

An EPR Study of Nitroxide Spin Probe Doped Illinois no. 6 Coal From
the Premium Coal Sample Program: Reactive Site Distribution

Lowell D. Kispert, Lalith S. Cooray, and Shing K. Wu

Chemistry Department, The University of Alabama,
Tuscaloosa, Alabama 35487

INTRODUCTION

The conversion of coal by an economically feasible catalytic method is an important area of research for our future energy requirements. However, knowledge of the coal structure is necessary before optimum use can be made of the catalyst. For instance, the catalyst must be able to diffuse into the coal sample so that hydrogenation catalysis can occur from within as well as the normal surface catalysis. This requires an estimation of the size, number, and shape of the pores in the coal before and after swelling with different solvents and the number distribution of different reactive sites within a coal sample. In the past, efforts have been made to estimate the total void volume (porosity) and distribution of pores by measuring the moisture content of coal and penetration by mercury as a function of pressure (1). It was concluded that the internal surface of coal is associated with a capillary system of < 4 nm pores connected by 0.5 - 0.8 nm passages. Liquid and vapor sorption studies (2) of porosity and internal surface of coal suggest that a definable pore structure may not exist and that accessibility is a better term to use.

Recently, we reported (3) a method to determine the relative pore (accessibility) size and number distribution in selected high-volatile bituminous coal samples by diffusing nitroxide spin probes of different shapes, varying in diameter or length from 0.47 nm to 3.5 nm, into the swellable pores of the coal samples. The relative spin probe concentration was measured by Electron Paramagnetic Resonance (EPR) methods for each sized spin probe. From these measurements, a relative number and size distribution was estimated for the swellable pores of Mary Lee (MRI, PSOC-271) and Black Creek (MRI) coal seams of Alabama and the Illinois no. 5 (PSOC-699) seam. The coal samples were obtained from the Mineral Resources Institute (MRI) at the University of Alabama and the Penn State Coal Sample Bank (PSOC) at Penn State University. The pore sizes deduced from these studies were consistent with those deduced by mercury penetration studies carried out as a function of pressure. It was found (3) that the size and number distribution of pores deduced from the spin probe concentration is different for each coal seam. For instance, there are 5 times as many swellable pores of the shape of a long chain stearamide (length 3.4 nm) in Mary Lee coal as there are in Black Creek coal, while there are 18 times as many short chain (1.2 nm length) cylindrical pores and only 0.3 times as many medium length cylindrical pores. Further details of the size and number

distribution reported earlier, can be found in Table 2 of reference 3.

It was also observed (3) that the nitrogen coupling in the principal z direction of the incorporated spin probe (those with a diameter or length greater than 1 nm) exhibited a temperature dependence above 250 K that is largely a result of librational motion of the nitroxide moiety about the N-C bond. Below 250 K, the temperature dependence of the nitrogen coupling is like that found for spin probes in solids that exhibit an equilibrium between a nonbonded and a hydrogen bonded state; the hydrogen bonded state exhibiting the larger coupling. The possibility of hydrogen bonding may suggest a mechanism whereby the spin probes are incorporated in the porous structure of the coal samples.

While the earlier study (3) dealt largely with determining the number distribution for swellable pores with diameters between 0.46 nm and 3.5 nm, no attempt was made to study reactive site distributions and whether a hydrogen bonding mechanism is an important mechanism for spin probe incorporation in pores of the coal samples.

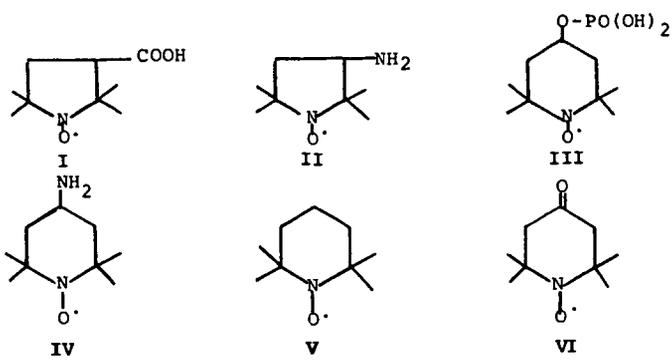
Thus this study reports the results of a series of similar but small sized spin probes (~ 0.6 nm in diameter), each containing a different reactive substituent, to determine the number distribution of reactive sites containing acid, phenol and amine substituents. The smaller size of the spin probes with reactive sites, will permit a measure of all accessible sites with diameters greater than approximately 0.6 nm.

