Reports

Acid-Base Structure of Coal-Derived Asphaltenes

Abstract. *Asphaltenes, the key intermediates in the liquefaction of bituminous coals, consist of hydrogen bonded complexes which can be separated into their acidic and basic components. The acidic components contain all, while the basic components contain none, of the exchangeable protons present. The significance of these findings with respect to coal structure and coal solubilization is discussed.*

It is generally agreed that asphaltenes, operationally defined as being soluble in benzene and insoluble in pentane, are the key intermediates in the conversion of coal to oil (*1*). We now have found that these asphaltenes have essentially an acid-base structure. Furthermore, the acidic and basic components can be separated by dissolving the asphaltenes in toluene and passing dry HCl gas through the solution. The basic component precipitates as an insoluble HCl adduct, while the acidic component remains in solution (*2*) and can be recovered by evaporation of the solvent.

Experiments including thin-layer chromatography, thin-layer electrophoresis, nuclear magnetic resonance (NMR), D_2O exchange, and determination of sodium-replaceable hydrogen suggest the composite structures for the acidic and basic components shown in Fig. 1.

The essential features of these structures are as follows. The oxygen in the acidic component is present as phenolic hydroxyl and the nitrogen as acidic nitrogen, as in pyrrole (*3*). The oxygen in the basic component is present as ring or ether oxygen, and the nitrogen as ring nitrogen as in pyridine. Complex formation occurs by hydrogen bonding between acidic phenol and basic nitrogen groups as indicated in Fig. 1.

Table 1. Ultimate analyses and molecular weights of asphaltenes and their acidic and basic components. The molecular weights were obtained by vapor pressure osmometry in benzene solution. Values for the HCl-free basic components were calculated (calc.).

Material	Composition (%)						Molecular weight
	C	H	O	N	S	Cl	
Asphaltene (415°C)	85.91	6.85	4.11	1.67	1.46		686
Acidic component	85.72	7.18	3.86	0.99	0.88	1.37	
Basic component (as HCl adduct)	81.27	6.39	4.63	2.12	1.05	4.54	
Basic component (calc. HCl-free)	85.25	6.57	4.86	2.22	1.10		
Asphaltene (450°C)	87.43	6.52	3.52	2.16	0.37		417
Acidic component	87.40	7.04	3.39	0.99	0.51	0.67	550
Basic component (as HCl adduct)	83.35	5.78	3.48	2.72	0.53	4.14	
Basic component (calc. HCl-free)	87.06	5.91	3.64	2.84	0.55		368

Table 2. Ultimate analyses and molecular weights of hexane-soluble fractions from coal liquefaction products. Oxygen values were obtained by difference, molecular weights by vapor pressure osmometry in benzene solution.

Temperature (°C)	Percentage of total liquefied product	Composition (%)					Molecular weight
		C	H	O	N	S	
415	76	89.02	9.69	0.68	0.43	0.18	289
450	60	87.57	8.49	2.42	1.10	0.42	225

The hydrogen bonded structure of asphaltenes is compatible with their solubility characteristics. In moderately polar solvents, such as benzene (*4*), the asphaltenes are soluble because the acidic and basic components are separately solvated. As the polar solvent is replaced by nonpolar solvents, such as pentane, hydrogen bonding takes place, a large complex is formed, and the asphaltenes precipitate as hydrogen bonded acid-base complexes.

Although more work will have to be carried out to confirm the structural details in Fig. 1, our experimental data leave no doubt that the acidic component contains all and the basic component none of the acidic (deuterium exchangeable) hydrogen present. This result precludes the possibility of the asphaltenes having an amphoteric structure.

That a complex mixture of compounds such as asphaltenes is composed of acids and bases is an unexpected result. It suggests that coal, too, may have an acid-base structure, contrary to the generally accepted view (*5*) that acidic and basic functional groups are randomly distributed over the whole coal molecule. It certainly seems extremely unlikely that conversion of coal to asphaltene could change such a random distribution of acidic and basic functional groups into one where these groups are segregated, that is, where acidic and basic functional groups are attached to different molecules.

An acid-base structure of bituminous coal is compatible with earlier experiments (*6*) which showed that bituminous coal can be solubilized by aromatic compounds at elevated temperatures. The solubility of coal in high-boiling aromatic compounds, like that of asphaltenes in benzene, may be attributed to solvation of hydrogen bonded acid-base complexes.

