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Section I

1. Overview

This is the Technical Progress Report for the seventh quarter of activities under DOE Contract No. DE-AC22-92PC91047 (contracted on 2/28/92, total 16 months project). Authorization to expend contract funds was not received until July 1992. Therefore, the activity was started on September 1, 1992. This report covers the period October 1 through December 31, 1993.

2. Contract Objectives

A series of reviews concerning the molecular nature of coal is available¹⁻³. Among them, a cross-linked three-dimensional macromolecular model occluding some solvent-extractable components has been widely accepted since van Krevelen⁴ reviewed the 'polymeric' character of coal in 1961. Wiser's⁵ and Shinn's⁶ models would be representative examples of the model. As their models show, it is thought that aromatic ring systems are linked by carbon or heteroatom bridges.

Relatively strong intra- and intermolecular (secondary) interactions play an important role in the structure of all ranks of coal, and their abundance is far more significant than generally believed⁷⁻⁹. Pyridine is one of the best solvents for coal, but can disrupt only a limited fraction of these relatively strong interactions. The importance of physical associations due to these relatively strong interactions in coal should not be underestimated¹⁰. The mechanism by which coal molecules may be covalently cross-linked (A) and/or physically associated (B) is illustrated in *Figure 0.1*. Direct evidence to verify the real state of the physical structure has not yet been obtained.

Figure 0.1 Illustration of the conventional network (A) and the associated (B) models

The objective of this project is to investigate the physical structure of coal illustrated in *Figure 0.1*. Coal structure should be well understood to guarantee effective utilization. A better understanding of this physical structure is the first step for effective development of coal utilization processes.

Solvent *swelling* and *extraction* are the two main investigative probes in this project. No single solvent tested to date can disrupt all of the relatively strong secondary interactions in coal. Various relatively strong secondary interactions must be solvated step by step using appropriate procedures. If physical association is considerable, coal should be readily extracted. Physical association will also be evaluated by coal swelling using conventional and new methods. To investigate the effects of low coal concentration and continuous mixing, a new method will be developed.

The focus of the work was directed toward a specific bituminous coal low in sulfur and iron. As requested by DOE, Blind Canyon (DECS-16) coal obtained from the Penn State Coal Bank has been used in this project.

3. Contract Activities - This Period

- (1) The swelling kinetics were evaluated by conventional procedures using glass tubes. Diffusion of solvent into the coal was small, and solvation of intra- and intermolecular interactions was the rate determining step for swelling.
- (2) A newly established technique using laser scattering has been used to evaluate interparticle aggregation and swelling. It was observed that particles from certain fractions of specific coals were selectively aggregated in particular solvents.
- (3) Pyridine extractability after soaking in phenol at 200-250°C was studied. Approximately 70 wt% of Blind Canyon (DECS-16) coal was extracted under the optimum condition. A significant amount of phenol, however, was physically retained.
- (4) The associated molecular structure of coal proposed has been supported by associative equilibria during soaking in poor and good solvents.

Section II

1. Swelling Kinetics

Introduction

Solvent swelling has been used to characterize the product coal as well as the unextracted residue. Since the volumetric swelling method using a glass tube is both easy and reproducible, this method has been widely used¹¹⁻¹³. Coal swelling is measured as the ratio between the height or volume of a swollen sample to an unswollen sample. There are, however, several important factors which affect the reliability of the results which have not been considered. These are the quantity of coal, the ratio of coal to solvent (C/S), and the dependence of the C/S value.

A quantity of coal is usually introduced into a glass tube and centrifuged. An initial height is determined after centrifugation. The height, however, will vary depending on the bulk density of the coal, even if fine particles are used for testing. Since this test uses necessarily small quantities of coal to investigate the dependence of coal concentration, the initial height often changes remarkably just by tapping the sample tube, even after centrifugation. This results in significant errors in initial heights, with the small amount of coal. Therefore, coal should be exactly weighed before insertion into the glass tube, and swelling ratios should be compared by swollen volume per mass (eg. $\text{cm}^3 \text{g}^{-1}$)¹⁴. Various important results have been obtained by considering these factors¹⁴⁻¹⁶.

Reproducible swelling ratios for small C/S values were obtained by exactly weighing the coal and solvent. Coal swelling was measured for a wide range of C/S values¹⁵, and was found to be highly dependent on coal concentration. The swelling was greatly enhanced with low concentrations, but the dependence was diminished at high concentration. Since volumetric swelling by other workers has been measured at higher concentrations of coal, the dependence of coal concentration on swelling has been largely overlooked.

Realizing that coal swelling is dependent on coal concentration is very important for the understanding of coal structure. Since coal molecules dissociate and swell more at low coal concentration, this implies that coal has an associative nature. This view of coal structure contradicts the widely accepted structural model which infers a covalently cross-linked three dimensional network.

Reversibility of coal swelling was tested to investigate the elastic property of coal¹⁵. Two coals of different rank were treated with solvents. Coal swelling was measured before and after

treatment. Swelling from both coals proved completely irreversible which was consistent with the change in solvent extractability for these coals after treatment. This irreversibility of coal swelling also contradicts the widely accepted conventional network model of coal.

Coal swelling in selected solvents was then examined for fractionated samples from two high-volatile C bituminous coals to investigate the role of physical associations in the coal structure¹⁶. It was thought that *residues* after extraction with pyridine show a network structure, while the *extracts* do not. However, the dependence of concentration on their swelling was similar. Swelling ratios of residues were significantly larger than those of extracts. This could just as reasonably be interpreted in terms of an associated model for the residues. The obvious conclusion is that significant portions (far more than generally believed) of coal molecules are physically associated.

