

# Electron Paramagnetic Resonance Spin-Probe Studies of Porosity in Solvent-Swelled Coal

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*An electron paramagnetic resonance (EPR) spin-probe method was used to examine the changes in the size and number distribution of the accessible regions in five Argonne Premium coal samples as a function of rank upon swelling with the solvents toluene, nitrobenzene, and pyridine. As the basicity of the solvent increased (from that of toluene to that of pyridine), the number and length of the cylindrical pores increased with decreasing coal rank. The number of cylindrical pores also increased with oxygen content (with decreasing rank), a result suggesting a destruction of the hydrogen-bond network upon swelling with pyridine.*

THE PORE STRUCTURE AND SWELLING PROPERTIES OF COALS have been studied in order to gain a better understanding of coal structure. Studies of surface area, pore-size distribution, pore volume, and even pore shape have been performed in order to understand the surface

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0065-2393/93/0229-0467\$06.00/0  
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properties of coals (1). Additionally, studies of coal-solvent interactions and the resulting changes in the pore structure of coals have been performed (2-6). As a complement to solvent-swelling studies, experiments have been carried out to determine how guest molecules diffuse into coal as it swells (7, 8). These studies not only lead to a better understanding of coal structure, but they are also important for understanding coal liquefaction and how liquefaction catalysts gain access to coal.

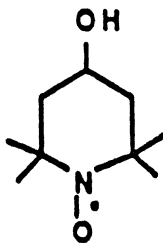
Coal consists of cross-linked macromolecular subunits. Cross-links consist of aliphatic bridges as well as hydrogen bonds. Cross-link density appears to increase with coal rank. Although not completely understood, the solvent swelling of coal apparently occurs via two mechanisms. Non-polar solvents such as toluene appear to swell coal by solvating molecules trapped within the pore structure. However, nonpolar solvents are not capable of disrupting the cross-links in coal and consequently cannot gain access to molecules trapped deep inside the coal particle. Thus, nonpolar solvents are not good swelling solvents for coal.

Hydrogen bonds are very important in cross-linking coal macromolecules (7). Polar, hydrogen-bonding solvents such as pyridine appear to replace the coal-coal hydrogen bonds with coal-solvent hydrogen bonds. This replacement decreases the cross-link density of the coal, a phenomenon that allows the coal to swell (8). Furthermore, the ability of a solvent to swell coal is related to its  $pK_b$  (7).

Hydrogen bonding in coal is most likely due to oxygen functionalities within the coal (9). Because oxygen content decreases with rank and cross-link density increases with rank, the cross-links in higher ranked coals must be primarily aliphatic bridges. Nonpolar swelling solvents have very limited access to the interior of the coal because of the high cross-link density, and hydrogen-bonding solvents have no means of reducing the cross-link density. Consequently, solvents are less able to swell high-rank coals.

Until the early part of the last decade, electron paramagnetic resonance (EPR) spectroscopy was used primarily to study the concentration of free radicals in coal and to determine  $g$  values. However, in 1981 Silbernagel et al. (10) showed the possibility of diffusing nitroxide spin probes into the coal structure and observing the probes by EPR spectroscopy. 4-Hydroxy-2,2,6,6-tetramethylpiperidinoxyl (TEMPOL, structure 1) was placed in a hexane solution and diffused into either Wyodak or Illinois No. 6 coal. The broadening and reduction of the nitroxide spin-probe EPR signal was associated with the diffusion of the TEMPOL molecules into the coal matrix. The results of this experiment suggested that surface absorption and diffusion of spin probes into coal was possible.

The aforementioned method was expanded in our laboratory (11), and EPR studies of doped Alabama (12), Pennsylvania State University



1

Coal Research Section (PSOC) (4), and Argonne (2, 3) Premium coals were performed. From these EPR studies, the relative accessibility of different-size spin probes to the pore structure of coals in the presence of a swelling solvent can be estimated. Nitroxide spin probes with different sizes and shapes were diffused into various coal samples that were swelled with toluene (an intermediate swelling solvent), benzene, and pyridine. Untrapped probe molecules were removed with a nonswelling wash solvent such as cyclohexane. Relative pore shapes and size distributions were then determined from the EPR spin probes trapped within the coal matrix.

More recently, the results of an EPR spin-probe study (2) showed that the relative number distribution of acidic functionalities measured by the spin-probe method is linearly related to the ratio of phenolic to alkyl -OH groups determined by diffuse reflectance infrared (DRIFT) measurements (13). Thus the relative number distribution of acidic functionalities can be measured by the spin-probe method. In addition, the predicted increase in elongated voids in Pittsburgh No. 8 (Argonne Premium coal sample [APCS] No. 4) upon swelling with pyridine was confirmed (2). This confirmation showed that pore-size distribution can be estimated by using the spin-probe method. An electron nuclear double resonance (ENDOR) study (14) of five nitroxide spin-probe-doped Argonne Premium coal samples was used to identify matrix protons in the coal, the protons of the nitroxide spin probe, and the interaction of the surrounding matrix-coal protons with the nitroxide spin probes.

