MASTER

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 asphaltenes and coal-liquids, and to seek possible correlations with the viscosity of the product oil. During the period October 1, 1978-December 31, 1978, the paper "Characterization of Coal-Liquid Fractions. Molar Enthalpies of Quinoline Interaction with Coal-Derived Asphaltenes and Heavy Oils", by K.C. Tewari, K.M. Egan, and N.C. Li has appeared in FUEL, 57, 712 (1978). The following two papers are in press: "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, Anal. Chem., and "Molecular Interaction of Quinoline with Coal Liquid Fractions", by K.C. Tewari, J.T. Wang, N.C. Li, and H.J.C. Yeh, Fuel. We have also completed a manuscript on "Influence of Hydrogen Bonding on the Viscosity of Coal Liquids," by K.C. Tewari, T. Hara, L-J S. Young, and N.C. Li. The details are as follows:

ABSTRACT

Solvent refined coal, SRC II process solvent, prepared by Pittsburgh and Midway Coal Company from Kentucky #9 and #14 blend bituminous coal, has been separated into acid/neutral and base fractions. Viscosity, infrared, and proton magnetic resonance studies are reported on the SRC II (before fractionation), and its acid/neutral fraction, and on the interaction of these coal-liquids with quinoline and triethylamine. The results obtained with the coal-liquids and with several model compounds suggest that hydrogen-bonding involving largely phenolic OH to nitrogen-containing bases, $-O-H^{\cdots}N-$, gives rise to proton-transfer complexes, $-O^{\cdots}H^+-N-$, and non-Newtonian flow of the coal liquids.

INTRODUCTION

The high viscosity at ambient temperature of coal liquids, derived from hydrogenation processes, has been related to their asphaltene (benzene-soluble and pentane-insoluble) and preasphaltene (benzene -insoluble and pyridine-soluble) fractions [1-6]. In defining the effect of asphaltene on the viscosity we recently reported [7] that in coal-liquids, asphaltene and pentane-soluble heavy oil fractions are associated intermolecularly through hydrogen bonding involving largely phenolic hydroxyl groups as proton donors and are, in part, responsible for the increase in the viscosity of the product oil.

In order to obtain stronger evidence and to assess further the effect of hydrogen-bonding interaction involving phenolic OH, on the viscosity of coal-liquids, we have compared viscosity data on coal-liquid-amine systems with those on a model system, o-cresol-amine mixtures. The results indicate that the contribution of hydrogen-bonding, $-O-H \cdots N-$, to the viscosity of the coal-liquid may be partially attributed to the size and concentration of the ionic proton-transfer complexes, $-O^- \cdots H^+ - N-$, formed from the hydrogen-bonded complexes.

EXPERIMENTAL

The SRC II process solvent used in this work was prepared by Pittsburgh and Midway Coal Company from Kentucky #9 and #14 blend bituminous coal. The liquid was separated into acid/neutral and base components by bubbling dry hydrogen chloride gas through a stirred benzene solution [8,9]. Quinoline, Fisher Scientific Company reagent grade, was doubly distilled from CaH_2 and kept under dry nitrogen for immediate use. o-Cresol and anisole, Fisher Scientific Company, were further purified by distillation. Triethylamine, Eastman Kodak Company, was distilled in the presence of KOH. Carbon tetrachloride and benzene, of Fisher pesticide grade, were dried over 4A molecular sieves.

Viscosity measurements were performed by means of viscometers of the Ostwald type and with the Brookfield viscometer equipped with a small sample adaptor. Number-average molecular weights were determined on a Mechrolab 301 A vapor pressure osmometer at 10-20 g/dm³ in toluene solutions. Infrared spectra were recorded from solutions in CCl₄ in a 5-mm KBr liquid cell with the solvent in the compensating beam or as thin film on a Beckman IR-20 infrared spectrometer. Proton magnetic resonance spectra were obtained with a Perkin-Elmer R-600 FT nmr spectrometer at 60 MHz as CDCl₃ solutions with TMS as internal reference.

