DOE/PC/90540--16

DE91 005751

**DETERMINATION OF THE EFFECT OF VARIOUS HYDROGEN BONDING FUNCTIONALITIES ON
THE VISCOSITY OF COAL LIQUIDS**

Final Report for the Period September 15, 1986–August 14, 1990

**Principal Investigator
Jing-Fong Wei**

November 15, 1990

Grant No. DE-FG22-86PC90540

**Prepared for
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania**

**By
Southern University
Department of Chemistry
Southern Branch Post Office
Baton Rouge, Louisiana 70813**

FINAL REPORT

date: November 15, 1990

TITLE: Determination of the Effect of Various Hydrogen Bonding
Functionalities on the Viscosity of Coal Liquids

PI: Jing-Fong Wei

INSTITUTION/ORGANIZATION: Department of Chemistry, Southern
University, Southern Branch Post Office, Baton Rouge,
Louisiana 70813. (504) 771-3990

GRANT NO. : DE-FG22-86PC90540

PERIOD OF PERFORMANCE: September 15, 1986 - August 14, 1990

Determination of the Effects of Various Hydrogen Bonding Functionalities on the Viscosity of Coal Liquids

Abstract

The trifluoroacetyl chloride (TFAC) and the TFAC/alkanoic acid derivatizations showed that phenolic and aromatic amino compounds behaved differently toward the derivatizations. To assess the effects of various hydrogen bonding functionalities on the viscosity of coal liquids, the above two derivatization methods were employed to eliminate only base-type hydrogen bondings and to eliminate both acid- and base- type hydrogen bondings. The viscosity changes due to derivatization were attributed to both the elimination of hydrogen bonding and the increase of average molecular weight. This study revealed that the effect of average molecular weight increase on the viscosity of low-boiling coal liquids severely overshadowed the effect of hydrogen bonding. It was strongly suggested that the effect of molecular weight increase must be measured before the derivatization methods can be used to quantitate the effects of various hydrogen bonding functionalities on the viscosity of coal liquids.

The viscosities were measured by using the cone/plate viscometer of Wells-Brookfield. The average molecular weights of coal liquids were measured by using the osmometer of Wescor. The percentages of phenols and amino compounds in coal liquids were determined by nonaqueous potentiometric titrations. The gas chromatography (GC) was used to quantitate the derivatization yields of model compounds and the GC/mass spectrometry was used to identify their derivatized products. The gas chromatography was also used to assess the removal of methylene chloride which was used as solvent in the derivatizations of coal liquids.

Determination of the Effect of Various Hydrogen Bonding Functionalities on the Viscosity of Coal Liquids

INTRODUCTION: The objective of this program was to differentiate and quantitate the effects of various hydrogen bonding functionalities on the viscosity of coal liquids. Emphasis was on separating and measuring the individual effect of phenolic (acidic) and aromatic amino (basic) hydrogen bonding functionalities on the viscosity of coal liquids. The elimination of both acidic and basic hydrogen bondings was attempted by using trifluoroacetyl chloride and butyric acid in derivatization; and the elimination of basic hydrogen bondings was attempted by using only trifluoroacetyl chloride in derivatization. The selectivity toward hydrogen bondings' elimination offered by these derivatizations was proven to be feasible from a study of model compounds' derivatizations. Nine narrow-boiling-range coal distillates were obtained from distilling the 1:1 mixture of 450x650°F and 650x950°F coal liquids of Wilsonville Run 245 and were used as coal liquid samples. Under the TFAC derivatization, a distillate's basic type hydrogen bondings were presumably eliminated; and under the TFAC/butyric acid derivatization, a distillate's acidic and basic hydrogen bondings were presumably eliminated. Same derivatization procedures except the omission of TFAC or TFAC/butyric acid was applied to the distillate to serve as a controlled blank.

