

## LOW TEMPERATURE SWELLING OF ARGONNE PREMIUM COAL SAMPLES: EFFECT ON PORE STRUCTURE

Dennis R. Spears, Lowell D. Kispert and Lidia Piekara-Sady

Box 870336, Chemistry Department,  
The University of Alabama, Tuscaloosa, AL 35487-0336

### ABSTRACT

Changes in the pore structure of Argonne Premium Coal Samples (APCS) upon slurrying at different temperatures with the solvents toluene, nitrobenzene and pyridine were followed using an EPR spin probe method. At room temperature, spherical shaped pores in coal slurried with nitrobenzene become elongated and cylindrical at 60°C. Coal slurried with pyridine exhibits few detectable spherical shaped pores at room temperature but exhibits significant concentrations of elongated pores at 60°C. This change in pore structure was attributed to the break-up of the hydrogen bonding network by the pyridine solvent.

### INTRODUCTION

The organic portion of coal consists of an entangled, extensively cross-linked network of high-molecular weight subunits. The subunits vary in composition and are cross-linked by both covalent and hydrogen-bonding linkages (1). The network, although polymeric in nature, is still not well understood. Adding to the difficulties in understanding coal structure is the porous nature of coal (2). Guest molecules of varying molecular weight are trapped within the network and within the pore system (3). Because coal is polymeric in nature, classical solvent swelling techniques have been used to better understand the structure of coal.

Solvent swelling of coal is important for several reasons. Solvent swelling studies have been used to estimate the average molecular weight between crosslinks (4), and to understand the bonding between subunits (5,6). Understanding solvent swelling is important because organic solvents affect the pore structure of coal, as well as density, mechanical strength, and spectral properties. Further, many coal beneficiation processes, especially liquefaction, take place in organic solvents.

The pore structure of coal has been extensively characterized (7,8). Swelling solvents act upon coal via diffusion into the pore structure. Catalysts can penetrate into accessible areas during conversion processes. Among the many techniques used to characterize the pore structure of coal has been the use of spin probes and electron paramagnetic resonance spectroscopy (EPR) (9-16).

Until the early part of this decade, EPR was used primarily to study the concentration of free radicals in coal and determine g-values. However, in 1981 Silbernagel et al. (9) showed the possibility of diffusing spin probes into coal as observed by EPR spectroscopy. TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) 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. This experiment suggested that surface adsorption and diffusion of spin probes into coal was possible (9).

This method has been expanded in our laboratory (10). EPR studies of doped Alabama and Penn State Coal Sample Bank (PSOC) coals were carried out, showing it possible to estimate the relative accessibility of different sized spin probes to the pore structure of coals in the presence of a swelling solvent (10-16). Spin probes of different sizes and shapes are diffused into different coal samples swelled with toluene. A nonswelling solvent such as cyclohexane is used to wash away the spin probes not trapped in the porous structure. Relative pore shapes and size distributions can then be

determined by EPR measurement of the spin concentration of the probes trapped within the matrix. In this paper, changes in both pore size and shape with coal rank and swelling solvent were determined as a function of swelling temperature for the Argonne Premium Coal Samples (APCS).

## EXPERIMENTAL

All eight Argonne premium coal samples were used in this study. The compositions of these coals on a dry, mineral matter-free basis are shown in Table 1. The coals were doped with spin probes using a procedure described previously (13-16). The coals were swelled with either toluene, nitrobenzene or pyridine solutions of the desired spin probes. This paper details the results of the spin probe commonly known as TEMPOL, I, spin probe V (4-octadecanoylamino-2,2,6,6-tetramethylpiperidine-1-oxyl) and spin probe XIII (4-nonylamino-2,2,6,6-tetramethylpiperidine-1-oxyl). The structures of these probes are given in Figure 1. I was obtained from Aldrich and V and XIII were obtained from Molecular Probes. Spin probe I is roughly spherical in shape while probes XIII and V are elongated. The coals were swelled either at room temperature or at 333 K.

## RESULTS AND DISCUSSION

The ability of a solvent to swell a given coal depends upon many factors, including the polarity of the solvent, temperature of solvolysis and rank of the coal. The swelling conditions used in this study were fairly mild. At room temperature with n-alkyl amine solvents, equilibrium swelling ratios require weeks to reach (17). The intention in this study was not to reach swelling equilibrium but rather an equilibrium uptake of the spin probe. This was found to occur after 12 hours.

Nonpolar solvents interact with coal in accordance with regular solution theory; polar solvents swell coal by disrupting hydrogen bonds. Coal is cross-linked with both covalent and hydrogen-bond cross-links. Hydrogen bonding is especially important for lower rank coals, but diminishes in importance with rank (5). Hydrogen bonding is believed to be associated with oxygen functionalities (18), and the oxygen content of coal decreases with rank. Thus, polar solvents show a lessened ability to swell higher ranked coals. Further, the degree of solvent polarity affects the ability of a solvent to disrupt hydrogen bonds and swell coal (19). Swellability also decreases with rank for nonpolar solvents, probably due to high covalent cross-link density in higher ranked coals.