Dried low rank coal, unlike that of higher rank bituminous, is slowly swollen in organic solvents. To further study the extent of this physical association, the swelling kinetics were analyzed with associative equilibria controlled by ionic forces¹⁷. It was concluded that solvation of ionic forces was the rate determining step during volumetric swelling of lower rank coal rather than solvent diffusion into the coal. This tends to contradict those that diffusion is the most important factor in swelling.

Pore diffusion has been studied using gases¹⁸⁻²⁵, nothing definitive has been reported about solvent diffusion during swelling. Larsen and Lee²⁶ investigated steric requirements for coal swelling by postulating amine bases with various sizes and branching of alkyl groups. They concluded that bulky groups inhibited the dissolution of organic molecules in coals. Since they were considering equilibrium swelling values, solvent diffusion during coal swelling could not be obtained. Basicity of solvents changes with the structure of substitutes and may affect the equilibrium swelling in addition to the bulkiness of alkyl groups. Aida *et al.*²⁷ examined the steric effect on the kinetics of solvent swelling using a piston type apparatus. However, swelling behavior noted in the glass tube differs from that in the Aida's method, because coal/solvent ratios are very large and coal and solvent are not mixed in the Aida's procedure. No reliable result on the steric effect of solvent is available.

To answer this need, the steric effect of solvents during swelling was evaluated in the previous quarter. Wyoming subbituminous coal was swollen in amines and pyridines with different alkyl groups. Although equilibrium swelling is different among these solvents, all swelling rates followed the first order equation. Therefore, we conclude that swelling kinetics

is controlled by associative equilibria rather than diffusion of solvent into the coal, and the steric effect of the solvent is small. In this quarter, swelling kinetics was further evaluated under various conditions for high-volatile bituminous coals and lignite.

Swelling kinetics. The kinetics of solvent sorption of coal and swelling of coal thin section samples was studied by Peppas and his co-workers^{28,29}. They proposed that these processes were controlled by both solvent diffusion into coal and relaxation of coal molecules during these processes. According to them, the simplified rate law that governs the "early period" of sorption and swelling may be represented as:

$$Q = (Q_{\infty} - Q_0) \times k t^n + Q_0 \quad (1)$$

where Q , Q_{∞} and Q_0 are swellings at arbitrary, ultimate, and initial times, k is the constant related to swelling rate and t is time. A constant n is 0.5 for Fickian diffusion, while n is generally between 0.5 and 1 for non-Fickian diffusion of coal. For the latter, the process is called case II diffusion in which relaxation of coal molecules changes the diffusion kinetics.

Otake and Suuberg³⁰ analyzed the kinetics of volumetric swelling using this equation. They concluded that volumetric swelling of coal is controlled by diffusion of solvent into the network, and calculated its activation energy. This volumetric swelling, however, is a different process from the sorption and swelling studied by Peppas *et al.*^{28,29}. Equation (1), used by these investigators, fits only the "early period" of their sorption and swelling. Care should be exercised for the proper interpretation of the kinetics in these procedures.

If associative equilibria induced by intra- and intermolecular interactions control the rate of coal swelling, this rate should follow the first order process similar to the process of solvent extraction controlled by relatively strong intermolecular interactions (Equation (2))⁹,

$$E = E_{\infty} \times (1 - e^{-k_1 t}) \quad (k_1: \text{constant}) \quad (2)$$

where E and E_{∞} are extraction yields at time t and ultimate time, respectively. For swelling, the following equation is expressed.

$$Q = (Q_{\infty} - Q_0) \times (1 - e^{-k_2 t}) + Q_0 \quad (k_2: \text{constant}) \quad (3)$$

Experimental

American Chemical Society reagents and h.p.l.c.-grade solvents were used. Blind Canyon (DECS-16), Illinois No. 6 (DECS-2), and North Dakota (ND) coals were obtained

from the Pennsylvania State University Coal Bank and the Argonne Premium Coal Sample Bank. Their elemental analyses are shown in *Table 1.1*.

The experimental procedure of coal swelling is based upon the earlier reported method¹⁴⁻¹⁶. The measurements were performed in a disposable Wintrobe Tube (Fisher Scientific) of 3 mm inner diameter and 115 mm length graduated in 1 mm divisions. After placing three weighed coal samples into the tubes, these tubes were centrifuged for 5 min (at 3600 rev min⁻¹ in a 30 cm diameter horizontal rotor). The bulk density (BD) of coal was determined by the average centrifuged height and its mass. Each initial height before solvent swelling was calculated from the mass of the sample by using BD. Solvent volume was measured and added to each weighed sample, and the content was vigorously stirred with a thin rod. The tubes were centrifuged for 5 min at 3600 rev min⁻¹. Experiments were generally carried out at a coal/solvent ratio of 4.4 ± 0.2 (wt/wt %). Separate samples were employed for determining the extent of swelling as a function of time. The volumetric swelling ratio (Q) was calculated by the difference between heights of samples. The specific swelling ratio (Q') defined by the following equation¹⁵ is used in this report.

$$Q' = Q / BD \quad (4)$$

The value Q' corresponds to the swollen volume (ml) of 1 g sample. Alternatively, the value Q' can be directly calculated by the height of a swollen sample and mass of the sample.