In addition, a study was made to differentiate hydrogen-bonding to the nitroxyl group from that of a substituent group in swellable pores with diameters of approximately 0.4-0.6 nm.

EXPERIMENTAL

Samples of Mary Lee (MRI), Black Creek (MRI) and Illinois no. 5 (PSOC-669) high-volatile bituminous coal from the stock samples previously studied (3) and samples of Illinois no. 6 obtained from the Premium Coal Sample Program at the Argonne National Laboratory were selected for study. The proximate and ultimate analyses for all coals except Illinois no. 6 have been previously given (3) while the ash free percentage by weight values of the Illinois no. 6 sample equal C (79%), H (5.6%), O (9.7%), and S (5.4%). All coal samples were stored under a blanket of N₂ except Illinois no. 6 which arrived in sealed ampoules under humid nitrogen. Upon opening, the samples were stored under N₂ or argon.

A 30 mg sized, dried and unmodified sample of each coal was added to a 10⁻³ M solution of nitroxide spin probe in toluene. Six different spin probes (I-VI), obtained from Molecular Probes, Inc. Junction City, Oregon, were used. These probes were selected because they are all of similar size and because spin probes I and III react with amines, spin probes II and IV react with acids and phenols and spin probes V and VI can be used to distinguish between hydrogen bonding to a ketone and to a nitroxyl group.



Each coal and spin probe mixture was stirred vigorously at 50-60°C in a sealed flask. After 16-18 hours, the excess toluene was suction-filtered off and the remaining solid material evacuated to dryness to collapse the coal around the spin probe. The dried material was washed with ethanol (a nonswelling solvent) to remove any spin probe attached to the exterior of the coal, suction filtered, packed into an EPR sample tube, evacuated and sealed. The prepared spin-probe-doped coal sample was stored under liquid nitrogen.

EPR powder spectra were recorded on a Varian E-12 EPR spectrometer interfaced to an IBM-XT for each sample as a function of temperature (77-335 K) using the standard Varian variable-temperature and liquid nitrogen accessory. The magnetic field was calibrated using a Bruker ER 035 M NMR Gaussmeter and the microwave frequency was measured with a model H/P 5246 L frequency counter. EPR spectra were recorded on disk with an IBM-XT using the EPRDAS software program from Adaptable Laboratory Software. For spectra recorded only on graph paper, input to disk was achieved by use of a Kurta Tablet Digitizer using Sigma-Scan software. A computer program has been developed using the ASYST language (MacMillan Software) to calculate the relative concentration of spin probes in different coal samples in the presence of the severe spectral overlap by the EPR spectrum of the undoped coal. The computer program has also been expanded to analyze temperature dependent coupling constants in terms of hydrogen-bond equilibrium or/and small amplitude librational motion. Output is to a H/P 7440 A Plotter.

RESULTS:

EPR spectra obtained from coal samples containing spin probes gave rise to a spectrum similar to that shown in Figure 1, consisting of an intense central line due to undoped coal (curve B) and, at high gain (curve A), resolved powder EPR lines at high and low magnetic fields due to the z tensor component of the nitrogen hyperfine coupling (A_{zz}) arising from the nitroxide spin probe dopant. The separation between the high and low field component equals $2A_{zz}$. The relative spin concentrations were determined by integrating the low field peak. The relative spin probe concentration is given in table I for probe I (reacts with amines), probe IV (reacts with acids and phenols), probe V (hydrogen bonding only to the nitroxyl group) and