In this study, the variation in the size and number of cylindrical pores was measured as a function of both rank and the degree of swelling for selected Argonne Premium coal samples in which the percent carbon (dry, mineral-matter-free [dmmf]) values vary from 74.05% (Beulah-Zap) to 91.81% (Pocahontas No. 3). Toluene, nitrobenzene, and pyridine were used as swelling solvents, and cyclohexane was used as the wash solvent. Our results extend earlier work (2) and were confirmed by independent small-angle neutron scattering (SANS) (5, 6) and DRIFT studies (13).

## Experimental Details

Five Argonne Premium coal samples (100 mesh) were used:

<i>APCS Number</i>	<i>Name</i>	<i>Rank</i>
3	Illinois No. 6	HVB
4	Pittsburgh No. 8	MVB
5	Pocahontas No. 3	LVB
6	Utah Blind Canyon	HVB
8	Beulah-Zap	L

ABBREVIATIONS: LVB, low-volatile bituminous; MVB, mid-volatile bituminous; HVB, high-volatile bituminous; and L, lignite.

The coal samples were doped with nitroxide spin probes by using a procedure that was found to be optimal and that was reported previously (2). A 30-mg sample of coal under an argon atmosphere was mixed with 2 mL of a  $10^{-3}$  M toluene, nitrobenzene, or pyridine spin-probe solution. The mixture was heated in an oil bath at 50–60 °C and was stirred for 18 h. The mixture was then filtered, and the solid residue was dried for 2 h at room temperature and  $10^{-1}$  torr (13.3 Pa). The dried coal was washed with 3 mL of dry cyclohexane for 3 min to remove any spin probe that was attached to the exterior of the coal or that was in pores or accessible regions too large to trap the probe. The mixture was filtered, washed with 5 mL of cyclohexane, and vacuum dried at room temperature for 0.5 h. After drying, 10 mg of the sample was placed in an EPR tube and evacuated for 0.5 h at  $5 \times 10^{-3}$  torr (0.67 Pa) and sealed. During the entire procedure, the doped coal was exposed to air for only a few minutes.

A swelling temperature of 50–60 °C was optimal, because in that temperature range the swelling probes did not decay and a swelling equilibrium was reached after 12 h (2). The spin concentration of the undoped coal was not studied as a function of solvent. The samples were stored under liquid nitrogen until the EPR spectra were recorded.

To determine the nitroxide-radical spin concentration for a particular sample, the area under only the low-field peak (*z* component of the nitrogen hyperfine coupling) of the spin-probe-doped-coal EPR spectrum was measured. The nitroxide-radical concentration could not be determined by integrating the entire EPR spectrum of the doped-coal sample because the radical concentration of the undoped coal is typically 10–100 times greater than the nitroxide radical concentration. The typical error in measuring radical concentration by EPR spectroscopy is 10–20% under the most ideal conditions (the system here is far from ideal),

and the error in determining the radical concentration in the undoped coal sample would exceed (up to a factor of 10) the spin-probe concentration. Furthermore, determining a base line for the low-field peak is difficult, so typical EPR integration programs fail. This difficulty was solved by using the Kurta tablet digitizer interfaced to an IBM PC AT microcomputer and Sigma Scan software (Jandel Scientific Corp.) that was designed for determining irregular areas.

The total area of the spin-probe EPR spectrum was compared to the area of the EPR spectrum of the Cr(III) intensity standard (SRM-2601) from the National Bureau of Standards, and an absolute spin concentration could then be determined by using methods described previously (2). The fraction of the total nitroxide spectral area measured (typically 10%) was established by determining the area under the low-field EPR peak of a frozen toluene or pyridine solution containing a 1 mM concentration of the same spin probe. To reduce integration errors, the spectra were integrated three times and then averaged.

The compositions of the undoped Argonne Premium coals are given in Table I. The following spin probes were used in this study:

- V, 4-octadecanoylamino-2,2,6,6-tetramethylpiperidinoxyl
- X, 4-amino-2,2,6,6-tetramethylpiperidinoxyl-4-pyridinecarboxaldimine
- XII, 4-hexylamino-2,2,6,6-tetramethylpiperidinoxyl
- XIII, 4-nonylamino-2,2,6,6-tetramethylpiperidinoxyl

Spin probes X, XII, XIII, and V are made up of 4-, 6-, 9-, and 15-carbon chains, respectively, attached to the same nitroxyl-radical substituent (see structures on page 473). Spin probes I–IX were defined previously (3), and the numbering system for spin probes I–XIII used in our previous papers is maintained here for consistency.

