

SOLVENT-INDUCED ASSOCIATIONS OF HIGH-VOLATILE BITUMINOUS COALS

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INTRODUCTION

It is known that solvent-induced crystallization of amorphous polymers can occur below their glass transition temperatures. This conformational change of the polymer chains into a lower free energy state is facilitated by the presence of the solvent. We recently reported a similar solvent-induced association between coal macromolecules. This is analogous to the solvent-induced crystallization of amorphous polymers in that the amorphous coal macromolecules are altered to increase relatively strong intermolecular interactions leading to a lower free energy state.

It was previously observed that the pyridine extractability and optical anisotropy of Pittsburgh No. 8 coal decreased after heating at 115°C in chlorobenzene under nitrogen for seven days. Immersion in pyridine at room temperature for one day, followed by eliminating pyridine, had the same effect on pyridine extractability as exposure to hot chlorobenzene for a week. Treatment of the pyridine extract from the same coal with chlorobenzene (115°C, 1 week) resulted in about half of the formerly soluble extract becoming pyridine-insoluble. The physical interactions responsible for the solvent-induced conformational changes of coal macromolecules are relatively strong, because some of these interactions cannot be overcome by solvation with pyridine.

In this paper, the solvent-induced associations of several high-volatile bituminous coals were investigated in several solvents for various times. The scope and magnitude of the phenomenon in bituminous coals was investigated in several solvents for various times. The scope and magnitude of the phenomenon in bituminous coals was explored, though not exhaustively. Additional structural information on the changes occurring in these samples was obtained using FT-IR and X-ray diffraction.

EXPERIMENTAL SECTION

ACS reagents and HPLC grade solvents were used. Tetrahydrofuran (THF) was distilled before use, and the other solvents were used without further purification. The coal samples were obtained from Exxon Research and Engineering Co. and the Pennsylvania State University Coal Bank. Their elemental

analyses were given in the previous paper.² Coal samples were ground and sifted under a nitrogen atmosphere. Minus 60-mesh size coal particles were used in the experiments.

Samples (two-gram) were extracted with 200 mL of pyridine for 24 hours in a Soxhlet apparatus under nitrogen atmosphere. The coal extracts were dried to constant weight in a vacuum oven at 50°C after evaporation of the pyridine.

Approximately 5 grams of each coal sample was placed in 100 mL of solvent in a 250 mL flask or a 300 mL autoclave and magnetically stirred under nitrogen. The mixture was either stirred at room temperature, heated, or mildly refluxed in an oil bath or in an autoclave heater. The cooled mixture was dried using a rotary evaporator, mixed with methanol, and filtered, while being rinsed with methanol several times. The coal was dried to constant weight in the vacuum oven at 50°C.

O-methylation was carried out following the method of Liotta.³ Two different O-methylated Pittsburgh No. 8 coals were prepared. One was obtained using normal conditions (exhaustive alkylation), and the other was partially alkylated by using a limited amount of alkylation reagents. For the latter reaction, 5 grams of coal samples was placed in 100 mL of THF, and 1.5 cm³ of 1M tetrabutylammonium hydroxide in methanol and 0.2 cm³ of iodomethane were used in the reactions.

Infrared spectra were obtained on an IBM 97/IR Series Fourier Transform Photoacoustic Infrared Spectrometer. Spectra were recorded from 256 scans at 8 cm⁻¹ resolution against a reference of carbon black. Samples for infrared spectra were further evacuated for 12 hours at 100°C.

X-ray diffraction studies were carried out at ambient temperatures on a Phillips APD 3600 Automated Powder Diffractometer (Phillips Electronics Instruments, Inc., Mahwah, NJ) using CuK radiation (1.5418 Å) at 45 kV, 40 ma. The diffractometer was equipped with a graphite monochromator, theta-compensating slit, scintillation counter, and pulse-height selector. The X-ray data were collected, stored, and displayed using the APD 3600 data system.

