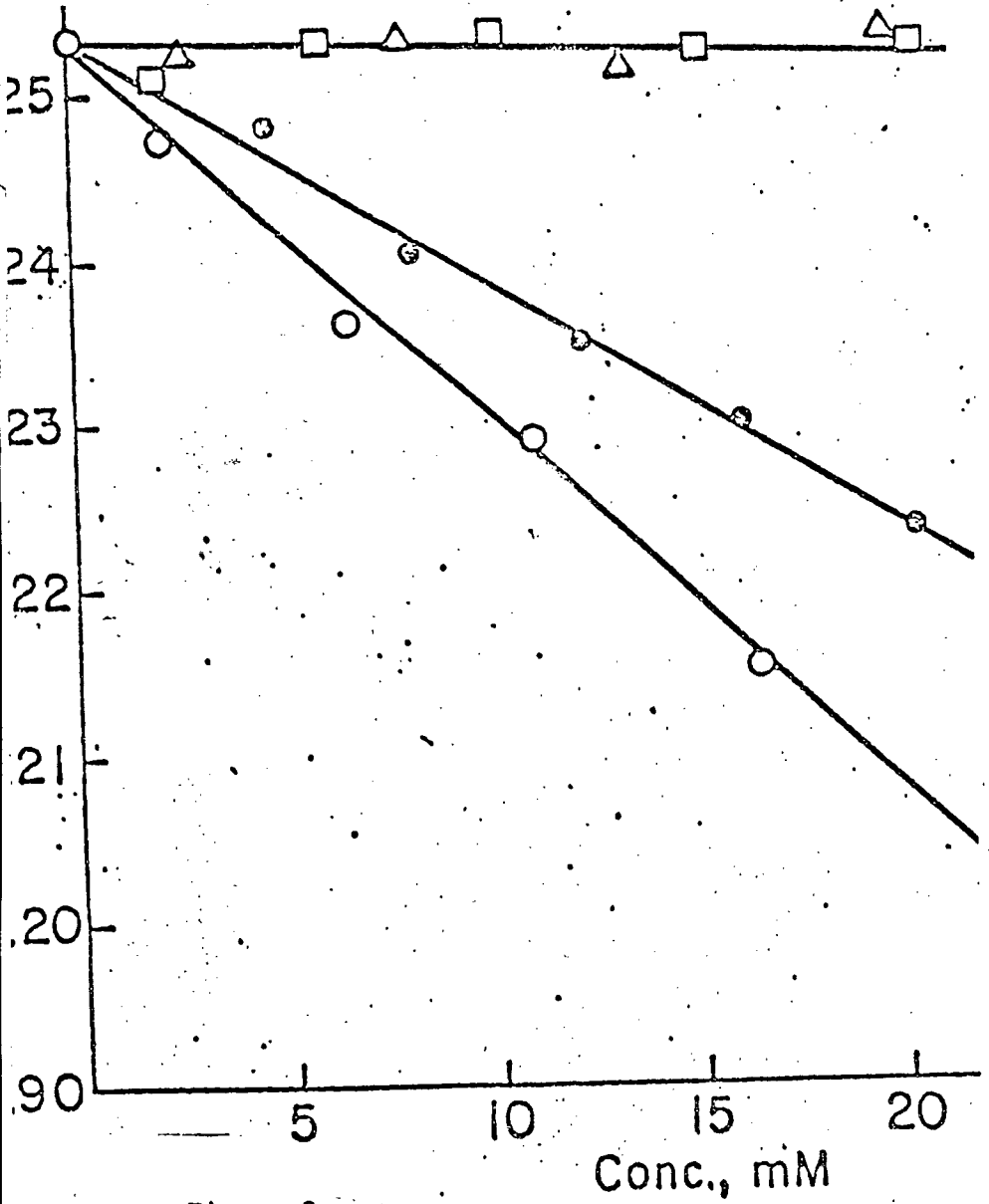

Figure 3

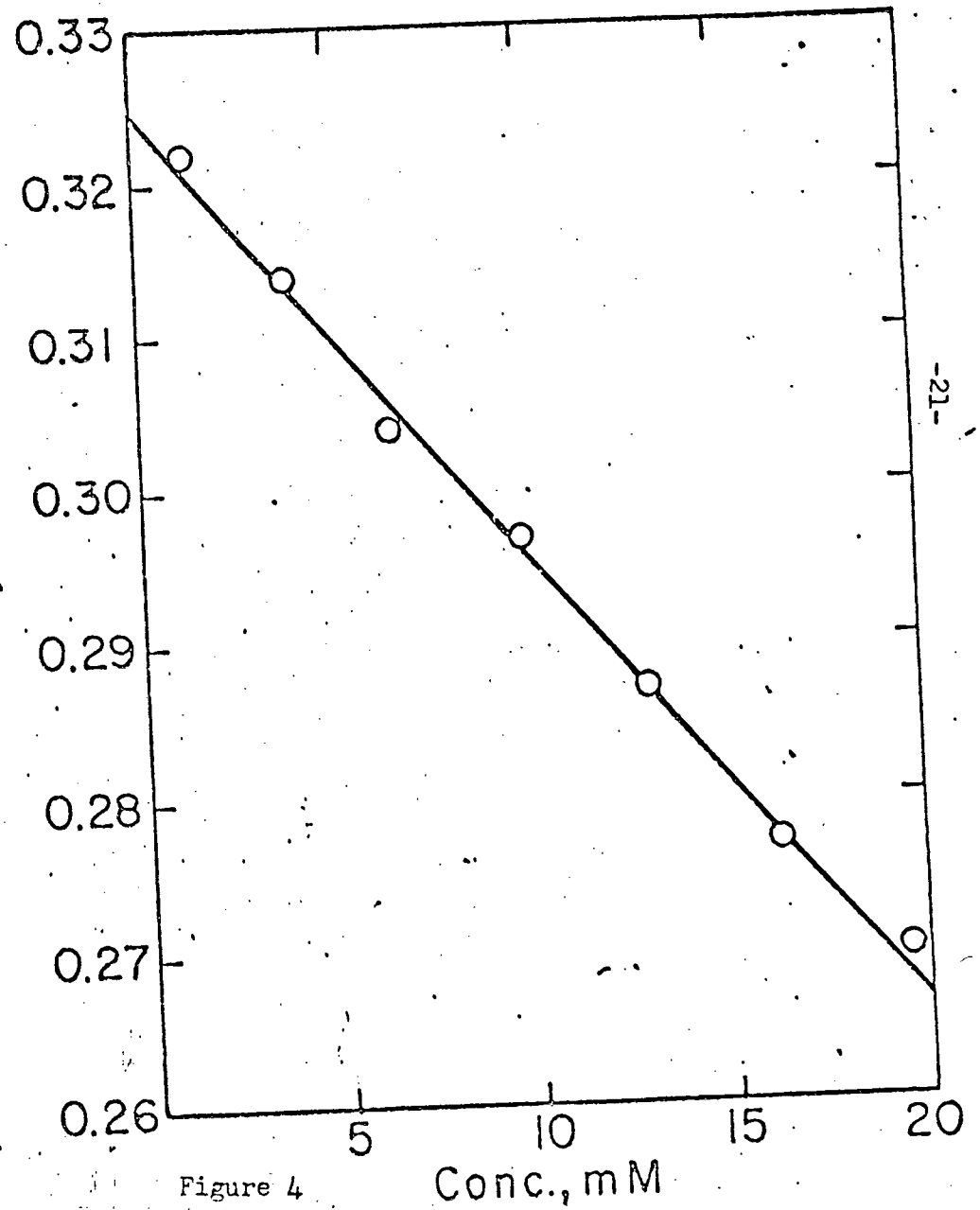

