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Ionomer-Like Structures and π -Cation Interactions in Argonne Premium Coals

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The increase in the amount of pyridine-soluble material obtained from Argonne Premium coals after acid treatment is examined. The amount of pyridine-soluble material in most of the coals increases significantly with acid treatment. In low and to some extent medium rank coals this is largely a result of the presence of ionic clusters formed by carboxylate groups. In higher rank coals we are proposing that π -cation interaction play a major role. These ion/coal interactions are of sufficient strength to act as "reversible" cross-links, in the same way as ionic clusters behave in ionomers.

Introduction

Ionomers are synthetic polymers containing a relatively small fraction of ionizable functional groups, a classic example being ethylene/methacrylic acid random copolymers containing about 5% methacrylic acid groups. When these acid groups are exchanged to form salts the resulting ionic groups micro-phase separate from the nonpolar hydrocarbon matrix to form small domains, often referred to as clusters or multiplets. Although the domain size is usually small, perhaps of the order of 6 Å or so in diameter for the copolymer mentioned above (see Eisenberg and Kim¹ and citations therein), these multiplets have a profound effect on properties, effectively acting as thermoreversible cross-links. For example, the region surrounding the multiplets is one of restricted mobility, greatly affecting relaxation processes.

In a recent study,² we suggested that Pittsburgh No. 8 coal has an ionomer-like structure, as the amount of pyridine-soluble material increased dramatically on treatment with acid and infrared spectroscopy showed that carboxylate groups were converted to carboxylic acid groups by this treatment. Obviously, it would be important to determine the generality of this observation. Accordingly, here we present results obtained from studies of the Argonne Premium coals before and after acid treatment.

Experimental Section

Materials. Coal samples were supplied by the Argonne National Laboratory. The samples were stored under nitrogen and used as received. The model compounds 2-hydroxy-9-fluorenone (2H9F) and 2-methylnaphthoquinone (2MNQ) were obtained from Aldrich and used without further purification.

Preparation of Phenolic Resins. Phenolic resins were synthesized by a condensation polymerization of (alkyl)phenol, dihydroxynaphthalene, and formaldehyde by a method described elsewhere.^{3,4} Essentially, the desired amount of (alkyl)phenol and dihydroxynaphthalene were dissolved in water. An oxalic acid catalyst was then added and the mixture was stirred and preheated at 65 °C for 30 min. Next, formaldehyde was added and the mixture was refluxed at 100 °C for 2 h. As the polymerization proceeded, the mixture gradually changed color. Finally, water was removed by heating under vacuum at a temperature of 200 °C and a black solid resin was obtained.

Preparation of Acid-Treated Coal Samples. The coal samples were acid-treated using the methodology we described in our previous work,² except that here we use 0.1 N HCl rather than 1 N HCl, to minimize any side reactions. Essentially, a 2.5 g coal sample was placed in 250 mL of 0.1 N HCl solution. The 0.1 N HCl solution was prepared by diluting concentrated HCl (37% in water) with THF so that 250 mL of the solution contains about 2 mL of concentrated HCl (and about 1 mL of water). The mixture was stirred at room temperature under a nitrogen atmosphere for 2 days. The THF and the trace amount of water were then removed from the coal using a rotary evaporator followed by high vacuum treatment at room temperature until it reached a constant weight.

The possibility that HCl reacts with THF is unlikely under the conditions we are using (at room temperature and without the use of any catalyst). THF is the least reactive cyclic ether in term of ring opening reactions.⁵ A strong initiator, such as a benzoyl cation ($\text{C}_6\text{H}_5\text{CO}^+ \text{SbF}_6^-$), is required to polymerize THF to polyTHF ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$)_n.⁶ To confirm this, we compared the FTIR spectrum of polyTHF to that of THF + HCl and found no evidence for polymerization as a result of simply mixing the two compounds.

Preparation of Alkali-Treated Model Compounds. The model compounds were treated by 0.1 N NaOH employing the

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Table 1. Pyridine-Extraction Yield (daf) of Original and Acid-treated Coal Samples, with the Number in Parenthesis Indicating Total Extraction Recovery

coal sample	ash ^a	extraction yield (wt %, daf)				
		original coal	acid-treated coal	Nishioka ^c	Fletcher et al. ^d	NMP/CS ₂ ^e
Beulah-Zap	9.7	8 (102)	36 (98)	15	3, 3	2
Wyodak-Anderson	8.8	15 (101)	39 (102)	24	7, 6	10
Illinois No. 6	15.5	34 (104)	45 (99) 48 (101) ^b	42	38, 32	33
Blind Canyon	4.8	32 (102)	39 (98)	—	29, 28	34
Lewiston Stockton	19.8	26 (104)	35 (100) 41 (103) ^b	—	34, 27	27
Pittsburgh No. 8	9.2	41 (103)	45 (101) 53 (102) ^b	42	17, 15	39
Upper Freeport	13.2	35 (100)	39 (99) 39 (97) ^b	45	17, 15	59
Pocahontas No. 3	4.8	6 (101)	13 (107)	5	1, 1	3

^a Results from the Argonne Premium coal database. ^b Soaked in 1 N HCl solution. ^c The extraction yield of original coals reported by Nishioka, ref 7. ^d The extraction yield of original coals (daf basis), recalculated from data reported by Fletcher et al., ref 9. The second set of data is the original result reported on a dry basis. ^e The extraction yield of original coals using NMP/CS₂ as mixed solvent, reported by Takanohashi and Iino, ref 10.

same procedure we previously applied to coal.² Essentially, solid NaOH was dissolved in as small amount of water as possible and then diluted with THF. The model compound was soaked in this solution at room temperature for 2 days. The solvent was then removed and the treated sample was placed in a vacuum at room temperature.