RESULTS

Pittsburgh No. 8 coal was immersed or mildly refluxed in the following hot solvents for times as long as 28 days: chlorobenzene, toluene, toluene/ethanol (95/5 vol %), and H₂O. O-methylated Pittsburgh No. 8 coals were similarly treated in toluene for one week. These solvent-treated coals were dried and Soxhlet extracted with pyridine. The pyridine extraction yields are plotted in Figure 1. Figure 2 shows the changes in pyridine extractability (Soxhlet) with time for various high-volatile bituminous coals heated at 115°C in chlorobenzene. The solvent treatment resulted in decreasing amounts of pyridine extracts for all coals studied. Table I shows the change in pyridine Soxhlet extractability for Illinois No. 6 coal treated in chlorobenzene at different temperatures for 24 hours.

Structural differences between the original and the solvent-treated coals were investigated using photoacoustic Fourier transform infrared spectroscopy.

Absorptions due to hydrogen bonds in these samples were slightly different. Figure 3 shows overlay spectra ($2810-3740\text{ cm}^{-1}$) of the original, two-day, and four-week chlorobenzene-treated Pittsburgh No. 8 coals. No absorbance change between $3200-3516\text{ cm}^{-1}$ was observed for the untreated coal after soaking in methanol and drying. The four-day, one-week and two-week chlorobenzene-treated coals gave spectra almost identical to that of the two-day treated coal.

Changes in aromatic parallel stacking due to solvent treatment were surveyed using the X-ray diffraction [002] band.⁴ The X-ray [002] diffraction peak of the Pittsburgh No. 8 coal is very weak, and no change resulted from chlorobenzene treatment. A pyridine extract from Pittsburgh No. 8 coal was treated with chlorobenzene at 115°C for a week, and the portion rendered insoluble by this treatment was isolated and subjected to X-ray analysis. No [002] band was observed.

DISCUSSION

One of the major secondary interactions in coals is hydrogen bonds.^{5,6} Toluene and chlorobenzene cannot break hydrogen bonds in coals at room temperature.^{5,7} However, it is possible that weak hydrogen bonds are broken thermally at higher temperatures, because such solvents swell coals more at higher temperatures. The ability of chlorobenzene to disrupt the weak secondary interactions in coals is expected to be slightly greater than that of toluene, because of its greater interaction with coals as revealed by its higher solvent-swelling values. The ability of toluene containing ethanol to disrupt the weak secondary interactions should be greater than pure toluene since ethanol can participate in and break coal-coal hydrogen bonds while toluene cannot. Pyridine can break most, if not all, hydrogen bonds in coals at room temperature and so thoroughly disrupts these interactions.^{5,7}

The relative rates of decrease in pyridine Soxhlet extraction yield of Pittsburgh No. 8 coal after solvent treatment (Figure 1) are consistent with the ability of the solvents to disrupt hydrogen bonds. The decrease was most rapid when the treating solvent was pyridine, slowest with toluene, and slightly faster with the toluene/ethanol mixed solvent than with pure toluene. The effect of chlorobenzene treatment was faster and larger than that of toluene over the 30-day period of the experiments. Hydroxyl groups can be capped by O-methylation, eliminating hydrogen bonds.³ This treatment enhanced the rate of decrease of the pyridine Soxhlet extractability of toluene-treated coals.

The effect of solvent treatment on the hydrogen bonds present in this coal were studied by FT-IR using the band assignments recently reported by Painter et al. There are four general types of hydrogen-bonded structures⁻¹ involving hydroxyl groups in coal. These are found between 3200 and 3516 cm^{-1} . In this study, the absorbance between 3200 and 3516 cm^{-1} was examined. The intensity of the aliphatic C-H stretching band at 2930 cm^{-1} was used as the reference in comparing the spectra. Weak hydrogen bonds were reduced after the solvent-induced conformational changes (Figure 3) as revealed by a decrease in the intensity of the IR peaks. Similar absorbance changes in hydrogen bonds have been observed for other coals used in this study. This loss is ascribed to a reduction in hydrogen bonding as a result of conformational changes.

It is proposed that solvent-induced conformational changes occur and that they require breaking secondary interactions. Direct structural evidence for hydrogen bond disruption has been obtained. Evidence for participation of other non-covalent interactions is indirect.

Pittsburgh No. 8 coal heated in boiling pyridine gave almost the same pyridine extraction yield as that of the starting coal if the pyridine was not removed from the treated coal.² Strong secondary interactions seem not to be produced in the pyridine-swollen state, but are formed during the pyridine-removal step. Probably, pyridine solvates the sites which can generate the strong secondary bonds so they form as pyridine is removed.

