

SMALL ANGLE NEUTRON SCATTERING STUDIES OF SWELLED COAL

Randall E. Winans and P. Thyagarajan

Chemistry Division, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439

INTRODUCTION

The objective of this study is to determine changes that occur in the physical structure of coals upon swelling in an organic solvent. It is known that bituminous coals will swell in solvents such as pyridine (1). The phenomenon of coal solvent swelling is being used to characterize coal structure especially in the determination of molecular sizes between cross-links. Swelling can affect coal reactivity in thermolysis reactions. Also, it is important to note that swelling increases reagent accessibility in chemical modification of coals (2). Small angle neutron scattering (SANS) is the approach used in this study to examine the changes in pore structure in a Pittsburgh #8 seam hvA bituminous coal, Argonne Premium Coal Sample #4 (3). Two perdeuterated solvents are used, benzene for non-swollen and pyridine for swelling conditions. The deuterated solvent provides a large contrast between the solvent and the solid coal for neutron scattering.

Coal porosity has been studied by SANS in the dry state (4,5,6) and in non-swelling deuterated solvents (4,6). These studies suggested that this technique can be useful for examining pore structure. Our current results show that the pore structure of a coal swollen in pyridine is dramatically altered from its original state.

EXPERIMENTAL

The SANS measurements were made at Argonne National Laboratory's Intense Pulsed Neutron Source (IPNS) using the Small Angle Diffractometer (SAD). Neutrons were produced in pulses by spallation from 450 MeV protons followed by moderation by solid methane (18°K) to produce wavelengths of 0.5 to 14 Å. The sample saw a 0.9 cm diameter beam. A 64x64 array position sensitive multidetector was used to detect neutrons scattered by the sample while the wavelength of the neutrons (λ) was determined by time-of-flight. The data were corrected for scattering from the cell and incoherent scattering. Finally, the intensity (I) was expressed as a function of the scattering vector, Q:

$$Q = (4\pi/\lambda) \sin \theta \quad (1)$$

where θ was half the scattering angle and:

$$I(Q) = K \langle \int_V (\rho_s - \rho_m) \exp(iQr) d^3r \rangle^2 \quad (2)$$

where K included all the experimental constants and ρ_s and ρ_m were the scattering length densities of the solvent and the matrix. A Q range of 0.005 to 0.35 Å⁻¹ was accessible on the SAD instrument at IPNS.

The preparation of the Argonne Premium Coal Sample has been described (3). A -100 mesh APCS #4 sample was used. (Preliminary analytical data, on a maf basis: C 83%, H 5.8%, N 1.6%, O 8% S(dry) 1.6% and ash(dry) 9%.) A sealed glass ampoule containing the coal was broken open in a nitrogen atmosphere glove box. The coal was well mixed and a portion transferred to a 2 cm diameter x 1.85 mm thick quartz cell leaving enough room for swelling. Perdeuteriosolvent was added to the coal and then the cell was sealed. The sample was allowed to sit for several days before doing the SANS experiment to insure complete swelling in the case of d_5 -pyridine.

RESULTS AND DISCUSSION

A Guinier plot (7), based on the relationship shown in Equation 2, for both solvents is shown in Figure 1. Even though d_6 -benzene and d_5 -pyridine have similar scattering length densities, 5.35 and $5.69 \times 10^{10}/\text{cm}^2$ respectively, there is a striking difference between the scattering data from the two solvents. The scattering data for both solvents exhibit a steep slope at low Q . These results are indicative of large pores with sizes up to 1000 Å. The largest pores that have been reported previously had a 500 Å limit which was constrained by the instrumentation (1). Further analysis of the d_6 -benzene data shows a distribution of pore sizes from 12 Å up to the 1000 Å limit. The difference of the porosity between the coal and swollen coal may be in the shape of the pores.

In low angle scattering it is possible to determine the shape of the pore or particle using a modified Guinier analysis (7). There are three types of pore shapes: spherical, elongated (tubular) and lamellar. From the Guinier analysis one can determine the radius for spherical, cross sectional radius and length ($1/Q$) for elongated, and thickness and area ($1/Q^2$) for the lamellar shapes due to the following scattering laws:

$$\text{Elongated: } I = I_c \cdot 1/Q$$

$$\text{Lamellar: } I = I_c \cdot 1/Q^2$$

To investigate the possibility of elongated pores $\ln(I \cdot Q)$ is plotted versus Q^2 in Figure 2. For d_6 -benzene there is no correlation, but for the d_5 -pyridine a negative slope is found. At low Q tubular pores with a radius of 9-11 Å are found. Figure 3 shows that lamellar pores are not seen in either sample since positive slopes are observed for both samples.

From these preliminary results we conclude that in a good swelling solvent the tertiary structure of this bituminous coal undergoes major rearrangement. Whereas the original coal contains a broad size range of roughly spherical pores, the swollen coal contains elongated pores with several distinct sizes. The pyridine appears to be determining the new pore dimension. Exactly five pyridines can be fitted into a 9 Å radius circle as shown in Figure 4. Table 1 lists the dependence of pore radius on the number of pyridines packed into a cross-section of the elongated pore. The size of the pyridine molecule has been estimated from space-filling computer models based on the van der Waals radii of the individual atoms. Even at high Q , up to the instrument limit, a negative slope for the modified Guinier analysis is

TABLE 1. Possible Packing Arrangements of Pyridine Molecules in Tubular Pores

Number of Pyridines	Radius of Pore (Å)
1	3.37
2	6.74
3	7.26
4	8.14
5	9.10
6	10.11
7	11.14

observed giving a radius of approximately 6 Å. This size of tubular pore could accommodate stacks of two or three pyridine rings. It is important to note that we are observing relative narrow elongated pores. These results could be explained by invoking hydrogen bonding between the pyridines and the phenols or other acidic hydroxyls on the surface of the tubular pores. In addition, it is thought from the NMR and ESR experiments that the motion of pyridine in a coal is restricted (8). Our SANS data argues against a layered, polycyclic aromatic structure for this coal. Possibly hydrogen bonding is more important in determining the tertiary structure.