Determination of the Pyridine-Extraction Yield. The Soxhlet extraction procedure and the calculation of extraction yields on a daf basis were the same as that described by Nishioka,⁷ as follows:

$$\text{Extraction Yield} = \frac{(\text{total extract})}{(\text{residue} - \text{ash} + \text{total extract})} \times 100 \quad (1)$$

FTIR Spectra. FTIR spectra were recorded on a Digilab model FTS-45 at a resolution of 2 cm⁻¹ by co-adding 100 scans. Samples for FTIR experiments were prepared as standard KBr pellets, using approximately 2 mg of coal or model compound samples in 250 mg of KBr.

Proximate Analysis. Proximate analysis was performed by the Center for Applied Energy Research, University of Kentucky.

Results

In our previous study² we focused our attention on Pittsburgh No. 8 coal and our results indicate that the formation of ionic clusters, which act as cross-linking zones, are responsible for the decrease in the extraction yield and the swelling ratio of this coal when it is soaked in chlorobenzene, a result reported earlier by Larsen et al.⁸ The FTIR spectra of the original and treated coal show that this is a consequence of the formation of carboxylate ions and carboxylic acid salts from carboxylic acid groups, presumably by exchange with ions from the coal mineral matter that become mobilized in the presence of chlorobenzene. The FTIR spectra of the subsequently acid-treated coal reveal the regeneration of carboxylic acid groups together with the disappearance of carboxylate bands. The removal of the ionic clusters, which act like cross links, results in an increase in the pyridine-extraction yield.

Here we broaden the study to cover the set of Argonne Premium coals. The pyridine-extraction yield of the original and (0.1 N) acid-treated coals, calculated on a daf basis, are shown in Table 1. These results are the average of multiple extraction experiments run on many of the coals. The numbers in parentheses indicate total recovery. The table also includes extraction yields reported by Nishioka,⁷ Fletcher et al.,⁹ and Takanohashi and Iino,¹⁰ the latter using an NMP/CS₂ mixed solvent system.

The results that are most directly comparable to ours are those of Fletcher et al.⁹ (which we converted to a daf basis). Nishioka⁷ used complex, multiple extraction schemes that varied from coal to coal and involved chemical modification (such as methylation) and, for low rank coals, treatment with strong acid solutions (2 N HCl). Accordingly, we do not believe these latter results are comparable to those presented here. We will comment on the NMP/CS₂ extraction yields obtained by Iino and co-workers¹⁰ later.

The largest increase in extraction yield is (unsurprisingly) observed in low rank coals, Beulah-Zap and Wyodak-Anderson coals (a 350%, and 160% increase in pyridine-soluble extraction yields, respectively). It is well-known that these coals contain exchangeable carboxylate groups, but the size of the increase in extraction yield obtained by the relatively mild acid treatment used here is, we believe, surprising, particularly compared to the results obtained by Nishioka⁷ using a much stronger acid treatment.

Moving up in rank, Illinois No. 6 coal also showed a significant increase in extraction yield (from about 34% to 45%), as did two of the high volatile bituminous coals, Blind Canyon and Lewiston-Stockton. Pittsburgh No. 8 coal and Upper Freeport coal had smaller (but reproducible) gains in extraction yields, however. Surprisingly, the highest rank coal in the set, Pocahontas No. 3, had a 117% increase in extractable material upon acid treatment. The high rank coals are believed to have little or no carboxylic acid content, of course.¹¹

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Table 2. Proximate Analysis Results of Selected Coal Samples Reported on a Dry Basis

coal sample	ash	calcite ^a	volatile matter	fixed carbon
Beulah Zap	9.0	1.7	48.4	42.6
	8.9		46.8	44.3
0.1 N HCl-treated Beulah Zap	8.9		48.9	42.2
	8.6		49.2	42.2
Illinois No. 6	16.2	1.9	39.8	44.0
0.1 N HCl-treated Illinois No. 6	15.8		42.1	42.1
	14.6		42.3	43.1
Pittsburgh No. 8	9.4	0.5	38.2	52.3
0.1 N HCl-treated Pittsburgh No. 8	8.5		39.1	52.4
	8.7		38.9	52.4
Upper Freeport	13.1	1.0	26.9	60.0
	12.3		28.3	59.4
0.1 N HCl-treated Upper Freeport	12.3		30.2	57.5
1 N HCl-treated Upper Freeport	12.7		28.3	59.0
	12.8		28.1	59.0

^a The carbonate content reported in wt % of calcite (dry coal basis), results from the Argonne Premium coal database.

As mention above, previous studies have shown that a removal of cations in low rank coals results in an increases in the pyridine extraction yield,^{7,12,13} (and of liquid yield on liquefaction¹⁴). Sugano et al.,¹³ for example, observed an increase in the pyridine extractability of low ranked coals after demineralization (by treating coals with 4.6 N HCl and 2.3 N HF aqueous solution, followed by a rinse with a large amount of water). However, the demineralization process employed by these authors, which removes almost 90% of the mineral matter from the coals, is different from the mild acid treatment procedure we applied in this study, where a low concentration of HCl (0.1 N) was used and the samples were not washed after the treatment.

