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HYDROGEN BONDING IN ASPHALTENES AND COAL

Progress Report
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DISCLAIMER

ABSTRACT

A calorimetric method is presented for the simultaneous evaluation of equilibrium constant, K, and molar enthalpy, ΔH^{o}, for 1:1 adduct formation of quinoline (Qu) with asphaltene (A), together with its acid/neutral (AA) fraction and its base (BA) fraction, isolated from a centrifuged liquid product(CLP) sample prepared from Kentucky hvAb coal at 27.6 MPa hydrogen pressure and 723K, with reactor charged with glass pellets. The same procedure was used to determine K and ΔH^{o} for 1:1 adduct formation of Qu with asphaltene and heavy oils obtained from CLP samples (FB-53) prepared with CoMo catalyst at different run times and process conditions. The effects of the CoMo catalyst, run time, and residence times on viscosity, molecular weight, ΔH^{o}, heteroatom content, contents of preasphaltene, asphaltene and heavy oil, aromaticity, and structural parameters, are determined. These findings lead us to conclude that hydrogen bonding plays an important role in determining viscosity, and contributes more to the enthalpy of interaction then does π- interaction.

We have also isolated the toluene-insoluble fraction, asphaltene (whole, acid/neutral and base fractions), and heavy oil from a solvent-refined-coal (SRC) conversion product. Data obtained from several infrared and viscosity experiments indicate that the behavior of different fractions isolated from SRC is similar to that of corresponding fractions isolated from CLP samples.

Objective and Scope of Work

The objective of this program is to investigate and to determine the nature and strength of hydrogen bonding and other molecular interactions that occur in asphaltene and coal, and to seek possible correlation with the viscosity of the product oil. The asphaltene components of samples of SYNTHOIL centrifuged liquid product, CLP, and solvent refined coal, SRC, product are isolated. The compositions of the asphaltenes are obtained by elemental analysis and the molecular weights obtained by vapor pressure osmometry. The acid and base components of the asphaltenes are separated and again elementary 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 preasphaltene and heavy oil fractions are also carried out.

During the period March, 1977 - August, 1977 the following tasks have been completed:

Part 1 Calorimetric study of quinoline interaction with o-phenyl phenol and coal-derived asphaltenes.

Part 11 Characterization of coal liquid fractions. Molar enthalpies of quinoline interactions with asphaltenes and heavy oils.

Part 111 Some studies with solvent-refined-coal, SRC.

The details of Parts 1 to 111 are as follows:

Part I

Calorimetric Study of Quinoline Interaction with o-Phenylphenol and Coal-Derived Asphaltenes

Krishna C. Tewari, Laurine G. Galya, Kenneth M. Egan and Norman C. Li

A calorimetric method is presented for the simultaneous evaluation of equilibrium constant, K, and molar enthalpy, ΔH^o, for 1:1 adduct formation of quinoline (Qu) with coal-derived asphaltenes in solvent benzene. Asphaltene (A), together with its acid/neutral (AA) and base (BA) fractions used in this study were isolated from a centrifuged liquid product (CLP) sample prepared from Kentucky hvAb coal at 27.6 MPa hydrogen pressure and 723K, with reactor charged with glass pellets. The computed K values for the interaction of Qu and A, AA, and BA are, within experimental error, the same, 18-19 $dm^3\ mol^{-1}$, whereas there is large variation in the ΔH^o values (Qu - A, -4.04 ± 0.05 kcal mol^{-1}; Qu - AA, -3.52 ± 0.01 kcal mol^{-1}; Qu - BA, -2.81 ± 0.01 kcal mol^{-1}). For Qu - A and Qu - AA systems, hydrogen bonding occurs between the aromatic phenols (present in A and AA) and quinoline, which is a strong hydrogen-bond acceptor, in addition to other molecular interactions. The hydrogen-bonding interaction in the Qu-BA system is lacking because both Qu and BA are hydrogen-bond acceptors. Since asphaltenes are really mixtures, we have taken a pure compound, o-phenylphenol (OPP), and obtained thermodynamic parameters for its interaction with quinoline (Qu). OPP was chosen to represent the aromatic phenols found in coal liquefaction products. Results obtained are:

