HYDROGEN BONDING IN ASPHALTENES AND COAL

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Objective and Scope of Work

The objective of this program is to investigate the nature and strength of hydrogen bonding and other molecular interactions that occur in asphaltene and coal liquids, and to seek possible correlation with the viscosity of the product oil. During the period July 1, 1978 - Sept. 30, 1978, the paper on "Molecular Interaction of Quinoline with Coal Liquid Fractions", by K.C. Tewari, J.T. Wang, N.C. Li, and H.J.C. Yeh, has been accepted for publication by FUEL. The content of the paper has been reported in a previous Progress Report, COO-63-9. We have also completed a manuscript on "Viscosity, Calorimetric, and Proton Magnetic Resonance Studies on Coal Liquid Fractions in Solution," by K.C. Tewari, N.S. Kan, D.M. Susco, and N.C. Li. The details are as follows:

Abstract

Two coal liquid products derived from the same Kentucky hvAb coal have been separated into toluene-insoluble, asphaltene, and pentane-soluble heavy oil fractions. Viscosity and calorimetric studies are reported of the interaction between heavy oil and asphaltene(A) and its acid/neutral(AA) and base(BA) components in solvent benzene. The increase in viscosity and molar enthalpy of interaction, ΔH° , in the order $BA > A > AA$, correlate well with the proton magnetic resonance downfield chemical shift of the OH signal of o-phenylphenol, as a function of added asphaltene (A, AA, BA) concentration in solvent CS_2 . The results suggest that when asphaltene and heavy oil are present together, hydrogen-bonding involving largely phenolic OH, is one of the mechanisms by which asphaltene-heavy oil interactions are achieved and, in part, is responsible for the viscosity increase of coal liquids.

The high viscosity at ambient temperature of coal liquids, derived from hydrogenation processes, has been a major concern in the direct use of the coal liquids as a boiler fuel. The viscosity of these liquid products has been related to the asphaltene (toluene-soluble, pentane-insoluble) and preasphaltene (toluene-insoluble, pyridine-soluble) fractions (1-5). Although the effect of preasphaltene concentration on the viscosity of coal liquids is dramatic, the increase caused by asphaltene materials has been suggested to be due to acid-base interactions (2,4) between hydroxyl or acidic nitrogen and basic nitrogen functions causing molecular aggregation and a corresponding trend toward highly viscous liquids. Recently, the effect of the heavy ends of coal liquids on viscosity has been studied by Schiller et al(6). They, however, observe that hydrogen bonding is more important in defining the effect of asphaltene on viscosity than are acid-base salt formation interactions.

We report here the effect of asphaltene concentration on the viscosity of benzene solutions containing pentane-soluble heavy oil (HO) fraction of the same coal liquid, and the observed correlation of viscosity change with calorimetric and proton magnetic resonance results. The data suggest that when asphaltene and HO are present together, hydrogen-bonding involving largely phenolic OH, is one of the mechanisms by which asphaltene-heavy oil interactions are achieved, and in part is responsible for the viscosity increase of coal liquids.

Experimental

Centrifuged liquid product (CLP) samples, FB53-59 and FB57-42 were obtained from 450 kg ($\frac{1}{2}$ ton) per-day Process Development Unit at Pittsburgh Energy Research Center, after 236 and 168 hours, respectively, and were prepared from the same feed coal, Kentucky hvAb, from Homestead Mine, at 27.6 MPa (4000 psi) hydrogen pressure and 723K reactor temperature. Run FB53-59 was made with the reactor packed with Harshaw 0402T CoMo catalyst, 11-min preheater and 3-min reactor residence time while run FB57-42 was made with reactor charged with glass pellets, 17-min preheater and 6-min reactor residence time (residence time of coal slurry feed in preheater and reactor was calculated from cold-Model studies). The isolation of toluene-insoluble (TI), asphaltene(A) and H₀ fractions from the two CLP samples was accomplished by solvent fractionation based upon solubility in toluene and pentane. The A fraction was further separated into acid/neutral (AA) and base (BA) components by bubbling dry hydrogen chloride gas through a stirred toluene solution. Details of these isolation methods have been previously described(7,8). Traces of residual solvent from dried asphaltene samples were removed by freeze-drying a dispersion of the isolated fraction in benzene. For liquid H₀ fraction, dry nitrogen was passed for 8-10 hrs at room temperature.