A proximate analysis of the samples before and after acid treatment reveals only minor changes in the mineral matter as a result of this treatment. These results are reported in Table 2. The analysis was performed by a laboratory outside our institution and the samples were sent in a random order and were not identified. There is a surprising amount of scatter in the data, but the results suggest that the mineral matter content decreases a small amount as a result of acid treatment. FTIR analysis indicates that this decrease is due to the removal of carbonates such as dolomite or calcite in these samples (the calcite content on a dry coal basis is shown in Table 2). For example, the infrared spectrum of Pocahontas No. 3 is shown in Figure 1. Also shown in this figure is the spectrum of the coal after acid treatment, together with a difference spectrum. Bands due to clays (between 1100 and 1000 cm^{-1} and 600 to 400 cm^{-1}) do not appear to be affected, but there is a significant decrease in the intensities of bands near 1435 and 870 cm^{-1} , characteristic of carbonate minerals.¹⁵ However, these bands are very intense in the spectra of pure minerals (work we performed nearly 20 years ago required using less than 0.1 mg of

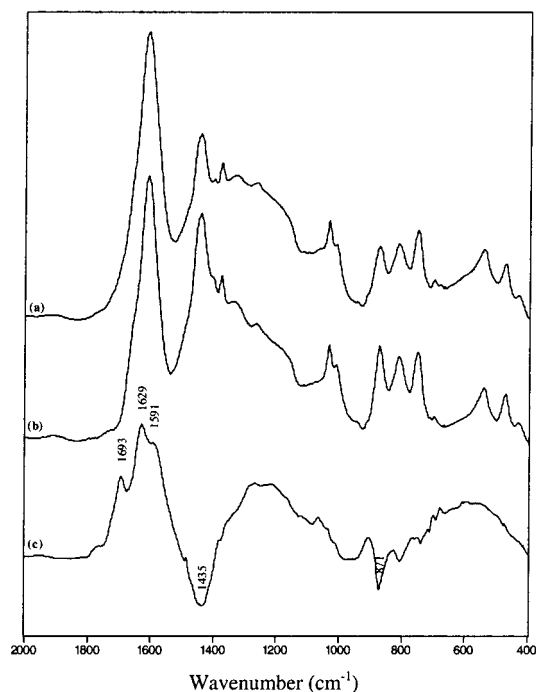


Figure 1. FTIR spectra of an acid-treated Pocahontas No. 3 (a), an original coal (b), and the difference (c).

material in a standard KBr pellet to get the bands within the Beer–Lambert law range -see ref 15). This indicates that there is only a small change in mineral matter content as a result of acid treatment, a conclusion supported by the proximate analysis results, where observed changes are almost within the scatter of the results. Such relatively small changes do not affect our conclusion that the extraction yield of soluble material increases significantly on acid treatment. Furthermore, there is no measurable increase in volatile matter, indicating that any free HCl has been completely removed (the boiling point of HCl is -85°C).

We now turn our attention to an elucidation of the changes that are occurring in coal structure as a result of acid treatment. This is fairly straightforward for low rank coals, but the results from higher rank coals are less easily interpreted. We will start with the former.

The 1800–1300 cm^{-1} region of the spectrum of the original Beulah-Zap coal, the acid-treated sample, and a difference spectrum are shown in Figure 2. The corresponding spectra for Wyodak-Anderson coal are shown in Figure 3. The difference spectra from the two coals show a decrease in the intensity of bands near 1555 and 1400 cm^{-1} and an increase in the intensity of a 1715 cm^{-1} band upon acid treatment. This change is similar to results we obtained many years ago in a study of the ionomeric polymer, ethylene-*co*-methacrylic acid^{16–19} and more recent FTIR results obtained from a neutralization of aromatic-acid model compounds; 4-hexylbenzoic acid and 4-hexyloxybenzoic acid (unpublished results; available upon request). The bands

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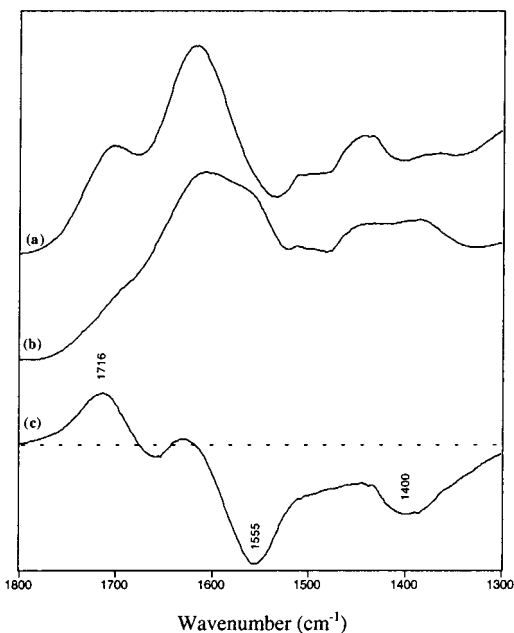


Figure 2. FTIR spectra of an acid-treated Beulah-Zap (a), an original coal (b), and the difference (c).

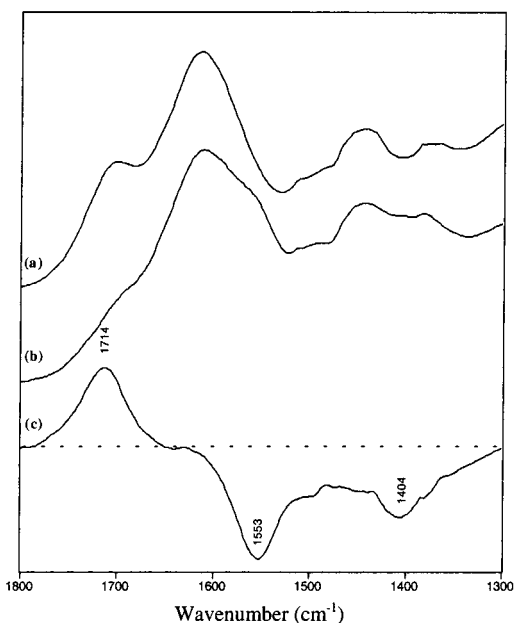


Figure 3. FTIR spectra of an acid-treated Wyodak-Anderson (a), an original coal (b), and the difference (c).

near 1555 and 1400 cm^{-1} are assigned to carboxylate groups and the decrease in the intensity of these modes implies that the coal loses ionic clusters upon acid treatment as a result of conversion to carboxylic acid groups. This is reflected in the appearance of the 1715 cm^{-1} band in the difference spectrum.