K, M^{-1}: 10.4 (in CS_2), 6.2 (in CCl_4); ΔH^o, kcal mol^{-1}: -7.50 (in CS_2), -6.64 (in CCl_4). The solvent effect is apparent. By using o-phenylanisole as a model non-hydrogen-bonding donor (Dietz, Blaha, Li, J. Chem. Thermodynamics in press), the relative contribution of H-bond to π-interactions in the total enthalpy change for the OPP-Qu system is estimated to be 3:1.

The deliverables of Part I are:

Table 1	Elemental analysis and molecular weights of asphaltene isolated from CLP sample, FB 57 batch 42. The run was made with Kentucky hvAb coal at 27.6 MPa hydrogen pressure at 723K, with reactor charged with glass pellets.
Table 2	Enthalpies of solution of o-phenylphenol in CCl_4 and CS_2, and of quinoline in C_6H_6.
Table 3	Thermodynamic constants of quinoline interaction with o-phenylphenol and asphaltene from FB 57-42.

TABLE 1

Ultimate Analysis of Asphaltene

Fraction	C	H	O	N	S	Cl	Molecular Weight
A	86.30	6.44	4.19	2.02	0.95	0.10	532
AA	85.45	6.73	4.68	1.21	0.77	1.16	429
BA (HCl-free)	86.04	6.09	3.45	3.03	1.15	0.24	680

TABLE 2

Enthalpies of solution* at 298 ± 0.5K

Solute	Solvent	Millimoles of solute added to 200cm3 of solvent	ΔH obsd. cal.	ΔH_s kcal mol^{-1}
OPP	CCl_4	0.623	2.94	4.72
		1.941	9.33	4.81
		3.757	18.10	4.82
		5.622	27.06	4.81
		6.322	30.60	4.84
				Ave. +4.80 ± 0.05
	CS_2	0.661	3.62	5.48
		1.371	7.49	5.46
		2.080	11.35	5.46
		2.844	15.63	5.50
		3.443	18.96	5.51
		4.087	22.39	5.48
				Ave. +5.48 ± 0.02
Qu	C_6H_6	5.660	0.41	0.072
		10.571	0.75	0.071
		16.375	1.17	0.071
		23.606	1.55	0.066
		29.266	1.98	0.068
		34.177	2.31	0.068
		39.981	2.71	0.068
		47.212	3.09	0.065
				Ave. +0.070 ± 0.003

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*Uncertainties are standard deviations.

TABLE 3

Summary of Thermodynamic Constants at 298 ± 0.5K

System	Solvent	K, $dm^3 mol^{-1}$	$-\Delta H^o$ kcal mol^{-1}
Qu + OPP	CCl_4	6.2	6.64 ± 0.01
Qu + OPP	CS_2	10.4	7.50 ± 0.02
Qu + A	C_6H_6	18.8	4.04 ± 0.05
Qu + AA	C_6H_6	18.2	3.52 ± 0.01
Qu + BA	C_6H_6	18.4	2.81 ± 0.01

Part II

Characterization of Coal Liquid Fractions. Molar Enthalpies of Quinoline Interaction with Asphaltenes and Heavy Oils.