WORK DONE

I. Development of Derivatization Procedures for Selective Elimination of Acidic and Basic Hydrogen Bondings

Model compounds representing phenolic and aromatic amino compounds in coal liquids were derivatized with TFAC. Gas chromatographic method was used to quantitate % yield by peak disappearance. Successful yield was observed for aromatic amino compounds like APAH (e.g. N-ethylaniline), N-PAH (e.g. 1,2,3,4 tetrahydroquinoline), however no yield was observed for phenols. This was explained by the following reactions:

When an alkanolic acid was added to the derivatization, both phenolic and amino compounds were successfully derivatized. Gas chromatography/mass spectrometry (GC/MS) confirmed that the product for a amino compound remained the same as without the alkanolic acid addition; however, the product for a phenolic compound was the alkyl ester instead of the highly labile trifluoroacetyl ester. Obviously, the highly labile trifluoroacetyl ester reacted with alkanolic acid to form a stable alkyl ester, as described by the following reaction .

The GC/MS identified the product by comparing the derivatized product to its model. An increase of 96 m/e units indicated the formation of the trifluoroacetyl ester or amide; and an increase of 70, when derivatized in the presence of butyric acid, indicated the formation of the alkyl ester or amide.

II. Derivatizing Coal Distillates

a) Preparing Nine Coal Distillate Samples

The 1:1 mixture of 450x650°F and 650x 950°F distillates of Wilsonville Run 245 was distilled into nine narrow-boiling range distillates, as 400x450°F, 450x475°F, 475x500°F, 500x525°F, 525x550°F, 550x595°F, 595x630°F, 630x660°F and above 660°F.

b) Derivatizing samples

All the above nine distillates were derivatized under the TFAC derivatization and the TFAC/butyric acid derivatization, the same procedures except the omission of TFAC or TFAC/butyric acid were

applied to these distillates to serve as controlled blanks. The elimination of basic only and both basic and acidic hydrogen bondings were presumably achieved under the TFAC and the TFAC/butyric acid derivatization respectively.

c) Removing Methylene Chloride

Since methylene chloride was used as solvent in the derivatizations, the removal of the solvent must be done before the measurements of viscosity and molecular weight. The methylene chloride was removed to about 0.05% or less by vacuum evaporation. Determination %CH₂Cl₂ in samples was done by GC external standard method using distilled toluene (free of low-boiling impurities) as solvent.

III. Measurements

a) Average Molecular Weight

The average molecular weights were determined using an osmometer. The toluene and tetrahydrofuran (THF) were tested for their adequacy as solvents. Figure 1 was the plots of average molecular weight versus various concentrations of samples in toluene, the non-horizontal lines, (1) and (2) for low-boiling samples, demonstrated the inadequacy of using toluene as the solvent in the determination of molecular weight in this study. The THF was used in the osmometry as it gave satisfactory result as showed in Figure 2.

b) Viscosity

The viscosities were measured at $50.00^{\circ} \pm 0.01^{\circ}\text{C}$ using a cone/plate viscometer.

c) Acid and Base Contents

The phenolic contents were determined by titrating samples in pyridine with tetra-n-butyl ammonium hydroxide (TBAOH) in 9:1 toluene/2'-propanol. The amino contents were determined by titrating samples in nitrobenzene with perchloric acid in 1,4-dioxane. To sharpen the titration curves, p-cresol was added as standard (spiking agent) in the determination of phenols and 2-

aminobiphenyl was for amino compounds of 3'-PANH like acridine, APAH like n-ethylaniline and N-PAH like tetrahydroquinoline. These standards were used because of their acidity and basicity were about the weakest among their own groups. The very weak bases/acids like carbazole and indole were not titrated in the above titration. The titrations of these very weak bases/acids were also found to be possible if adequate solvent and spiking standard were used. However, the effect of hydrogen bondings from these compounds was too weak to be considered in this study.

Results and Discussion

The results are listed in Table 1. The followings summarize their scientific importance.

a) It was manifested that the derivatization procedures were applied properly. This was evidenced by i) the molecular weights, ii) the -OH contents and iii) the -NH contents measured for the two controlled series being extremely close.

b) The derivatization procedures were adequate to use in the selective elimination of various hydrogen bondings. The -OH contents decreased only very slightly for coal distillates after the TFAC derivatization; no -OH remained in coal distillates after the TFAC/butyric derivatization. The -NH contents for coal distillates after both TFAC and TFAC/butyric acid derivatizations were decreased to about the same levels; the remaining -NH was accounted for 3'-PANH which were presumably unable to derivatize.

