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"Magnetic Relaxation - Coal Swelling, Extraction, Pore Size"

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A Study of Coal Extraction with Electron Paramagnetic Resonance (EPR) and Proton Nuclear Magnetic Resonance Relaxation Techniques

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Abstract

An electron spin and proton magnetic relaxation study is presented on the effects of the solvent extraction of coal on the macromolecular network of the coal and on the mobile molecular species that are initially within the coal. The eight Argonne Premium coals were extracted at room temperature with a 1:1 (v/v) *N*-methylpyrrolidinone (NMP)-CS₂ solvent mixture under an inert atmosphere. As much solvent as possible was removed from extract and residue by treatment in a vacuum ($\sim 10^{-2}$ torr) oven at 145 - 150 °C until constant weight was achieved. The extraction, without further washing with other solvents, results in substantial uptake of NMP, apparently by H-bonding or acid-base interactions, which tends to be higher in coal matter with higher heteroatom (N,O,S) content. The mobilization of molecular free radicals by the solvent and the exposure of free radicals in the macromolecular matrix to solvent or to species dissolved in the solvent, results in a preferential survival of residue radicals of types that depend on the particular coal and results in the apparently fairly uniform loss of all types of radicals in bituminous coal extracts. The surviving extract and residue free radicals are more predominantly of the odd-alternate hydrocarbon free radical type. The spin-lattice relaxation (SLR) of these coal free radicals has previously been inferred (Doetschman and Dwyer, *Energy Fuels*, **1992**, *6*, 783) to be from the modulation of the intramolecular electron-nuclear dipole-interactions of the CH

groups in a magnetic field by rocking motions of the radical in the coal matrix. Such a modulation would depend not only on the rocking amplitude and frequency but also upon the electron spin density at the CH groups in the radical. The observed SLR rates decrease with coal rank in agreement with the smaller spin densities and the lower rocking amplitudes that are expected for the larger polycondensed ring systems in coals of higher rank. The SLR rates are found to be generally faster in the extracts (than residues) where the molecular species would be expected to have a smaller polycondensed ring system than in the macromolecular matrix of the residue.

Introduction

The extraction of molecular species by solvent from the macromolecular matrix of the organic part of the coal depends on a number of factors that are relevant to practically all coal utilization or derivitization processes. The molecular structure of the coal is important, particularly in regard to its flexibility and permeability to smaller molecular species. One may regard the problem in terms^{1,2} of a hydrogen-bonded, polymeric or polycondensed network within which the mobility of smaller molecular species is desirable. The extraction process takes place as a result of mobile solvent molecule penetration into the network and as a result of the mobilization and dissolution of small coal molecular species. The language of this hypothesis^{1,2} that coals comprise an intractable molecular matrix and smaller molecular species, put forth most recently^{1,2} to explain nuclear magnetic resonance (NMR) relaxation in coals,²⁻⁷ will be employed extensively in this paper. Yokono and Sanada³ studied the proton NMR spin-spin relaxation of several whole coals and detected multiple decay components in them. They also examined the proton NMR spin-lattice relaxation (SLR) times in whole coals and their pyridine extracts and residues, finding a different, but single, decay component in each.³ Jurkiewicz *et al.* in the debate of Derbyshire *et al.* concerning the macromolecular-molecular hypothesis also discussed the proton NMR relaxation in pyridine-swollen coals and pyridine-swollen pyridine-extracted coal residues,^{4,5-7} finding distinguishable macromolecular and small molecular spin-spin relaxations. The NMR

relaxation results on coals undergoing thermal softening show that the coals contain mobile regions or structures, as well as immobile or rigid regions or structures,^{8,9} results that also conform to the macromolecular-molecular hypothesis. Takanohashi and Iino¹⁰ have made an electron paramagnetic resonance (EPR) study of the lineshapes of whole coals and the residues and extracts from a three-step, multiple-solvent extraction of the coals, which showed considerable changes in the linewidths, g-values and spin concentration upon extraction.¹⁰ They observed an increase in the g-value in an acetone-soluble fraction that suggested preferential solubility of heteroatom-bearing free radicals, whose linewidths suggest that they have decreased degrees of aromatic ring condensation.¹⁰ Evidence was also found that the total number of free radicals in the original whole coals was not conserved in the course of extraction.¹⁰ These results together with recent characterizations^{11,12} of whole Argonne Premium coals by EPR relaxation methods suggested that a systematic study should be done of the EPR and NMR relaxation characteristics of this representative, well-characterized set of whole coals and their extracts and residues. In particular, the SLR in the maceral constituents of the whole Argonne coals were shown to be from the modulation of the electron-proton magnetic dipolar interaction.¹¹ Thus SLR is sensitive to the flexing of the matrix or host of the free radical,¹¹ as well as upon the chemical structure of the free radical that governs the magnitude of the interaction.^{14,15} Thus one would expect SLR to give information about the dynamics and chemical characteristics of the free radicals in the molecular matrix and in the molecular species that survive the extraction process.

Within the macromolecular-molecular hypothesis, the primary role of the extracting solvent is to present the molecular species with a milieu in which they are more soluble than in the coal macromolecular matrix. However, a secondary role of the solvent is to enter the macromolecular matrix and, if possible, alter its structure, so as to expose the coal molecules to solvent. Given the common chemical origins of the coal molecular species and the macromolecular matrix, a good solvent molecule may be attracted to the macromolecular matrix almost as strongly as it is to the molecular species. Thus coal swelling is a well-known characteristic, being greatest in the best coal-solvent combinations.¹⁶ A number of NMR studies of pyridine bound to or sorbed onto coals

reveal a pyridine whose rotational freedom is hindered in ways that depend on the type of coal.¹⁷⁻²⁰ This interaction is thought to be through Lewis acid-base or H-bonding interactions with the N lone pair of pyridine.²¹ In the present study similar information is obtained about NMP retention from our extraction yields, extract characterization and NMR studies.