Should the acid-base structure of bituminous coal be confirmed, this

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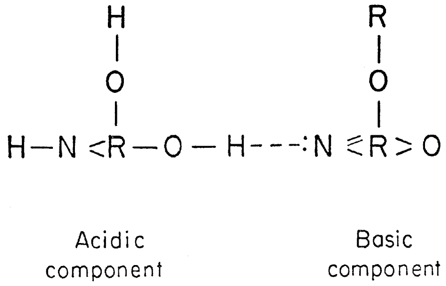

Fig. 1. Acidic and basic components of asphaltenes. The hydrogen attached to the nitrogen in the acidic component represents an acidic hydrogen as in pyrrole. This illustration merely indicates the type of hydrogen bonding that may occur between acidic and basic components; it does not imply that asphaltenes consist of acidic and basic components in a 1/1 ratio.

would raise the question of how coalification of plant material could lead to a segregation of acidic and basic functional groups.

The two coal-derived asphaltenes described in this report were isolated from coal liquefaction products made from Kentucky hvAb (high volatile A bituminous) coal by the Synthoil process (*7*) at 415°C and an H_2 pressure of 4000 pounds per square inch (psi) and at 450°C and an H_2 pressure of 2000 psi (1 psi ≃ 50 torr). The asphaltenes from 415°C represented 24 percent and those from 450°C represented 40 percent of the liquefaction product. Ultimate analyses and molecular weights (number average) obtained by vapor pressure osmometry of the original asphaltenes and their acidic and basic components in benzene are listed in Table 1 (*8*). Ultimate analyses and molecular weights of the hexane-soluble fractions (*9*), which represented 76 and 60 percent of the liquefaction products at 415° and 450°C, respectively, are shown in Table 2.

For the molecular weight determination, NMR analyses, and D_2O exchange reactions, the HCl adduct of the basic component was freed of HCl by stirring a suspension of adduct in a mixture of toluene and dilute aqueous alkali. The liberated basic component was now soluble in toluene and could be recovered by removal of the solvent. The acidic and basic components of the 415°C asphaltenes were obtained in a weight ratio of 42/58, and those of the 450°C asphaltenes in a weight ratio of 37/63.

It is of interest to compare the molecular weight of 417 obtained for the 450°C asphaltene complex with the molecular weights obtained separately for the acidic (550) and basic (368) components. Assuming complete dissociation in benzene solution, 37 weight percent of acidic component having a molecular weight of 550 and 63 weight percent of basic component having a molecular weight of 368 should give a molecular weight of 420. This value is in excellent agreement with that of 417 found for the molecular weight of the asphaltene fraction by direct determination.

It is also of interest to speculate on the molecular weight of the undissociated asphaltene complex. From the weight ratio of 37/63 of acidic component to basic component and from their respective molecular weights of 550 and 368, it follows that the undissociated asphaltene complex contains the acidic and basic components in a ratio of 2/5. This corresponds to a molecular weight of 2940, which is of the order of the molecular weight found in bituminous coal (*10*).

Thin-layer chromatography of the acid fraction gave direct reproducible evidence of a number of polynuclear aromatic phenols and some indole-type nitrogens, while no phenols were observable in the base fraction. The base fraction, which required the more drastic solvent conditions, gave evidence of polynuclear aromatic base nitrogen.

Thin-layer electrophoresis results showed that only the acidic fraction responded to the voltage potential between *p*H 2.2 and 4.5 (acetic acid–formic acid mixture). The resulting zones on spraying gave clear evidence of phenolic character. No indication of phenolic character was observed for the basic fraction.

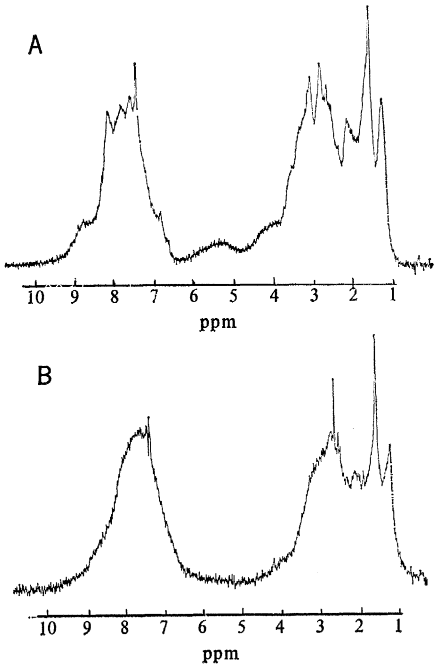

Fig. 2. Nuclear magnetic resonance spectra (^1H; 250 Mhz) of (A) the acidic and (B) the basic component of coal-derived asphaltenes in $CDCl_3$.