Table 1.1 Elemental analyses of coals used (wt%)

Symbol	Sample	H ₂ O	Ash	Element (daf)				
				C	H	N	S	O (diff.)
DECS-2	Illinois No. 6 (hvbC)	10.4	14.5	78.1	5.4	1.3	5.4	9.8
DECS-16	Blind Canyon (hvb)	5.2	13.2	81.0	5.9	1.5	0.6	11.0
ND	North Dakota (lignite)	32.2	6.6	72.9	4.8	1.2	0.9	20.2

Results and Discussion

Swelling kinetics of high-volatile bituminous coal. Since the swelling rate of dried lower rank coal is small and highly dependent on temperature, its swelling kinetics can be evaluated in contrast to that of high-volatile bituminous coal. Some of the results were reported in the previous quarterly report. It is, however, difficult to study swelling kinetics of high-volatile bituminous coal. High-volatile bituminous DECS-16 coal was swollen in various solvents at various temperatures. Results showed that this dried coal was very slowly swollen in N-methyl-2-pyrrolidinone (NMP) at 25°C and highly dependent on temperature. Therefore, this dried coal and NMP solvent were used to evaluate the effects of solvent diffusion into coal and solvation of secondary interactions.

The DECS-16 coal was swollen in NMP at 25-75°C (coal/solvent ratio: 4.4 wt/wt %). Figure 1.1 shows observed and calculated specific swelling ratios versus time. Calculated values were obtained from Equation (3), in which solvation of secondary interactions is assumed to be a main factor. The parameters were determined by curve fitting using SigmaPlot® and produced the following equations:

$$Q' = 1.42 \times (1 - e^{-0.263 t}) + 1.40 \quad (25^\circ\text{C}) \quad (5)$$

$$Q' = 1.52 \times (1 - e^{-1.04 t}) + 1.44 \quad (40^\circ\text{C}) \quad (6)$$

$$Q' = 1.52 \times (1 - e^{-1.65 t}) + 1.40 \quad (50^\circ\text{C}) \quad (7)$$

$$Q' = 1.59 \times (1 - e^{-4.75 t}) + 1.39 \quad (75^\circ\text{C}) \quad (8)$$

The calculated values agree very well with observed values at temperatures ranging from 25°C to 75°C. The conventional Equation (1), in which diffusion of the solvent into coal and relaxation of coal molecules are assumed to be the main factors, does not coincide with the observed values. Solvation of secondary interactions were the rate-determining step controlling the swelling of Wyoming subbituminous coal, and the effects of diffusion during swelling, as discussed above, were small. The result obtained in this study shows that swelling of high-volatile bituminous coal is similarly controlled by solvation of secondary forces.

The dependence of the k value on temperature may be expressed as¹⁷:

$$k = A \cdot \exp(-\Delta H / R \cdot T) \quad (9)$$

where A , ΔH , R , and T are a constant, activation energy, gas constant and absolute temperature, respectively. The activation energy, ΔH , can be determined by the following Arrhenius plot.

$$\ln k = -\Delta H / R \cdot T + B \quad (B: \text{constant}) \quad (10)$$

Figure 1.1 Specific swelling ratios (Q') of dried DECS-16 coal in N-methyl-2-pyrrolidinone at 25°C (●), 40°C (○), 50°C (■), and 75°C (□) (coal/solvent ratio: 4.4 w/w %)

Figure 1.2 Arrhenius plot of the swelling constant k for the results in Figure 1.1

From the results shown in *Figure 1.2*, the activation energy under the condition is determined as follows:

$$-\Delta H / R = -5.86 \times 10^3 \quad (11)$$

$$\therefore \Delta H = 5.86 \times 10^3 K \times 8.31 J \cdot K^{-1} \cdot mol^{-1} \quad (12)$$

$$= 48.7 kJ \cdot mol^{-1} (12 kcal \cdot mol^{-1}) \quad (13)$$

Extraction kinetics. The above results suggest that swelling of high-volatile bituminous coal is primarily controlled by solvation of relatively strong secondary interactions. Extraction was also controlled by solvation of secondary interaction, and its rate was expressed by the first order process (Equation (2))⁹. If the diffusion of a solvent into coal is small during swelling in an extraction process, extractability for solubles and coal may follow the same kinetics. The basic structure of the PS is not a network, but the coal may contain network entities. Therefore, if solvent diffusion into the network controls extractability, kinetics of toluene extraction is different between the two samples. To confirm this, toluene extractability for Illinois No. 6 high-volatile bituminous (DECS-2) coal and its pyridine extract (PS) were evaluated.

Ultimate toluene extractability of the dried coal was 0.8 wt% (daf), while that of the PS was 9.8 wt% (3 wt% (daf) of the coal). Larger extractability from the PS may be explained as follows: Pyridine can solvate relatively strong secondary interactions more effectively than toluene. If toluene solubles strongly interact with the residue, the solubles cannot be extracted. If the interactions can be broken with pyridine before toluene extraction, more solubles would be extractable with toluene.

Extraction yields divided by ultimate extraction yields (E_{∞}) (normalized extractability) are shown in *Figure 1.3* as well as calculated values using Equations (14) and (15).

$$E / E_{\infty} = 100 \times (1 - e^{-0.0506 t}) \quad (PS) \quad (14)$$

$$E / E_{\infty} = 100 \times (1 - e^{-0.0562 t}) \quad (coal) \quad (15)$$

The results show that extraction kinetics is essentially the same for these two samples. This means that the effect of solvent diffusion into coal during extraction is small, and the results support the projected swelling process.