The organic free radicals observed by ESR in coals and other carbonaceous materials have properties consistent with stable, odd-alternate, polycondensed, ring systems.^{14,15} Less clear, however, is the exact chemical nature of the heteroatom-containing species in coals known to impart positive ESR g-value shifts that correlate with oxygen, nitrogen and sulfur content.^{14,15} It has been argued that the unusual stability of the odd-alternate hydrocarbon system is responsible for the persistence of odd-alternate, polycondensed free radicals over the long coal lifetime. However, this argument might be questioned for the apparently highly reactive phenoxy, semiquinone, etc. radicals proposed for g-shifted species in coals.^{14,15} Thus further clarification is needed as to whether (a) heteroatom incorporation into more stable odd-alternate hydrocarbon ring systems gives the observed g-shifts or whether (b) *immobilization* of reactive, heteroatom-containing free radicals leads to their longevity.

When coal is treated with an extracting solvent, the molecular species are mobilized by the solvent, and while the macromolecular matrix may be mobilized to a much lesser extent, it is exposed to other coal molecular species and to solvent molecules at previously protected regions. There have been conflicting reports about the conservation or non-conservation of the numbers of spins in coal samples upon solvent treatment or extraction.^{10,22-24} Some authors report that the numbers of spins decrease in room temperature extraction,^{22,23} one reports little change upon NMP extraction at 202 °C²⁴ and another reports that NMP extraction at room temperature leads to small increases in the total number of spins in some coals but to minor decreases in others.¹⁰ The present NMP extractions have been performed at room temperature but the resulting coal fractions were treated at 145 - 150 °C under vacuum oven conditions for as much as 24 h in order to drive solvent off. Both processes were performed under strictly oxygen-free conditions. Present results show the total number of free radicals in the original whole coals is not conserved in the course of

extraction. Takanohashi and Iino have also performed elemental analyses of the Argonne Premium coal extracts and residues¹⁰ that also bear on the relative heteroatom contents and degrees of aromatic ring condensation in general. While there were previous indications from g-value changes upon extraction that there is a preferential solubility of heteroatom-bearing free radicals,¹⁰ the present results point to an apparently fairly representative extraction of free radical types except in the lignite.

Experimental

The eight Argonne coals were repeatedly extracted with 1:1 (v/v) NMP-CS₂ solutions at room temperature. After thorough mixing, approximately 5 gram samples of the coals were removed in a pre-pure grade N₂(g) atmosphere glove box from the vials in which they were shipped¹⁵ and placed in preweighed round bottom flasks. The samples in the stoppered flasks were weighed and then dried by careful rotoevaporation (Buchi/Brinkman RE111) (*in vacuo* with N₂(l) trap) to a constant weight in a bath at 145 - 150 °C. The rotoevaporator was outfitted with a pre-pure grade N₂(g) tank for flushing the system at the times of unstoppering/flask-attachment and flask-removal/ stoppering. To the flasks of dried coal in the glove box were added 100 ml of the NMP-CS₂ solution. The NMP was Aldrich HPLC grade and the CS₂ was Aldrich spectrophotometric grade. The flasks were stoppered and placed in the initially room temperature bath of a Quantrex Q210 ultrasonic agitator for 30 min. The temperature of the bath typically rose 5 °C in the course of the sonication. The stoppered coal and extract solutions were centrifuged for 30 min at 15,000 r.p.m. (17,540 RCF) in a Sorvall RC-5B centrifuge and decanted, filtered and washed through 1 µm Millipore filters in the glove box. The extractions of the solids were repeated in like manner until the extract achieved an optical density < 2 at 505 nm, collecting all washings and extracts in a large flask. The CS₂ and NMP solvents in the preweighed flasks of extract or residue were removed by rotoevaporation to constant weight with a procedure identical to the initial drying. Final weights were recorded. Extraction is believed to be quantitative except in the case of the Beulah Zap coal where material loss is encountered due to the "explosion" of the sample caused

by the release of adsorbed gases when the sample is lowered into the rotoevaporator heat bath.

EPR and NMR sample tubes, preweighed with caps, were loaded, respectively, with approximately 40 mg and 150 mg of whole coal, extract and residue in the glove box. The capped, loaded tubes were reweighed and then in the glove box silica wool wads were pushed into the tubes over the samples in order to prevent dispersal of the sample during the subsequent evacuation. The samples were attached via o-ring fittings to a diffusion pump-equipped Kontes vacuum line and pumped to less than 10^{-3} $\mu\text{m Hg}$ pressure. Finally, the samples were flame-sealed under vacuum and stored in the dark at about -10 $^{\circ}\text{C}$ except when being examined. The remainder of the samples were stored, as required for other analyses, in vials under nitrogen atmosphere in the glove box.

The extract samples were characterized beyond the work of Takanohashi and Iino¹⁰ by the following methods. Transmission infrared (IR) spectra of the extracts, pressed into KBr pellets (6.3 mg extract and 1 g KBr), were run (600 cm^{-1} to 400 cm^{-1}) on a Perkin-Elmer 1420 IR spectrometer. Solution proton NMR spectra of solutions of known extract concentrations by weight in pyridine- d_5 were examined and compared quantitatively with a standard proton NMR spectrum of an NMP solution of known concentration in pyridine- d_5 (Merck Isotopes). NMR spectra were acquired on a Bruker AM360 300 MHz spectrometer with $\pi/2$ pulses (12 μsec) at a repetition times of 5 sec, by calculating the Fourier transform (FT) of the resulting free induction decay (FID). A solid-echo²⁵ proton NMR ($\pi/2_x$ - τ - $\pi/2_y$) technique was employed to examine and compare the solid extract and whole coal spectra. The spectra were obtained on the spectrometer described above with 12 μsec $\pi/2$ pulses and intervals $\tau = 10\text{ }\mu\text{sec}$ with a repetition period of 20-30 sec. In order to quantify the NMP retained in the solid extracts on a relative basis with an FID-FT spectrum, the same length, single $\pi/2$ pulse was employed with a repetition period of 1 sec. In all cases the FT of the FID or the solid-echo was calculated to obtain the NMR spectra of the coal, coal extract or retained NMP.

The residues have been further characterized in the following experiments. Weighed amounts of the residues were washed by sonication with acetone- d_6 (Merck Isotopes) and filtered and then

the solution proton NMR spectra of the washings were examined. The amount of washable NMP retained in the residues was determined by comparison with a proton NMR spectrum of a standard solution of NMP in acetone- d_6 . Solid-echo and FID experiments similar to those done on the extracts were performed on the solid residue samples.

