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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 April 1, 1978 - June 30, 1978, the task on "Molecular Interaction of Quinoline with Coal Liquid Fractions" has been completed, and a manuscript on this topic by K.C. Tewari, J.T. Wang, N.C. Li, and H.J.C. Yeh, has been submitted to FUEL. The details are as follows:

ABSTRACT

A direct calorimetric method has been used to determine sumultaneously the molar enthalpy, $\Delta H°$, 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 C_6H_6. 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 $\Delta H°$ 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, $-\Delta H°$ values increase with decrease in molecular weight of A(TMS), while $-\Delta S°$ 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 and largely depends upon some unusal entropy effects.

INTRODUCTION

The molecular composition and chemical behavior of coal liquid fraction vary widely as a function of source materials, conversion process conditions and methods of their extraction. In order to obtain a better understanding of the thermodynamics of molecular interactions in solution from which coal liquid subfractions are derived, we recently reported[1,2] a direct calorimetric approach for simultaneous determination of equilibrium constant and molar enthalpy for donor-acceptor type adduct formation between quinoline and coal-derived asphaltene (toluene soluble-pentene insoluble) or heavy oil (pentane soluble) fractions in solvent benzene. The present report substantiates further the hydrogen-bonding nature of the interactions involved and illustrates the applicability of calorimetric method to study of systems in which hydrogen-bonding and other types of rapidly reversible intermolecular interactions in solution occur.

EXPERIMENTAL

Centrifuged liquid product (CLP) samples used in this study, FB53, batches 1 and 59, and FB57, batch 42, were obtained from 450kg (½ ton) per-day Process Development Unit at Pittsburgh Energy Research Center after 4, 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. Among the two runs chosen, FB53 was made with the reactor packed with Harshaw 0402T CoMo catalyst, 11-min preheater residence time and 3-min reactor residence time, while run FB57 was made with the reactor charged with glass pellets, 17-min preheater residence time and 6-min reactor residence time. The residence time of coal slurry feed in preheater and reactor was calculated from Cold-Model Studies. The isolation of asphaltene(A) and heavy oil (HO) from the CLP was accomplished by solvent fractionation based upon solubility in toluene and pentane. The asphaltene fraction was further separated into acid/neutral (AA) and base (BA) components by bubbling dry hydrogen chloride gas through a stirred

toluene solution. Detail of these isolation methods have been previously described.[1,2]

Quinoline (Qu), Fisher Scientific Co. reagent grade, was doubly distilled from CaH_2 and kept under dry nitrogen for immediate use. Fisher pesticide grade, benzene, dried over 4A molecular sieves, was used as solvent. The molecular weights were determined on a Mechrolab 301A vaporpressure osometer at 12-20 g/dm^3 in benzene solutions. Proton magnetic resonance (PMR) spectra were obtained on Jeol FX-100 spectrometer as $CDCl_3$ solutions with tetramethylsilane (TMS) as an internal reference.

Hydroxyl silylation: Silylation of coal and coal-derived asphaltenes has been described by several authors[3-5]. In our method, 20 cm^3 of hexamethyldisilazane and 10 cm^3 of N-trimethylsilyldiethylamine were added to 100 cm^3 of benzene containing 2g asphaltene sample. The resulting mixture was put to slow reflux, under nitrogen for 18 hrs. After reflux was complete, solvent and unreacted reagents were removed on a Rotavap at 333K. Nitrogen was then flushed to ensure dryness. The residue was repeatedly dissolved in dry benzene and dried as before. To ensure complete removal of reagents, the residue was finally freeze dried from 10 cm^3 of benzene for 3 hrs. The formation of asphaltene trimethylsilyl ether was checked by infrared spectroscopy for complete disappearance of the free phenolic or alcoholic OH absorption at 3600 cm^{-1}. No significant change in intensity of IR absorption band at 3480 cm^{-1}, assigned[6] to free NH groups of pyrrole or carbazole, was observed after silylation. We conclude, therefore, the NH groups were not silylated and the silylated asphaltene derivative was substantially derived from hydroxyl moieties. The number of silyl groups attached to asphaltene, hence the percent hydrogen as OH, was calculated from integration of PMR spectrum in $CDCl_3$. The weight percent oxygen as OH on a moisture and ash free basis was then calculated from the elemental analysis of the original sample.