Further investigation of swelling kinetics. According to the proposition of solvent diffusion, swelling kinetics should be the same with no dependence on the coal to solvent ratio. Based on the solvation proposition, however, swelling kinetics should change with changes in

Figure 1.3 Normalized toluene extraction yields versus time for DECS-2 pyridine extract (●) and dried DECS-2 coal (○)

the coal to solvent ratio. This comes about since solvation is controlled by the equilibrium between coal and solvent, which is dependent on the coal to solvent ratio. To investigate this theory, the swelling kinetics of the dried DECS-16 coal was evaluated at different coal to solvent ratios. Test results are presented as *Figure 1.4* with calculated values shown as Equations (16)-(18).

$$Q' = 1.42 \times (1 - e^{-0.263 t}) + 1.40 \quad (\text{coal/solvent} = 4.4 \text{ w/w}\%) \quad (16)$$

$$Q' = 1.26 \times (1 - e^{-0.357 t}) + 1.32 \quad (\text{coal/solvent} = 7.1 \text{ w/w}\%) \quad (17)$$

$$Q' = 0.87 \times (1 - e^{-0.351 t}) + 1.35 \quad (\text{coal/solvent} = 11 \text{ w/w}\%) \quad (18)$$

We conclude that the swelling rate and ultimate swelling ratios are small at high coal to solvent ratios. This supports the solvation mechanism of intra- and intermolecular interactions during swelling.

Swelling of North Dakota lignite was also investigated to confirm the solvation proposition. The swelling ratio of this coal was very small and did not change with time in NMP at 25°C as shown in *Figure 1.5*. Swelling of this coal, however, increased with time by adding CS₂ in NMP, and *Figure 1.5* shows swelling in the mixed solvent of NMP/CS₂ (50/50 vol/vol %). Swelling of this coal was enhanced even in NMP at 75°C. The followings are the equations used for these calculations.

$$Q' = 1.10 \times (1 - e^{-0.558 t}) + 1.20 \quad (75^\circ\text{C in NMP}) \quad (19)$$

$$Q' = 0.42 \times (1 - e^{-0.136 t}) + 1.34 \quad (25^\circ\text{C in NMP/CS}_2) \quad (20)$$

These results cannot be explained by solvent diffusion, and support the solvation mechanism proposed.

Figure 1.4 Specific swelling ratios (Q') of dried DECS-16 coal in N-methyl-2-pyrrolidinone at 25°C, concentration of coal/solvent = 4.4 w/w % (●), and coal/solvent = 7.1 w/w % (○), coal/solvent = 11 w/w % (■)

Figure 1.5 Specific swelling ratios (Q') of dried North Dakota coal in N-methyl-2-pyrrolidinone at 75°C (●), in N-methyl-2-pyrrolidinone/CS₂ (1/1 v/v) at 25°C (○), and in N-methyl-2-pyrrolidinone at 25°C (■) (coal/solvent ratio: 4.4 w/w %)

2. Coal Swelling Using a Laser Scattering Method

Introduction

Swelling of coal with incomplete dissolution in any solvent has been used as evidence for the three-dimensional cross-linked macromolecular network model of coal structure. Sanada and Honda³¹ applied the statistical theory of rubber elasticity to coal swelling. Since then, coal swelling has been used to characterize the macromolecular nature of coal by many workers³²⁻⁴⁰. Four major methods have been used: the volumetric method using glass tubes^{12,13,30}, the gravimetric method^{31,33,34}, the method requiring a piston type of apparatus^{40,41,42}, and direct observation using a microscope^{36,43-45}. The easiest and most commonly used is the volumetric method.

The conventional volumetric technique using glass tubes was selected to examine the physical structure of coal in this investigator's recent papers¹⁴⁻¹⁷. Some steps in the method were modified. Coal samples and solvents were weighed, and the initial height of each sample before swelling was calculated from the mass and bulk density of the samples. This was necessary to obtain reproducible results, particularly at low coal concentrations. From this study, it was found that coal swelling is strongly dependent on coal concentration¹⁵.

The results also showed that swelling ratios, Q , did not change in the common range of C/S from 10-20 %, but significantly increased at $C/S < 5$ %. The intrinsic swelling ratio, $[Q]$, independent of coal concentration, was introduced (Equation (12))¹⁵.

$$[Q] = \lim_{\log(C/S) \rightarrow 0} Q \quad (21)$$

The $[Q]$ values were consistently more than two times larger than those conventionally observed. Therefore, conventionally observed swelling ratios are apparent values. During this work, it was also found that the degree of mixing of coal and solvent was an important factor for coal swelling. This strongly suggests that solvent swelling should be measured at very *low* coal concentrations with *continuous mixing* for a given period of time. An apparatus specifically designed for these purposes is necessary.

One of the objectives of this project is to explore a new method to measure coal swelling for low coal concentrations with continuous mixing. For this purpose, the measurement of particle size distribution of coal by laser scattering has been studied. The swelling ratio measurement by particle size distribution was first suggested by Turpin *et al*⁴⁴., but details were not reported. Therefore, the method has been reevaluated in this project with some results reported in the previous quarterly reports. The method proved satisfactory under the desired

conditions. Coal swelling is determined from the difference in the particle size range using poor and good solvents.

It was notable that the particle size distribution of coal in pyridine and methanol was nearly equal, considering that the volumetric swelling in pyridine was much larger than that in methanol. In addition, the distribution in pyridine reversibly changed from time to time, while in methanol it did not change. The results imply equilibrium between aggregation and disaggregation of coal particles. Decreases in particle size due to disaggregation may be compensated by increases in particle sizes due to coal swelling. This could explain the minimal differences shown by particle size distributions in poor and good solvents. If this interpretation is correct, the number of coal particles should increase in good solvents due to disaggregation. This number can be measured as a function of the light scattered back to the probe by the apparatus. The change in the number of coal particles during swelling was evaluated in the previous quarter. Number of coal particles with small diameters increased in line with better solvents for coal; methanol < toluene < chloroform < pyridine. The result supported the disaggregation interpretation in good solvents. Therefore, coal particles swell in good solvents, but concurrently disaggregate. Disaggregation was experimentally observed for particles with small diameters. *Figure 2.1* presents the proposed behavior of aggregation and swelling for coal particles.

