

Separation and Characterization of Hydroxyl Aromatics in Oils
and Asphaltenes from Nondistillable, Pyridine Soluble Coal-Liquids

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Introduction

Hydroxyl aromatics are an important class of compounds in coal liquefaction processes (1-6). The separation and characterization of hydroxyl aromatics are particularly important for the development of coal liquefaction processes and for an understanding of coal liquefaction chemistry. It has been shown that oils and asphaltenes in high-boiling distillates and nondistillable, pyridine soluble coal-liquid samples produced in an SRC-I process consist of the same major compound classes: hydrocarbons, nitrogen compounds, and hydroxyl aromatics (5). However, as reported by Boduszynski et al. (5) oils and asphaltenes differ in the concentrations of hydrocarbons, nitrogen compounds, and hydroxyl aromatics. In this work, hydroxyl aromatic fractions were isolated from oils and asphaltenes in non-distillable ($> 427^{\circ}\text{C}$) Wyodak and Kentucky pyridine soluble coal-liquid samples using procedures developed by Boduszynski et al. (7, 8). The fractions were further separated by normal-phase and reversed-phase liquid chromatography and then characterized by nuclear magnetic resonance, infrared, and field-ionization mass spectrometry. In addition, elemental analysis data were obtained on some of the fractions.

Experimental

Using methods developed by Boduszynski et al. (7, 8) nondistillable, pyridine soluble coal-liquid samples were separated into solvent-derived fractions and compound-class fractions. Coal-liquid fractions rich in hydroxyl aromatics from oils and asphaltenes were obtained from both Wyodak and Kentucky pyridine soluble coal-liquid samples. Each of these hydroxyl aromatic fractions was then separated into fractions containing monohydroxyl and dihydroxyl aromatics by liquid chromatography with a bonded-phase amino column and chloroform:2-propanol mobile phases. The monohydroxyl aromatic fraction was first eluted from the bonded-phase amino column with chloroform:2-propanol (95:5, v/v), and the dihydroxyl aromatic fraction was subsequently eluted with chloroform:2-propanol (75:25, v/v).

Fractions containing monohydroxyl aromatics from oils were isolated with the bonded-phase amino column and further separated by reversed-phase liquid chromatography. In reversed-phase liquid chromatography experiments, the monohydroxyl fraction from Wyodak oils was separated in two steps. First, isocratic conditions with a Resolvex C_8 column and a acetonitrile:tetrahydrofuran:water (15.2:27.8:57.0, v/v/v) mobile phase were used. Then, a linear gradient to 100% tetrahydrofuran was employed.

Field-ionization mass spectral data were obtained from SRI International, Menlo Park, California on several of the monohydroxyl and dihydroxyl aromatic fractions from oils and asphaltenes. Elemental analysis data were obtained from Huffman Laboratories, Inc., Wheatridge, Colorado.

Results and Discussion

Weight Percent and Elemental Analysis Data

Table I gives the approximate weight percent (wt%) data for fractions containing monohydroxyl aromatics and dihydroxyl aromatics isolated from the oils and asphaltenes of Kentucky and Wyodak nondistillable, pyridine soluble coal-liquid samples. It is clear from the data in Table I that the monohydroxyl aromatic fractions contain significantly more material than the dihydroxyl aromatic fractions. Table II gives the elemental analysis data obtained for three of the monohydroxyl aromatic fractions and one of the dihydroxyl aromatic fractions. The elemental analysis data clearly show that the fractions contain a large amount of oxygen; however, nitrogen is also present but in smaller amounts. Infrared data and the chromatographic data indicated that hydroxyl oxygen was present in the fractions. The infrared experiments also showed that pyrrolic nitrogen was in most of the fractions.

Chromatographic and Field-Ionization Mass Spectral Data

Chromatographic data from thirty-four monohydroxyl and dihydroxyl aromatic standards indicated that these compounds could be separated into monohydroxyl and dihydroxyl aromatic fractions with a bonded-phase amino column and chloroform:2-propanol mobile phases. Application of this approach to hydroxyl fractions from coal-derived oils and asphaltenes yielded two distinct fractions which had retention characteristics similar to the model monohydroxyl and dihydroxyl aromatic compounds, respectively.