Calorimetric measurements: The calorimeter was essentially that designed by Arnett.[7] For a 1:1 complex formation in a donor-acceptor type reaction $A + B \rightleftarrows C$, the molar

enthalpy, $\Delta H°$, and equilibrium constant, K, were determined simultaneously from equation (1)

$$K^{-1} = \frac{\Delta H'}{v\ \Delta H°} + \frac{A_o B_o v\ \Delta H°}{\Delta H'} - (A_o + B_o) \qquad (1)$$

where A_o and B_o 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 the complex corrected for the heat of solution of added reagent at the corresponding concentration. The range of reactant concentrations were chosen to satisfy as nearly as possible the criteria outlined by Conrow, et al.[8]

RESULTS AND DISCUSSION

The structural parameters[2] of A and HO fractions isolated from the three CLP samples and the thermodynamic parameters[1,2] of Qu interactions with A, AA, BA, and HO fractions in solvent benzene have been reported previously. For comparison purposes the thermodynamic constants are reproduced in Table 1. It was observed that for a given system, Qu + A and Qu + HO, the values of equilibrium constant, K, within experimental error, remained the same, while the molar enthalpy of interaction, $\Delta H°$, increased markedly with the increase in oxygen content of the coal liquid fraction, in the order FB53-1 < FB57-42 < FB53-59. Since the C/H ratio, aromaticity, f_a, aromatic/benzylic hydrogen ratio and other structural parameters were the same for the three HO fractions and decreased in order of FB53-1 > FB57-42 >FB53-59 for A fractions[2], the observed variation of $\Delta H°$ was attributed to hydrogen-bonding interactions involving largely aromatic phenols which serve as hydrogen donors to Qu. The contributions involving acidic NH as hydrogen donors were neglected since the pK_a of phenol and pyrrol at 293K are 9.89 and ~15, respectively.

The fact that the computed K values, Table 1, for the interaction of Qu with AA and with BA fractions are, within experimental error, the same as those of Qu + A systems, leads us to believe that the observed variation in $\Delta H°$ values also

can be largely due to hydrogen-bonding acidity, involving OH groups, of these fractions. Contrary to thin-layer chromatographic (TLC) analyses of Sternberg, et al.[9], it is interesting to note that IR spectrum[4] of the base component 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 to substantiate further the hydrogen-bonding nature of interaction, the percent hydrogen as OH in each of A, AA, BA and HO fractions was calculated from the integration of PMR spectra in $CDCl_3$. Representative PMR spectra for HO and silylated asphaltene, A(TMS), fractions are shown in Figure 1 (a) and (b). The spectrum of HO fraction shows a distinct phenolic OH signal at 5.6 ppm downfield from TMS. This was confirmed by deuterium exchange where the OD signal is chemically shifted out of the spectrum and an HDO signal appears.[10] The integrated intensity of the OH resonance was used directly to calculate percent phenolic hydrogen in HO sample. The OH signal of A, AA, and BA fractions, however, remains under the aromatic hydrogen envelope. The percent hydrogen as OH in asphaltene fractions was calculated from the integrated area under trimethylsilyl proton signals, 0-0.4 ppm from internal TMS. The results are summarized in Table 1. As can be seen, on silylation the number of trimethylsilyl groups introduced correspond to 40% of the oxygen present in BA fraction as OH.

The hydrogen-bonding nature of interaction involving phenolic OH can be seen from the plot of $\Delta H°$ values, Table 1, for Qu interaction with asphaltene (A, AA, and BA) and HO fractions, with the phenolic oxygen contents of the fractions as shown in Figure 2. The linear correlation indicates the dominance of hydrogen-bonding effects, associated with phenolic OH, over other types of molecular interactions in these systems.

It is interesting to point out that Dietz, et al.[11], using the "pure base" method of Arnett et al.[12], report that the enthalpy of hydrogen bonding of o-phenylphenol (OPP) with quinoline is 22.6 kJ mol^{-1}. Since OPP contains 16 g of phenolic oxygen per mol, Figure 2 would put the value of - $\Delta H°$ at 18.9 kJ mol^{-1}. Part of the discrepancy is that in the work of Dietz et al., the solvent is the pure base quinoline, while in Figure 2, the solvent is benzene. Moreover, Figure 2 is based on the coal liquid fractions obtained from one feed coal, Kentucky hvAb, only. Since the phenols present in the coal would be much more restricted then OPP, we would expect the enthalpy of hydrogen bonding between the pure compound OPP and quinoline to be larger than that indicated by Figure 2. This comparison with the pure compound OPP shows that Figure 2 is useful in correlating - $\Delta H°$ with phenolic oxygen content of coal liquid fractions, obtained from one feed coal.

