HYDROGEN BONDING IN ASPHALTENES AND COAL - Short Interim Annual Report
(Annual Summary)

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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. During the year 1978, the following papers have appeared in print or are in press:

- Paper A: S.R. Taylor and N.C. Li, "Nature of Hydrogen Bonding in Coal - Derived Asphaltenes," Fuel, 57, 117 (1978).
- Paper B: 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, 57, 245 (1978)
- Paper C: K.C. Tewari, K.M. Egan, and N.C. Li "Characterization of Coal Liquid Fractions: Molar Enthalpies of Quinoline Interaction with Coal-Derived Asphaltenes and Heavy Oils," Fuel, in press.
- Paper D: K.C. Tewari, J.T. Wang, N.C. Li, and H.J.C. Yeh, "Molecular Interaction of Quinoline with Coal Liquid Fractions," Fuel, in press.
- Paper E: K.C. Tewari, N.S. Kan, D.M. Susco, and N.C. Li, "Viscosity, Calorimetric, and Proton Magnetic Resonance Studies on Coal Liquid Fractions in Solutions," Anal. Chem., in press.

Abstracts of Papers A - E, and a Summary of work on SRC I, II are as follows:

Abstract of Paper A. Near infrared (n.i.r.) and proton magnetic resonance (p.m.r.) studies are reported of hydrogen bonding between the hydroxyl group of o-phenylphenol (OPP) and two coal-derived asphaltenes, and their acid and base components. The asphaltenes were isolated from two centrifuged liquid product (CLP) samples prepared from West Virginia, Ireland Mine bituminous coal under the same reaction conditions, except that CLP FB44-56 was prepared with the reactor charged with a CoMo catalyst, while CLP FB50-17 was prepared with glass pellets in place of the catalyst. The base asphaltene components from both FB44-56 and FB50-17 cause a decrease in the OPP-OH absorbance at $1.44 \mu\text{m}$ in CS_2 and a downfield shift of the OPP-OH p.m.r. resonance in CS_2 , while these changes are not observed for the original asphaltenes or their acid components. Furthermore, the base asphaltene component from CLP-44-56 is more effective in decreasing the OPP-OH absorbance when compared with the base asphaltene component from CLP FB50-17. Also, the absorbance of a pentane-soluble fraction of the acid asphaltene component at $1.42 \mu\text{m}$ in CS_2 from CLP FB50-17 is decreased upon addition of the corresponding base asphaltene component. Our results lead to the conclusion that the use of a CoMo catalyst leads to a base asphaltene component of lower molecular weight and higher hydrogen-bond acceptor strength.

Abstract of Paper B. A calorimetric method is presented for the simultaneous evaluation of equilibrium constant, K, and molar enthalpy ΔH° , 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 723 K, 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 dm³ mol⁻¹; whereas there is large variation in the ΔH° values (Qu-A, -16.92 + 0.21 kJ mol⁻¹; Qu-AA, -14.74+0.04kJ mol⁻¹; Qu-BA, -11.76+0.04kJmol⁻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(dm³ mol⁻¹): 10.4 (in CS₂), 6.2 (in CCl₄); ΔH° (kJ mol⁻¹): -31.40(in CS₂), -27.80(in CCl₄). The solvent effect is apparent. By using o-phenylanisole as a model non-hydrogen-bonding donor (Dietz, Blaha, Li, J. Chem. Thermodynamics, 1977,9,783), 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.

Abstract of Paper C. The toluene-insoluble (TI), asphaltene (A), and heavy oil (HO) fractions were isolated from three centrifuged SYNTHOIL liquid product (CLP) samples, prepared under different process conditions at 450°C, 4000 psi hydrogen pressure from the same feed coal, Kentucky hvAb, from Homestead Mine. Run FB 53 was made with CoMo catalyst, 11-min preheater residence time, and 3-min reactor residence time. The much higher viscosity of FB53-59 compared to BF53-1, correlates with the larger contents of its toluene insolubles, larger molecular weight and smaller aromaticity of its asphaltene, and the larger enthalpy of interaction (ΔH°) of its asphaltene with quinoline in benzene. The average molecular weight and percentage of heteroatoms of the heavy oil from FB 53-59 are also greater than that from FB 53-1, and the value of ΔH° of the heavy oil with quinoline follows the same order.

Run FB 57 was made with glass pellets, 17-min preheater residence time and 6-min reactor residence-time. 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 is larger, while the heavy oil content of FB 53-59 is smaller than that of FB 57. This comparison indicates that a larger residence time preheater and reactor may, to some extent, favor conversion as well as decrease the viscosity of the product oil. The values of ΔH° 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 > FB 53-1, and attributed to the varying degree of hydrogen-bonding effects involving largely aromatic phenols which serve as hydrogen donors to quinoline.

Abstract of Paper D. A direct calorimetric method has been used to determine simultaneously the molar enthalpy, ΔH° , and equilibrium constant, K, for quinoline (QU) interaction with coal-derived asphaltenes (A), acid/neutral (AA) and base (BA) components of A, silylated asphaltenes (A(TMS)) and heavy oil (HO) fractions in solvent C₆H₆. Solvent fractionated A and HO fractions were from three centrifuged liquid product (CLP) samples prepared in the 450kg (½ ton) per-day Process Development Unit at Pittsburgh Energy Research Center, at different process conditions from the same feed coal, Kentucky hvAb. For a given system, Qu-A (AA or BA), Qu-HO, the almost constant value of K and linear

variation of ΔH° with the phenolic oxygen content of coal liquid fractions, have been attributed to the dominance of hydrogen-bonding effects, involving phenolic OH, over other types of molecular interactions in solution. In Qu-A(TMS) system, $-\Delta H^\circ$ values increase with decrease in molecular weight of A(TMS), while $-\Delta S^\circ$ values increase with increase in aromaticity of A fraction. The degree of complexation, in absence of OH groups, is much smaller than Qu-A system.

Abstract of Paper E. 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 CS₂. 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.

Summary of Work on SRC I and II

SRC I is from Kentucky bituminous coal obtained from the Tacoma Pilot Plant. Elemental analysis: Hydrogen, 6.1%; carbon, 85.5%; nitrogen, 2.0%; sulfur, 0.7%. SRC II is a liquid product with initial boiling point 180°C, extending into end boiling point of 392°C. Elemental analysis for SRC II: hydrogen, 8.7%; carbon, 89.0%; nitrogen, 0.8%; sulfur, 0.3%; oxygen, 1.2%. The liquid product has a flash point of 80°C and 26.7 ml. coal tar acids/100 g.

A mixture of 30% SRC I and 70% SRC II (by weight) was prepared by heating at 140-150 °C for 2.5 hours (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 insoluble, 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 unfractionated mixture, 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.

By using a preparative liquid chromatograph-Waters LC/System 500, we have separated SRC II into the following hydrocarbon types: saturates, aromatics, non-basic heterocyclics, monophenols, polyphenols, basic heterocyclics, and high molecular-weight highly functional compounds. The Chemistry Department at Duquesne University now have a 60-MHz FT NMR spectrometer (Perkin-Elmer R-600), and we plan extensive proton magnetic resonance studies on SRC II and mixtures of SRC I and II.

Personnel

During 1978, the Principal Investigator devoted one-third time during the academic year and full-time in the summer months, to the work of the contract. Dr. K.C. Tewari devoted 40 hours/week through out the year. Dr. Takao Hara arrived on September 1 from Japan and has carried out full-time research since then. The following students have participated:

Dan Croitoru, David Susco, Robert Maurer and Miann Jones (up until June);
Lilly Young, Dan Croitoru, David Susco and John Barkin (up until December).