Krishna C. Tewari, Kenneth M. Egan and Norman C. Li

The toluene insoluble (TI), asphaltene (A), and heavy oil (HO) fractions from three centrifuged liquid product (CLP) samples, prepared from the same feed coal, Kentucky hvAb, from Homestead Mine, were isolated. Run FB 53 was made with CoMo catalyst, 11-min preheater residence time, and 3-min reactor residence time at 723K, 27.6 MPa hydrogen pressure. Batches 1 and 59 of FB 53 represent samples taken at 4 and 236 hours, respectively, after the run started. The viscosities of FB 53-1, FB 53-59 are 25.1 and >700 SSF, respectively, at 355K, and the viscosity increase has been attributed to partial deactivation of the catalyst bed as the run time increases. We find that the much greater viscosity of FB 53-59 correlates with the larger contents of its toluene-insolubles and asphaltene, larger oxygen and sulfur contents of its asphaltene and toluene-insolubles, larger molecular weight and smaller aromaticity of its asphaltene, and the larger enthalpy of interaction (ΔH^o) of its asphaltene with quinoline in benzene. These correlations indicate that hydrogen-bonding plays a more important role in determining viscosity than π-interactions, since the asphaltene from FB 53-59 has smaller aromaticity than that from FB 53-1, and yet the observed ΔH^o with quinoline is greater for the asphaltene made from batch 59. A larger oxygen content for the asphaltene from 53-59 indicates that this sample contains more phenols, hence it acts as a stronger hydrogen donor to quinoline that does the asphaltene from FB 53-1. The oxygen content of the heavy oil from FB 53-59 is also greater than that from FB 53-1, and the value of ΔH^o of the heavy oil with quinoline follows the same order. Since a majority of oxygen is in the form of hydroxyl groups and since the aromaticity of the heavy oil from 53-1 and 53-59 is about the same, the higher ΔH^o of the quinoline-HO (from 53-59) indicates that hydrogen bonding contributes more to the enthalpy of interaction than does π-interaction.

Run FB 57 was made with glass pellets in the reactor at 723K, 27.6 MPa hydrogen pressure, 17-min preheater residence time and 6-min reactor residence time (longer residence times than FB 53). Since in FB 53-59, the CoMo catalyst has lost part of its activity, a comparison of FB 53-59 with FB 57 yields information on the effect of residence times on the properties. The toluene insoluble and asphaltene contents, as well as the viscosity, of FB 53-59 are larger, while the heavy oil content of FB 53-59 is smaller than that of FB 57. This comparison indicates that the conversion, as well as the viscosity of the product oil, become more favorable with a larger residence time preheater and reactor. The values of ΔH^{o} for the interaction of quinoline with the heavy oil and asphaltene fractions obtained from the three CLP samples are in the order:

FB 53-59 > FB 57-42 > FB53-1.

The deliverables of Part II are:

Table 1	Viscosities and solvent analysis of coal liquid products
Table 2	Ultimate analysis of fractions of liquid products
Table 3	Proton distribution and structural parameters of asphaltenes and heavy oils
Table 4	Summary of thermodynamics constants at 298K

Table 1

Viscosities[11] and solvent analyses of liquid products

CLP	Viscosity SSF at 355K	Distribution, wt. percent, ash-free		
		Toluene-insolubles (TI)	Asphaltene (A)	Heavy Oil (HO)
FB53-1(Co Mo Catalyst)	25.1	5.6	19.0	75.4
FB53-59(CoMo Catalyst)	>700*	10.4	33.3	56.3
FB57-42(glass pellets)	122-133**	9.3	28.4	62.3

*Too viscous for measurement.

**Viscosity of batches 41 to 43.

Table 2

Ultimate analysis of fractions of liquid products (maf)

Source	Fraction	Sp. gravity 22°C	C	H	O	N	S	Cl	Atomic C/H ratio	$\overline{\text{Mn}}$ Mol. wt.
FB53-1	A		88.17	5.90	3.10	1.95	0.77	0.11	1.25	683
	HO	1.0297	88.18	8.70	1.72	0.87	0.39	0.14	0.84	238
	TI		83.44	4.80	6.11	2.28	2.29	0.38	1.45	-
FB53-59	A		85.83	6.46	4.42	2.02	0.88	0.39	1.11	742
	HO	1.0583	86.28	8.61	3.17	1.05	0.73	0.16	0.84	289
	TI		71.79	4.41	11.48	2.05	9.86	0.41	1.36	-
FB57-42	A		86.30	6.44	4.19	2.02	0.95	0.10	1.12	532
	HO	1.0421	86.76	8.48	2.88	1.13	0.64	0.11	0.85	264
	TI		77.17	4.83	8.40	2.55	6.89	0.16	1.33	-