o-Phenylphenol (OPP) was obtained from Eastman Kodak Co., purified by recrystallization from ether and stored in a vacuum desiccator at 130 Pa (1mm Hg) at room temperature. Benzene was of Fisher pesticide grade dried over 4A molecular sieves. Carbon disulfide (CS₂) was purified as described previously(9). The molecular weights were determined on a Mechrolab 301A vapor pressure osmometer at 10-20 g/dm³ in toluene solutions. The solution viscosities were determined by Ostwald viscometer at 293K. Viscosity data reported here are with respect to water whose viscosity(10) was taken as 1.002 centipoise at 293K. Proton magnetic resonance (PMR) spectra were obtained at 220 MHz and 60 MHz as CS₂ solutions with tetramethylsilane (TMS) as an internal reference.

Hydroxyl silylation: 20 cm³ of hexamethyldisilazane and 10 cm³ of N-trimethylsilyldiethylamine were added to 100 cm³ of benzene containing 2g asphaltene or HO sample. The mixture was slowly refluxed under nitrogen for 18 hrs. The solvent and unreacted reagents were removed on a Rotavap at 333K. Nitrogen was then flushed to ensure dryness. The residue was repeatedly dissolved in benzene and dried as before. To ensure nearly complete removal of reagents, the silylated asphaltene residue was finally freeze-dried from 10 cm³ of benzene for 3 hrs. In case of silylated HO fraction, dry nitrogen was passed for 8-10 hrs. The formation of HO or asphaltene trimethylsilyl ether was checked by infrared spectroscopy for complete disappearance of the free phenolic or alcoholic OH absorption at 3600 cm⁻¹. Representative partial infrared spectra of HO fraction before and after silylation are shown in Figure 1. No significant change in intensity of infrared absorption band at 3480 cm⁻¹, assigned(11) to free NH groups of pyrrole or carbazole, was observed after silylation, indicating that the silylated HO or asphaltene derivative was substantially derived from hydroxyl moieties.

Calorimetric measurements: The calorimeter was essentially that designed by Arnett(12), except that the systematic base-line drifts on the recorder were compensated by extremely slow passage of dry nitrogen through the teflon top well over the solution surface in the cell. All solutions were prepared in a dry box. A gas-tight Hamilton syringe with chaney adaptor was used for the introduction of the liquid sample of HO in benzene. The heat of reaction, corrected for the heat of dilution, was determined by injecting a benzene solution of HO of known concentration into the calorimeter cell containing known amount of asphaltene fraction in benzene. Each successive measured heat and the moles of HO injected in the cell solution were added to the previous total measured heat and moles injected. The range of reactant concentrations were chosen to satisfy as nearly as possible the criteria outlined by Conrow et al.(13). Accuracy of the calorimeter was checked against accepted value for the heat of solution of potassium chloride(14,15) in water.

The molar enthalpy, ΔH° , and equilibrium constant, K, for a 1:1 complexation

in a donor-acceptor type reaction $A + B \rightleftharpoons C$, were determined simultaneously from the Bolles and Drago(16) equation

$$K^{-1} = \frac{\Delta H'}{v\Delta H^{\circ}} + \frac{A_0 B_0 v \Delta H^{\circ}}{\Delta H'} - (A_0 + B_0) \quad (1)$$

where A_0 and B_0 are the initial concentrations of A and B respectively, v is the volume in dm^3 of the solution and $\Delta H'$ is the measured heat of formation for an unknown amount of complex corrected for the heat of solution of the added reagent at the corresponding concentration.

RESULTS AND DISCUSSION

The viscosities(17) at 355K of the two CLP samples, FB53-59 and FB57-42, from the same feed coal Kentucky hvAb, were >700 and ~128 Saybolt seconds, respectively. The high viscosity of the catalytic run, FB53-59, may be attributed largely to partial deactivation of the catalyst bed. Solvent fractionation gave the weight percent distribution of TI, A and HO fractions in FB53-59 as 10.4, 33.3 and 56.3 respectively, and in FB57-42 as 9.3, 28.3 and 62.3 respectively. Further separation of A from FB53-59 and FB57-42 into AA and BA components gave the weight ratio AA/BA of 53.1/46.9 and 46.7/53.3 respectively. The results indicate that the low viscosity liquid, FB57-42, contains lower weight content of TI, A and higher weight percent of BA in A fraction. The long-residence-time preheater and reactor seem to favor conversion as well as decrease the viscosity of the product oil. The results of ultimate analyses and molecular weight determinations for the asphaltene and HO fractions are given in Table I. It is interesting to note that asphaltene (A,AA, BA) and HO fractions isolated from the low viscosity liquid, as compared to similar fractions from the high viscosity liquid product (FB53-59), have lower molecular weight, lower oxygen content, higher nitrogen content, and higher C/H ratio.