Figure 2.1 Proposed concurrent changes in aggregation and swelling of coal particles in solvents

The pyridine soluble (PS) fraction from the DECS-16 coal was fractionated into three fractions; pyridine soluble and tetrahydrofuran insoluble (PS•TI), tetrahydrofuran soluble and chloroform soluble (TS•CI), and chloroform soluble (CS). Association of these fractions in pyridine solution was previously studied in this project by evaluating viscosity. Significant association of the PS•TI fraction was suggested from the following results.

1. The dependence of temperature on specific viscosity of this fraction was the largest among the fractions.
2. Specific viscosity remarkably decreased by adding small amount of triethylamine (electron donor) or N-methyl-2-pyrrolidine (NMP) (electron donor and acceptor).
3. The dependence of specific viscosity on concentration was the largest for this fraction.

It is expected that higher molecular association may lead to higher particle association (or aggregation). Aggregation of coal particles was observed with the laser scattering method. Therefore, this method was used to evaluate aggregation of coal particles of the particular fraction, PS•TI. The effect of temperature on aggregation was also studied for medium-volatile bituminous coal which shows thermally-induced dissociation⁹.

Experimental

Blind Canyon (DECS-16) and Upper Freeport (UF) coals were obtained from the DOE Coal Bank at the Pennsylvania State University and the Premium Sample Program at Argonne National Laboratory, respectively. All the reagents and solvents were obtained from Aldrich Chemical Co. (Milwaukee, WI) and Fisher Scientific (Pittsburgh, PA), and HPLC-grade solvents were used without further purification. This DECS-16 coal (10 g) was Soxhlet-extracted with pyridine for 72 h, and pyridine was removed with a rotary evaporator to form a viscous sample (~10 cm³). Approximately 300 cm³ of tetrahydrofuran (THF) was added to this sample, and the mixture filtered. The recovered THF-solution was concentrated and treated with chloroform using the procedure described above. By this procedure, pyridine soluble/THF insoluble (PS•TI), THF soluble/chloroform insoluble (TS•CI), and chloroform soluble (CS) fractions were obtained with the yields shown in *Figure 2.2*. The pyridine soluble (PS) fraction was obtained for comparison. *Tables 2.1 and 2.2* show elemental analyses and molecular weight of these extract fractions. The NMP/CS₂ soluble and pyridine insoluble

*Values in parentheses denote yields in the PS fraction.

Figure 2.2 Yields (wt%) of fractionated samples

fraction (E-PI) from Upper Freeport coal was obtained from Dr. Iino (Tohoku University, Japan)⁴⁶. The fractionation scheme for this fraction is shown in *Figure 2.3*.

Model LAB-TEC 1000 particle size analyzer (LASENTEC, Bellevue, WA) was used for this study. This analyzer is a scanning laser type apparatus⁴⁷. When the focal spot intercepts a particle, some light is scattered back to the probe and converted into an electronic pulse. This is converted to size by the relationship:

$$d = v/t \quad (22)$$

The duration of the pulse represents the time (t) the focal spot illuminated the particle. Since the velocity (v) of the focal spot is known, the distance (d) for the focal spot scanned across the particle can be determined. This distance represents the length of a chord of the particle. Pulses representing the chord lengths are classified by counting circuits, then transferred to a computer for processing and presentation on a display or printer. The LAB-TEC 1000 classifies particles into 29 channels, ranging from 0.2 to 250 μm . The distribution is presented in two ways in this study. Scanned count is the uncorrected random chord frequency distribution. Volume diameters are the distribution of volume, derived from the scanned count data. The mean volume diameter and the mean diameter with scanned counts are shown as D_v and D_c , respectively. The measuring unit contains the probe, focus mechanism, and stirring plate. The probe contains the laser diode, scanning optics, detectors, and associated support circuits. The Main Unit contains the counting circuits and power supplies, as well as support circuits for the probe scanner motor drive. LASENTEC[®] measuring beakers (100 ml) were used for sample containers. Samples were agitated with a magnetic stirrer during the measurement. For tests of the effect of temperature, a heating mat confined the sample beaker. A thermocouple was immersed in the sample beaker for temperature control.

Elemental analyses of the fractions were conducted by Geochemical Testing (Somerset, PA). Molecular weight of the samples were measured in pyridine with vapor pressure osmometry by Huffman Laboratories, Inc. (Golden, CO).

Table 2.1 Elemental analyses of Blind Canyon coal and its extracts (wt%)

symbol	sample	H ₂ O	ash	element (daf)					H/C (atom/atom)
				C	H	N	S	O (dif.)	
DECS-16	Blind Canyon coal	5.2	13.2	81.0	5.9	1.5	0.6	11.0	0.87
PS	Pyridine solubles	-	-	81.6	7.1	2.3	0.6	8.4	1.04
PS•TI	Pyridine solubles and THF insolubles	-	-	78.2	6.5	2.4	0.4	12.5	1.00
TS•CI	THF solubles and chloroform insolubles	-	-	79.0	5.9	2.3	0.4	12.4	0.90
CS	Chloroform solubles	-	-	86.5	9.1	0.7	0.3	3.4	1.26

Table 2.2 Molecular weight of samples fractionated from DECS-16 PS solubles

symbol	sample	molecular weight
PS	Pyridine solubles	800
PS•TI	Pyridine solubles and THF insolubles	1,460
TS•CI	THF solubles and chloroform insolubles	1,230
CS	Chloroform solubles	550