The SLR times of the solid extract and residue samples were measured from the recovery of (the FT of) the solid echo described above, as a function of delay time after a (24 μ sec) π inversion pulse. The repetition times were 20 - 30 sec. The T_1 were determined from a least squares fit of the equation,

$$I = a - be^{-T/T_1}, \quad (1)$$

to the FT intensity, as a function of delay time T at a particular chemical shift in the spectrum, chosen so as to avoid the NMP peak. T_1 were otherwise independent of the choice of chemical shift. No evidence of multiexponential or multiphasic recovery was found away from the NMP line to be discussed in the **Experimental Section**.

Several types of CW and pulsed EPR measurements were made on the extract and residue samples. Measurements made on the whole Argonne Premium coals have been published separately in a paper¹¹ that describes the experimental details of each type of measurement. All experiments were performed on a Bruker ESP-380 pulsed EPR spectrometer. The numbers of spins in the broad-line components of the coal fractions were determined with reference to a standard¹¹ from the integrated intensities of the magnetic field sweeps of the two-pulse echo, corrected for spectrometer dead-time from the echo decay. The numbers of spins in the narrow-line (inertinite) components were determined with reference to a standard¹¹ from the integrated FID FT spectra, similarly corrected for spectrometer dead-time from the FID. Broad-line g -values were determined from the centers of the CW EPR spectra at 90 dB power attenuation, as were the broad-line linewidths from the widths, and the narrow-line g -values were determined from proton NMR gaussmeter (Micronow 515-1) field measurements at the center of the FID, as determined by visual oscilloscope examination of the FID, together with microwave frequency measurements.

Narrow-line Lorentzian linewidths (and T_2 values) were determined from the decay time of the FID. Broad-line spin-spin relaxation times T_2 were determined from the low-magnetization pulse turning angle (θ) limit of the two-pulse echo decay coherence memory time, T_M , from an appropriate plot of $1/T_M$ versus a function of θ . Broad-line SLR times T_1 were determined from the two-pulse echo saturation recovery after a picket-fence, multipulse saturation sequence designed to achieve saturation over a broad frequency range in order to avoid spin diffusion contributions to the recovery. The narrow-line T_1 were determined directly from the inversion recovery of the on-resonance FID decay at a particular decay time in the FID without intermediate Fourier transformation.

Results

Extraction

The extract yields by weight from the Argonne Premium Coals are shown as a function of rank in Figure 1. The data were determined from the weights of extract plus residue and from the proportioning of the NMP retained in them, as determined from the NMP retained in the extract on the basis of solution NMR, which will be described in the next section. All mineral matter was assumed to remain with the residue and negligible materials losses were assumed. Internal consistency checks regarding retained solvent show that the materials losses were no more than about 10%, except for the omitted Beulah Zap results (see Experimental Section). Except for the very high solubility of the Upper Freeport (UF) coal, the yields all lie between 20% and 40%. While we do not have quantitative results, it should be noted that the Beulah Zap extraction yield appears qualitatively to be still less than the Wyodak Anderson (WA) coal. The BZ yield was so low, in fact, that some of the measurements that were made on other extracts were not possible for the BZ samples. While the trends with rank are consistent with the results of Iino *et al.*,¹¹ there are too few data to see clearly the rising yield with rank, the peaking at 85 - 87% C and the rapidly decreasing values above 87% C which were demonstrated by them. A plot of extract yield versus heteroatom content¹³ (N,O,S) in the organic fractions of the coals reveals essentially no

more than the reverse of this trend with coal rank.

The IR spectra of the extracts display the kinds of trends with coal rank that are generally expected. The aromatic C-H out-of-plane bending and C-C stretching bands are observed to increase with the rank of the parent coal above about 80% C but are weak and not clearly identifiable in the extracts of coals of lower rank. This is in accord with increasing aromaticity of the parent coal with increasing rank. The methyl and methylene C-H stretching peaks in the extracts of all eight coals are observable and have intensities that decrease with parent coal rank. Also noteworthy is the fact that the ratio of methyl to methylene C-H stretching peak intensities appear to increase with coal rank. This suggests that, as the aliphatic nature of the coal extracts increases with decreasing parent coal rank, there is a tendency toward longer chains with relatively more methylene groups per chain (usually terminated with a methyl group). A broad band of C-O stretching modes, superimposed by that of NMP in some of the coal extracts, is found between 1550 cm^{-1} and 1750 cm^{-1} throughout the range of extracts. The broad band exhibits relatively subtle changes in shape from one sample to another and is probably from a variety of functional groups that contain the C=O group. The overall intensity of the broad C-O stretching band appears to be more a function of the particular coal than a function of parent coal rank. The absence of the strong, sharp C-O stretching peak characteristic of coal air-oxidation is missing in all samples, presumably because of the oxygen-free extraction and sample preparation. The fact that the broad, weak C-O peaks are observed in the extracts of all of the coals probably reflects the strong ability of the NMP in the solvent to extract the molecules with polar functional groups, across the range of coal ranks.

The solution proton NMR spectra of the extracts exhibit broad lines or bands in the aromatic(7-8 ppm) and aliphatic(2.2-3 ppm) regions. Because of the breadths of the bands and the small samples employed, the intensities are weak relative even to the impurity proton NMR peaks in the NMR grade deuterated solvents. Therefore quantitative integrations of these bands was not feasible, permitting only qualitative observations. Somewhat surprising to us was the fact that the relative intensities of the aromatic and aliphatic bands did not differ markedly through the

range of ranks of parent coals. The intensity of the aromatic region, which is somewhat less obscured by solvent peaks than the aliphatic region, increases from a negligible level below 75% C in the parent coal to a maximum at around 85% C in the parent coal and decreases again to an undetectable level again above 89% C in the parent coal. The constant relative NMR intensities of the aliphatic and aromatic proton bands may reflect the particular extracting character of the solvent across the range of coal ranks. The intensity change in the extract spectrum with coal rank suggests that, as the coals increase in aromaticity, there is a corresponding increase in numbers of aromatic protons up to around 85% C in the parent coal. Then, as one progresses from the more aliphatic to the more aromatic coal beyond 85% C in the parent coal, the extracted molecules suffer not only a loss of aliphatic protons but also a comparable loss of aromatic protons as a result of aromatic ring condensation.