EPR powder spectra were recorded on a Varian E-12 continuous-wave (CW) EPR spectrometer at room temperature. The magnetic fields were calibrated by using a Bruker ER035M NMR gaussmeter, and the microwave frequency was measured with a Hewlett–Packard 5246L frequency counter.

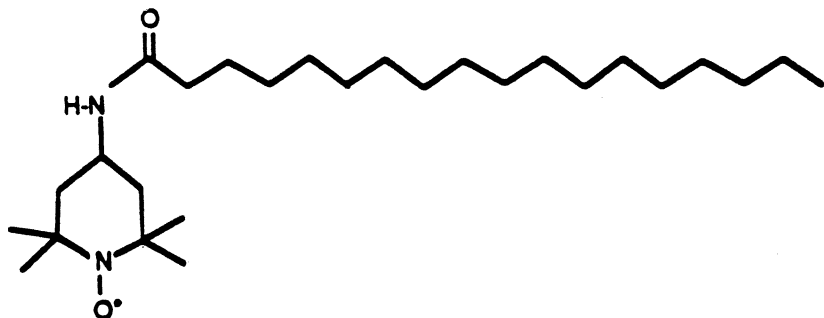
## ***Results and Discussion***

In Figure 1, the radical concentration of coals swelled with toluene solutions of spin probes V, X, XII, and XIII is shown as a function of carbon content. The radical concentration of doped coals swelled with toluene showed a similar dependence with carbon content for probes I, II, and V (2). Thus, although there are differences in spin-probe radical concentration as a function of percent carbon, the radical concentration decreases with rank until a level of 85% carbon and then levels off or increases. For spin probe X, the smallest probe for which results are reported here, the radical concentration decreased from  $15.4 \times 10^{17}$  spins/g at 74.05% carbon

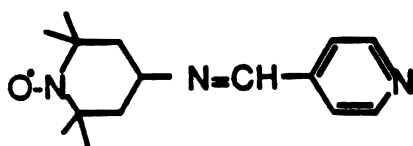
Table I. Analytical Data for the Argonne Premium Coal Samples Studied

APCS Number	Coal	C	H	N	S <sub>org</sub>	Cl	F	O
8	Beulah-Zap	74.05	4.90	1.17	0.71	0.04	0.00	19.13
3	Illinois No. 6	80.73	5.20	1.40	2.47	0.06	0.00	10.11
6	Blind Canyon	81.32	5.81	1.59	0.37	0.03	0.00	10.88
4	Pittsburgh No. 8	84.95	5.43	1.68	0.91	0.12	0.00	6.9
5	Pocahontas No. 3	91.81	4.48	1.34	0.51	0.20	0.00	1.66

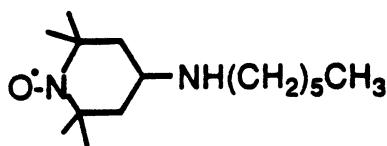
NOTE: Dry, mineral-matter-free (dmmf) values are given in percent, except for sulfur values, which are given in dry percent of the coal sample.



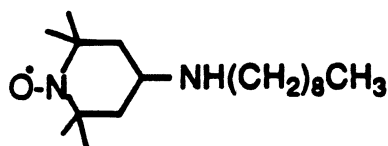
V



X



XII



XIII

(dmmf) (APCS No. 8) to  $1.0 \times 10^{17}$  spins/g at 84.95% carbon (APCS No. 4) and then increased to  $3.0 \times 10^{17}$  spins/g at 91.81% carbon (APCS No. 5). Similar behavior was noticed by Goslar for a toluene solution of spin probe II, which is a probe very similar in structure to X.

Spin probes XII, XIII, and V have similar shapes and differ from each other primarily in length. Spin probe XII is slightly longer than spin probe X. For coals doped with XII, the radical concentration decreased rapidly from  $16.5 \times 10^{17}$  spins/g at 74.05% carbon (APCS No. 8) to  $3.2 \times 10^{17}$  spins/g at 81.3% carbon (APCS No. 6), then decreased much more slowly to  $0.5 \times 10^{17}$  spins/g at 91.81% carbon (APCS No. 5).