Figure 2.3 Fractions from Upper Freeport coal using NMP/CS₂ mixed solvent

Results and Discussion

The particle size distribution of the PS•TI fraction from the DECS-16 coal was measured in three different solvents, methanol, toluene, and THF. Changes in the distribution with time are shown in *Figure 2.4*. The particle size in methanol was the largest among these solvents, and did not significantly change with time up to 7 d. Alternatively, the distribution in toluene significantly changed with time. The distribution was broad at an initial time, and the abundance of larger particles then decreased. The abundance of larger particles similarly decreased in THF with time, but the change in particle size distribution was small. It should be noted that the particle size distribution of the PS from the same coal was approximately the same in these three solvents, as previously reported. Therefore, the difference in particle size distributions between PS and PS•TI fractions is significant. Since methanol is a non-swelling solvent, the larger particle size in this solvent is probably due to interparticle aggregation. Particle size distribution in toluene and THF can be interpreted as follows: THF is the best solvent for coal among three solvents. Toluene is a better solvent than methanol but a poorer solvent than THF. Particles in toluene presumably aggregate but tend to disaggregate with time. Aggregation may be smallest in THF, and the change in the particle size distribution is also smallest since it is the best solvent. This would explain the small change in the particle size distribution in THF with time.

To confirm this aggregation/disaggregation proposition in different solvents, the particle size distribution of another E-PI fraction from UF coal was examined. *Figure 2.5* shows the results using toluene, THF, and pyridine. For this particular fraction, the change in the particle size distribution was small in toluene with time, but changed in THF. The distribution did not change in the better solvent, pyridine. It is thought that the same aggregation/disaggregation occurs for this fraction, but the interaction between particles and solvent seems different from that between the fraction PS•TI and solvents. Since this fraction has more high-molecular-weight residue than the PS•TI fraction because of its insolubility in pyridine, better solvents are presumably necessary to disaggregate particles.

The effect of temperature on interparticle aggregation/disaggregation was evaluated at temperatures ranging from 25°C to 70°C. The particle size distribution of the UF raw coal was measured in NMP and pyridine (*Figure 2.6*). The average particle size in NMP was larger at 25°C to 35°C. The particle size decreased with an increase in temperature, and became a broad distribution at temperatures of > 65°C. The results suggest that disaggregation proceeds with

an increase in temperature and swelling becomes appreciable at $> 65^{\circ}\text{C}$. The particle size distribution in pyridine, however, did not significantly change with an increase in temperature. Since pyridine is less effective than NMP for this coal, we conclude that the solvation capability of pyridine to disaggregate particles is not sufficient.

The above results show that the fraction which is soluble in pyridine does associate to a large extent but shows significant interparticle associations in poorer solvents than pyridine. Aggregated coal particles for particular coal samples disaggregate under mild heating. This equilibria can easily be detected by laser scattering. Therefore, the laser scattering method developed here is very useful for observing the behavior of interparticle aggregation in addition to swelling. Consideration of the concurrent changes in swelling and aggregation-/disaggregation is needed to interpret the particle size distribution.

Figure 2.4 Change in particle size distributions with time of the PS-TI fraction from DECS-16 coal in (a) methanol, (b) toluene and (c) tetrahydrofuran (D_v : mean volume diameter (μm))

Figure 2.5 Change in particle size distributions with time of the E-PI fraction from Upper Freeport coal in (a) toluene, (b) tetrahydrofuran and (c) pyridine (DV: mean volume diameter (μm))

Figure 2.6 Change in particle size distributions with temperature of UF coal in (a) NMP and (b) pyridine (Dv: mean volume diameter (μm))

3. Coal Extraction

Introduction

There is a long history, over a century, of coal-solvent extraction. Only a small fraction of most coals is extractable with organic solvents; the average ranging from 20-30 wt%. Hydrogen bonds along with weak van der Waals' forces^{48,49} were assumed to be broken with one of the best solvents, pyridine. Caution, however, is advised when considering the limited extractability of coal, since the solubilization of relatively strong intra- and intermolecular (secondary) interactions caused by polyfunctional groups in coal has not been fully considered.

The overlapping $2p_z$ orbitals on each sp^2 -hybridized carbon between polycyclic aromatic compounds (PAC) generate an electron cloud over and under the planar PAC molecules, as reviewed by Haenel and Schweitzer⁵⁰. Electronically excited complexes formed by the so-called π - π interaction in higher rank coal has been recently pointed out^{7,51,52}. However, other kinds of relatively strong secondary interaction in lower rank coals have been poorly understood. Charge-transfer interactions have been proposed as relatively strong secondary forces in high-volatile bituminous coal and initiate the solvent-induced association^{8,53}. Although there are indications of the presence of the ionic force in lower rank coal^{54,55}, its effect on solvent extractability has not been thoroughly reported. The significant effect of the ionic force on pyridine extractability, however, has been recently observed for lower rank coal by Nishioka *et al.*⁸.

These relatively strong ionic, charge-transfer, and π - π interactions are present in addition to hydrogen bonds and weak van der Waals' forces and are not completely overcome with pyridine. No single solvent can solvate all of these secondary interactions. The abundance of diverse functional groups in coal are highly rank-dependent, and the strength and importance of individual interactions change according to rank. Therefore, each interaction has to be solvated step by step using procedures dictated by coal rank.