Solvent Retention

There are many indications that the NMP from the extraction solvent is retained in the extracts and residues. Firstly NMP is observed in both the IR (by its prominent CO stretching band) and solution proton NMR spectra of the extracts by comparison with authentic NMP or NMP added to the sample. Extracts that exhibit obvious NMP peaks at *ca.* 1670 cm^{-1} (authenticated with the IR spectrum of an NMP sample) were the Illinois No. 6 (IL), Pittsburgh No. 8 (PI), Lewiston Stockton (LS) and Pocahontas No. 3 (PO) coals. The possible presence of NMP IR peaks in the BZ and WA extracts cannot be ruled out because of the presence of substantial C-O stretching intensity in this region from other sources. When the residues are washed with acetone- d_6 , the resulting solutions exhibit the proton NMR spectrum of NMP ($\delta_{\text{CH}_3} = 2.73$; $\delta_{\text{CH}_2} = 1.98, 2.17, 3.35$). There is also an additional broad singlet peak in the proton NMR FID and solid echo spectra of both the solid extracts and residues whose chemical shift range overlaps those of the solution NMP peaks. This broad peak is missing in the proton NMR spectra of the dried, solid, whole coals, which have not been subjected to extracting solvent. Finally there is a substantial increase in the total weight of extract plus residue compared with the original weight of the whole

dry coal. In view of the high CS₂ volatility, the temperature (145 °C - 150 °C) and pressure (~ 15 μm Hg) "vacuum oven" conditions in the solvent removal and the absence of a CS₂ peak in the C¹³ NMR spectra of the extract and residue wash solutions, we assumed that only NMP is retained from the extraction solvent.

In Figure 2 are shown the total amounts of NMP retained in the organic matter in the extract and residue. The data are based on the difference between the sums of the weights of the extract and residue and the original weights of the whole coal. The calculations included a correction for the ash content of the whole coal¹³ and assumed negligible material losses, except for the omitted Beulah Zap result (see Experimental Section). Thus the results are underestimated by no more than about 15%. It could be argued on the basis of the results in Figure 2 that there is an increasing tendency for NMP to be retained with increasing (O,S) heteroatom content.

Figure 3 presents individually the amounts of NMP retained (a) in the extract and (b) in the residue that can be washed from it with acetone. The values (a) were determined from the integrated NMP NMR intensities of pyridine-d₅ solutions of the extracts in comparison with a standard pyridine-d₅ solution of NMP ($\delta_{\text{CH}_3} = 2.69$; $\delta_{\text{CH}_2} = 1.82, 2.15, 3.19$). The values (b) were likewise determined from the integrated NMR intensities of the acetone-d₆ washings of the residues in comparison with a standard acetone-d₆ solution of NMP. Based on the signal-to-noise levels of the integrated intensities of the NMP peaks, the largest estimated standard deviations in the values plotted are 0.14 grams NMP/100 g extract and 0.78 grams/100 g residue organic matter. These measures of NMP retention in extract and residue bear a good correspondence to one another, with the exception of the PO residue from which a relatively greater amount of NMP is washed than is retained in the extract. These trends also roughly parallel the total retention in Figure 2, with the exception of the WA coal. The rather different PO coal extract and residue NMP retentions in Figure 3 may, at first glance, appear not to be in agreement with the total PO NMP retention in Figure 2. However, the PO residue NMP retention predominates because of the low, *ca.* 20%, extract yield and is in line with the total PO NMP retention. The sums of the weights of extract NMP and the weights of NMP washed from the residue agree well with the

weight increase upon extraction for the PO, LS and BC coals. The shortfalls, which represent NMP that cannot be washed from the residue, are about 8 g (UF), 15 g (PI), 20 g (IL) and 40 g (WA) per 100 g organic matter.

Figure 4 shows the LS example of the broadened NMP line that is observed on top of the broad spectrum of the coal fraction in the solid-echo and FID-FT proton NMR spectra of the solid extracts and residues but is not observed for the whole coals. The spectrometer deadtime in the FID-FT spectra may be too long to observe accurately the full width of the coal spectrum. On the basis of the behavior of pyridine adsorbed onto coal solids,¹⁷⁻²⁰ we assume that the broadening is the consequence of the hindered rotation of NMP molecules in the samples. The broadened lines attributed to NMP have distinctly different SLR T_1 -times (0.69 sec) from most of the rest of the coal NMR lines (0.05 sec - 1.5 sec). Somewhat surprising to us is the fairly uniform 4 ppm linewidth observed for this feature over the whole range of coal extracts and residues. No other evidence of NMP lines of greater breadth was found either directly in the spectrum or in the form of multiexponential SLR behavior elsewhere in the spectrum. Similar looking NMR spectra have been observed for adsorbed water in coals.²⁶ However, the absence of the peak in the dried whole coals and the fact that the "vacuum oven" conditions for the isolation of the extracts and residues were similar to those used for drying the whole coals seems to preclude natural or chemically generated water as the source of this NMR line.

In Figure 5 are presented the relative NMP NMR intensities in the solid extracts and residues versus the sum of the oxygen and sulfur contents in the organic matter of the fraction. The intensities of NMP were determined from the integrated intensity of each single, broadened NMP proton NMR line, as shown in the example in Figure 4. The residue values were corrected for the mineral content of the whole coal,¹³ which was assumed to remain with the residue. Standard deviations estimated from the signal-to-noise ratio of the integrals are 0.6 on the arbitrary scale presented in Figure 5. It is clear by comparison with Figure 3(a), that for the solid PO extract one is observing at most 4 g NMP/100 g of extract by solid NMR. It follows from the data in Figure 5 that at most about 0.4 g NMP/100 g of organic matter are being observed by solid NMR for any

of the other extracts and in all of the residues. Thus the percentage of NMP observable by solid NMR in the residues and extracts other than the PO and WA extracts can be seen from Figure 3 to be at most 30 - 40% of the total NMP present and as little as 3%! Even though relatively small amounts of NMP are retained in the PO extract (see Figure 3(a)), Figure 5 also shows that the amount of observable solid NMP is around ten-fold greater than in any other extract or residue and that the PO coal fractions have the smallest combined oxygen and sulfur content.¹⁰ Given that there has to be 40 - 45 g NMP/100 g organic matter in the WA residue and that at most 0.4 g NMP/100 g organic matter are observable shows that less than 1% of the WA residue NMP is observable by NMR. The WA residue has the highest combined oxygen and sulfur content.¹⁰