For coals doped with the two largest spin probes studied, XIII and V, the radical concentration decreased with percent carbon. For example, the concentration of XIII decreased linearly from  $11.1 \times 10^{17}$  to  $1.4 \times 10^{17}$  spins/g, and the radical concentration of V decreased from  $1.5 \times 10^{17}$  to

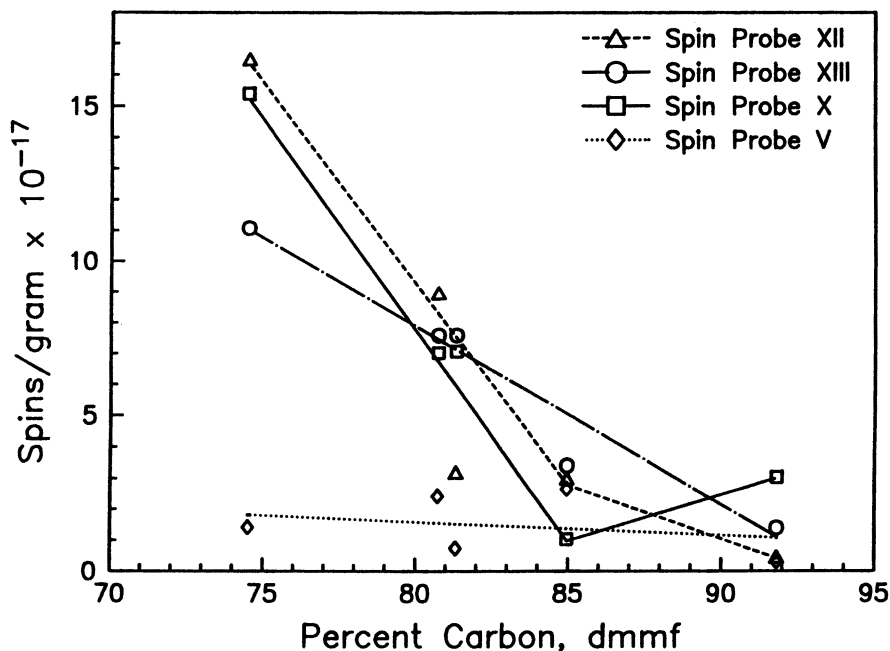


Figure 1. Nitroxide radical concentration vs. percent carbon for APCS Nos. 3, 4, 5, 6, and 8 swelled with a toluene solution of spin probes X, XII, XIII, and V.

$0.3 \times 10^{17}$  spins/g over the range of coals studied. Upon swelling with toluene, apparently fewer pores can accommodate spin probe V than can accommodate spin probe XIII.

In general, the carbon content of coal increases with rank (15). Figure 1 shows that for all spin probes studied, the nitroxide-radical concentration decreased with carbon content and, consequently, with rank. This result indicates that as the rank of the coal samples increases, the degree of swelling will be lower, and fewer areas will be accessible to the spin probes.

In Figure 2, the concentration of nitroxide radicals within the pores of the coal swelled with nitrobenzene solutions of different spin probes is shown as a function of oxygen content. As noted earlier, the nitroxide-radical concentrations of doped coals that were swelled with polar solvents seems to relate to percent oxygen rather than to percent carbon. Nitrobenzene is a stronger swelling solvent than toluene and thus causes a larger change in the pore structure. Consequently, the spin-probe concentrations are different for coals swelled in nitrobenzene. The nitroxide-radical concentration of coals doped with spin probe X increased from  $0.10 \times 10^{17}$  spins/g at 1.66% oxygen (dmmf) (APCS No. 5) to  $3.0 \times 10^{17}$