To understand the effect of asphaltene fraction on the viscosity of the liquid product and the nature of interaction involved, the viscosities at 293K were

measured of benzene solutions of H₀(0.305M) containing varying amounts of individual asphaltene fractions. The relative viscosity (η_r) change with concentration of AA and BA, isolated from FB57-42, are shown in Figure 2 (curves 2 and 5). The results indicate that at a given temperature and concentration (above 0.035M) BA has a larger effect on viscosity than AA. Although the limited solubility of unfractionated A restricted the viscosity measurement above 0.035M, where marked changes in viscosity were observed, however, it is interesting to note that Bockrath, et al. (4), have shown that the viscosity values for BA in pure H₀ are slightly greater than that of A in H₀. The observed order of increase in η_r (BA > AA) correlates well with the increase in molecular weight, nitrogen content and decrease in oxygen content, Table I, of the added asphaltene fraction. Since coal-derived asphaltenes are known to associate even in dilute solution and more significantly in non-polar solvent (18), the contribution of molecular size and molecular weight on the observed viscosity could be seen qualitatively from the variation of η_r with concentration of added asphaltene fraction in pure benzene as solvent, as shown in Figure 2, curves 1, 3, and 4. It should be noted that at a given temperature and concentration, η_r varies linearly with the molecular weight of the added fraction (Figure 2, curves 1, 3, and 4 refer to asphaltene fractions of molecular weight 430, 620, and 680, respectively). At a given concentration, for a given fraction (AA or BA), the value of η_r in benzene as solvent is smaller than that for the same fraction in benzene containing H₀ as solvent. Furthermore, in the presence of H₀ and at a given concentration of asphaltene, the increase in η_r for BA is larger than that observed for AA. Since solvent benzene is less polar than benzene containing H₀, and since nitrogen and oxygen are largely present (2) as basic ring nitrogen and ring or ether oxygen in BA and as acid nitrogen and phenolic hydroxyl in AA, it is reasonable to assume that beside the molecular weight of the added asphaltene fraction, part of effect on viscosity is due to the functional groups. The H₀ fraction contains phenolic or alcoholic hydroxyl as well as acidic NH

groups which serve as hydrogen donors in intermolecular association. PMR analysis of the silylated H₀ fractions from FB53-59 and FB57-42 shows respectively 83% and 80% of the oxygen present is in the form of phenolic/or alcoholic hydroxyl. The contribution involving pyrrol type imino groups as hydrogen donors, however, is negligible since pK_a of phenol and pyrrol at 293K are 9.89 and -15 respectively. Furthermore, A, AA and BA having phenolic H, can likewise act as proton donors to H₀ in these systems. It must be mentioned that contrary to thin-layer chromatographic (TLC) analyses of Sternberg *et al.*(2) the infrared spectrum(19,20) of the base component (BA) of coal-derived asphaltene shows distinct absorption of free phenolic/or alcoholic OH and NH at 3600 cm^{-1} and 3480 cm^{-1} respectively.

In order to obtain stronger evidence and substantiate further the hydrogen bonding nature of interaction, calorimetric method was used to determine simultaneously the molar enthalpy, ΔH° , and equilibrium constant, K, for the interactions of A, AA and BA with H₀ in benzene. The applicability of calorimetric method and reliability of the assumed 1:1 complexation, can be seen from the excellent agreement, Figure 3, of observed heat values with those calculated from equation(1). The values of thermodynamic constants are summarized in Table II.

It is interesting to note that the computed K values, within experimental error, are the same while the molar enthalpy of interaction, ΔH° , increases markedly with the increase in molecular weight, nitrogen content and decrease in oxygen content of the asphaltene fraction, in the order $AA < A < BA$, and show a direct correlation with the viscosity results shown in Figure 2. It must be realized that coal liquid fractions are complex mixtures of substituted heterocyclic aromatics. The interaction of H₀ with asphaltene (A,AA,BA) in solution can only be viewed as a system involving varying degree of hydrogen-bonding and other types of rapidly reversible intermolecular interactions. The observed values of K and ΔH° , therefore, correspond to the total interaction involving these equilibria.