The concentration of spin probe I as a function of swelling solvent and carbon content of the APCS coals, at 298 K, is shown in Figure 2. Carbon content was used as an indicator of rank throughout this study. Of the three solvents used in this study, pyridine was the most polar, toluene the least. At room temperature, the spin concentration of spherical TEMPOL in the swelled coals decreased with rank for coals swelled with either toluene or nitrobenzene. For coals below about 85 % carbon content (dmmf) swelled in nitrobenzene contained a higher spin probe concentration than coals swelled in toluene. For coals with greater than 85 % carbon content (dmmf), there was no significant difference in spin probe concentration regardless of rank or swelling solvent. Coals swelled with pyridine did not retain TEMPOL to any significant degree.

Coal has been shown by SANS (20, 21) experiments to contain spherically shaped pores. Coal swelled in a mild swelling solvent like toluene at room temperature still retains a significant quantity of spherical pores. At room temperature, nitrobenzene, a moderately polar swelling solvent, caused an increase in the number of the spherically shaped pores and a subsequent increase in the number of trapped smaller spherical shaped probe I. However, when coal underwent more severe swelling, such as in pyridine, pores lost their sphericity and became enlarged and elongated or cylindrical (20, 21) in shape. As a result, the spherical TEMPOL molecules are not retained when the coals were washed with cyclohexane.

The severity of swelling is not only affected by solvent polarity, but also by temperature. An increase in swelling temperature from 288 K to 333 K, while small, had a significant effect on the pore

structure of coal. In Figure 3, the concentration of spin probe I as a function of swelling solvent and carbon content of the APCS coals at 333 K is shown. Again, for higher ranked coals (above 85 % carbon content), spin probe concentration did not vary significantly regardless of rank or swelling solvent. For lower ranked coals, toluene-swelled coals retained a significant number of spherically shaped pores, while coals swelled in pyridine did not. Interestingly, at 333 K, coals swelled in nitrobenzene no longer contain significant quantities of spherically shaped pores.

The swelling process using nitrobenzene and pyridine result in a break-up of the hydrogen bonding system, causing an elongation of the pore structure. For nitrobenzene this was most noticeable using spin probe XIII at 298 K and at 333 K. Spin probe XIII is long and cylindrical in shape. When the APCS coals were swelled in nitrobenzene at room temperature (Figure 4), a significant number of cylindrical pores were present, as were numerous spherical pores. When the swelling temperature was increased to 333 K, the spherical pores all but disappeared, and the number of cylindrical pores increased significantly (Figure 5).

Lack of space prevents a discussion of the effect of temperature on the optimal elongation length deduced using several different spin probes for each solvent as a function of coal rank. However using spin probe V shows that almost no detectable spin probes of the size for which probe V would be trapped occurred at room temperature for toluene, or nitrobenzene or pyridine. However at 333 K, pyridine exhibited significant and measurable concentration of elongated pores similar to that of probe V while none were observed for toluene or nitrobenzene solvents. The variation in concentration with coal rank was similar to that exhibited by spin probe XIII in nitrobenzene.

The effect of temperature on the spin probe concentration of spin probe I depicted in Figures 2-5 appears to suggest the following. For coals swelled in toluene, the number of spherically shaped pores increased with temperature. Higher temperatures increased the ability of toluene to swell coal, but not enough to cause pore elongation. For nitrobenzene, spin probe concentration of I decreases with temperature. Like toluene, higher temperatures increase the ability of nitrobenzene to swell coal. At room temperature, nitrobenzene swelled the APCS coals enough to open up spherical pores. At 333 K, conditions were severe enough for nitrobenzene to cause pore elongation. Pyridine was such a severe swelling solvent for coal that even at room temperature pore elongation occurred.

Extensive Electron Nuclear Double Resonance (ENDOR) studies have shown that little chemical interaction occurs between the coal structure and the spin probes. Lack of space prevents a full discussion of the probe location in the pores of the coal.

## CONCLUSION

The use of nitroxide spin probes with swelling solvents is a simple way in which to gain an understanding of the pore structure of coals and how it changes in the presence of swelling solvents. Coal contains significant quantities of spherically shaped pores increasing with decreasing rank. If coal is mildly swelled with nitrobenzene, the number of spherically shaped pores increases. As solvent polarity increases, or as swelling temperature increases such as with pyridine, swelling conditions become more severe. As swelling severity increases, pores become elongated as evidenced by a decrease in the number of spherically shaped pores and a similar increase in the number of elongated pores. Finally, regardless of the severity of swelling conditions within the range studied, the pore structure of high rank coals changes very little.