It is well-known that carboxylate groups are present in low rank coals. However, to our knowledge an analogy to ionomers has not previously been made. This is important, because randomly dispersed groups of the type COO^-M^+ would not provide the connectivity necessary to change swelling and solubility. It is the clustering of these groups in microdomains that is crucial to changing properties.

We now jump to a consideration of the highest rank coals in this sample set; first, because their spectroscopic

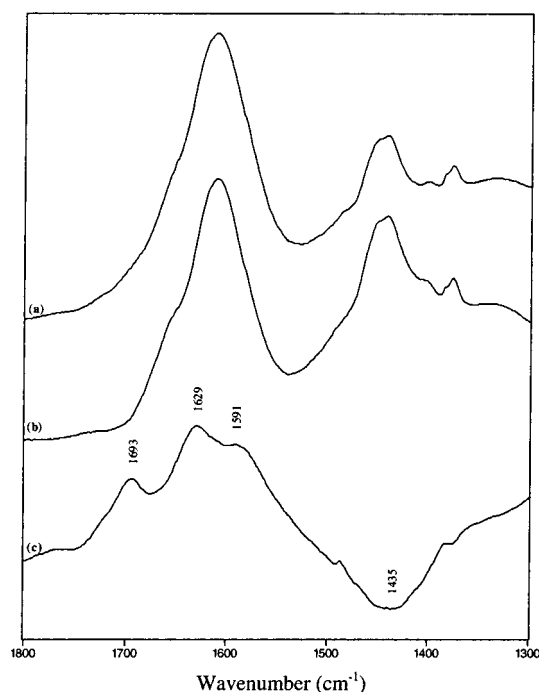


Figure 4. FTIR spectra of an acid-treated Pocahontas No. 3 (a), an original coal (b), and the difference (c).

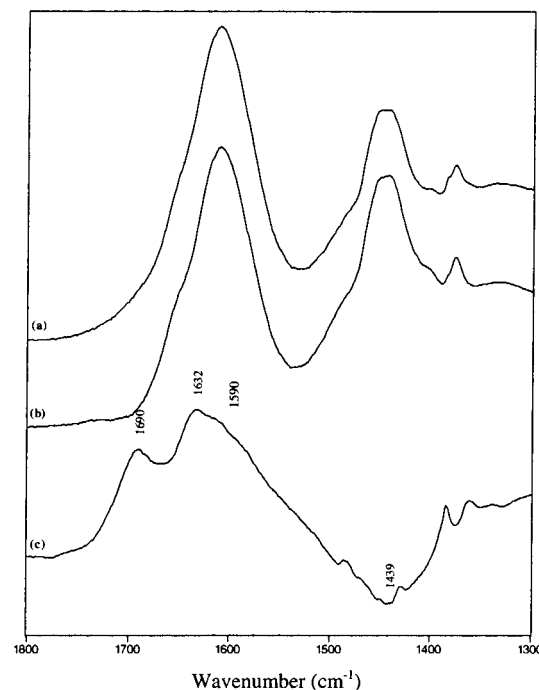


Figure 5. FTIR spectra of an acid-treated Upper Freeport (a), an original coal (b), and the difference (c).

characteristics are distinct from the low rank coals; second, because the coals of intermediate rank show elements of both types of behavior, so it is useful to examine the extremes first.

The infrared spectra of Pocahontas No. 3 and Upper Freeport coals are shown in Figures 4 and 5, respectively. Unlike the low rank coals, where the intensities of the OH stretching modes near 3400 cm^{-1} in the infrared spectrum of the acid-treated and original samples appeared comparable, these coals had more intense OH modes, due to the presence of some bound water. We chose not to dry these samples at elevated

temperature because any oxidation would interfere with our interpretation of the spectra. Accordingly, we used the aliphatic CH stretching modes (near 2900 cm^{-1}) as an internal standard, (as opposed to a 1:1 subtraction based on weight), on the assumption that these groups would be little affected by mild acid treatment under nitrogen. As a result, the difference spectra shown in Figures 4 and 5 display a band near 1630 cm^{-1} due to water, which we can ignore. Just as in the pair of low rank coals in this set, the pair of the highest rank coals display remarkably similar changes. There is a negative (below the baseline) band in the difference spectra (acid treated-original coal) near 1430 cm^{-1} , indicating the presence of some carbonate mineral or minerals removed by acid treatment. There are also positive difference bands near 1693 and 1590 cm^{-1} that appear upon acid treatment. The alkyl carboxylic acids that appear in the spectrum of low rank coals have bands that appear at wavenumbers above 1700 cm^{-1} . Bands below 1700 cm^{-1} usually indicate the presence of conjugated carbonyl groups of some type. Aromatic acids are one possibility. These have not been detected in other studies of coals, but they are stronger acids than alkyl carboxylic acids and phenols and so may have remained undetected in the titration and exchange procedures usually used to detect such groups. Of course, this means that we would anticipate some sort of negative difference peak round about $1550\text{--}1500\text{ cm}^{-1}$, characteristic of carboxylate groups in the original sample. Unfortunately, the presence of any such group is masked by the difference band due to the elimination of carbonate minerals.