ACKNOWLEDGMENTS

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, and Material Sciences (IPNS), U.S. Department of Energy, under contract number W-31-109-ENG-38.

REFERENCES

1. T. Green, J. Kovac, D. Brenner and J.W. Larsen, in "Coal Structure", R.A. Meyers Ed., Academic Press, p. 199 (1982).
2. R. Liotta, Fuel 58, 724, (1979).
3. K.S. Vorres and S.K. Janikowski, Preprints, Div. Fuel Chem., ACS., 32 (1), 492, (1987).
4. H. Kaiser and G.S. Gethner, Proceedings, Inf. Conf. Coal Science, 300, (1983).
5. M.J. Tricker, A. Grint, G.J. Audley, S.M. Church, V.S. Rainey and C.J. Wright, Fuel 62, 1092, (1983).
6. G.S. Gethner, J. Appl. Phys. 59, 1068, (1986).
7. A. Guinier and G. Fournet, "Small Angle Neutron Scattering" trans. by C.B. Walker and K.L. Kudowitch, Wiley, NY p. 19, (1955).
8. B.G. Silbernagel, L.B. Ebert, R.H. Schlosberg and R.B. Long, in "Coal Structure", M.L. Gorbaty and K. Ouchi Eds., ACS Adv. Chem. Series 192, 23, (1981).

Figure 1. Guinier plot for SANS of the Pittsburgh #8 Bituminous coal, APCS #4

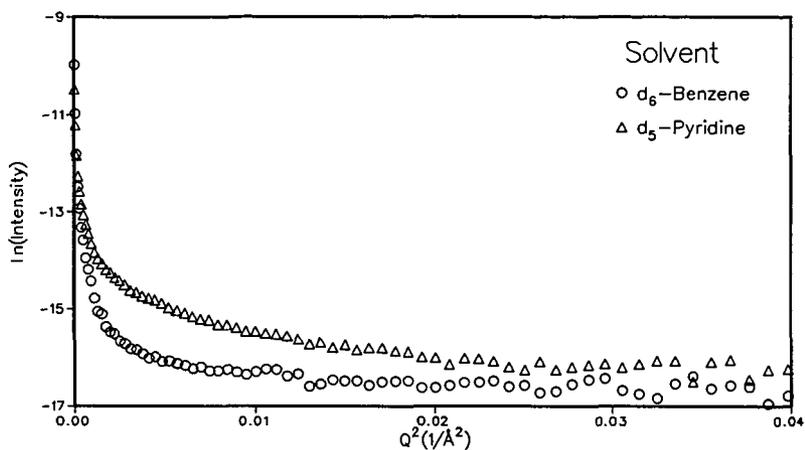


Figure 2. A modified Guinier plot of SANS data for APCS #4 to evaluate the possibility of tubular pores

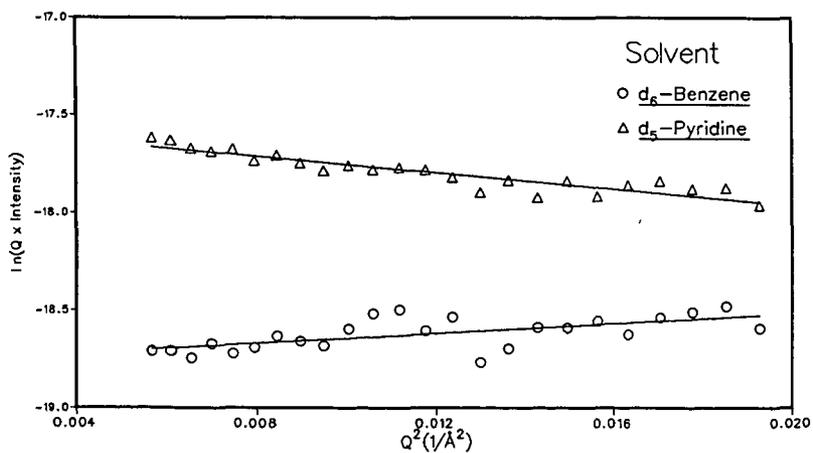


Figure 3. A modified Guinier plot of SANS data for APCS #4 to evaluate the possibility of sheet-shaped pores

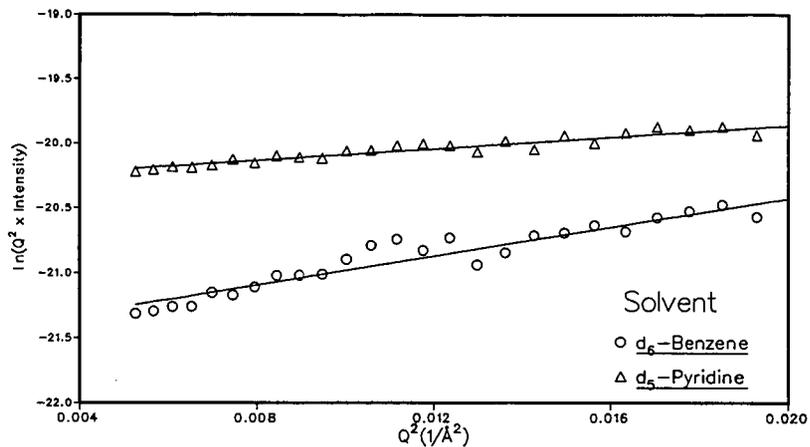


Figure 4. Possible arrangement of five pyridine molecules in a 9 Å radius elongated pore.