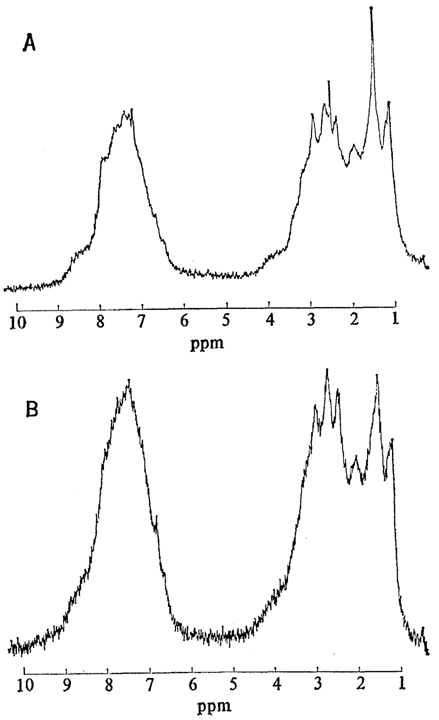

Fig. 3. Nuclear magnetic resonance spectra (^1H; 250 Mhz) of (A) the combined acidic and basic components and (B) the original coal-derived asphaltene in CS_2.

Nuclear magnetic resonance spectra were obtained with the 250-Mhz NMR spectrometer at the Carnegie-Mellon University. Figure 2 shows the ^1H NMR spectra of the acidic and basic components of the parent asphaltene in $CDCl_3$ solution. The most outstanding difference is the broad resonance at 5.35 parts per million (ppm) downfield from tetramethylsilane in the acid fraction (Fig. 2A). When a drop of D_2O is added to the acid sample, the resonance at 5.35 ppm disappears and a sharp HDO resonance at 5.0 ppm appears. This is good evidence that the signal represented replaceable protons —the hydroxyl protons of the acidic component. No deuterium-exchangeable protons were observed for the basic component.

When the acidic and basic components are physically mixed together, the resulting ^1H NMR spectrum (Fig. 3A) closely resembles that of the original asphaltene (Fig. 3B). It was also observed that when the basic component is added incrementally to the acidic component, the OH NMR resonance shifts toward lower field and broadens. This is highly indicative of the formation of a hydrogen bonded complex. To date, our investigation shows that the proton spectrum of a model phenol, *o*-phenylphenol, is shifted downfield on the addition of the basic component. We have also observed that the ^{14}N NMR signal of 5 percent pyridine in CS_2 solution broadens and is chemically shifted toward higher field with the addition of either the acidic component or the model phenol.

It is of interest to note that asphaltenes derived from petroleum also have an acid-base structure. By treating asphaltenes isolated from a California crude with HCl gas in toluene solution, as described for coal asphaltenes, we obtained acidic and basic components in a weight ratio of 44/56.

In the case of asphaltenes derived from petroleum, the NMR spectrum of the acidic component was not definitive for the presence of a hydroxyl resonance. This is probably due to the very high molecular weight range of petroleum-derived asphaltenes (~ 3000) (*11*) compared to that of coal asphaltenes (~ 500). It was, however, possible to confirm the presence of aromatic phenols in the acidic component of petroleum asphaltene by thin layer chromatography and use of visualization sprays.