Anisotropic solvent swelling of coals has been studied using thin sections.^{7,9} Coals swell more perpendicular to the bedding plane than parallel to it. After swelling with pyridine and removing it with a nitrogen flow, the coal shrank parallel to the bedding plane and expanded perpendicular to it. Similarly, the coal initially shrinks parallel to the bedding plane and expands perpendicular to it when thin sections are¹⁰ treated with hot chlorobenzene or toluene and then dried with nitrogen.

Optical anisotropy in coals is well known.¹¹ Birefringence in coal thin sections and swollen thin sections was observed by Brenner. The loss of optical anisotropy in solvents at room temperature^{9,12} coincided with the solvent's ability to break secondary interactions. The Birefringence of high-volatile bituminous coals apparently stems from a low degree of molecular orientation.¹² When macromolecules are in the glassy state, all large molecular chain motions are restricted, but segmental motion is not necessarily restricted.¹³ The presence of a solvent in the coal macromolecules lowers the glass transition temperature.¹⁴ Coal macromolecules may not be completely in the glassy state in cold pyridine, hot chlorobenzene or toluene, and some movement of coal can occur. The optical anisotropy of Pittsburgh No. 8 coal diminished after soaking in hot chlorobenzene.² The observed loss of optical anisotropy of Pittsburgh No. 8 coal after exposure to hot chlorobenzene provides additional evidence for conformational rearrangements in the swollen coal.

Pyridine breaks most or all of the hydrogen bonds in coals. Therefore, coal-coal hydrogen bonding will give no or a small effect on pyridine extractability. Since the pyridine extractability of the solvent-treated coal is smaller than that of the starting coal, it is likely that strong secondary interactions which are not hydrogen bonds are produced during the solvent-induced conformational change. An X-ray study of the effects of solvent treatment on the [002] band reveal no changes. The enhanced association does not include increased amounts of parallel face-to-face aromatic stacking. These imply that unknown complexes are involved in the new interactions.

A number of lines of evidence point to the solvent-induced association of coal molecules to a lower free energy state. Mined coals are in a metastable, strained state.⁷ The existence of coals in a non-equilibrium state was shown by swelling and vapor uptake hysteresis.^{15,16} These observations are presumably concerned with the initial movement of coal macromolecules during relaxation of the strained state as the coal is swollen by solvents. In high-volatile bituminous coals, physical interactions which cannot be broken by boiling pyridine are formed during pyridine removal, but are hardly formed in

the coal while it is fully pyridine swollen. The pyridine extract can aggregate during hot chlorobenzene treatment. These results demonstrate that the solvent-induced conformational change of coal macromolecules occurs with the coal achieving a lower free-energy state after relaxation. Secondary interactions originally present in the coal are broken and other secondary interactions are generated by the solvent-treatment. One view of this is schematically shown in Figure 4. The rates of disruption and formation of these secondary interactions will be dependent upon original coal properties, the interaction between the coal and the solvents used, and system conditions.

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REFERENCES

1. Jameel, H., Waldman, J., and Regenfeld, L., J. Appl. Polym. Sci., 1981, 26, 1975-1811, and references cited in the paper.
2. Nishioka, M. and Larsen, J. W., Energy & Fuels, submitted.
3. Liotta, R., Fuel, 1979, 58, 724-728.
4. Hirsh, P. B., Proc. Royal Soc. (London), 1954, A226, 143-169.
5. Larsen, J. W. and Baskar, A. J., Energy & Fuels, 1987, 1, 230-232.
6. Painter, P. C., Sobkowiak, M., and Youtcheff, J., Fuel, 1987, 66, 973-978.
7. Cody, G. D., Jr., Larsen, J. W., and Siskin, M., Energy & Fuels, 1988, 2, 340-344.
8. Sanada, Y. and Honda, H., Fuel, 1966, 45, 451-456.
9. Brenner, D., Fuel, 1985, 64, 167-456.
10. Jeffreys, H. E. and Cody, G. D., Jr., unpublished data.
11. van Krevelen, D. W., Coal; Elsevier: New York, 1961, Chapter 17.
12. Cody, G. D., Jr., Larsen, J. W., and Siskin, M., unpublished data.
13. Barr-Howell, B. D., Howell, J. M., and Peppas, N. A., Energy & Fuels, 1987, 1, 181-1186.
14. Lucht, L. M., Larson, J. M., and Peppas, N. A., Energy & Fuels, 1987, 1, 56-58.
15. Ritger, P. L. and Peppas, N. A., Fuel, 1987, 66, 1379-1388, and the preceding series of papers.
16. Hsieh, S. T. and Duda, J. L., Fuel, 1987, 66, 170-178.