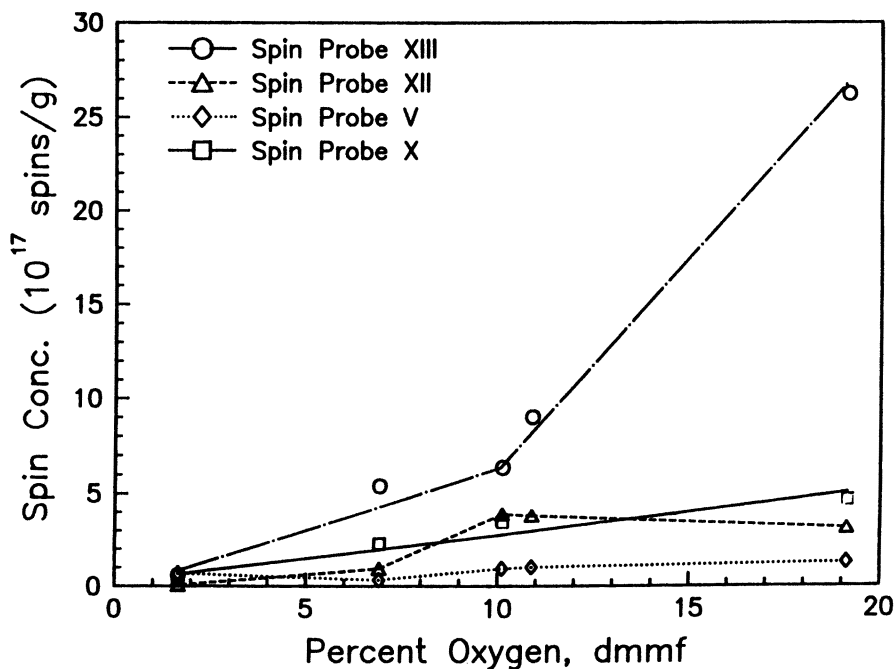


Figure 2. Nitroxide radical concentration vs. percent oxygen for APCS Nos. 3, 4, 5, 6, and 8 swelled with a nitrobenzene solution of spin probes X, XII, XIII, and V.

spins/g at 10.88% oxygen (APCS No. 6) and then levels off. Coals doped with spin probe XII behave in a similar manner. The concentration of nitroxide radicals within the pores of the coal increased from  $0.1 \times 10^{17}$  spins/g at 1.66% oxygen (APCS No. 5) to  $3.9 \times 10^{17}$  spins/g at 10.11% oxygen (APCS No. 3) and then decreased slightly to  $3.1 \times 10^{17}$  spins/g at 19.13% oxygen (APCS No. 8).

Of the two largest spin probes studied with nitrobenzene, the coals doped with XIII had the highest nitroxide-radical concentrations, and coals doped with V had the lowest nitroxide-radical concentrations. For coals doped with XIII, the radical concentration increased from  $0.6 \times 10^{17}$  spins/g at 1.66% oxygen (APCS No. 5) to  $9.0 \times 10^{17}$  spins/g at 10.88% oxygen (APCS No. 6) then increased to  $26 \times 10^{17}$  spins/g at 19.13% oxygen (APCS No. 8). The nitroxide-radical concentration in coals doped with V increased from  $0.3 \times 10^{17}$  to only  $1.3 \times 10^{17}$  spins/g over the range of coals studied. Like toluene, nitrobenzene did not swell the coals sufficiently to accommodate spin probe V.

In Figure 3, the nitroxide-radical concentration in coals swelled with pyridine solutions of different spin probes is shown as a function of oxygen content. Pyridine is a much stronger swelling solvent than either tol-

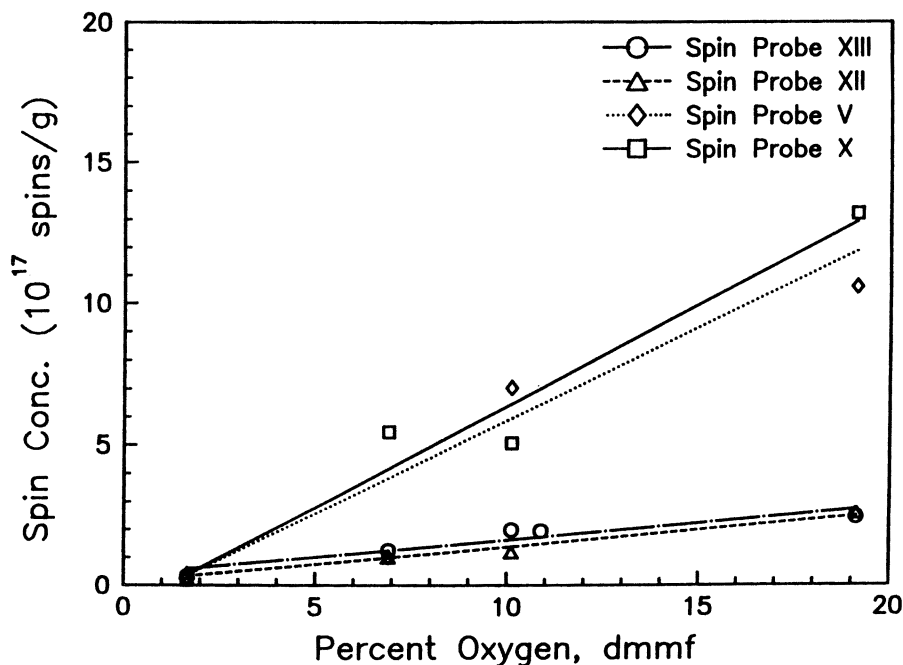


Figure 3. Nitroxide radical concentration vs. percent oxygen for APCS Nos. 3, 4, 5, 6, and 8 swelled with a pyridine solution of spin probes X, XII, XIII, and V.