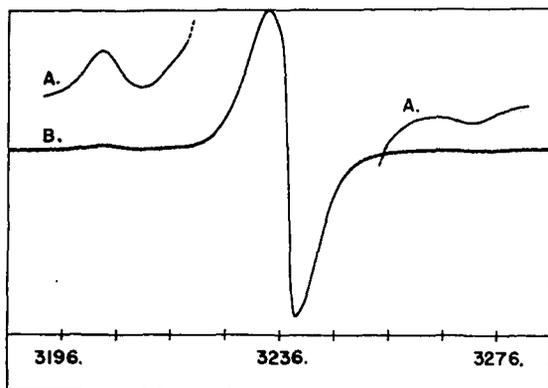


Figure 1. EPR spectrum of a spin probe in a sample of Black Creek coal at (A) high gain (X10) and (B) at low gain (X1) at 300 K.

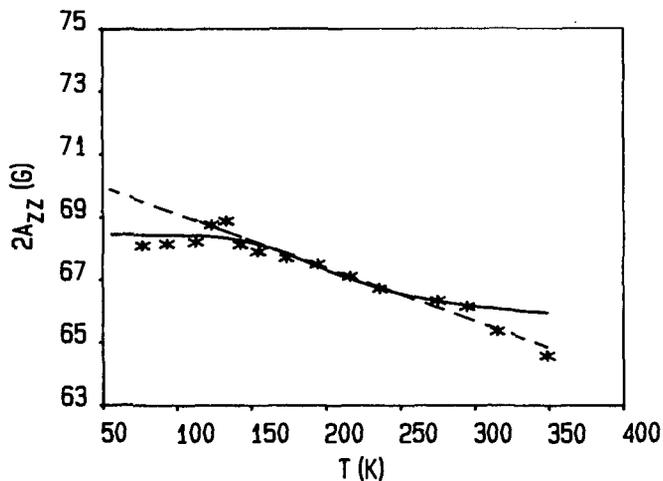


Figure 2. $2A_{zz}$ against temperature for spin probe VIII (DCT-Tempamine) incorporated in a sample of Illinois no. 6 (premium coal): *, experimental data; -----, librational model; _____, hydrogen-bond equilibrium.

probe VI (hydrogen-bonding to ketone and nitroxyl groups). The results for spin probes II and III are not reported here.

Table I. Relative Site Distribution for Spin Probes I, IV, V and VI.

Coal Sample	Spin Probes*			
	I (COOH) Base/acid reaction	IV (-NH ₂)	NO V (sub.) hydrogen bonding	VI (=O)
Mary Lee	220	67	24.0	1.0
Black Creek	230	1550	5.3	5.0
Illinois no. 5	100	53	4.1	17.0
Illinois no. 6	14	164	4.9	11.0

*Relative spin probe concentration normalized to probe VI in Mary Lee coal.

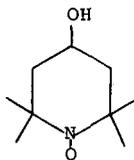
Notably, the ratio of pores containing acid or phenolic groups to those containing amine groups is 1/3; 6.7/1; 0.5/1; and 12/1 for Mary Lee, Black Creek, Illinois #5 and Illinois #6 respectively. In addition, Black Creek coal has approximately 25 more sites containing acid or phenol groups than either Mary Lee or Illinois no. 5 coal samples, and nearly an order of magnitude greater than that found in the Illinois no. 6 sample. The sites containing amine functions are similar except for the Illinois no. 6 sample for which the amine concentration decreases by nearly an order of magnitude. It is interesting to note that more spin probe V (factor of 23) can be incorporated into Mary Lee (only one site available for hydrogen-bonding), than spin probe VI (2 sites for spin probe hydrogen-bonding), while the presence of hydrogen-bonding sites does not seem to matter for spin probe incorporation in Black Creek coal, but is a factor of 4 greater for VI in Illinois no. 5 and a factor of 2 greater for incorporation of VI in Illinois no. 6. It is apparent from these measurements that the presence of an additional site for hydrogen bonding is of little importance in determining the amount of spin probe incorporated in small (0.4 to 0.6 nm) pores in samples of Mary Lee and Black Creek coal.