Interaction of Qu with A(TMS) in benzene may be viewed as a system involving rapidly reversible intermolecular interactions other than hydrogen-bonding involving phenolic OH. The applicability of calorimetric method in the system Qu + A(TMS) and reliability of the assumed 1:1 complexation for the computation of $\Delta H°$ and K, Table 2, can be seen from the excellent agreement, Figure 3, of observed heat values with those calculated from equation (1).

It is interesting to note that the calculated K values of Qu-A(TMS) systems are not the same for the three A(TMS) fractions studied and are quite small compared to those observed for Qu-A system, Table 1. The results, Table 2, indicate that even though the strength of interaction, $\Delta H°$, is appreciable, the degree of complexation, in absence of phenolic OH, largely depends upon some unusual entropy effect. Although it is difficult to speculate on the factors influencing entropy in Qu - A(TMS) systems, it is, however, interesting to note that the observed $\Delta H°$ values increase in the order of decreased molecular weight, hence size of A(TMS) "molecule". The decrease of entropy of the Qu - A(TMS) complex with the increase in aromaticity, f_a, of A fraction, indicates the possible restriction associated with Qu molecule joining the larger polynuclear condensed aromatic framework of

A(TMS) "molecule".

We conclude that in systems involving coal liquid fractions in solution, hydrogen-bonding largely involving phenolic OH as proton donor, is the dominant intermolecular interaction responsible for the strength and degree of complexation. For a given system in solution, in presence of phenolic OH the equilibrium constant is generally large and remains the same irrespective of the size and polynuclear condensed framework of coal liquid fraction.