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2. The fraction remaining in solution and referred to here as the acidic component contains some neutral material. Mass spectrometric analysis indicates the presence of perylene, 1,12-benzoperylene, coronene, and possibly dibenzopyrene. At present we know that the neutral material comprises less than 50 percent of the acidic component, since 50 percent of this fraction, which is now free of asphaltene bases, is soluble in hexane. A hexane-soluble, neutral material could not be present in the acidic component, since the asphaltenes were prepared by precipitation with excess hexane from toluene solution.
3. This conclusion is based on the following evidence. The acidic component, dissolved in toluene, was treated with metallic sodium at reflux temperature to replace acidic hydrogen. Decomposition of the resulting sodium compound with water and titration of the sodium hydroxide formed gave the amount of hydrogen that had been replaced by sodium. This amount of hydrogen was larger than could be accounted for by assuming that all of the oxygen in the acidic component was present as phenolic hydroxyl. The amount of acidic hydrogen could, however, be accounted for by assuming that all the nitrogen in the acidic component was present as acidic nitrogen, that is, as a nitrogen with an acidic (sodium replaceable) hydrogen such as pyrrole or indole. Since oxygen-carbon bonds of the ring or ether type are not cleaved by metallic sodium, we conclude that all oxygen in the acidic compound is OH oxygen.
4. A literature survey shows that benzene and other π-electron systems participate in hydrogen bonding. See, for examp Z. Yoshida and E. Csawa, *J. Am Chem. Soc.* **88**, 4019 (196 R. Mathur, E. D. Becker, N. C. Li, *J. Phys. Chem.* **67**, 2190 (1963).
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8. The difference in molecular weights between the 415° and 450°C asphaltenes is due to the difference in the severity of thermal degradation at these temperatures. At 415°C, thermal degradation is less severe, that is, fewer bonds are broken than at 450°C. Consequently, the fragments produced at 415°C are larger and have a higher molecular weight than those produced at 450°C.
9. It is interesting to note that these fractions have a relatively low molecular weight. Evidently, the conversation of asphaltenes to oil is the result of considerable degradation. On the basis of the ultimate analyses, it is evident that there has been a considerable loss of oxygen, nitrogen, and sulfur, probably due to hydrogenolysis.

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12. F.K.S. is a National Research Council postdoctoral fellow. The 250-Mhz NMR spectrometer facility is supported by PHS grant RR 00292.

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Ice-Rafted Sediments as a Cause of Some Thermokarst Lakes in the Noatak River Delta, Alaska

Abstract. *Irregular, barren polygonal sheets of mud scattered over the landscape of the western portion of the Noatak River Delta are derived from lake-bottom sediments, ice-rafted during flooding. The evidence suggests that the sheets of mud change the albedo and the thermal regime of the soil, induce the development of thermokarst, and lead to the formation of ponds and lakes. The angular perimeters, especially of the small ponds, support the suggested mode of formation.*

The western portion of the Noatak River Delta (67°03′N, 162°40′W), Alaska, covers about 7 km^2 and is punctuated by lakes constituting about three-fourths of the area. Many of the lakes have angular perimeters ranging from triangular to trapezoidal, or irregularly polygonal (Fig. 1). The unusual perimeters of the lakes are especially evident in the case of small ponds with well-defined sides (Fig. 2) and vertical edges. Rounded and cuspated shores occur mainly in large lakes (Fig. 1). I suggest here a mode of formation for these lakes that, to my knowledge, has not yet been described in the literature.

The mechanism invoked involves as a first step the complete freezing of existing shallow lakes, channels, and tidal flats. The lakes and other shallow bodies of water that freeze to the bottom incorporate, in the lower part of the ice, bottom sediments such as silt, algal mats, decomposed organic material, anoxic ooze, mosses, or, as observed in one case, sediments with aquatic plants. Subsequent river flooding in the spring and autumn, or storms from the sea, lift jagged ice floes with adhering sediments and float them over the delta. Once the flooding recedes, the ice floes are deposited on the landscape and, upon melting, leave silty sediments and the other material that was frozen to the ice. The suggested process does not necessarily explain all the lakes in the delta, some of which probably form as thaw lakes starting in thermal contraction cracks and others of which form in different ways from the one outlined here.

Dionne (*1*) proposed a mechanism for the formation of pitted schorre—shallow angular depressions filled with water in salt tidal marsh—in the St. Lawrence estuary. This mechanism involves the tearing and rafting of pieces of the marsh surface, including the vegetation and soil previously encased in ice, by ice floes driven ashore during spring flooding. Although there is an apparent resemblance between the geometry of the shallow ponds in the Noatak River Delta and of those in the St. Lawrence estuary, the mode of formation is different. In the case of Dionne's mechanism, the ice-rafted sediments are derived from the marsh surface, as evidenced by the presence of grass rafts and sod encased in ice blocks. In the case of the Noatak, the ice-rafted sediments are derived from the bottoms of the lakes as evidenced by the presence of gastropods, algal ma-