The relatively uniform 4 ppm widths of the solid NMR peaks in solid extract and residue spectra (see Figure 4) are assumed to result from motional narrowing of the powder pattern of fully immobilized NMP molecules. Our estimate of the average width of the powder pattern from the magnetic dipole interactions between the protons of the NMP methylene groups gives a width of 72 ppm. This estimate, together with the observed 4 ppm linewidth, gives an estimate of 1.35×10^{-6} s for the rotational correlation time τ_c of these observable NMP molecules in the solid fractions. We feel that NMP molecules, whose motional narrowing leads to lines broader than 80 ppm, would go altogether undetected under the conditions employed. (We find no SLR evidence for any NMP spectrum narrower than 80 ppm except for the 4 ppm line.) Since this represents, in most cases, the vast majority of the NMP, one concludes that, except for the small fraction of relatively unhindered NMP with $\tau_c \sim 1.35 \times 10^{-6}$ s, the bulk of the NMP is sufficiently firmly bound to have $\tau_c > 2.7 \times 10^{-5}$ s.

EPR Experiments

The numbers of electron spins per (dmmf-dry mineral matter free) gram of whole coal before the extraction¹¹ are compared in Figure 6 with the numbers of spins found in the extracts and in the organic matter of the residues from the original (dmmf) gram of the whole coal. The latter were calculated from the actual EPR spin number measurements, the weights of the extract or

residue samples, the yields of extract or residue and the appropriate corrections for mineral matter¹³ in the residues. BZ extraction data are omitted because the extraction was not quantitative and these calculations could not be performed. The ratios of the sums of spins after extraction to the original numbers of spins, which range from 60% to perhaps as little as 5% in a generally decreasing trend with rank, point out that there are substantial losses of free radicals in the extraction and isolation processes. (The pulsed EPR method employed may overestimate the numbers of spins in the high spin concentration coals, LS and PO.¹¹) There are also substantial losses in the numbers of spins in the inertinite fractions, as shown in Table 1 which compares the numbers of spins in the whole coal and residues. The whole coal numbers of inertinite spins for the WA, BC and PI coals were not measurable in our previous study¹¹ and were not repeated in the present study under a set of conditions that are apparently more sensitive. There are usually more spins found in the extracts than are left behind in the residues, with the exceptions of the IL and LS coals. Practically no narrow line EPR signals are found in the extracts. The largest fraction of inertinite spins that survives is 5% in the IL coal and the smallest survival is as low as 0.6% in the UF coal, assuming that all of the inertinite maceral remains with the residue (i.e., negligible extraction occurs).

The EPR g-values of the free radicals in the broad, non-inertinite, whole Argonne Premium coals and their extracts and residues are given in Table 2, together with the linewidths, ΔH , of the broad, non-inertinite parts of the EPR lines of each. Figure 7 shows the differences between the g-shift of the coal fractions and the g-shifts of the whole coals. The g-changes of all of the extracts, except for the substantial negative g-change of the BZ lignite are practically zero. On the other hand, there are significant g-changes, both positive and negative, in the residues, with the exception of the highest rank UF and PO residues. The extracts with significant (> 0.0001), positive g-changes all come from coals with higher sulfur content (0.9% - 5.6%) than the sulfur content of the coals whose residues have negative g-changes (0.6% and 0.7%).¹³

The EPR linewidth values, ΔH , in Table 2 exhibit extract values that range from less than or comparable to residue values at low rank to extract values comparable with or greater than residue

values at higher rank. The whole coal linewidths range from values considerably greater than or comparable to the values of their fractions at lower rank to whole coal values that are markedly less than the values of the fractions at higher rank.

The EPR SLR T_1 times are shown in Figure 8 for the whole coals and their extracts and residues. The non-inertinite and inertinite residues generally have SLR rates decreasing (T_1 increasing) with coal rank (from 25 - 30 μsec at 75% to > 100 μsec above 90 %C). The T_1 of the residues are generally greater than or comparable with the extracts, a trend that goes with a fairly uniform extract T_1 ($30 \pm 10 \mu\text{sec}$) across the whole range of coal ranks. We note that there are individual differences in the SLR of the whole coals. The T_1 of the UF (160 μsec ; 88 %C), PO (130 μsec ; 92 %C), LS (74 μsec ; 85.5 %C) and IL (64 μsec ; 80.5 %C) coals are considerably longer than their extracts and residues while the PI (17 μsec , 85 %C) and BC (15 μsec , 81.5 %C) are considerably less. We also note in Table 3 that the T_1 of the inertinites in the residues (720 - 1010 μsec) are longer than in the inertinites (390 - 400 μsec) in the whole coals before extraction.

The EPR spin-spin relaxation time, T_2 , values in the broad, non-inertinite lines of the whole Argonne Premium Coals and their extracts and residues are presented in Table 4. The extract T_2 values are greater than the whole coal with the possible exception of the WA case. The residue T_2 values are all less than the extract T_2 except for the PO case. The residue T_2 values are in some cases greater and in other cases less than the values of the whole coal. We have shown that there is little correlation of spin-spin relaxation rate, $1/T_2$, with the actual concentrations of spins in the extracts and residues, whereas a good correspondence is observed¹¹ for the whole coals.

The EPR T_2 times for the narrow, inertinite lines of the residue are compared with the whole coal values in Table 5. Based upon the whole coal data available from our previous study,¹¹ there appears to be a uniform increase in residue inertinite T_2 with whole coal inertinite T_2 . The residue inertinite T_2 are all significantly reduced from the values in the whole coals, with the possible exception of the significance of the LS difference.

NMR Experiments

The proton NMR SLR T_1 time measurements of the Argonne Premium Coals and their extracts and residues are shown in Figure 9(a). The results are superficially similar to the EPR T_1 results shown in Figure 8. The residue T_1 rise fairly uniformly with the rank of the whole coal except for the high BC residue T_1 value. The whole coal and extract T_1 values have overall rising trends with whole coal rank but with less uniformity. Like the EPR results, the proton NMR whole coal T_1 are mostly greater than or comparable with the T_1 of the extracts and residues. Unlike the EPR results, the extract proton NMR T_1 are often longer than the residue T_1 . The data are plotted against the individual C contents¹⁰ of whole coal, extract and residue in Figure 9(b). It can be seen from the uniformity of the T_1 dependence on C content that much of the variation between the T_1 of a given whole coal and its extract and residue is simply a function of C content. The BC and UF extract T_1 appear to be lower than the overall trend. (Interestingly, a presentation of the EPR T_1 data versus individual C content similar to Figure 9(b) does not eliminate the disparities between the T_1 of a given whole coal and its extract and residue observed in Figure 8.)