Figure 4

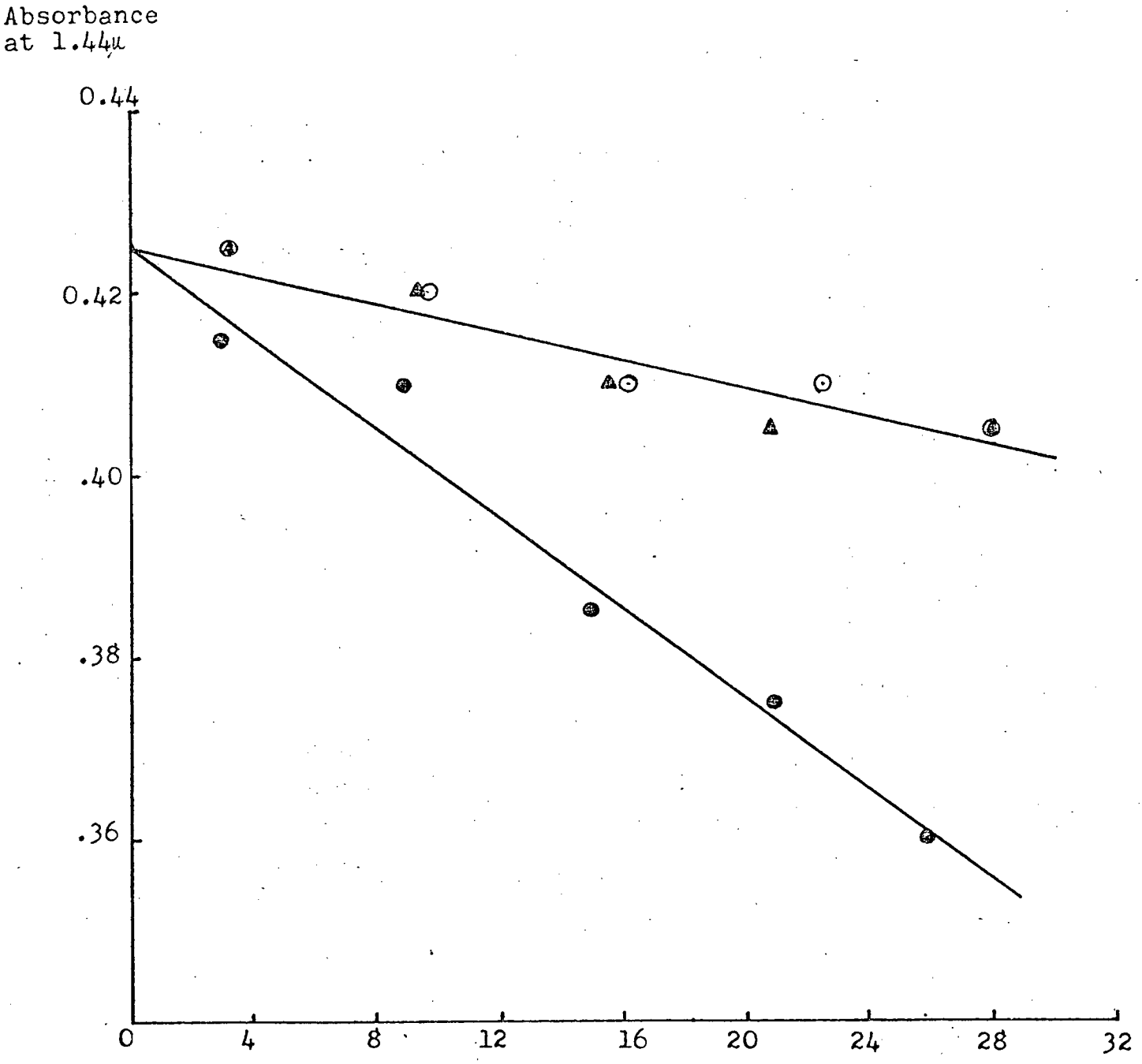
Absorbance
at 1.44μ
0.44
0.42
.40
.38
.36
0
4
8
12
16
20
24
28
32
concentration, mM
▲ , asphaltene; ○ , acid asphaltene; ● , base asphaltene