c) The coal distillates decreased their molecular weights after the derivatizations. The average molecular weights of coal distillates after the TFAC/butyric acid derivatization were greater than those after the TFAC derivatization. The molecular weight increase was resulted from the derivatizations due to a much heavier group replacing a hydrogen atom. More compounds were derivatized in the TFAC/butyric acid derivatization than in the TFAC derivatization.

d) The viscosities were decreased as expected only for higher boiling distillates. For low boiling distillates, the viscosities

caused by derivatization overshadowed the effect of hydrogen bonding on the viscosity. This overshadowing effect caused by molecular weight increase was severer for lower boilings because the increase of molecular weight was relatively more.

e) The increase in viscosity persisted to higher boiling up to 550'x595'F for the case of the TFAC derivatization, as compared to only up to 450'x475'F for the case of the TFAC/butyric acid derivatization. This may imply that the effect of the phenolic hydrogen bonding on viscosity is more important than that of the amino hydrogen bonding.

CONCLUSION

Figures 3 and 4 showed the plots of viscosity versus mid-boiling point, no obvious change in viscosity was shown for both cases. Figures 5 and 6 showed the plots of viscosity versus molecular weight, the effect of hydrogen bonding on viscosity was clearly shown; however, the effect of molecular weight was still very prominent. It was suggested that the correction for the effect of molecular weight on viscosity must be done before the effect of hydrogen bonding on the viscosity can be quantitated by the derivatization methods.

Figure 1. Plots of molecular weights of coal distillates determined from the osmometry using toluene as solvent.

Figure 2. Plots of molarcular weights of coal distillates determined from the osmometry using tetrahydrofuran as solvent.

Table 1. Results of Derivatization of Coal Distillates

boiling range, °F	derivatized with TFAC/butyric acid				controlled blank				derivatized with TFAC				controlled blank			
	m.wt	η	-OH	-NH	m.wt	η	-OH	-NH	m.wt	η	-OH	-NH	m.wt	η	-OH	-NH
400x450	172.6	2.91	N.D.	0.075	159.7	2.55	2.83	0.203	167.6	3.14	2.54	0.084	160.3	2.58	2.82	0.221
450x475	182.4	2.82	N.D.	0.125	164.3	2.75	2.21	0.217	170.3	3.11	1.97	0.130	164.4	2.88	2.23	0.196
475x500	192.2	3.04	N.D.	0.113	173.5	3.04	1.81	0.199	180.1	3.35	1.50	0.104	173.4	3.11	1.79	0.191
500x525	199.2	3.33	N.D.	0.123	184.4	3.52	1.32	0.188	190.3	3.76	1.18	0.121	183.8	3.51	1.31	0.192
525x550	217.6	3.80	N.D.	0.119	198.2	4.02	0.98	0.162	201.3	4.36	0.85	0.119	198.2	4.08	0.98	0.171
550x595	220.3	5.10	N.D.	0.096	205.4	5.90	0.57	0.152	216.1	6.15	0.53	0.107	205.7	6.01	0.56	0.154
595x630	247.5	10.30	N.D.	0.094	239.2	13.75	0.43	0.142	242.1	12.50	0.35	a	239.4	13.70	0.42	0.141
630x660	279.1	38.40	a	a	267.3	44.40	a	a	271.2	43.70	a	a	267.0	46.60	a	a
> 660	287.3	205.8	a	a	274.6	236.7	a	a	276.3	227.2	a	a	274.4	240.2	a	a

N.D. not detected

a not determined due to the shortage of sample

η viscosity in centipoise

-OH phenolic content in milliequivalent per gram of sample

-NH amino content of APAH, 30-PANH and N-PAH in milliequivalent per gram of sample

Figure 3. Viscosity change after the TFAC/
butyric acid derivatization, viscosity
was plotted versus mid-boiling point.

Figure 4. Viscosity change after the TFAC derivatization, viscosity was plotted versus mid-boiling point.

Figure 5. Viscosity change after the TFAC/butyric acid derivatization, viscosity was plotted versus the molecular weight of derivatized samples.

Figure 6. Viscosity change after the TFAC derivatization, viscosity was plotted versus the molecular weight of derivatized samples

END

DATE FILMED

02 / 07 / 91