Quinone and semi-quinone groups are another possibility for the origin of the 1690 cm^{-1} band. We will discuss why bands due to these groups may become more apparent upon acid treatment later. Finally, one cannot rule out that at some stage in our handling of the samples some mild oxidation occurred, despite our attempts to limit this by using a nitrogen atmosphere, etc. In this regard, it should be noted that we do not see bands near 1690 cm^{-1} in the spectra of lower rank coals, which we would expect to be more liable to oxidation (methylene groups adjacent to aromatic rings being particularly susceptible).

In addition to the difference band near 1690 cm^{-1} , there is one clearly resolved near 1590 cm^{-1} in the Pocahontas No. 3 difference spectrum and present as a shoulder in the Upper Freeport difference spectrum. This band is most likely due to aromatic groups that have been shifted from their position near 1600 cm^{-1} in the spectra of the original coals, for reasons we will make clear below.

The $1800\text{--}1300\text{ cm}^{-1}$ region of the spectra of the remaining four coals are shown in Figures 6–9. The Blind Canyon coal (Figure 6) shows changes similar to but less pronounced than those observed in the low rank coals. The Lewiston-Stockton and Pittsburgh No. 8 coals show spectroscopic characteristics that are closer to the higher rank coals, but the carbonyl or carboxylic acid band is much broader and probably a composite of contributions from bands observed at wavenumbers above and below 1700 cm^{-1} . Illinois No. 6 coal shows only small spectroscopic changes in the band near 1600

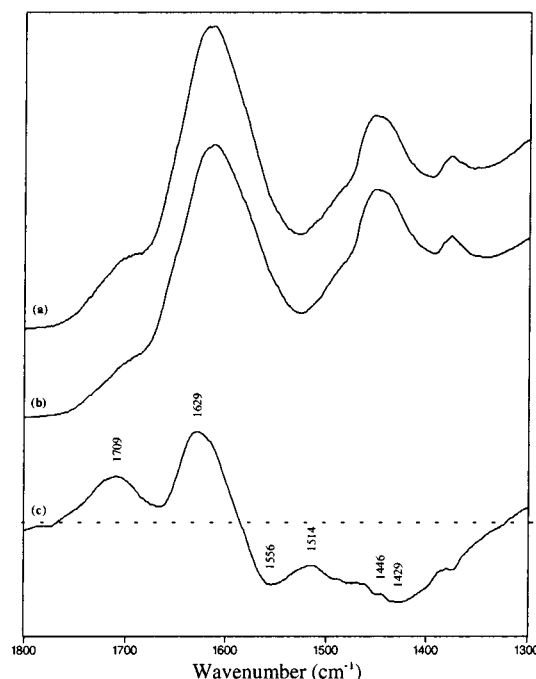


Figure 6. FTIR spectra of an acid-treated Blind Canyon (a), an original coal (b), and the difference (c).

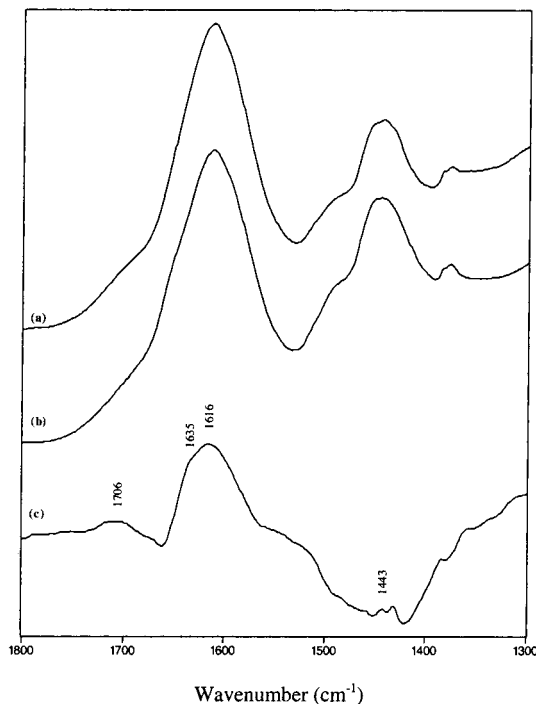


Figure 7. FTIR spectra of an acid-treated Illinois No. 6 (a), an original coal (b), and the difference (c).

cm^{-1} and this is partly masked by the 1630 cm^{-1} water band.

This leaves a conundrum; it is clear that extraction yields increases significantly with acid treatment, but the origin of this effect in anything but the low rank coals is not at all obvious from the infrared studies. However, these will provide some supporting evidence for other results that we will now consider.

This paper is not as we originally wrote it. Thanks to various constructive criticisms from the reviewers of our initial effort we rethought the original interpretation

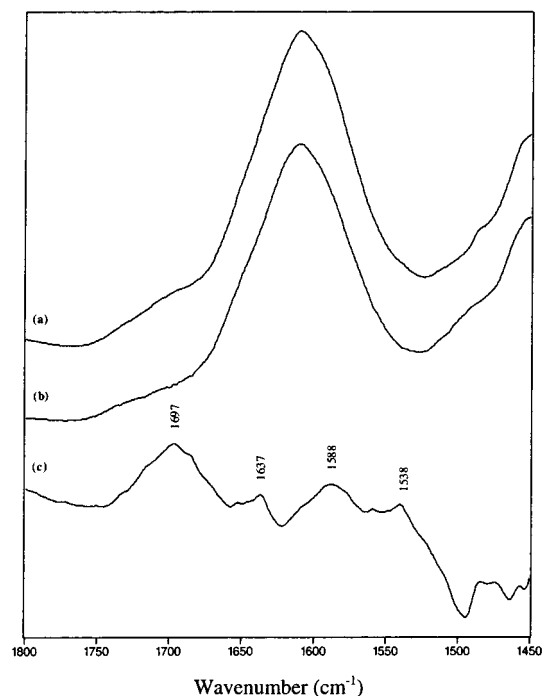


Figure 8. FTIR spectra of an acid-treated Lewiston-Stockton (a), an original coal (b), and the difference (c).