The charge-transfer interaction is significant in high-volatile bituminous coal⁸. Soaking the coal with electron donors and/or acceptors is suggested to solvate the charge-transfer interactions¹⁰. Soaking with electron donors and acceptors, however, to solvate the charge-transfer interactions should be conducted at temperatures above 200°C, for the following reasons:

1. Solvent-induced associations caused by the charge-transfer interactions are promoted at higher temperatures up to 200°C⁵³. The association cannot be solvated with the good

electron donor solvent, pyridine, with Soxhlet extraction.

2. Solvent-induced associations are initiated between 115-130°C, even in the presence of pyridine (electron donor) or maleic anhydride (electron acceptor)^{7,56}.

3. It is known that the coal can be solubilized by soaking in anthracene oil and polycyclic aromatic hydrocarbons, which are electron donors and acceptors, only at > 300°C¹⁰.

Electron donors and acceptors are known to be strongly retained by soaking. This adsorption is enhanced with an increase in soaking temperature⁵⁷. It can be interpreted that coal-coal complexes with charge-transfer interactions are replaced with coal-solvent complexes. Therefore, tests to evaluate the retention of solvents as well as extractability have been carried out after soaking at 150-250°C.

Experimental

Materials. Coal samples were obtained from the DOE Coal Bank at the Pennsylvania State University. Their ultimate analyses are shown in *Table 3.1*. All the reagents and solvents were obtained from Aldrich Chemical Co. (Milwaukee, WI) and Fisher Scientific (Pittsburgh, PA), and HPLC-grade solvents were used without further purification.

Tests of retention and extraction with a microreactor. Coal samples (2 g) and phenol (15 ml) or NMP/CS₂ (1/1 vol/vol) mixed solvent (15 ml) were charged in a 27 ml microreactor, and purged with N₂ (100 psi, @25°C). The reactor was heated in a fluidized sand bath controlled to 200 ± 3 °C for 24 h, while the reactor was horizontally shaken with the shaker unit for 20 min every 1 h. After soaking, the contents of the reactor were washed with pyridine into a beaker and filtered through a preweighed thimble. The residues in the thimble were Soxhlet-extracted with pyridine for 24 h. The solvent was removed with a rotary evaporator (mostly

Table 3.1 Elemental analyses of coals used (wt%)

Symbol	Sample	H ₂ O	Ash	Element (daf)				
				C	H	N	S	O (diff.)
DECS-8	Wyodak (subbC)	28.4	9.9	74.4	5.2	1.0	0.9	18.5
DECS-2	Illinois No. 6 (hvbC)	10.4	14.5	78.1	5.4	1.3	5.4	9.8
DECS-16	Blind Canyon (hvb)	5.2	13.2	81.0	5.9	1.5	0.6	11.0
DECS-12	Pittsburgh No.8 (hvbA)	2.4	10.0	83.3	5.7	1.4	1.3	8.3
DECS-3	Dutch Creek (mvb)	1.1	5.3	87.4	5.9	1.7	0.7	4.3

pyridine) and in a dish heated on a hot plate at 130°C (mostly phenol or NMP) purging with air. Residues and extracts were then dried at 95°C overnight. The weight gain after drying was regarded as retained phenol or NMP.

Tests of retention and extraction with a 250 ml autoclave. Coal samples (3 g) and phenol (50 ml) or NMP/CS₂ (1/1 vol/vol) mixed solvent (50 ml) were charged in a 250 ml autoclave (Model 4576; Parr Instrument Co., Moline, IL), and purged with N₂ (100 psi, @25°C). The autoclave was maintained at desired temperatures for 24 h while the samples were stirred at 500 rpm. After soaking, the contents of the reactor were washed with pyridine into a beaker and filtered through a preweighed thimble. The residues were Soxhlet-extracted with pyridine for 24 h. The solvent was removed with a rotary evaporator (mostly pyridine) and then in a dish heated on a hot plate at 130°C (mostly phenol or NMP) while purging with air. Residues and extracts were dried at 95°C overnight. The weight gain after drying was regarded as retained phenol or NMP.

Calculation of extractability and retention. Extractability and solvent retention were calculated following Equations (23)-(26), (coal and residue: daf base). When 7,7,8,8-tetracyanoquinodimethane (TCNQ) was added, the weight of TCNQ was subtracted from the weight of residues.

$$\text{extraction yield \%} = 100 \times \text{extract} / \text{coal} \quad (23)$$

(based on extract recovered)

$$\text{extraction yield \%} = 100 \times (1 - \text{residue} / \text{coal}) \quad (24)$$

(based on residue recovered)

$$\text{normalized extraction yield \%} = 100 \times \text{extract} / \{ (\text{extract} + \text{residue}) \} \quad (25)$$

$$\text{retained solvent \%} = 100 \times \{ (\text{coal} - \text{extract} - \text{residue}) \} / \text{coal} \quad (26)$$

Phenol analysis. The approximate phenol quantity was analyzed by the University of Pittsburgh Applied Research Center (Pittsburgh, PA) using gas chromatography. The peak area of phenol in samples were compared to that of the phenol standard.

Results and Discussion

Pyridine extractability after soaking in solvents with electron-donor and acceptor capability has been studied. Temperatures of 200-250°C were selected for the reasons discussed above. As an example, *Table 3.2* lists the result obtained from soaking DECS-16 coal in phenol at 200°C using the 250 ml autoclave. A large portion of the phenol was incorporated into the extract and the residue. This incorporation was ~28 wt% as shown by the mass balance before and after pyridine extraction. Because of the large phenol incorporation, extraction yields were different between extract and residue bases. Therefore, *normalized* extraction yields calculated by Equation (25) are presented as extraction yields in this report.