Field-ionization mass spectral data were obtained from eight monohydroxyl and dihydroxyl aromatic fractions isolated from Wyodak and Kentucky nondistillable, pyridine soluble coal-liquid samples. The spectra revealed the extreme complexity of these samples. Table III gives the weight average molecular weight for the fractions.

To obtain field-ionization mass spectra that were less complex, the monohydroxyl aromatics from Kentucky oils were divided into four fractions using a bonded-phase amino column. Then field-ionization mass spectra were obtained from these four fractions. Even though the field-ionization mass spectra were simplified, relatively complex spectra were still observed. However, major structural assignments were made and several homologous series were characterized.

Reversed-phase liquid chromatography experiments with the monohydroxyl fraction from Wyodak oils showed that the compounds could be completely eluted from a reversed-phase column. Under the reversed-phase conditions, first a highly resolved chromatographic profile of low molecular weight compounds was obtained, and then with the application of a reversed-phase gradient elution step, two major chromatographic bands were observed. Figure 1 shows the overall chromatogram obtained from the monohydroxyl fraction from Wyodak oils. In related experiments, field-ionization mass spectra were obtained from the total material of the highly resolved chromatographic bands and the total material from the reversed-phase gradient step from the monohydroxyl fraction of Kentucky oils. The field-ionization mass spectrum of the highly resolved chromatographic bands was somewhat simple, giving a weight average molecular weight of 291. The spectrum from the reversed-phase gradient step was rather complex and showed a weight average molecular weight of 465.

Acknowledgement

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References

1. Whitehurst, D. D.; Mitchell, T. O.; Farcasiu M. "Coal Liquefaction"; Academic Press: New York, 1980.
2. Kamiya, Y.; Sato, H.; Yao, T. Fuel 1978, 57, 681.
3. Schiller, J. E.; Mathiason, D. R. Anal. Chem. 1977, 49, 1225.
4. White, C. M.; Li, N. C. Anal. Chem. 1982, 54, 1570.
5. Boduszynski, M. M.; Hurtubise, R. J.; Silver, H. F. Fuel 1984, 63, 93.
6. Cronauer, D. C.; McNeil, R. I.; Galya, L. G.; Danner, D. A. Am. Chem. Soc., Div. Fuel Chem. Preprints 1984, 29(5), 130.
7. Boduszynski, M. M.; Hurtubise, R. J.; Silver, H. F. Anal. Chem. 1982, 54, 372.
8. Boduszynski, M. M.; Hurtubise, R. J.; Silver, H. F. Anal. Chem. 1982, 54, 375.

Table I. Approximate wt% Values of Monohydroxyl Aromatic and Dihydroxyl Aromatic Fractions From Oils and Asphaltenes in Solvent-Refined Coal-Liquid Samples

<u>Oils</u>			
<u>Wyodak</u>		<u>Kentucky</u>	
Monohydroxyl	Dihydroxyl	Monohydroxyl	Dihydroxyl
4.3	1.0	3.8	0.2
<u>Asphaltenes</u>			
<u>Wyodak</u>		<u>Kentucky</u>	
Monohydroxyl	Dihydroxyl	Monohydroxyl	Dihydroxyl
17.0	7.4	17.8	5.2

Table II. Elemental Analysis Data for Monohydroxyl and Dihydroxyl Aromatic Fractions¹

<u>Oils</u>	<u>Wt%</u>			
	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>
Wyodak-monohydroxyl	81.1	7.3	9.1	0.73
Kentucky-monohydroxyl	80.6	7.5	9.5	0.47
<u>Asphaltenes</u>				
Wyodak-monohydroxyl	84.3	6.3	8.5	1.0
Wyodak-dihydroxyl	80.1	6.2	11.3	0.90

¹Data provided by Huffman Laboratories, Inc.