TABLE I. PYRIDINE SOXHLET EXTRACTION YIELDS (WT %) OF ILLINOIS NO. 6 COAL AFTER SOAKING IN CHLOROBENZENE AT DIFFERENT TEMPERATURES FOR 24 HOURS

<u>Temperature</u> (°C)	<u>Extraction Yield</u> (wt %)
23	27
115	19
200	16
300	24 + tar (20)*

*Tar was recovered during methanol rinsing.
The yield is wt % of the coal.

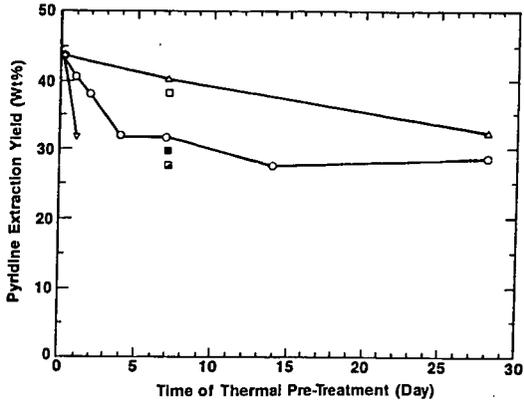


Figure 1. Change of pyridine extractability (Soxhlet) of Pittsburgh No. 8 coal immersed in solvents and dried, (V) room temperature pyridine, (O) 115°C chlorobenzene, (Δ) 100°C toluene, (□) 107°C toluene/ethanol (95/5 vol %) and 100°C toluene for completely (◻) and partly (◼) 0-methylated coal.

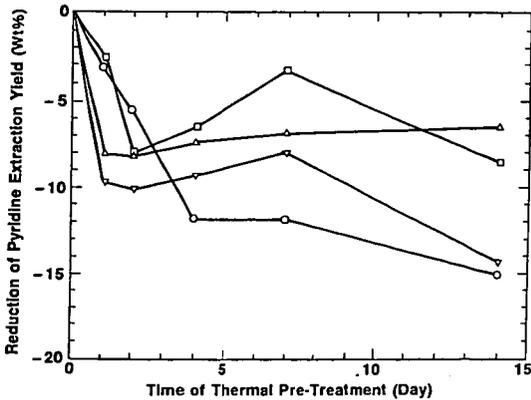


Figure 2. Difference of pyridine extraction (Soxhlet) yields between chlorobenzene-treated coals and starting coals for various ranks of high volatile bituminous coals. Key: (Δ) Wandoan, (V) Illinois No. 6, (O) Pittsburgh No. 8, and (□) PSOC-1336.

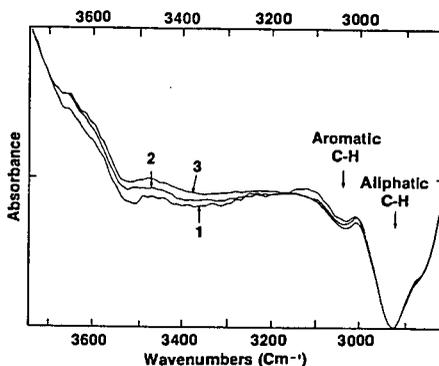


Figure 3. Overlay photoacoustic infrared Fourier transform spectra of (1) starting, (2) 2-day chlorobenzene-treated, and (3) 4-week chlorobenzene-treated Pittsburgh No. 8 coals.

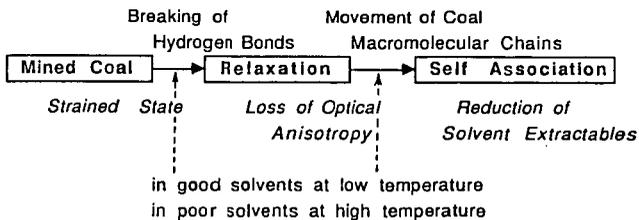


Figure 4. Schematic diagram for solvent-induced conformational changes of macromolecules in high-volatile bituminous coals.