uene or nitrobenzene, and the behavior of the spin probes is considerably different than in coals swelled by either of the two latter solvents. Of the spin probes studied, coals doped with either the largest (V) or the smallest (X) spin probe showed the highest nitroxide-radical concentrations. For coals doped with X, the nitroxide-radical concentration linearly increased from  $0.2 \times 10^{17}$  to  $13 \times 10^{17}$  spins/g over the range studied. For coals doped with V, the nitroxide radical concentration increased from  $0.3 \times 10^{17}$  to  $11 \times 10^{17}$  spins/g over the range of coals examined. Pyridine opens up the pore structure large enough that even the large probe (V) can be trapped before pyridine is removed. The reasoning behind the seemingly unusual behavior of spin probe X will be discussed in more detail later. For coals doped with XII and XIII, the nitroxide radical concentration increased from 0.3 and  $0.4 \times 10^{17}$  to 2.5 and  $2.6 \times 10^{17}$  spins/g, respectively, over the range of coals studied.

Figures 2 and 3 show the spin-probe content of coals swelled with nitrobenzene and pyridine, respectively, as a function of oxygen content. Oxygen content decreases with rank. For all solvent systems and all spin probes studied, the nitroxide radical concentration decreased with decreasing oxygen content and, consequently, with increasing rank. Again, this

indicates that the ability of the solvent to swell the coal and open areas of accessibility for the spin probes decreases with rank.

One further interesting observation from Figures 1–3 is that for the highest ranked coals the nitroxide radical concentration changes very little regardless of probe or swelling solvent. This result confirms that in higher ranked coals cross-linking consists of covalent bonds rather than hydrogen bonds.

The ability of solvents to swell coals and open areas of accessibility is strongly dependent upon coal rank. This observation leads to the question of how the pore structure changes with swelling within a given coal rank. By using SANS measurements of Pittsburgh No. 8 coal, Winans and Thiagarajan (6) determined that pores in unswelled coal are spherical, and that pores in coal swelled by pyridine are elongated, needlelike voids. Goslar and Kispert (2) confirmed their result by using a spin-probe study. The five Argonne coals used in the study by Goslar and Kispert (2) were swelled in toluene or pyridine using either a spherical or cylindrical probe. The results are shown in Table 3 of reference 2. Toluene mildly swells the coal and should change the pore structure only minimally. Mildly swelled coals doped with the spherical probe (I) contained significant radical concentrations, a result indicating that a significant number of spherically shaped pores were present (2). However, for severely swelled coals (i.e., those swelled with pyridine), the radical concentration of coals doped with I was very small, a result indicating that spherically shaped pores had all but disappeared.

On the other hand, coals doped with the cylindrically shaped probe (II) and swelled with toluene had significant radical concentrations. Swelling with pyridine slightly decreased radical concentrations in APCS Nos. 8 and 5, and in the three high-volatile bituminous (HVB) coals (APCS Nos. 3, 4, and 6) radical concentration was significantly increased. This result shows that in severely swelled coals the pores become cylindrical.

Several questions immediately arise:

- Upon learning the shape of pores in swelled coals, can the size of these pores be further defined?
- How does the pore structure of coal change when solvents with intermediate swelling ability are used?
- How does the size distribution of the pores change as the coal is swelled?
- How does the shape of the pores change with swelling?

To answer these questions, the five Argonne Premium Coal samples described in the "Experimental Details" section were swelled with either toluene, nitrobenzene, or pyridine and were labeled with three spin probes

(XII, XIII, and V) that are similar in shape and width but that differ in length. Toluene has an electron donor number of 0.1, the electron donor number of nitrobenzene is 4.4, and that of pyridine is 33.1. The electron donor number has been used (15) as a measure of coal swelling ability, although the variation in size and shape among various solvents makes the correlation a poor one (7). A better measure of swelling ability is the basicity of the solvent and the solvent's ability to break hydrogen bonds.

In Figure 4, the radical concentration in the labeled coals is shown as a function of spin probe length for coals swelled with toluene. For the toluene system, spin probe XII results in the highest radical concentrations of the five Argonne coals. As the probe size increased, the probe concentration decreased. Toluene, a poor swelling solvent, has a limited capacity to open areas of accessibility to spin probes. The pores are elongated only slightly, and larger spin probes had difficulty entering the coals.