## ACKNOWLEDGEMENT

This work was supported by the U. S. Department of Energy, Pittsburgh Energy Center, University Coal Research Program grant No. DE-FG22-90PC90284.

## REFERENCES

1. Peppas, N. A.; Larsen, J. W.; Lucht, L. M.; Sinclair, G. W. *Proc. Int. Conf. on Coal Science*, Pittsburgh, 1983, 280.
2. Bartholemew, C. H.; White, W. E.; Thornock, D.; Wells, W. F.; Hecker, W. C.; Smoot, L. D. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 1988, 33, 24.
3. Given, P. H. In *Coal Structure*; Gorbaty, M. L.; Larsen, J. W.; Wender, I.; Eds.; Academic: New York, 1984, Vol. 3.
4. Lucht, L. M.; Peppas, N. A. *Fuel* 1987, 66, 803.
5. Larsen, J. W.; Green, T. K.; Kovac, J. J. *Org. Chem.* 1985, 50, 4729.
6. Quinga, E. M. Y.; Larsen, J. W. *Energy and Fuels* 1987, 1, 300.
7. Mahajan, O. P. In *Coal Structure*; Meyer, R. A.; Eds.; Academic: New York, 1982.
8. Tricker, M. J.; Grint, A.; Audley, G. J.; Rainey, V. S.; Wright, C. J. *Fuel* 1983, 62, 1092.
9. Silbernagel, B. G.; Ebert, L. B.; Schlosberg, R. H.; Long, R. B. *Adv. Chem. Ser.* 1981, No. 192, 23.
10. Wu, S. K.; Kispert, L. D. *Fuel* 1981, 64, 1681.
11. Kispert, L. D.; Corray, L. S.; Wu, S. K. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 1987, 32, 286.
12. Cooray, L. S.; Kispert, L. D.; Wu, S. K. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 1988, 33, 32.
13. Goslar, J.; Cooray, L. S.; Kispert, L. D. *Fuel*, 1989, 68, 1402.
14. Goslar, J.; Kispert, L. D. *Fuel*, 1990, 69, 564.
15. Goslar, J.; Kispert, L. D. *Energy and Fuels* 1989, 3, 589.
16. Spears, R.; Goslar, J.; Kispert, L. D. In *Techniques in Magnetic Resonance for Carbonaceous Solids*; Botto, R.; Sanada, Y., Eds.; ACS Symposium Series No. 229; American Chemical Society: Washington, DC, 1991, in press.
17. Green, T. K.; West, T. A. *Fuel* 1986, 65, 298.
18. Larsen, J. W.; Baskar, A. J. *Energy and Fuels* 1987, 1, 230.
19. Hall, P. J.; Marsh, H.; Thomas, K. M. *Fuel* 1988, 67, 863.
20. Gethner, J. S. *J. Appl. Phys.* 1986, 59, 1068.
21. Winans, R. E.; Thiyagarajan P. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 1987, 32, 227.

Table 1. Major element composition of Argonne Premium Coal Samples, dmmf basis.

| Coal             | % C   | % H  | % N  | % S  | % O   |
|------------------|-------|------|------|------|-------|
| Upper Freeport   | 88.08 | 4.84 | 1.60 | 0.76 | 4.72  |
| Wyodak-Anderson  | 76.04 | 5.42 | 1.13 | 0.48 | 16.90 |
| Illinois No.6    | 80.73 | 5.20 | 1.43 | 2.47 | 10.11 |
| Pittsburgh No. 8 | 84.95 | 5.43 | 1.68 | 0.91 | 6.90  |
| Pocahontas       | 91.81 | 4.48 | 1.34 | 0.51 | 1.66  |
| Blind Canyon     | 81.32 | 6.81 | 1.59 | 0.37 | 10.88 |
| Lewis-Stockton   | 85.47 | 5.44 | 1.61 | 0.67 | 6.68  |
| Beulah-Zap       | 74.05 | 4.90 | 1.17 | 0.71 | 19.13 |

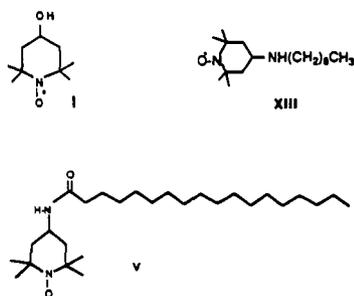


Figure 1. Molecular structure of spin probes I, V and XIII.