RESULTS AND DISCUSSION

Separation of SRC II process solvent into its acid/neutral and base components gave the weight ratio acid/base of 90.7/9.3. SRC II process solvent and its acid/neutral fraction are henceforth referred as SRC II and SRC II-Acid, respectively. The elemental analysis, molecular weight and viscosity at 298 K of the two coal-liquids are given in Table 1. The results indicate that although the O/C and C/H ratios of the two coal liquids are the same, the SRC II-Acid fraction compared to SRC II has lower nitrogen content, higher molecular weight and higher viscosity. Incorporation of a large amount of chlorine into the SRC II-Acid fraction is similar to that reported previously for the incorporation of chlorine into the acid/neutral fraction of coal-derived asphaltenes [2].

The proton magnetic resonance spectra of SRC II and SRC II-Acid are very similar. 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, $H_o + 1$, and the hydrogen/carbon ratio for the hypothetical unsubstituted aromatic nuclei, H_{ar}/C_{ar} , using Brown and Ladner [10] equations are given in Table 2.

The results indicate that both SRC II and SRC II-Acid have large fraction of hydrogens bound to aliphatic carbons, β or further from the aromatic rings, H_o , and have about the same structural parameters. This is in agreement with the constant atomic C/H ratio observed in Table 1.

Partial infrared spectra of SRC II and SRC II-Acid in CCl_4 solution are shown in Fig. 1. In the dilute solution (0.02M) both liquids show distinct absorption for the free phenolic OH and NH at 3600 cm^{-1} and 3480 cm^{-1} , respectively. The appearance of a relatively broad band at $3200\text{--}3450\text{ cm}^{-1}$ in SRC II-Acid signifies a highly hydrogen-bonded structure even in dilute solutions. The absorption band indicates intramolecular bonding and intermolecular self-association of SRC II-Acid, involving the phenolic OH. The self-associated structure, in part, may be responsible for the observed higher viscosity of SRC-II-Acid compared to the unfractionated SRC II.

Hydrogen-bonding interaction in coal liquids, to a large extent, involves aromatic phenols and basic ring nitrogens. To demonstrate the effect of hydrogen-bonding on the viscosity of the liquid phase, the viscosities of mixtures of pure compounds, o-cresol + quinoline (Qu), o-cresol + triethylamine (Et_3N), anisol + Qu, and o-cresol + CCl_4 , were measured at 293 K. The results are shown in Fig. 2. The self-association of o-cresol, as expected, shows a gradual increase in viscosity with increase in the mol fraction of o-cresol in CCl_4 (curve 2). In the absence of phenolic OH, no such effect was observed in the system anisol + CCl_4 (not shown). It is interesting to note that in the systems o-cresol + Qu and o-cresol + Et_3N , involving acid-base interaction, $-OH...N$, the viscosity of the mixtures as a function of phenol mol fraction show a single maximum (curves 3 and 4) at mol fraction 0.6 and 0.8, respectively. The height of the viscosity peak is greater with Et_3N , a stronger electron donor, than with Qu. In absence of hydrogen-bonding interaction, no enhancement in viscosity is observed, as in anisol-Qu system. The results in Fig. 2 are similar in nature to those

reported by Felix and Huyskens [11] for mixtures of phenol and aliphatic amines, where spectacular variation of viscosity, electric conductivity, and volume contraction have been well correlated with the concentration of ionic proton-transfer complexes, $-O^- \cdots ^+HNR_3$. The R_3NH^+ cation forms a hydrogen bond with a lone pair of electrons of the oxygen atom of the phenol. The viscosity depends not only on the concentration of the cationic proton-transfer complexes which are responsible for the conductivity but also on the size of these ions.

Felix and Huyskens [11] have shown that a 1:1 or 2:1 phenol: amine complex is not principally responsible for ion formation and for the increase of the viscosity, but that one needs to have ionic complexes of higher stoichiometry, $n \geq 2$ (n : 1 phenol : amine). Outside the maximum, a given value of viscosity appears at two different mol fractions (x_A) of phenol and the authors conclude that, at the lower value of x_A , the same viscosity is obtained by a lower concentration of ions and that the size of the ions is greater than at the upper value of x_A .