Table 3

Proton distribution and structural parameters of asphaltenes and heavy oils

Samples	Fraction	Area percent, PMR spectra			Aromatic/Benzylic	f_a	σ	$H_o/H_\alpha + 1$	$\frac{H_a}{C_a}$
		Aromatic H_a	Benzylic* H_α	Aliphatic* H_o	H_a/H_α				
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

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*Separation point between H_α and H_o chosen at 1.94 ppm

Table 4

Summary of Thermodynamic Constants at 298 ± 0.5K

System	Source	K^{-1} mol dm^{-3}	$-\Delta H°$ Kcal mol^{-1}
Qu + HO in C_6H_6	FB53-1	0.0323	1.01 ±0.01
	FB53-59	0.0352	1.98 ±0.02
	FB57-42	0.0328	1.79 ±0.03
Qu + A in C_6H_6	FB53-1	0.0515	3.58 ±0.03
	FB53-59	0.0585	6.22 ± 0.03
	FB57-42	0.0532	4.04 ±0.05

Part III

Some studies with solvent-refined coal, SRC

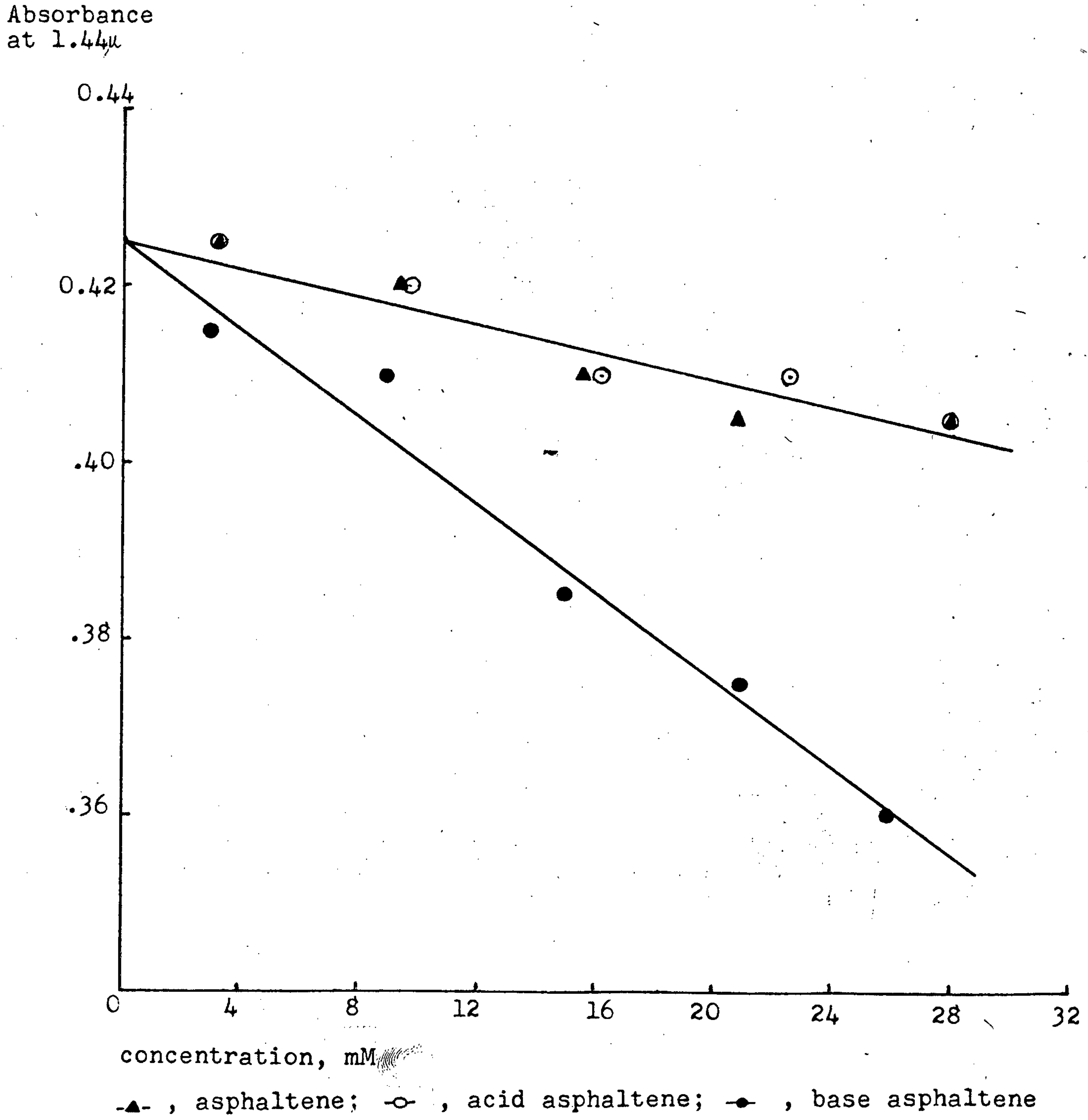
From a solvent-refined-coal conversion product, obtained from a mixture of No. 9 and No. 14 seams of Kentucky coal, we have isolated the toluene-insoluble fraction, asphaltene, and heavy oil. The asphaltene was further separated into acid/neutral and base components by precipitation of the base component 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.