Table III. Weight Average Molecular Weight for Hydroxyl Aromatic Fractions¹

<u>Oils</u>			
<u>Wyodak</u>		<u>Kentucky</u>	
Monohydroxyl	Dihydroxyl	Monohydroxyl	Dihydroxyl
496	503	477	505
<u>Asphaltenes</u>			
<u>Wyodak</u>		<u>Kentucky</u>	
Monohydroxyl	Dihydroxyl	Monohydroxyl	Dihydroxyl
571	543	566	556

¹Data provided by SRI International.

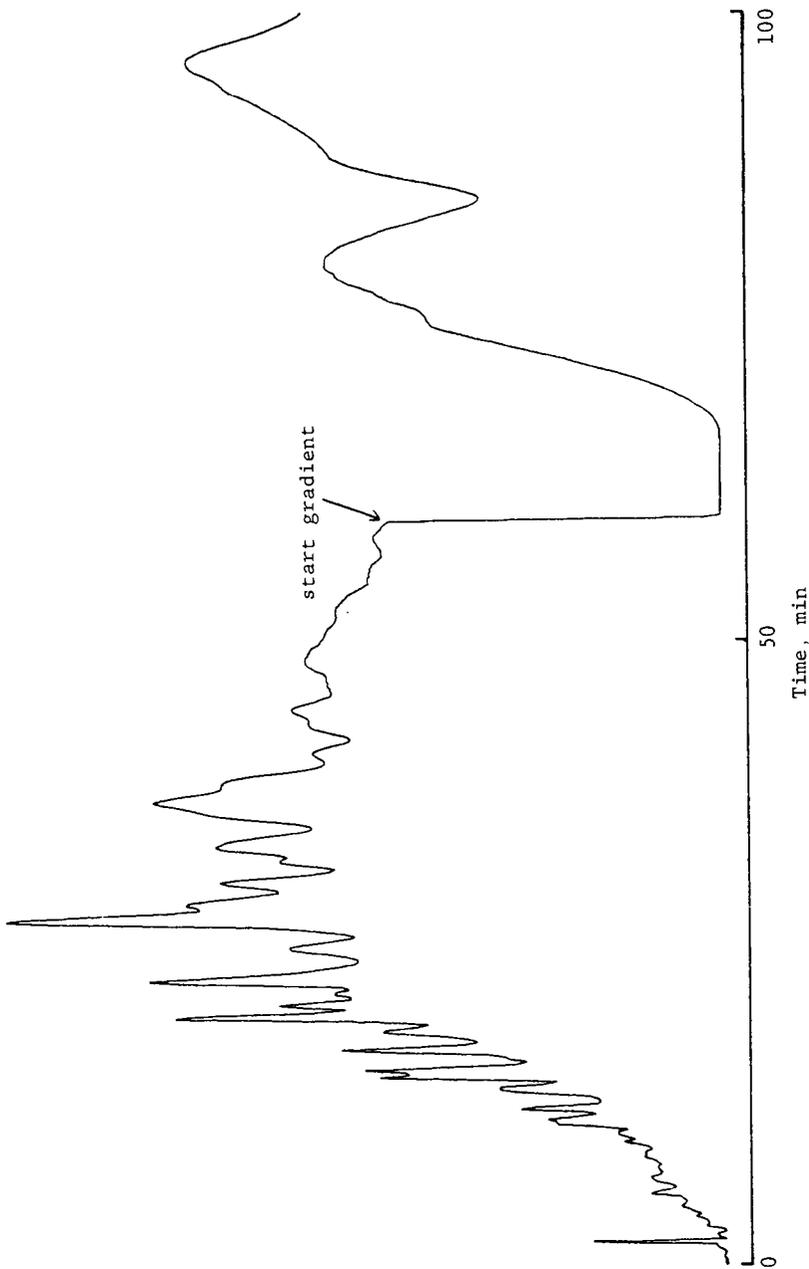


Figure 1. Reversed-phase chromatogram obtained from the monohydroxyl fraction from Wyodak oils with a C₈ column and acetonitrile:tetrahydrofuran:water (15.2:27.8:57.0, v:v:v) mobile phase (0-60 min) and a gradient step to 100% tetrahydrofuran (60-100 min) at 1.0 mL/min. The chromatogram from 0-60 min represents about 22% of the fraction and the chromatogram from 60-100 min represents about 78% of the fraction.