To evaluate qualitatively the hydrogen-bonding contribution in the observed

ΔH° , asphaltene (A, AA, BA) and HO fractions isolated from FB53-59 were examined by high resolution proton magnetic resonance at 220 MHz in CS_2 solutions. 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 rings, $\frac{H_o}{H_a} + 1$, and hydrogen/carbon ratio for the hypothetical unsubstituted aromatic nuclei, H_{au}/C_a , using Brown and Ladner(20) equations, are given in Table III. Both AA and HO fractions show a larger fraction of the hydrogens bound to aliphatic carbons, β or further from the aromatic rings, H_o . A and BA show larger aromaticities, larger percent of aromatic hydrogens and smaller aliphatic branches as compared to AA and HO fractions. It is interesting to note that both A and BA, within experimental error, show the same structural parameters and an even distribution of hydrogen bound to aromatic, benzylic and aliphatic carbons. This is in agreement with the nearly constant C/H ratio for the two fractions (Table I). It could be inferred, therefore, that the contribution of the π -bonding form of associations to the observed ΔH° values of HO interaction with A and with BA, to a large extent, would be the same. The observed large increase of ΔH° value, in the order $AA < A < BA$, therefore, is due to the varying degree of hydrogen-bonding basicity of these fractions. In systems involving coal liquid fractions, the dominance of hydrogen-bonding effects, largely involving phenolic H as hydrogen donors, over other types of molecular interactions in solution is in line with our previous observations(7,8,20) on quinoline (QU) interaction with coal-derived asphaltene (A, AA, BA) and HO fractions in solvent benzene. It was observed that for a given system, Qu + asphaltene (A, AA, BA) and Qu + HO, the values of K, within experimental error, were the same while ΔH° of interaction increased linearly with the increase in the phenolic oxygen content of the coal liquid fraction.

As shown in Figure 4, additional support for the presence of hydrogen-bonding interaction, involving phenolic hydroxyl protons, can be obtained from the PMR

downfield chemical shift (δ) of phenolic OH signal of OPP, a model chosen for phenolic OH in H₀, as a function of added asphaltene (A, AA, BA) concentration in solvent CS₂. OPP was chosen as the model because it is a moderately hindered phenol and any self-association(22) at the concentration (0.2M) studied can be neglected. Although the chemical shift of a proton resonance is the sum of contributions from several factors(23), however, it is interesting to note that the observed shift of OPP-OH signal at a given asphaltene (A, AA, BA) concentration is fairly large, downfield in the order BA > A > AA and correlates well with the viscosity and calorimetric results reported earlier. The extent of observed OPP-OH downfield shift with asphaltene (A, AA, BA) concentration, therefore, represents a qualitative measure of the relative hydrogen-bonding basicity of the asphaltene fraction. The chemical nature of the hydrogen-bonding bases in asphaltenes, containing heteroatoms, is probably multifunctional so that any conclusions drawn from the present work would be merely speculative. However, since nitrogen in BA is largely present as free basic ring nitrogen as in pyridine and the aromaticity of BA is the same as that of A (Table III,) the calorimetric and OPP-OH chemical shift results indicate that nitrogen is largely responsible for the high hydrogen-bonding basicity of BA fraction. The near absence of OH-- π interactions in systems involving ortho substituted hindered phenols and pyridine is well recognized(24). Furthermore, addition of silylated asphaltene, A(TMS), into 0.2M OPP in CS₂, Figure 4, moves the OPP-OH signal considerably downfield compared to that observed for A addition. This is expected since the acid-base structure(2) of A involves hydrogen bonding between acidic phenols and basic ring nitrogens. Removal of phenolic hydrogens on silylation would leave an appreciable amount of basic ring nitrogens available for association with OPP-OH protons. On the other hand, oxygen is probably responsible for the hydrogen-bonding basicity of AA fraction, since AA contains no basic nitrogens and addition of AA(TMS) shows no significant difference on the OPP-OH chemical shift compared to that observed as a function of AA concentration.

The above qualitative correlation of viscosity, calorimetric and PMR results, therefore, suggests that in coal-liquids, asphaltene and pentane-soluble heavy oil fractions are associated intermolecularly through hydrogen-bonding involving largely phenolic hydrogens as proton-donors. The hydrogen-bonding is, in part, responsible for the increase of viscosity of the product oil.