Discussion

The extraction yields generally conform to the classic shape of extraction yield versus C content that has been observed for a wide sampling of many coals by Iino *et al.*,¹⁶ in which extraction yields increase to a maximum at 85 - 87% C and drop rapidly above this rank. It is at this range of C content that the intensity of the aromatic proton NMR region of the extract maximizes and begins to drop off, presumably as a result of the increasing polycondensation of aromatic rings and loss of H. Heteroatom content also tends to drop off more rapidly with rank above 87% C.¹⁰ As the C content of the whole coal decreases below 85% C, we observe methyl and methylene CH stretching intensity ratios in the IR of the extracts that are indicative of increasingly longer aliphatic chain structures, which is, of course, being accompanied by an increasing heteroatom content.¹⁰ There is a well known propensity of coals with decreasing rank to retain increasing amounts of water or pyridine solvent, like the similar trend demonstrated here

for NMP, probably through acid-base interactions or H-bonding.¹⁴ Given the natural, biological origin of coals, together with these facts, it seems likely that from 85% C downward, the coals become increasingly polymeric, resembling the biopolymers from which they derive in regard to H-bond cross-linkage.

Thus the amount of extractable molecular species increases with rank to 85 - 87% as the polymeric, H-bonded macromolecular network breaks up. Above 85 - 87% C the extractable, largely aromatic molecular species have been increasingly transformed with increasing rank into an increasingly polycondensed, insoluble, macromolecular matrix. This picture is also consistent with the elemental analyses of the extracts and residues from the Argonne coals. Except for the BZ lignite, the C content of the soluble, more aromatic extract is greater than the C content of the more aliphatic, insoluble, polymeric residue below 87% C. The situation reverses for the PO coal, in which the insoluble, polycondensed, aromatic residue is richer in C and the soluble, more aliphatic extract is poorer in C. Likewise, except for the BZ lignite, the heteroatom content of the soluble, more aromatic extract is less than the heteroatom content of the more aliphatic, Lewis and Brönsted acid-rich, polymeric residue below 87% C. The situation reverses for the PO coal, in which the insoluble, polycondensed, aromatic residue is poorer in heteroatoms and the soluble, more aliphatic and acid-functionality-rich extract is richer in heteroatoms. The BZ lignite is probably an exception because of the small degree of coalification of the organic matter. What very little material that can be extracted from BZ, because it is almost entirely polymeric, has a composition almost identical to the residue.¹⁰

The weight increases upon extraction indicate that solvent is being retained in spite of the rigorous vacuum heating to constant weight under strictly oxygen-free conditions. The extract IR spectra, the extract solution proton NMR spectra, the proton NMR spectra of the acetone-d₆ washings and the proton NMR spectra of the solid extract and residue spectra all show the retention of NMP. The absence of any detectable CS₂ in the extract or in the acetone wash C¹³ NMR spectra, together with the rigor of the "vacuum oven" conditions of solvent removal relative to the high CS₂ vapor pressure and low boiling point, indicates that it is only NMP that is being

retained.

The total amount by weight of NMP that is retained in the extraction shown in Figure 2 appears to rise generally with heteroatom content in the whole coal, perhaps with LS and BC coals dropping below the trend. (We have chosen to associate heteroatom content with the combined O and S content only because the N content is generally small and not highly variable.¹⁰) The amount of NMP that cannot be washed from the residues increases roughly with heteroatom content of the residue, suggesting that not only does NMP retention *increase* with heteroatom content but that it is *more tightly bound*. The fact that the amount of NMP retained in the extract so very closely follows the amount that can be washed from the residue (except for the PO fractions), as shown in Figure 3, suggests that the entities to which NMP binds tightly are largely absent in the extract. More specific evidence about the tightness of NMP binding comes from the solid proton NMR studies in which it was found that only a fraction of the total NMP retained had rotational correlation times short enough (1.35×10^{-6} s) to observe the NMR peak of NMP. This fraction drops precipitously with heteroatom content or, in other words, the fraction of highly immobilized NMP increases dramatically with heteroatom content. These results appear to be consistent with the H-bonding or acid-base immobilization mechanism that has been proposed²¹ for pyridine-coal interactions. The unusually large amount of solid NMR-observable NMP in the PO residue seen in Figure 5 may have to do with a substantial depletion of the heteroatom-containing sites to which NMP can tightly bind, resulting in the disappearance of NMP from the NMR line. Even the PO extract, which has almost twice the combined O and S content,¹⁰ has enough tight binding sites to suppress the observable NMP NMR.

It is evident from the data presented in Figure 6 that there is a substantial loss of free radicals in the extraction process, carried out in the strict absence of oxygen. The survival of both extract and residue free radicals decreases with increasing rank. This suggests that it may be the *more* aromatic free radical molecules that fail to survive. It is well established and confirmed here to some extent by our IR and NMR characterization that the aromaticity of the coals, extracts and residues increase with coal rank. Also generally more free radicals are extracted than remain in

the residue, as can be seen in Figure 6 except for the IL and LS coals. In many coals the ratio of extract radicals to residue radicals exceeds the ratio (by weight) of extract to residue. If the extract radicals, like extract material in general, tend to be more aromatic than the residue material (with the possible exception of the PO extract), one of two outcomes would result. One is that the extract radicals, being more aromatic, have a lower survival rate and, contrary to observations, the residue radicals predominate. Clearly then, in spite of the disadvantage of low survival, the free radicals are overwhelmingly in the aromatic material. This trend is dramatically displayed in the well known increase in spin concentration with rank, also shown for the Argonne coals in Figure 1. The evidence for the chemical lability of the aromatic free radicals appears to run counter to arguments in the literature for their exceptional stability, mentioned in the **Introduction**.