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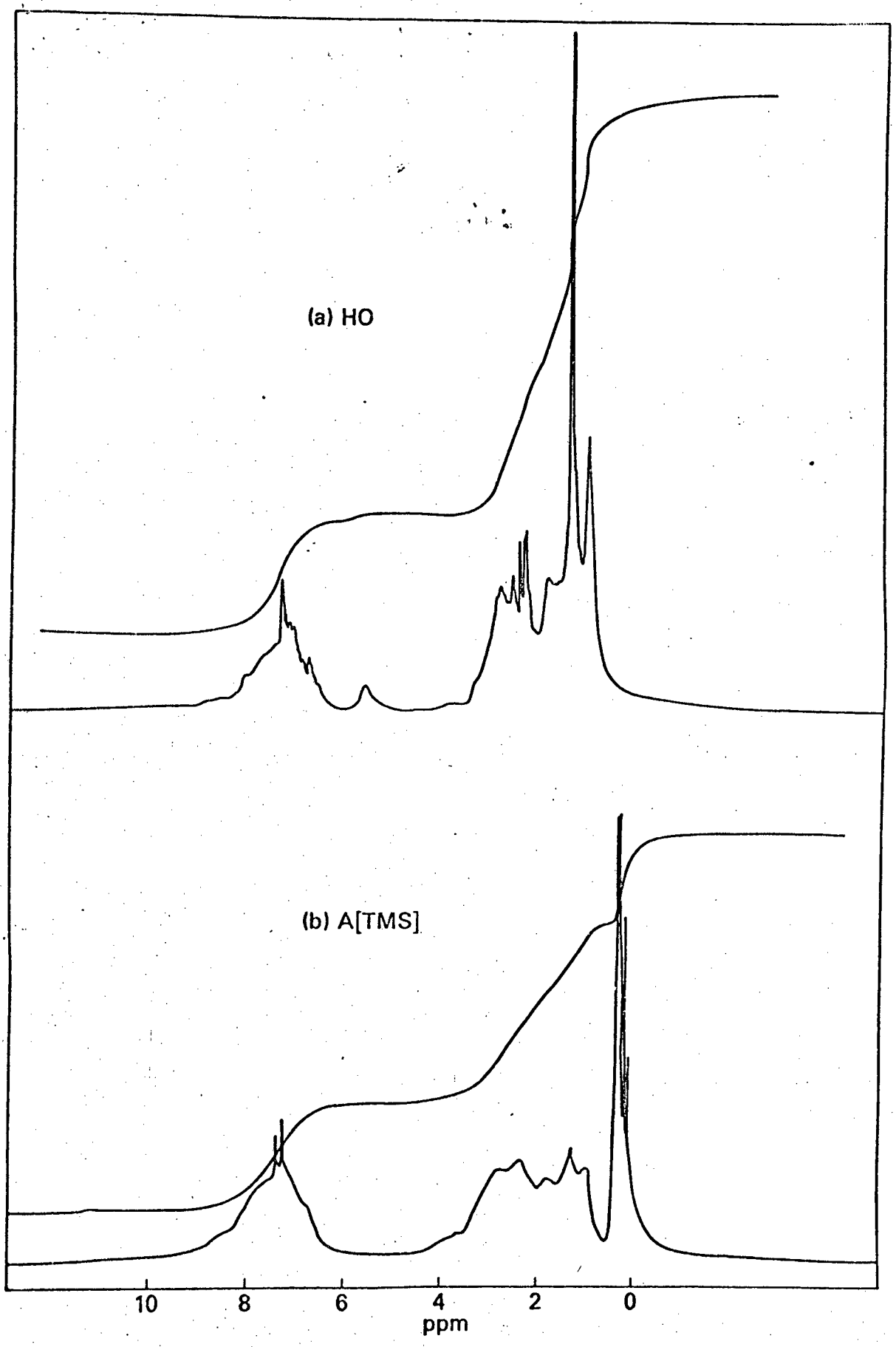
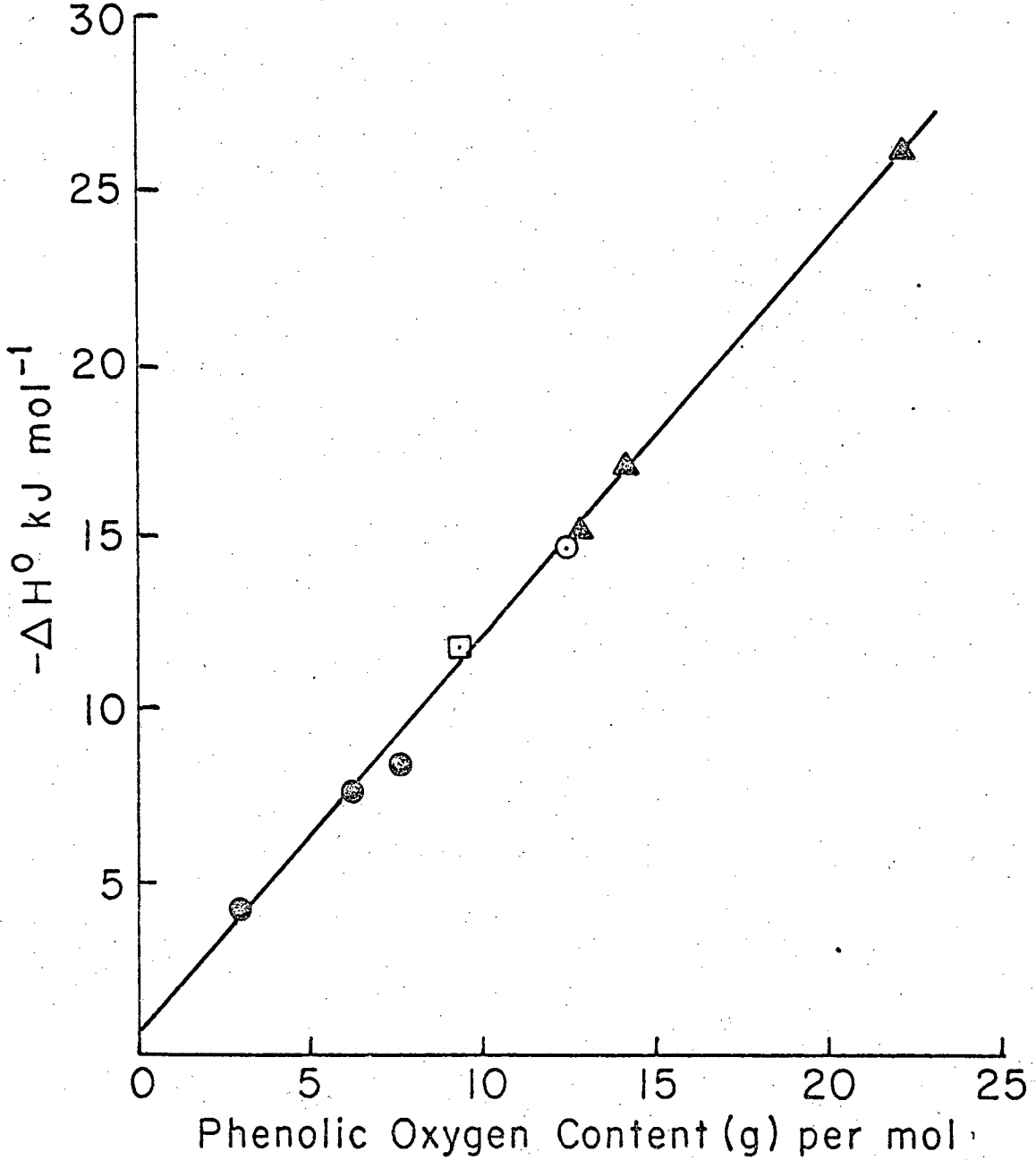
Figure Legends