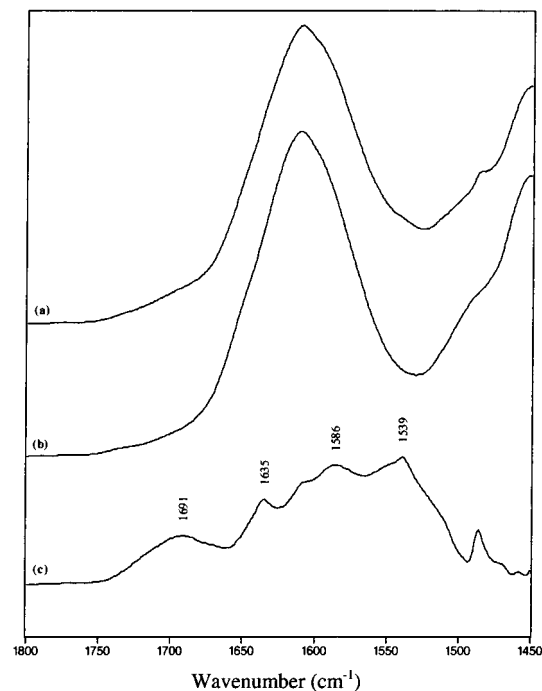


Figure 9. FTIR spectra of an acid-treated Pittsburgh No. 8 (a), an original coal (b), and the difference (c).

of our results. During this process we became aware of a recent body of work dealing with π -cation interactions in aromatic systems (see references 20–22 and citations therein). Essentially, it has been shown that cations bind to the π face of an aromatic structure through a surprisingly strong interaction (19 kcal/mol for K^+ /benzene in the gas phase). Recent work indicates that

for cations such as Li^+ and Na^+ the interaction predominantly involves induction forces. Coal, of course, is not only a complex organic system but also one that is almost invariably found with various types of mineral matter. We suspected that π -cation interactions could well exist in coal. Indeed, given the nature of coal and recent work demonstrating both the strength and ubiquity of this interaction^{20–22} it would now be surprising to us if they were not present. But, could such interactions act as cross-links, reducing the solvent swelling and extractability of coal? We have argued that point interactions such as hydrogen bonds with “strengths” or enthalpies of the order of 4–5 kcal/mol cannot. This interaction is apparently four or five times “stronger” than hydrogen bonds and would therefore behave very differently.

In previous work we have demonstrated that phenolic resins are good models for coal^{3,4} and for the purposes of this study we synthesized three resins, using dihydroxynaphthalene, phenol, and ethylphenol in various proportions, all reacted with formaldehyde. The extraction yields obtained from these networks was determined before and after treatment with 0.1 N NaOH and 0.025 N NaOH. In each case about 1 g of resin was treated with 50 mL of THF to which was added the appropriate amount of a 1 N aqueous solution of NaOH to obtain the desired NaOH concentration. The ratio of NaOH to phenolic OH groups was about 1:5 for the 0.1 N NaOH-treated samples and 1:20 for the 0.025 N NaOH-treated samples. Accordingly, it seems unlikely that there is significant ionization of the (weakly) acidic phenolic OH groups under these conditions in this medium. Nevertheless, there is a significant reduction in the amount of pyridine-soluble material in these samples, as shown in Table 3. The three resins we synthesized had a range of cross-link density, such that the amount of pyridine-soluble material varied from a high of 94% in the first sample to a low of 12% in the third. All displayed a marked reduction in pyridine extraction yields, the most surprising being the first sample, where the amount of pyridine-soluble material decreased from 94% to 3% when treated with 0.1 N NaOH and from 94% to 79% when treated with 0.025 N NaOH.

If the origin of this reduction is π -cation interactions, which are nonspecific and do not involve particular functional groups, then we would only expect to see subtle changes in the spectrum, related predominantly to the ring modes. Indeed, this is largely the case. The spectrum of a copolymer made from ethylphenol and 1,5-dihydroxynaphthalene (50:50) reacted with formaldehyde shows a broadening of the characteristic ring mode near 1600 cm^{-1} and a shift to lower frequency, near 1590 cm^{-1} , as shown in Figure 10, similar to the changes observed in medium and high rank coals. We obtained these spectra in diffuse reflectance in order to examine the OH stretching region, shown in Figure 11, where there are also significant shifts and intensity changes. π -cation interactions would be expected to change the distribution of electrons in an aromatic system, thus affecting various band frequencies and intensities and this type of interaction might be significantly stronger in heterocyclic systems (there is not much work in the literature on this point as yet, most studies have focused