In coal-liquid systems, SRC II + Et₃N, SRC II-Acid + Et₃N and SRC II-Acid + Qu, the observed viscosities of the mixtures as a function of mol fraction of coal-liquid are shown in Fig. 3. Since the phenolic OH groups in the unfractionated liquid, SRC II, already exist in the bonded form, therefore, in the system SRC II + Et₃N, no maximum in the viscosity vs. mol fraction curve was observed. The liquid mixtures show Newtonian behavior in the entire mol fraction region. However, the dominant role of hydrogen-bonding interaction involving phenolic OH as proton donor, in defining the viscosity and rheological properties of coal-liquid can be seen from Fig. 3, curves 2 and 3. The viscosity data for SRC II-Acid + Et₃N and SRC II-Acid + Qu systems are at shear rate of 3.96 s⁻¹ and 7.92 s⁻¹, respectively. It is interesting to note that hydrogen-bonding not only defines the viscosity, but also the plastic nature of these systems. This is shown in Fig. 4 where, at a given mol fraction of SRC II -Acid in Et₃N, a linear relationship is obtained on a log-log plot of

rate of shear vs. viscosity in cp.

The maxima in viscosity, Fig. 3, for the systems SRC II-Acid + Et_3N and SRC II-Acid + Qu are, respectively at 0.75 and 0.92 mol fraction of the coal liquid. Since Felix and Huyskens [11] have concluded that the size of the ionic complexes in the mol fraction region below the maximum is larger than the ionic complexes in the mol fraction region above the maximum, we have determined the number-average molecular weight of SRC II-Acid + Et_3N mixtures at various mol fractions. The results are listed Table 3, and definitely show that at mol fraction below the observed maximum (at mol fraction 0.75) the number-average molecular weight is indeed larger than on the other side of the maximum. For mol fraction >0.75 , the observed molecular weight decreases with increase in mol fractions. Column 3 of Table 3 lists the number-average molecular weights calculated from the mol fractions and the molecular weights of SRC II-Acid (210) and Et_3N (101), assuming no complex formation.

The transition from a hydrogen-bonded complex $\text{O}-\text{H}\cdots\text{N}$ to a proton-transfer complex $\text{O}^-\cdots\text{H}^+-\text{N}$ can be followed by infrared spectroscopy. The infrared spectra of SRC II-Acid and SRC II-Acid + Et_3N mixture at 0.69 mol fraction of SRC II-Acid are shown in Fig. 5. The appearance of absorption bands at 2680 cm^{-1} and 2500 cm^{-1} , (for the mixture of SRC II-Acid and Et_3N), ascribed to $\text{N}^+-\text{H}\cdots\text{O}$ [12], and a broad absorption band at $3200-3600\text{ cm}^{-1}$ clearly indicates the presence of both $\text{O}-\text{H}\cdots\text{N}$ and $\text{O}^-\cdots\text{H}^+-\text{N}$ species in the system. The self-association of SRC II-Acid is obvious from the infrared spectrum of neat SRC II Acid shown in Fig. 5.

Fig. 6 shows the infrared spectra as CCl_4 solutions of the mixtures SRC II + Et_3N and SRC II-Acid + Et_3N . A comparison of Fig. 1 and Fig. 6 shows that the effect of the addition of Et_3N to SRC II-Acid is to reduce markedly the hydrogen-bonding absorption at $3200-3450\text{ cm}^{-1}$ observed for SRC II-Acid in CCl_4 , Fig. 2, with the appearance of strong $\text{N}^+-\text{H}\cdots\text{O}$ bands [12] at 2630, 2610, and 2500 cm^{-1} . On the other hand, the addition of Et_3N to SRC II shows no significant

absorption bands in the region $2500-2800\text{ cm}^{-1}$. The decrease in free OH absorption at 3600 cm^{-1} , both for SRC II-Acid and SRC II, is estimated to be 10%. It is therefore concluded that the high viscosity and plastic nature of coal liquids, involving both phenolic OH and basic nitrogens, are probably due to the increased concentration of large complexed ions formed in the transition from hydrogen-bonded complex, $\text{O-H}\cdots\text{N}$, to proton-transfer complexes, $\text{O}^-\cdots\text{H}^+\text{N}$.

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Table 1.

Elemental analysis of coal-liquids (% maf)

	C	H	O	N	S	Cl	C/H	Mol. Weight	Viscosity at 298 K, cp
SRC II	86.8	8.4	3.1	1.29	0.36	0.12	0.86	190	20.0
SRC II-Acid	85.9	8.3	3.1	0.82	0.3	1.57	0.86	210	38.5

Table 2.