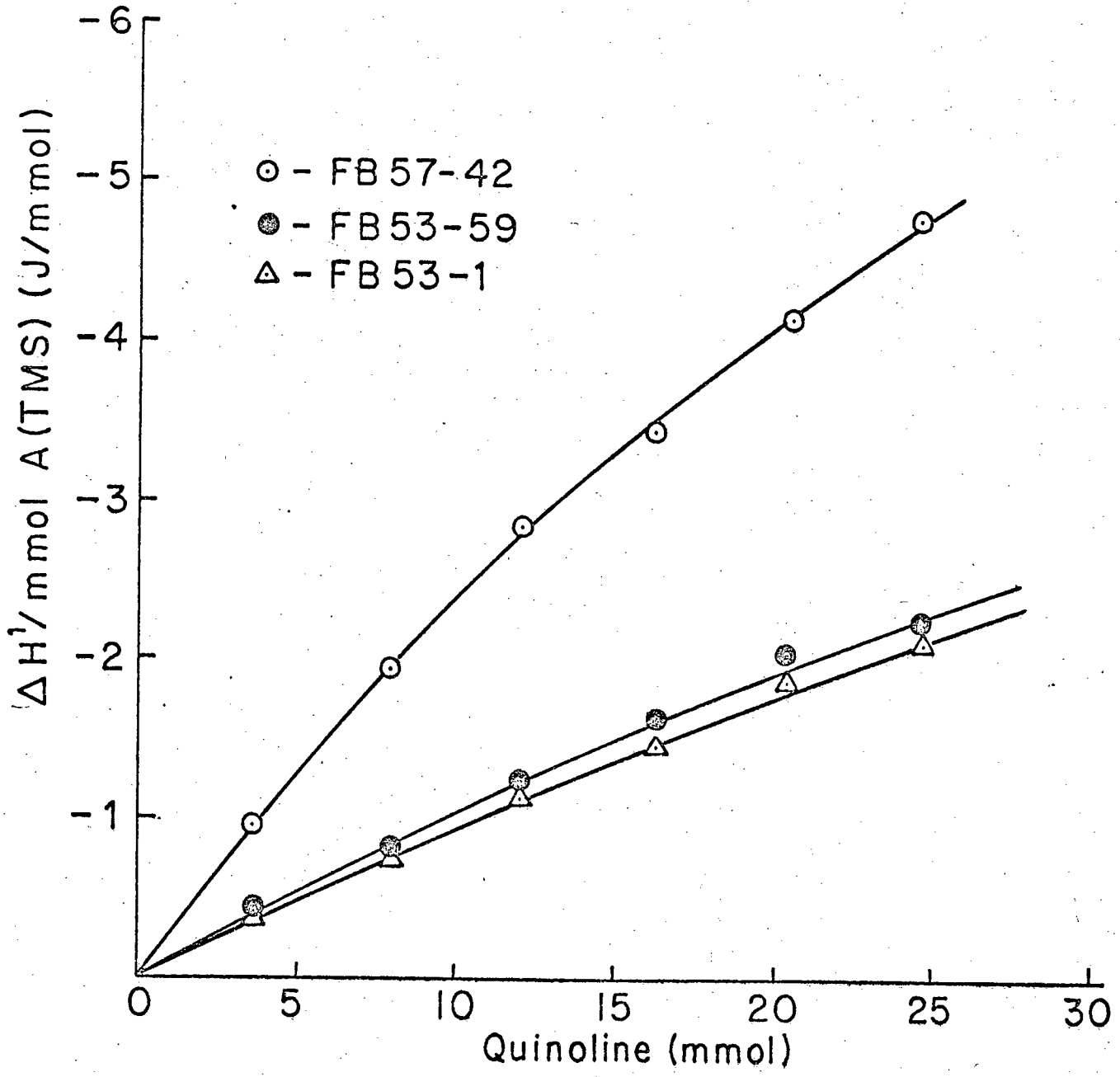
Figure 1. 100 MHz proton magnetic resonance spectra of coal liquid fractions in $CDCl_3$ (a) pentane soluble HO (b) A(TMS)

Figure 2. Dependence of $\Delta H°$ value on the phenolic oxygen content per mole of coal fraction. -▲-A, -O- AA, -□- BA and -●- HO.