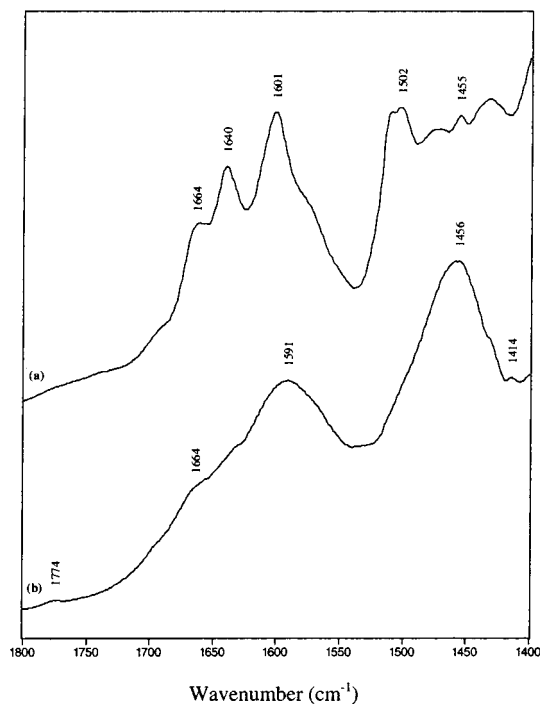
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Table 3. Extraction Yields (in pyridine) Obtained from Phenolic Resins

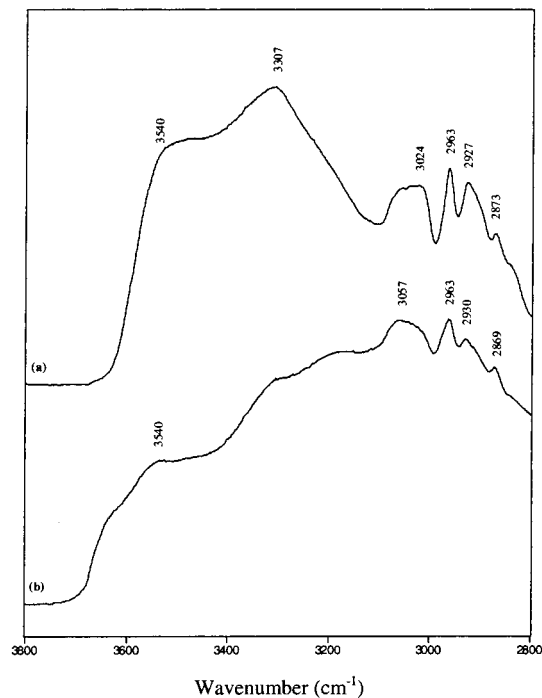
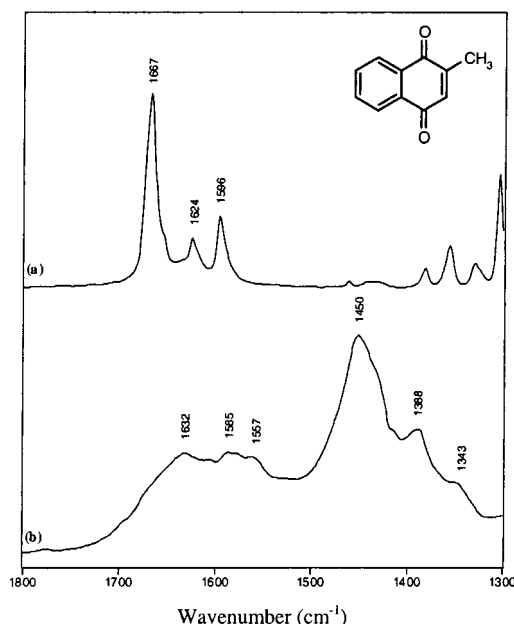
resins	original sample	extraction yield (wt %)	
		treated sample (0.025 N NaOH)	treated sample (0.1 N NaOH)
40% 2,7-dihydroxynaphthalene/ 60% phenol/formaldehyde	94	79	4
50% 1,5-dihydroxynaphthalene/ 50% ethylphenol/formaldehyde	35	—	2
40% 1,5-dihydroxynaphthalene/ 60% phenol/formaldehyde	12	9	—

**Figure 10.** FTIR spectra of poly(ethylphenol₅₀-co-dihydroxynaphthalene₅₀/formaldehyde) resin (a), and the resin after treatment with 0.1 N NaOH (b).

on biological systems). Indeed the spectra of samples of a quinone and semi-quinone before and after NaOH treatment, shown in Figures 12 and 13, respectively, also show significant changes in the aromatic modes. Again, the aromatic ring-stretching mode near 1600 cm^{-1} is shifted to 1590–1580 cm^{-1} and, interestingly, the band near 1670 cm^{-1} in the quinone is eliminated and the 1690 cm^{-1} carbonyl band in the semi-quinone is reduced significantly in intensity. The C=O vibrations in quinones are coupled strongly to the ring modes, so these changes are not unexpected if the π bonds of the system are strongly perturbed by an interaction. (Note that a strong band near 1450 cm^{-1} appears in both spectra. NaOH has a band at this frequency, so we cannot attribute this to a change in the system). These results suggest that the band near 1690 cm^{-1} in the spectra of the acid-washed coals may be due to a removal of cations, hence π -cation interactions upon acid treatment.

Discussion

These results are by no means as definitive as we would like, partly because π -cation interactions, which we suspect are significant in medium and high rank coals, are not specific in the sense that, say, hydrogen bonds are and are thus less easy to characterize

**Figure 11.** FTIR spectra of poly(ethylphenol₅₀-co-dihydroxynaphthalene₅₀/formaldehyde) resin (a), and the resin after treatment with 0.1 N NaOH (b).**Figure 12.** FTIR spectra of 2-methylnaphthoquinone (2MNQ) (a) and 2MNQ after alkali treatment (b).

spectroscopically. Nevertheless, the results we obtained from treating phenolic resins indicate that such interactions could have a pronounced effect on solubility. In