In Figures 5 and 6, the radical concentration in the labeled coals is shown as a function of spin probe length for coals swelled with nitrobenzene and pyridine, respectively. In Figure 5, the maximum spin concentration at the probe length corresponds to that of spin probe XIII. This

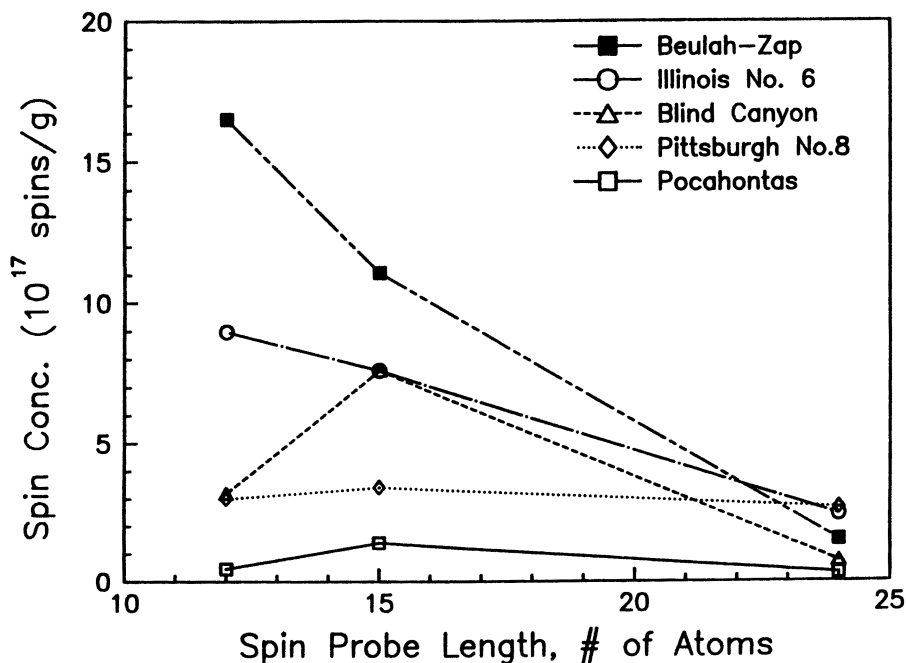


Figure 4. Nitroxide radical concentration for five coals swelled with a toluene-spin probe solution vs. spin probe length.

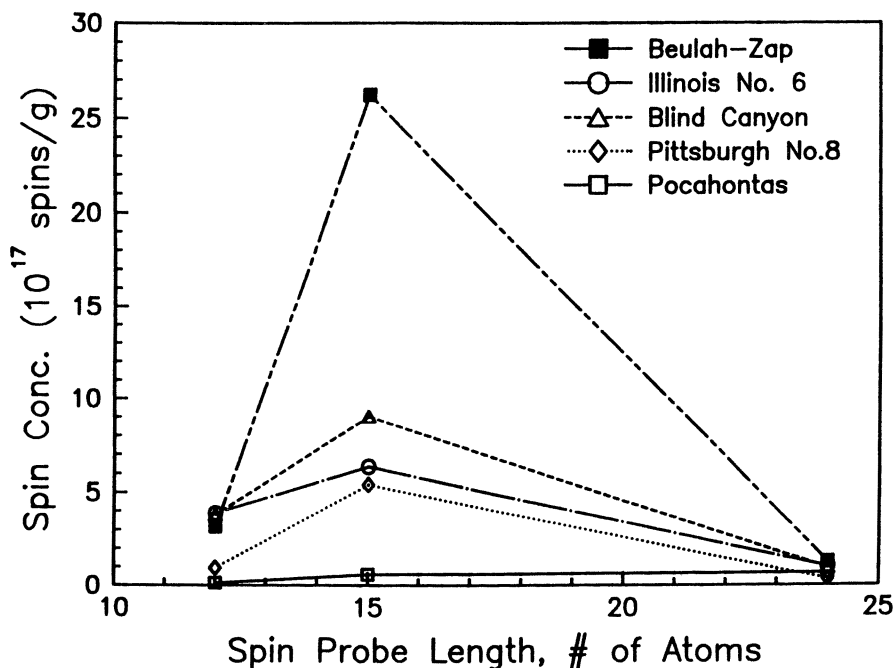


Figure 5. Nitroxide radical concentration for five coals swelled with a nitrobenzene-spin probe solution vs. spin probe length.

probe was the right size to be trapped within the pore structure of the swelled coal without being removed by the cyclohexane wash, as apparently happened to the smaller probes. However, nitrobenzene is only a moderate swelling solvent, and larger probes such as V have difficulty gaining access to the interior of the coal. On the other hand, there is no apparent maximum in Figure 6; the largest spin probe studied (V) had the highest concentration of all the spin probes. Pyridine, the best swelling solvent studied, opens up the pore structure of the coals to the greatest extent. Large spin probes such as V have easy access to the interior of the coal, and small spin probes are easily washed out. These results lead to two additional questions:

- How large a spin probe can be readily introduced into pyridine-swelled coals?
- What effects do solvents with even larger electron donor numbers have on the pore structure of coals?

Our hope is that these questions will be answered in a later study.