Fig 5

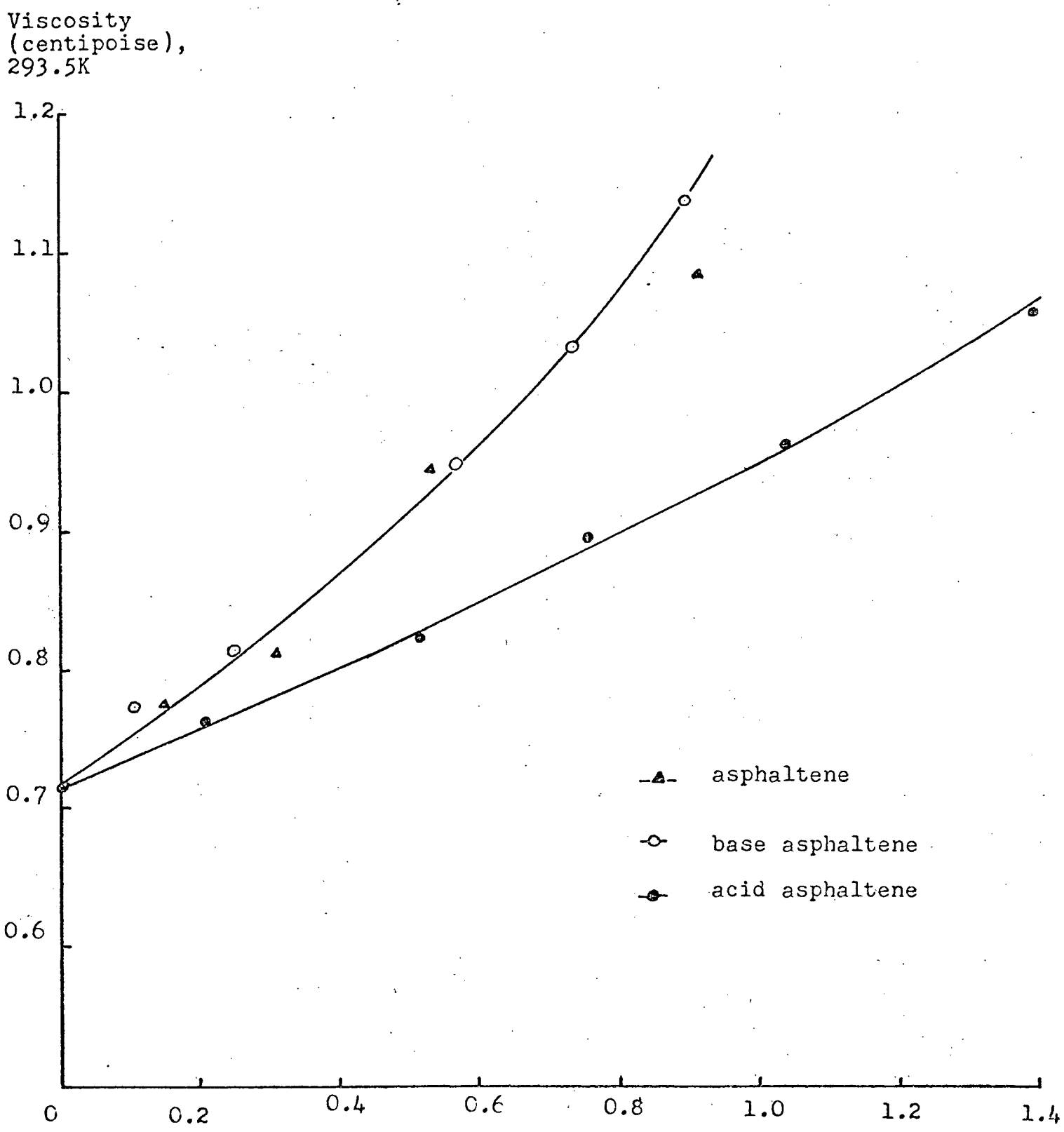
Viscosity
(centipoise),
293.5K
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
asphaltene
base asphaltene
acid asphaltene
Millimoles in 6 ml benzene containing 1.2 millimoles HO

Fig 6

Fig. 2

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   (b) B.C. Bockrath, private communication.

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PERSONNEL

The Contract, EY-76-S-02-0063, is for the period October 1975 to September 1977. The Principal Investigator devoted 1/3 of his time to the work of this Contract throughout this period. Dr. K.C. Tewari devoted 40 hours/week during calendar year 1977. The period October 1977 to March 31, 1978 represents a no-fund extension.

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