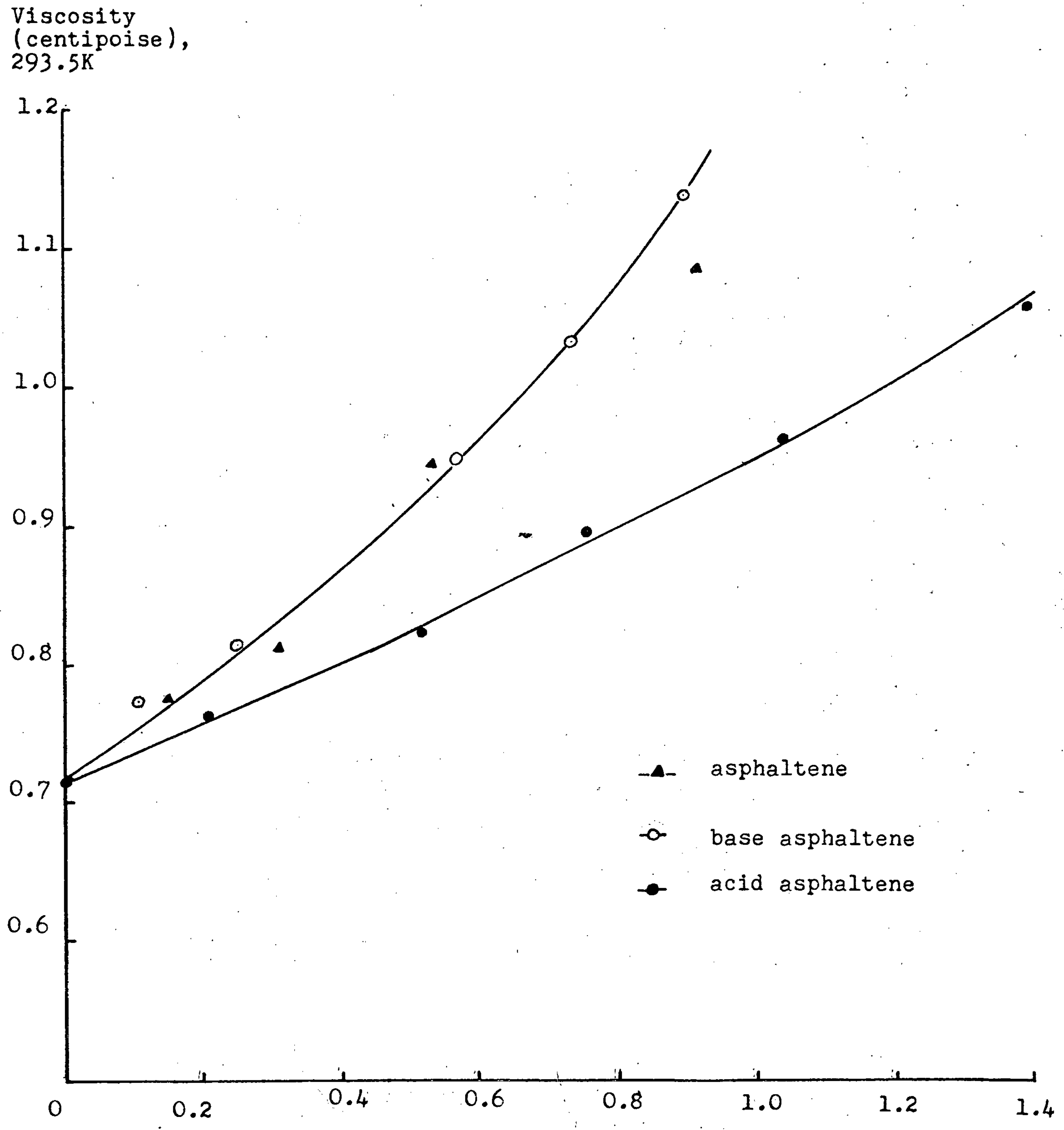
The base asphaltene component causes a noticeable decrease in the o-phenylphenol (OPP)-OH asborbance at 1.44 μ in CS_2, while the whole asphaltene and the acid/neutral asphaltene component cause only slight decrease, as shown in Figure 1. This is in agreement with the result obtained by Taylor and Li[1] 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 downfield 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. 2. 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.