Figure 3. Plots of $\Delta H'$/(mmol of A(TMS)) vs quinoline (mmol) added. Points are experimental; solid lines are calculated from equation (1), using values of K^{-1} and $\Delta H°$ listed in Table 2.


(a) HO
(b) A[TMS]
10
8
6
4
2
0
ppm


30
25
20
15
10
5
0
5
10
15
20
25
$-\Delta H^{\circ}$ kJ mol^{-1}
Phenolic Oxygen Content (g) per mol


⊙ - FB 57-42
● - FB 53-59
△ - FB 53-1
ΔH¹/mmol A(TMS) (J/mmol)
-6
-5
-4
-3
-2
-1
0
5
10
15
20
25
30
Quinoline (mmol)

13

Fig. 3

Table 1

Hydroxyl distribution in coal-derived liquid fractions and thermodynamic parameters* of their interaction with Qu in solvent benzene at 298 ± 0.5K

Source	Fraction	% H as OH ± 5%	% O as OH ± 10%	Phenolic oxygen (g) per mol	Thermodynamic constants of Qu Interaction		
					K^{-1} mol dm^{-3}	$-\Delta H°$ kJ mol^{-1}	$-\Delta S°$ J mol^{-1} deg^{-1}
FB53-1	A	2.0	61	12.9	0.0515	14.98 ± 0.13	25.5
	HO	0.9	73	3.0	0.0323	4.23 ± 0.04	-14.2
FB57-42	A	2.6	64	14.3	0.0532	16.92 ± 0.21	32.2
	AA	2.7	62	12.5	0.0549	14.74 ± 0.04	25.3
	BA	1.4	40	9.4	0.0543	11.77 ± 0.04	15.2
	HO	1.7	80	6.1	0.0328	7.49 ± 0.12	-3.3
FB53-59	A	2.9	68	22.3	0.0585	26.02 ± 0.13	63.6
	HO	1.9	83	7.6	0.0352	8.28 ± 0.08	0.0

*taken form reference 1 and 2.

Uncertainties in $\Delta H°$ values are standard deviations. Error in K^{-1} is about 10%.

Table 2

Asphaltene structural parameters and thermodynamic constants for system, Qu-A(TMS) in C_6H_6 at 298 ± 0.5 K.

Source	Asphaltene structural parameters				Thermodynamics constants,* Qu-A(TMS)		
	C/H	f_a	Mol wt. A	Mol wt. A(TMS)	K^{-1} mol dm^{-3}	$-\Delta H°$ kJ mol^{-1}	$-\Delta S°$ J mol^{-1} deg^{-1}
FB53-1	1.25	0.75	680	770	0.6309	13.31 ± 0.25	40.8
FB57-42	1.12	0.72	530	660	0.2354	14.14 ± 0.22	35.5
FB53-59	1.11	0.70	740	830	0.4553	10.84 ± 0.35	29.8

*Uncertainties in $\Delta H°$ values are standard deviations. Error in K^{-1} is about 10%. Initial mmol of A(TMS): FB53-1, 2.512; FB57-42, 1.910; FB53-59, 1.558.

Work in Progress

The toluene-insoluble, asphaltene and heavy oil fractions of centrifuged liquid product and solvent refined coal, supplied by the Pittsburgh Energy Research Center, are isolated by solvent fractionation, and the acid/neutral and base components of the asphaltenes are further separated. Trimethylsilyl ethers (TMS ethers) of select liquid fractions are being prepared. Experiments are going on for the purpose of assessing the importance of hydrogen bonding in determining the viscosity of the solutions.

Personnel

During the period April 1, 1978 - June 30, 1978, the Principal Investigator devoted 1/3 of his time to the work of the Contract in April, and 40 hr/ week in May and June. Dr. K.C. Tewari devoted 40 hrs/week throughout this period. The following students are participating in the project:
Dan Croitoru, David Susco, Robert Maurer and Miann Jones.