The extract free radicals have very small and only slightly positive g-value differences from the corresponding whole coals except for the BZ and PO coals. Thus the free radicals in the extracts are fairly representative of the free radicals in the original whole coals. This is to be expected from the fact that more radicals are extracted than remain in the residue. The well-established correlation of positive g-shifts with coal heteroatom content^{14,15} suggests that the extract free radicals may be slightly more heteroatom-rich than the original whole coal. This is also in agreement with the previous conclusion that the heteroatom-rich free radicals have a greater survival rate than the aromatic free radicals. The PO extract and residue free radicals exhibit no g-value changes, as might be expected if the heteroatom content in the coal is too small for any differentiation. The large negative g-change of the BZ extract would seem to imply that the extract contains more heteroatom-poor, aromatic free radicals than the whole coal, a situation that differs from the slightly more heteroatom-rich character of the extract material as a whole.¹¹ It is interesting that the residues with the largest negative free radical g-changes are those with the highest S content and are all among the residues that are heteroatom-enhanced by extraction. This would appear to imply that either the S-containing free radicals, that remain predominantly with the heteroatom-enhanced residue, are either preferentially destroyed or loose S. Free radicals containing other heteroatoms are stable.

The ESR, SLR rates (T_1^{-1}), shown as T_1 in Figure 8, do not correlate well with either electron spin concentration or the relatively small variations in H content, as is required respectively by electron or nuclear intermolecular dipolar interactions. Therefore one concludes that modulation of intermolecular interactions, such as the Zeeman or molecular electron-proton dipolar interactions by flexing of the radicals in their sites in the coal matrix, are the operative SLR mechanisms. Since the g anisotropies in aromatic hydrocarbon radicals are small, one would expect that only the heteroatom-containing free radicals would be influenced by this mechanism. However, there appears to be no strong correlation of SLR rate (T_1^{-1}), shown as T_1 in Figure 8, with heteroatom content (e.g., the heteroatom contents of BZ and its fractions are *ca.* 20 times greater than those of UF but only 2 - 3 times greater than those of UF, comparisons that are not consistent with the corresponding relative SLR rates). The only remaining and often considerably stronger mechanism at the fields employed in these experiments is the modulation of molecular electron-proton dipolar interactions¹¹ and we will attempt to show that it is reasonable in terms of the observed SLR rates in Figure 8.

SLR occurs as a consequence of components of time varying local magnetic fields at the Larmor frequency of the electron spins that induce transitions, much as does the applied microwave magnetic field.²⁷ Generally two distinct, but not easily experimentally distinguishable factors contribute to the amplitude of the local magnetic field induced on the electron spin by the varying electron-proton dipolar interaction by the flexing of the free radical in its matrix. One factor is the actual angular amplitude of the motion of the free radical at the Larmor frequency in its site in the solid matrix. The other factor is the magnitude of the anisotropy of the electron-proton dipole interaction in the free radical molecule. The latter is a molecular property of the free radical and scales as the spin density mainly at the CH groups in odd-alternate, polycondensed ring systems. We were not successful in separating these two factors by employing observed linewidth as a measure of the dipolar anisotropy, perhaps because there remains a distribution of g -values that contributes to the linewidth.

The non-inertinite and inertinite whole coal and residue free radicals display a generally

increasing T_1 with coal rank (from 25 - 30 μsec at 75% C to as much as 1000 μsec above 90% C). This is consistent with both the decreasing CH spin densities and the decreasing flexing amplitude of increasingly large polycondensed ring systems. The T_1 of the residues are generally greater than or in some cases comparable with the extract T_1 . This would be consistent with a generally more rigid macromolecular matrix free radical environment than the molecular environment in the extract, if it is assumed that the sizes of the odd-alternate, condensed aromatic hydrocarbon free ring systems are comparable in extract and residue. The relatively flat extract T_1 trend with rank is somewhat puzzling. It would be consistent with the opposing trends with decreasing rank toward more rigid H-bonding or dipolar intermolecular binding forces but greater CH spin densities in the smaller molecular polycondensed free radical systems or conversely with the opposing trends with increasing rank toward less rigid van der Waals binding forces but smaller CH spin densities in larger molecular polycondensed free radical systems.

The NMR SLR results, shown in the two T_1 presentations in Figure 9, exhibit a markedly monotonic increasing trend with C content of the individual coal or coal fraction. Since there is no obvious *direct* connection between T_1 and C content, we look for other potential causative factors that correlate strongly with C content, such as electron spin concentration or H content. However, T_1 fails to correlate very well with either factor. The failure to correlate with spin concentration, can be seen, for example, as a failure of the T_1 to follow the loss of electron spins that occurs upon extraction, shown in Figure 6. We speculate that it is either the progressive loss of flexible or rotating, fast aliphatic chain protons with rank and/or the increase in rigidity of the increasingly polycondensed molecules whose aromatic protons begin to predominate with increasing rank. These questions could be answered more specifically with T_1 measurements of separate functional groups in magic-angle spinning solid state NMR experiments. We believe that the rigidity of the matrix must also be playing some role in determining NMR SLR rates. The whole coal T_1 would otherwise tend to be an average of extract and residue values, whereas they are observed to be greater than the average in all but one case.

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Table 1. Concentrations of the numbers of spins per gram of inertinite found in the narrow EPR lines of the whole Argonne Premium Coals and their residues. (No appreciable narrow-line signal was found in the extracts.)

Coal	Spins per Gram of Inertinite x 10 ⁻¹⁹	
	Whole Coal ^a (dmmf)	Residue (dmrnf)
Wyodak Anderson	---	0.0044
Illinois No. 6	3.6	0.19
Blind Canyon	---	0.17
Pittsburgh No. 8	---	0.36
Lewiston Stockton	6.5	0.11
Upper Freeport	10.5	0.064
Pocahontas No. 3	13.3	0.47

^a From reference 11.

Table 2. The g-values and linewidths of the broad EPR line in the whole Argonne Premium Coals and their extracts and residues.