Proton distribution and structural parameters

Area %, pmr spectra								
	aromatic H_a	benzylic H_d	aliphatic H_o	$\frac{H_o}{H_a}$	f_a	σ	$\frac{H_o+1}{H_d}$	$\frac{H_{ar}}{C_{ar}}$
SRC II	33.8	27.3	38.9	1.24	0.62	0.32	2.42	0.93
SRC II-Acid	33.0	26.8	40.2	1.23	0.61	.32	2.5	0.92

Table 3

Number-average Molecular weight of SRC II-Acid + Et₃N mixtures

Mol fraction of SRC II-Acid	M _{obs}	M _{calc} *
0.677	250	175
0.763	230	184
0.805	220	189
1.000	210	210

*Calculated from mol fractions and molecular weights of SRC II-Acid (M=210), and Et₃N (M=101); assuming no complex formation.

Legends of Figures

- Fig. 1. Infrared spectra of SRC II and SRC II-Acid in CCl_4 (a) SRC II, 0.02M; (b) SRC II-Acid, 0.02 M. 5-mm cell (KBr)
- Fig. 2. Viscosity, in cp, as a function of mol fraction of the phenol at 293 K. Curves: 1, anisol and Qu; 2, o-cresol and CCl_4 ; 3, o-cresol and Qu; 4, o-cresol and Et_3N .
- Fig. 3. Viscosity, cp, as a function of the mol fraction of the coal liquid at 298 K. Curves: 1, SRC II and Et_3N ; 2, SRC II-Acid and Et_3N ; 3, SRC II-Acid and Qu.
- Fig. 4. Effect of rate of shear ($\dot{\gamma}$) on the viscosity (η) of SRC II-Acid and Et_3N mixtures. Mol fraction of SRC II-Acid: (a) 0.491, (b) 0.795, (c) 0.689.
- Fig. 5. Infrared spectra, neat: (a) SRC II-Acid; (b) SRC II-Acid and Et_3N (mol fraction of SRC II-Acid, 0.69).
- Fig. 6. Infrared spectra in CCl_4 solutions, 5 mm cell (KBr).
(a) SRC II (0.02 M), Et_3N (0.01M)
(b) SRC II-Acid (0.02 M), Et_3N (0.01 M)

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Work in Progress on Upgrading of Solvent Refined Coal

Two kinds of SRC liquids were used as feed material for upgrading. One is a mixture of 30% SRC I and 70% SRC II by weight. The other is SRC II itself.

SRC I is from Kentucky bituminous coal obtained from the Tacoma Pilot Plant. Elemental analysis; hydrogen, 6.05%; carbon, 85.47%; nitrogen, 2.01%; sulfur, 0.74%; ash, 0.12%; oxygen (by difference), 5.61%. The preasphaltene, asphaltene, and heavy oil fractions, isolated by solvent fractionation of SRC I, occur to the extent of 34.1%, 48.8%, and 17.1% respectively. SRC II is a liquid product with initial boiling point 180°C and extending into end boiling point of 392°C. Elemental analysis for SRC II: hydrogen, 8.70%; carbon 88.98%; nitrogen, 0.84%; sulfur, 0.28%; oxygen, 1.16%. The liquid product has a flash point of 80°C, contains 26.7 cm³ coal tar acids/100g and 0.012% pyridine insolubles.

The mixture of 30% SRC I and 70% SRC II, was prepared by heating at 140-150°C for 2.5 hrs (nitrogen atmosphere). Yield of the liquid product was 95.8%. Viscosity of the mixture, determined at 60°C, is 36.0 cp. The preasphaltene (pyridine soluble, toluene insoluble), asphaltene (toluene soluble, pentane insoluble), and heavy oil (pentane soluble) fractions of the mixture, as isolated by solvent fractionation, occur to the extent of 10.2%, 18.5%, and 71.3%, respectively. Gel permeation chromatograms of the mixture and its preasphaltene, asphaltene, and heavy oil fractions have been obtained and the preasphaltene fraction is shown to be composed of larger molecules than the other fractions (Fig. 7). The mixture of 30% SRC I and 70% SRC II was chosen as feedstock for upgrading, because the boiling point ranges and high percentages of asphaltenes, organic sulfur and nitrogen are typical of coal-derived liquids such as mixtures of atmospheric bottoms and vacuum bottoms of H-coal.