The separation between the high and low field EPR lines ($2A_{zz}$) for each spin probe exhibits a temperature dependence between 350 and 77 K. It was previously shown for bulky or long chain spin probes (3) that at high temperature, the temperature dependence of A_{zz} is due to librational motion of the NO group of the spin probe with respect to the CNC plane of the nitroxide ring and is given by Equation 1

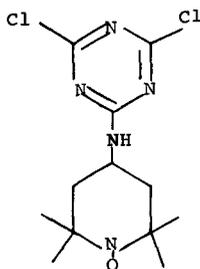
$$2A_{zz}(t) = A_{zz}^0 [1 + \cos(kt/E_a)]^{0.5} \quad 1)$$

where E_a = the barrier to librational motion and A_{zz}^0 is a temperature independent hyperfine coupling. At temperatures below 270 K, the temperature dependence can be fit to an equation derived from the assumption that the spin probe exists in an hydrogen-bond equilibrium between two states, one with a larger coupling due to hydrogen-bonding and the second to a non-bonding state. This type of dependence follows the solid line in Figure 2 and is noted by the near temperature independence at low temperature (3). Similar behavior is observed for spin labels tightly bound within hemoglobin (4).

Temperature dependent studies of 4-aminotempo-(IV) in Illinois no. 6 coal, Mary Lee, Black Creek, and Illinois no. 5, showed a very interesting dependence. A near perfect fit to the librational model (dashed line in Figure 2) occurred for the $A_{zz}(t)$ value observed for IV in the Illinois no. 6, Mary Lee and Black Creek and a small dependence of a hydrogen-bond model was observed for IV in Illinois no. 5 coal. In addition when the smaller spin probe tempo. (VII),



VII



VIII

(the OH substituted for NH_2 in IV) was incorporated in Illinois no. 6 it gave a temperature dependence of A_{zz} that was clearly due only to a librational motion as the temperature dependence follows a straight line relationship. However the temperature dependence of DCT-tempamine, (VIII) incorporated in Illinois no. 6 exhibits a behavior like that found for other large spin probes - librational behavior at high temperature and evidence of hydrogen-bond equilibrium below 200 K (See Figure 2).

In Table II are given the energy barriers to librational motion of the spin probes deduced from the temperature dependent hyperfine coupling parameter A_{zz} . Although the variation is not large, the large sized spin probe VIII does have a higher barrier to rotation than IV, as would be expected for a large size probe trapped in the swellable coal pores.

Table II: Energy Barrier to Librational Motion of Spin Probes in Four Coal Samples.

Coal	Spin Probe	E_a (kJ/Mole)
Illinois no. 6	IV	6.69 (± 0.04)
Illinois no. 6	VII	7.57 (± 0.04)
Illinois no. 6	VIII	8.59 (± 0.04)
Mary Lee	IV	8.61 (± 0.03)
Black Creek	IV	7.88 (± 0.02)
Illinois no. 5	IV	7.26 (± 0.04)

CONCLUSION

The reactive site distribution detected by spin probes approximately 0.6 nm in diameter, varies from coal seam to coal seam. The detected acid and phenolic sites in Black Creek Coal and the Illinois No. 6 coal (Premium Coal Sample Program) exceed the detected amine sites by approximately an order of magnitude while slightly more amine than acid or phenolic sites are detected in samples of Mary Lee and Illinois no. 5. On the other hand, the greatest number of reactive acid and phenolic sites were detected in Black Creek coal. The ability for the coal pore to hydrogen bond to a spin probe was shown not to be an important process for incorporating spin probes in Mary Lee and Black Creek coal and only a slight factor in samples of Illinois no. 6, and Illinois no. 5. Because of this the number of swellable pores containing spin probes V and VI was at least an order of magnitude lower than the reactive sites containing I and IV. Spin probes V and VI exhibited large librational motion in the swellable pores.

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