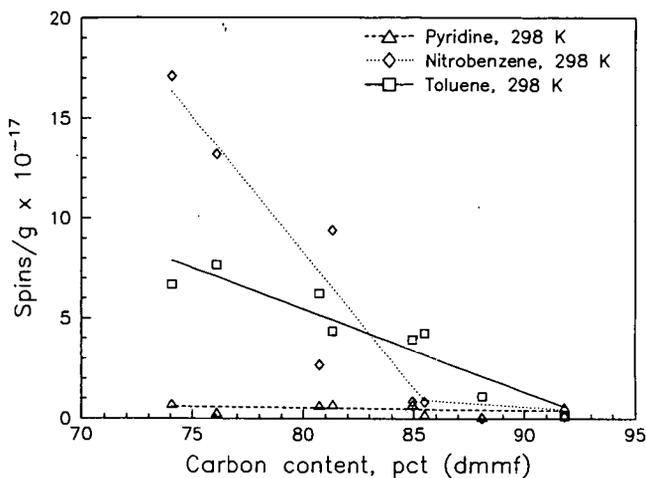


Figure 2. Spin probe concentration of spin probe I (spins/g  $\times 10^{17}$ ) vs. carbon content (pct (%), dmmf basis) for APCS coals swelled 298 K in toluene (□), nitrobenzene (◊), and pyridine (Δ).

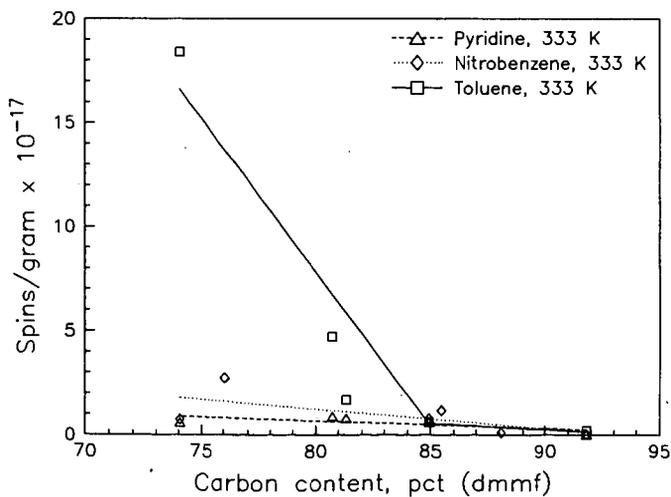


Figure 3. Spin probe concentration of spin probe I (spins/g  $\times 10^{17}$ ) vs. carbon content (pct (%), dmmf basis) for APCS coals swelled 333 K in toluene (□), nitrobenzene (◊), and pyridine (Δ).

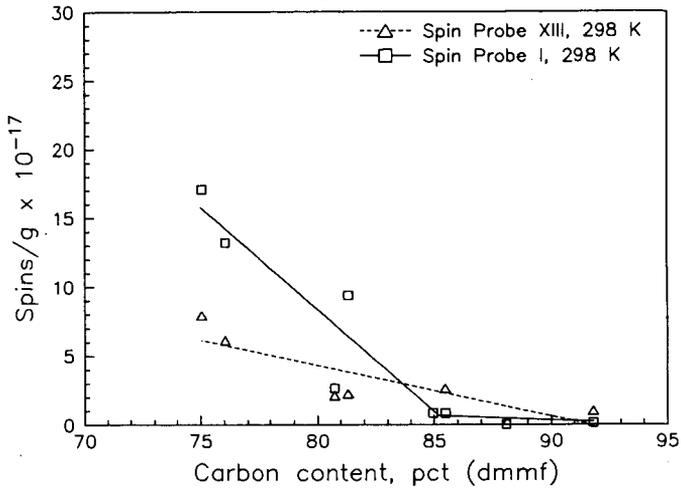


Figure 4. Spin probe concentration of spin probe I (□) and XIII (Δ) in nitrobenzene at 298 K vs. carbon content (pct (%), dmmf basis) for APCS coals.

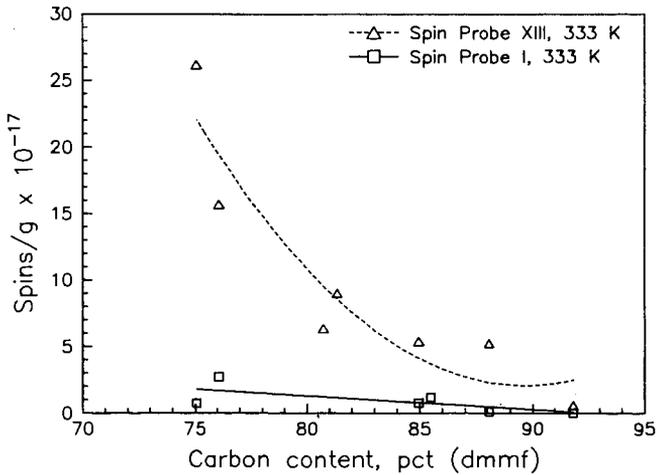


Figure 5. Spin probe concentration of spin probe I (□) and XIII (Δ) in nitrobenzene at 333 K vs. carbon content (pct (%), dmmf basis) for APCS coals.