The infrared spectra of SRC II and of the mixture of 30% SRC I and 70% SRC II, neat, are very similar, and show the presence of strongly hydrogen-bonded OH groups as well as large content of aromatic compounds. Fig. 8 gives infrared spectra of

Fig. 7 GPC of the mixture (SRC I + SRC II)
and its fractions

Fig. 8 IR Spectra of feed materials in CCl_4 solution.

(a) heavy oil fraction of the mixture (3.99 g/l)

(b) SRC II (3.84 g/l), 5 mm cell (KBr)

CCl_4 solutions of (a) heavy oil fraction of the mixture and (b) SRC II. The solubility of the mixture in CCl_4 is low, because of the preasphaltene and asphaltene components, hence only the heavy oil fraction of the mixture is shown in Fig. 8 (a). A broad peak at $3,250 \text{ cm}^{-1}$ appears only in Fig. 8 (a), and not in (b), indicating that the mixture of SRC I and SRC II contains hydroxyl groups which are strongly hydrogen-bonded. The NH absorption peak, at $3,475 \text{ cm}^{-1}$, appears in both (a) and (b).

Upgrading of the mixture and SRC II was carried out by Dr. Yuan C. Fu at the Pittsburgh Energy Technology Center, using a Ni-Mo catalyst (Nalco NM 1504) in a trickle-bed reactor at space velocity (LHSV) of 0.5 hr^{-1} , hydrogen pressure of 2,000 psi and 694°K . IR spectra of the upgraded oils from the mixture and SRC II, neat, are shown in Fig. 9. The intensity of the aromatic peaks at $3,030 \text{ cm}^{-1}$ and $1,620 \text{ cm}^{-1}$ for the upgraded oils is very much smaller than that for the materials before upgrading. The reduction in the aromatic content is greater for the upgraded oil from SRC II than for the upgraded oil from the mixture.

NMR spectra are shown in Fig. 10-12. Proton distribution data, based on the NMR spectra, are listed in Table 4. The NMR spectra, as well as the data listed in Table 4, show conclusively that the content of aromatic hydrogens are in the order SRC II > upgraded oil from the mixture > upgraded oil from SRC II and that the values of H_o and $(H_o/H_a) + 1$ increase in the order SRC II < upgraded oil from the mixture < upgraded oil from SRC II. The reduction in the aromatic content on upgrading the mixture and SRC II, obtained from NMR data, fully support the IR data. On upgrading, the content of aliphatic hydrogens increases, accompanied by an increase in the average length of alkyl substituents on the aromatic rings.

Activities in upgrading of coal liquids have been intensified in recent times, because of the necessity of having acceptable quality fuels for transportation and

Fig.10 NMR Spectrum of SRC II

Solvent : CDCl_3

Concentration : 11 % (by volume)

Fig. 11 NMR Spectrum of the upgraded oil from SRC II

Solvent : CDCl_3

Concentration : 14 % (by volume)

Fig.12 NMR Spectrum of the upgraded oil from the mixture (SRC I + SRC II)

Solvent : CDCl_3

Concentration : 14 % (by volume)

Table 4 Proton distribution and structural parameters of liquids before and after upgrading

Samples	Aromatic	Area % Benzylic *	Aliphatic	$H_O/H_\alpha + 1^{**}$
	H_a	H_α	H_O	
SRC II	37.7	29.7	32.6	2.10
upgraded oil from the mixture	12.9	19.6	67.5	4.44
Upgraded oil from SRC II	4.7	9.6	85.7	9.93

* separation point between H_α and H_O chosen at $\delta = 2.10$ ppm

** average length of alkyl substituents on the aromatic rings.

industrial use. We plan to continue active investigation on characterization and study of interactions with the coal liquids after various stages of hydro-processing and upgrading.

Personnel

The Principal Investigator devoted 1/3 time, during Sept. - Dec. 1978, to the work of the contract. Dr. K.C. Tewari and Dr. Takao Hara devoted 40 hrs/week in this period. The following students have participated: Lilly Young, Dan Croitoru, David Susco and John Barkin.