Spin probe X has a different structure than the other three spin probes studied. Spin probe X is shorter in length and, because of its steric

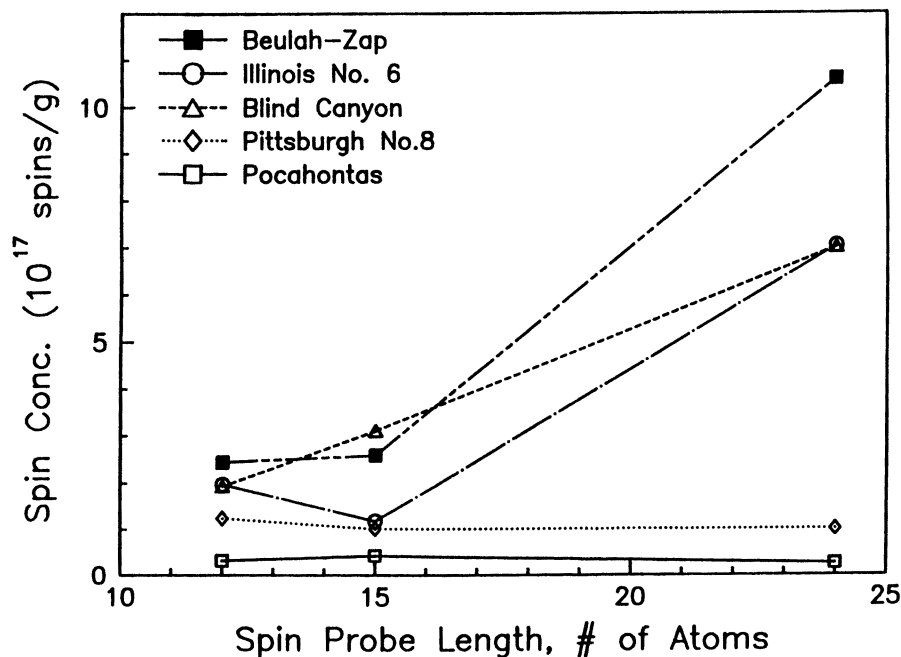


Figure 6. Nitroxide radical concentration for five coals swelled with a pyridine-spin probe solution vs. spin probe length.

rigidity, less bulky than spin probe XII, the smallest of the other three probes studied. In Table II, the nitroxide radical concentration is shown as a function of the swelling solvent for Argonne coals labeled with spin probe X. The radical concentration passes through a minimum when nitrobenzene is used as the swelling solvent. Both toluene- and pyridine-swelled coals retain significant amounts of probe X within the pore structure. This phenomenon is supported by data from earlier work (2). In toluene-swelled coals, the pore structure is opened up only slightly, and the result is that small cylindrical probes are trapped. Coal also contains a micropore system that is too small to be accessed by these probes when the coal is only mildly swelled. Nitrobenzene opens up areas of accessibility large enough to prevent retention of X and XII (Figure 4), but does not significantly open the micropore system. Pyridine, however, is a much stronger swelling solvent than either toluene or nitrobenzene. Pyridine apparently not only opens areas of accessibility large enough for spin probes like V, but also opens the micropore system enough to allow access by X. Thus the coal swelling process undergoes several stages.

**Table II. Nitroxide-Radical Concentration for Coals Swelled with Solutions of Spin Probe X and Various Swelling Solvents**

<i>APCS</i>				
<i>Number</i>	<i>Coal</i>	<i>Toluene</i>	<i>Nitrobenzene</i>	<i>Pyridine</i>
8	Beulah-Zap	15.4	4.6	13.2
3	Illinois No. 6	7.0	3.4	5.0
6	Blind Canyon	7.1	—	9.4
4	Pittsburgh No. 8	1.0	2.6	5.4
5	Pocahontas No. 3	3.0	0.1	0.20

NOTE: Concentrations are given in spins per gram  $\times 10^{17}$ .

## Conclusions

In conclusion, the use of spin probes with swelling solvents is a convenient method with which to increase understanding of the pore structure of coals and how the pore structure changes in the presence of swelling solvents. As coal swells, the pores become cylindrical and elongated. As the severity of the swelling solvent is increased, the pores become larger until even the micropore system opens up to allow access to fairly large molecules. Regardless of the severity of the swelling solvent, the pore structure of high-rank coals changes very little. Finally, a spin-probe EPR spectroscopic study can be used to observe changes in coal structure as solvents of different donor or swelling strength are used.

## Acknowledgment

We gratefully acknowledge the U.S. Department of Energy, Pittsburgh Energy, Technology Center, University Coal Research Program, for financial support under Grant No. DE-FG 22-86 PC90502. We gratefully acknowledge Xinahi Chen for technical support.

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RECEIVED for review June 7, 1990. ACCEPTED revised manuscript December 5, 1990.