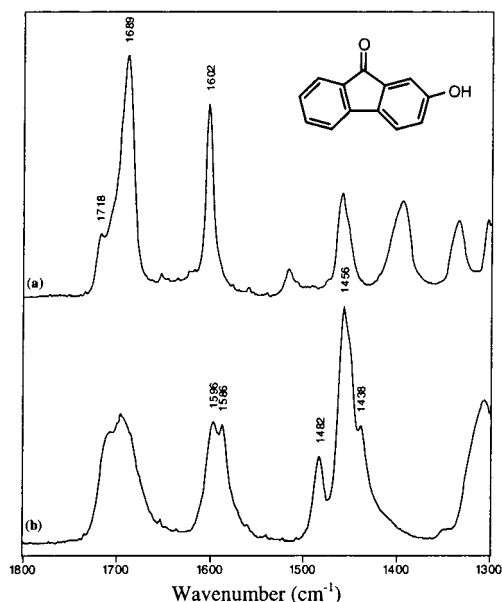


Figure 13. FTIR spectra of 2-hydroxy-9-fluorenone (2H9F) (a) and 2H9F after alkali treatment (b).

this regard, the recent results of Takahashi et al.,²³ that anions with a small radius or large electronegativity increase the amount of soluble material obtained in the NMP/CS₂ extraction of coal is important. Such anions would be expected to preferentially bind to the cations involved in any π -cation complex, thus removing the junction zones that such complexes might provide.

No doubt other possible causes for the increased solubility of these coals upon acid washing can be invoked, but we have attempted to account for these. Radicals generated from THF could be involved in breaking covalent bonds, for example. To preclude this possibility we simply soaked some coals in THF and measured their extraction yields. No increase in pyridine-soluble material was observed. Also Chen et al.²⁴ reported that hydrolysis of some weak ester and ether bonds can occur during treatment with concentrated acid/alkali solutions (40 g of coal with 160 mL of 3 N HCl or 1.5 N NaOH for 1 h at 180 °C). There is no evidence for any appreciable amounts of esters (bands near 1730 cm⁻¹) in the original spectra of these coals and it seems unlikely to us that ethers would cleave under these mild room-temperature conditions. Accordingly, we believe the evidence presented here indicates that in most coals there are "reversible" cross-links associated with ionic structures (low to medium rank coals) and with π -cation interactions in higher rank coals. This, in turn, suggests that we should now start to think about cross-links in coal in a different way, classifying them into two types; first "permanent" covalent linkages that cleave only at high temperatures or through chemical reaction; second, "reversible" cross-links, largely associated with ionic structures such as carboxylate salts and probably π -cation complexes. Others would add hydrogen bonds to this list, but these are relatively weak interactions compared to the link-

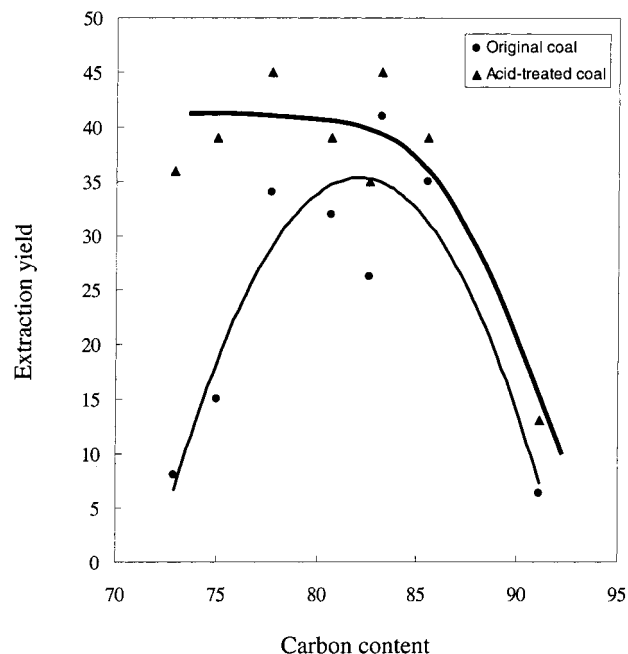


Figure 14. The pyridine-extraction yields of original and acid-treated coals with various carbon content.

ages considered above and the contacts are transient above the T_g or in solution.

There is a school of thought that regards coal as largely an associated structure, based largely on the seminal work of Iino and co-workers.^{25,26} However, much of this work is based on results obtained from a single coal, Upper Freeport, about 59% of which is soluble in NMP/CS₂ mixtures compared to only 35% in pyridine. This coal appears to be anomalous. The NMP/CS₂ solubility of the Argonne Premium coals are also shown in Table 1 and it can be seen that with the exception of the Upper Freeport coal the yields are comparable to those obtained with pyridine before acid treatment.

Finally, we believe these results have a number of ramifications. First, the cross-link density of coal as a function of rank has historically been regarded as reaching a minimum for coals of about 86%C, based on the observation that coals of about this carbon content swell more and give the highest extraction yields using solvents such as pyridine. If we now just focus on "permanent" cross-links, the pattern is different, as shown in Figure 14. The trend appears to be an exponential (e^{-x}) variation, with pyridine extraction yields ranging from values of about 43% for low rank coal, dropping slowly to near 40% for coals of carbon content of about 86%, followed by a precipitous decline at higher rank. These "permanent" cross-links presumably have a greater effect on properties than their ionic counterparts, which at least in synthetic polymers are thermoreversible.

Conclusions

The results presented here indicate that ionic clusters formed by carboxylate groups in low rank coals and π -cation interactions in higher rank coals are significant

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components of coal structure and act as “reversible” cross-links. The nature of the ionic clusters varies with coal rank, with carboxylates dominating in low rank coals, and π -cation interactions probably dominating in high rank coals. Between, both mechanisms appear to play a role. The existence of these ionic structures is responsible for significantly lowering the solvent extractability of coal and presumably affects other properties in a significant manner.

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