Coal	Percent ^a (dmf)	g-Value ^b			ΔH^c (Gauss)		
		Extract	Residue	Whole Coal	Extract	Residue	Whole ^d Coal
Beulah Zap	74.0	2.0033	2.0039	2.0042	5.9	6.8	7.4
Wyodak Anderson	76.0	2.0037	2.0039	2.0036	5.9	5.8	7.9
Illinois No. 6	80.7	2.0033	2.0025	2.0031	6.4	6.1	6.0
Blind Canyon	81.3	2.0032	2.0037	2.0031	6.4	6.1	7.6
Pittsburgh No. 8	85.0	2.0033	2.0025	2.0031	5.9	6.2	4.7
Lewiston-Stockton	85.5	2.0032	2.0027	2.0031	6.6	6.2	4.8
Upper Freeport	88.1	2.0033	2.0033	2.0032	6.6	5.9	4.4
Pocahontas No. 3	91.8	2.0032	2.0032	2.0032	5.9	5.9	5.2

^a Whole coal, rounded to nearest tenth of 1%.

^b Estimated uncertainties are 0.0001.

^c Measured from peak to trough of EPR derivative spectrum; 0.1 G estimated uncertainty.

^d From the selected values in reference 14.

Table 3. The spin-lattice relaxation times T_1 of the narrow EPR lines in the whole Argonne Premium Coals and their residues. Standard deviations are given in parentheses.

Coals	Percent C ^b	T_1^a (μ sec)	
		Residue ^c	Whole Coal ^d
Lewiston Stockton	90.2	720(150)	500
Illinois No. 6	90.4	820(30)	390
Pittsburgh No. 8	91.2	1010(50)	480
Pocahontas No. 3	91.8	810(10)	490

^a Standard deviations are given in parentheses.

^b Selected values in reference 14.

^c Traces of a narrow line signal are found in the extract with identical T_1 .

^d From reference 11.

Table 4 The spin-spin relaxation times T_2 of the non-inertinite macerals of the whole Argonne Premium coals and of their extracts and residues. Uncertainties are given in parentheses.

Coal	T_2 (nsec)		
	Whole Coal Non-Inertinite Macerals	Extract	Residue
Beulah Zap	1020(160)	1590(45)	355(14)
Wyodak Anderson	1340(160)	1140(110)	623(38)
Illinois No. 6	464(35)	2840(550)	1045(80)
Blind Canyon	950(100)	1970(180)	705(93)
Pittsburgh No. 8	355.8(8.8)	3860(890)	1680(260)
Lewiston Stockton	1450(110)	1710(370)	724(71)
Upper Freeport	390(20)	1470(230)	2490(240)
Pocahontas No. 3	507(54)	1570(210)	910(130)

Table 5. The spin-spin relaxation times, T_2 , of the narrow EPR lines of the whole Argonne Premium coals and their residues. (No appreciable narrow line signal was found in the extracts.) Standard deviations are given in parentheses.

Coal	T_2 (nsec)	
	Whole Coal ^a	Residue
Wyodak Anderson	---	490(10)
Illinois No. 6	370(40)	297(3)
Blind Canyon	---	290(40)
Pocahontas No. 3	830(100)	626(5)
Pittsburgh No. 8	---	358(1)
Lewiston Stockton	370(50)	322(5)
Upper Freeport	660(50)	420(20)

^a From reference 11.

Figure Captions

1. Equivolume NMP-CS₂ extraction yields by weight from Argonne Premium Coal versus C content in the whole coal or coal rank. The results have been corrected for retained NMP and are presented on a dry-mineral-matter basis. The Blind Canyon coal extraction was not quantitative and is omitted. See text for abbreviations.
2. Total amounts by weight of NMP retained in extracts and residues on the basis of weight increase per 100 grams of organic matter in the original whole Argonne Premium Coals presented versus the combined O and S atom contents of the whole coals.
3. Individual amounts of NMP retained in the extracts and residues from the extracted Argonne Premium Coals, as determined from quantitative NMP proton NMR measurements of solutions of the extracts and from acetone washings of the residues, respectively. Results are presented on the basis of dry weight of organic matter in the fractions and plotted versus the yield of extract.
4. The 360 MHz proton Ft NMR spectrum of the narrow line (expanded) that is assigned to retained NMP, shown atop the broader coal extract NMR line of the solid Lewiston Stockton coal extract. magic angle spinning was not employed.
5. Relative amounts of retained NMP observable in the proton NMR spectra of the Argonne Premium Coal extract and residue solids. The data are plotted versus the combined O and S atom content in the individual coal fractions.
6. Concentrations of unpaired electron spins in the Argonne Premium Coals and their extracts and residues on a dry-mineral-matter-free (dmmf) basis versus whole coal C content (rank).

In order to make additivity comparisons, the spin concentrations in the fractions are given on the basis of the dmmf grams or original whole coal. The sums of the spins in the combined fractions are also shown.

7. Changes in the ESR g-values, Δg , of the Argonne Premium Coal extracts and residues from the g-values of the whole coals are presented versus the C content of the whole coals.
8. ESR spin-lattice relaxation times T_1 of the broad ESR lines in the Argonne Premium Coals and their extracts and residues. The data for the narrow lines are also shown for the whole coals and their residues. No narrow lines appear in the extracts. Data are shown versus C content (rank) of the whole coal or the inertinite in the whole coal, respectively.
9. Proton NMR spin-lattice relaxation times T_1 of the Argonne Premium Coals and their extracts and residues. Data are shown at the top versus C content (rank) of the whole coal. Data at the bottom are displayed with only a few outlying points labeled as a function of the individual C content of the whole coal or fraction.

Figure 1.

NMP Retained in Extract and Residue from Extract & Residue Weights

Figure 3.

NMP Retained in Extract from Solution NMR

NMP Retained in Residue from Acetone Wash

Figure 4-

EXTRACT 701 SHARP LINE

E101.FID

3F 360.134
3Y 120.0
31 5000.000
3I 512
3D 512
3W 125000.000
3Z/PT 488.281

3W 9.8
3D 1.000
3Q .002
3G 10
3S 64
3E 295

W 250000
2 0.0
P 63L P0

B 0.0
B .500
X 25.00
Y 14.00
1 176.347P
2 -169.390P
Z/CM 4.980E3
PM/CM 13.829
3 3991.30

NMP Retained in Fractions Observable by Solid NMR

Spin Concentrations

Figure 7.

Spin-Lattice Relaxation

Extract Residue Coal

Figure 9
Spin-Lattice Relaxation

NMR T1 vs Percent Carbon

**DATE
FILMED**

10 / 25 / 93

END