Our result with solvent-refined-coal products on viscosity changes is similar to that found by Bockrath et al. for SYNTHOIL process liquid product[2].

1. S.R. Taylor and N.C. Li, Fuel.
2. B.C. Bockrath, R. B. La Count, and R.P. Noceti, private communication.


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


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
Millimoles in 6 ml benzene containing 1.2 millimoles HO
▲ asphaltene
○ base asphaltene
● acid asphaltene

Personnel

The Contract, EY-76-S-02-0063, is for the period October 1, 1975 to Sept. 30, 1977. The Principal Investigator devotes 1/3 of his time to the work of this Contract throughout this period. Persons who have contributed to this investigation described in this Progress Report are:

Research Assocate: Dr. K.C. Tewari, 100% time

Assistant Prof. Chemistry: Dr. J.T. Wang, one-month, July, 1977

Students: Laurine G. Galya, Kenneth M. Egan, Robert Maurer

Technician: Shian-Shi Shu, 100% time

Publications

1. S.R. Taylor, L.G. Galya, B.J. Brown, N.C. Li, Hydrogen Bonding Study of Quinoline and Coal-Derived Asphaltene Component with o-Phenylphenol by Proton Magnetic Resonance, Spectroscopy Lett., 9, 733 (1976).
2. A.G. Dietz, C. Blaha, N.C. Li, Enthalpies of Hydrogen-Bonding of Quinoline with o-Phenylphenol and of Hydrogen-Bonding Reactions Involving the Acid and Base Components of a Coal-Derived Asphaltene, J. Chem. Thermodynamics, in press.
3. S.R. Taylor and N.C. Li, On the Nature of Hydrogen-Bonding in Coal-Derived Asphaltenes, Fuel.
4. K.C. Tewari, L.G. Galya, K.M. Egan, and N.C. Li, Calorimetric Study of Quinoline Interaction with o-Phenylphenol and Coal-Derived Asphaltenes, Fuel.
5. K.C. Tewari, K.M. Egan, and N.C. Li, Characterization of Coal Liquid Fractions, Molar Enthalpies of Quinoline Interactions with Coal-Derived Asphaltenes and Heavy Oils, manuscript in preparation for Fuel.