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Legend of Figures

1. Partial infrared spectra of pentane-soluble heavy oil, (HO), and silylated heavy oil, HO(TMS), fractions in CS_2 solution.
2. Relative viscosity change with added asphaltene concentration in C_6H_6 and in 0.305M solution of HO in C_6H_6 at 293K. Sample FB57-42: 1, AA in C_6H_6 ; 2, AA in HO + C_6H_6 ; 4, BA in C_6H_6 ; 5, BA in HO + C_6H_6 ; Sample FB53-59: 3, AA in C_6H_6 .
3. Plots of $\Delta H' / (\text{mmol of asphaltene})$ vs. heavy oil (mmol) added. Points are experimental; solid lines are calculated from equation (1), using the values of K and ΔH° listed in Table II.
4. Chemical shift changes (at 60 MHz) of the proton-OH resonance of o-phenylphenol (0.2M) as a function of asphaltene concentration in CS_2 solution. Added asphaltene: 1, A; 2, AA; 3, BA; 4, A(TMS) and 5, AA(TMS).

Figure 1

Figure 2

Figure 3

Figure 4

Table 1

Ultimate analyses (maf) and molecular weights of asphaltene and heavy oil fractions

SOURCE	FRACTION	C	H	O	N	S	Cl	ATOMIC C/H RATIO	$\bar{M}_n$ Mol. wt.
FB 53-59	A	85.85	6.5	4.4	2.02	0.88	0.39	1.10	740
	AA	84.0	7.2	5.5	1.03	0.96	1.34	0.97	620
	BA	85.3	6.6	4.2	2.79	0.70	0.44	1.08	950
	HO	86.3	8.6	3.2	1.05	0.73	0.16	0.84	290
FB 57-42	A*	86.3	6.45	4.2	2.02	0.95	0.10	1.12	530
	AA*	85.45	6.75	4.7	1.21	0.77	1.16	1.06	430
	BA*	86.05	6.1	3.45	3.03	1.15	0.24	1.18	680
	HO	86.8	8.5	2.9	1.13	0.64	0.11	0.85	260

* Taken from ref (7)

Table II

Summary of thermodynamic constants* at $298 \pm 0.5\text{K}$

Source	System	$\text{dm}^3 \text{ K mol}^{-1}$	$-\Delta H^\circ$ kJ mol^{-1}
FB 53-59	$\text{HO} + \text{A in C}_6\text{H}_6$	9.3	19.12 ± 0.57
	$\text{HO} + \text{AA in C}_6\text{H}_6$	9.1	15.02 ± 0.48
	$\text{HO} + \text{BA in C}_6\text{H}_6$	9.4	25.90 ± 0.78

*Uncertainties in ΔH° values are standard deviations. Error in K is about 10%.

Table III

Proton distribution and structural parameters of asphaltene and heavy oil fractions isolated from FE53-59

Fraction	Area percent, PMR Spectra			f_a	σ	$\frac{H_o}{H_\alpha} + 1$	$\frac{H_{au}}{C_a}$
	Aromatic H_a	Benzylic* H_α	Aliphatic* H_o				
A	32.6	34.5	32.9	0.70	0.40	1.95	0.70
AA	25.6	22.9	51.6	0.62	0.39	3.25	0.70
BA	32.9	32.4	34.7	0.69	0.38	2.07	0.71
HO	23.8	31.9	44.3	0.54	0.43	2.39	0.93

* Separation point between H_α and H_o chosen at 1.94 ppm

Work in Progress

The preasphaltene , asphaltene and heavy oil fractions of a mixture of solvent refined coal (3 parts SRC I and 7 parts SRCII) are isolated by solvent fractionation. The elemental analysis of the fractions, along with their molecular weights, infrared, proton and carbon-13 nmr spectra, are being obtained. The molecular size distribution profiles of the unfractionated mixture and the various fractions are being determined and possible correlations with viscosity attempted.

We have purchased a preparative liquid chromatograph-Waters LC/system 500 and have used liquid chromatographic approach to separate SRC II into hydrocarbon types: saturates, aromatics, non-basic heterocyclics, mono-phenols, polyphenols, basic heterocyclics and high molecular-weight highly functional compounds. Experiments are in progress to characterize and investigate the molecular interactions in these fractions.

Personnel

The Principal Investigator devoted full time in July and August, and 1/3 time in September to the work of the contract. Dr. K.C. Tewari devoted 40 hrs./wk, June-September. We are happy to welcome Dr. Takao Hara who arrived on Sept. 1 from Japan. He has carried out full-time research in September, and has already made significant contributions. The following students participated in the project: Lilly Young, Dan Croitoru and David Susco.