Table 3.2 Example of extraction and its calculation

DECS-16 coal: pyridine extraction after soaking in phenol at 200°C for 24 h

Result

	Sample		Weight (g)
1	Starting coal	(total)	3.00
2	"	(dry base)	2.84
3	"	(daf base)	2.45
4	Ash in starting coal		0.40
5	Additive	(non-volatile)	0.00
6	Extract		1.48
7	Residue	(total)	2.04
8	"	(daf base)	1.65
9	Ash in residue		0.40

Yield

	Calculation ^a	Extraction Yield (wt%, daf)
Extract base	6/3	60.4
Residue base	1-(8-5)/3	32.8
Normalized yield	6/(6+8-5)	47.3
Solvent Incorporation	(6+8-5)/3-1	27.6

^aSee the above table for numbers

Extraction after soaking in phenol at high temperatures. DECS-16 raw and its PI were soaked in phenol at 200°C, filtered, and extracted with pyridine. Figure 3.1 shows results obtained using the 250 ml autoclave and the microreactor. Extraction yields of this coal were 42-47 wt%. Extractability obtained using the autoclave was 10-15 wt% higher than that obtained using the microreactor. This presumably stems from the better mixing of coal and phenol in the autoclave, where the contents were vigorously mixed with a continuous mode. The pyridine extraction yield of the raw coal (~ 25 wt% (daf)) was added to the yields for PI. Extractability of PI was 10-15 wt% lower than that of the whole portion of coal. This can be attributed to the influence of pyridine solubles which help solvate coal during soaking. The same effect was observed for high-temperature soaking in coal liquids at 350°C⁶¹. Retained phenol in PI, however, was lower than that in the whole coal.

It is not known whether retained phenol is physically or chemically incorporated after soaking under the conditions imposed. Although quantitative analysis is very difficult⁶², recovery of retained phenol was attempted to evaluate the extent of physical incorporation. Two separate tests were conducted. In one, the DECS-16 coal was soaked in phenol at 200°C and 250°C for 24 h and Soxhlet-extracted with pyridine. These pyridine extracts were vacuum-dried after evaporation of phenol and further Soxhlet-extracted with methanol for 3 d. Significant amounts of methanol solubles (22-35 wt% of pyridine extracts) were obtained, as shown in Table 3.3. Quantities of phenol retained in these samples were 12 and 15 wt%, respectively. Since methanol dissolves phenol but is a poor solvent for coal, these recoveries are remarkably high. Only a small portion of the methanol seems to be recovered with the above procedure, because phenol is strongly adsorbed on coal and its recovery is very difficult even with good solvents⁵⁷. The results demonstrate that a significant amount of phenol is physically retained after the soaking step.

Figure 3.1 Extraction yields and retention of phenol after soaking in phenol at 200°C for DECS-16 and its PI

Table 3.3 Recovery of retained phenol

(1)

DECS-16 coal	phenol	pyridine		
5.00 g	200°C			
	24 h			
			PS	2.23 g
			PI	3.74 g
			PS	2.00 g
			methanol	
			Soxhlet	
			3 d	
			solubles (35 %)	0.70 g
			insolubles	1.29 g
phenol content in solubles: 12 wt%				

(2)

DECS-16 coal	phenol	pyridine		
5.00 g	250°C			
	24 h			
			PS	3.37 g
			PI	2.41 g
			PS	2.00 g
			methanol	
			Soxhlet	
			3 d	
			solubles (22 %)	0.44 g
			insolubles	1.53 g
phenol content in solubles: 15 wt%				

In the second test, the effect of temperature on extractability was evaluated at 150-250°C using the autoclave for the same DECS-16 coal (*Figure 3.2*). Extractability increased with an increase in temperature, and reached 70 wt% at 250°C. Triethylamine (TEA, 0.5 ml) or TCNQ (0.5 g) was added to 2 g of the DECS-16 PI to evaluate the effect of electron donors and acceptors. TEA is a electron donor, while TCNQ is an electron acceptor. *Figure 3.3* shows the results obtained using the microreactor where the effects on extractability were positive.

In summary, high-volatile bituminous coal can be solvated by soaking in selected solvents at temperatures exceeding 200°C. Higher soaking temperatures increase solvation. The solvents, to a large extent, are physically incorporated during soaking. Electron donors and acceptors effectively solvate, but are strongly incorporated in coal. These results support the proposition that coal-coal complexes with charge-transfer interactions are solvated by replacement with coal-solvent complexes.

Figure 3.2 Extraction yields and retention of phenol after soaking in phenol at 150-250°C for DECS-16 coal

Figure 3.3 Extraction yields and retention of phenol after soaking in phenol added triethylamine (TEA) and TCNQ at 200°C for DECS-16 PI

Effects of coal rank and solvent. The effects of coal rank and retention of phenol on extractability were studied at 200°C using the microreactor. Extractability and retention slightly increased with an increase in the rank of the coal (Figure 3.4). More than 60 wt% of coals were extracted by adding TCNQ (coal/TCNQ = 2 g/0.5 g) regardless of the rank of coal, but phenol retention was significant for medium-volatile bituminous DECS-3 coal. The DECS-16 coal was soaked in other electron donor and acceptor solvents at 200°C, and extracted with pyridine. Solvents used were pyridine, NMP/CS₂ (1/1 v/v), and *n*-butylamine (Figure 3.5). Pyridine was not effective for solubilization but TCNQ (coal/TCNQ = 2 g/0.5 g) was effective for all solvents. Since phenol and butylamine were retained to a smaller extent but effective for solubilization, the coal was soaked in this mixture under the same conditions and Soxhlet-extracted with pyridine. Figure 3.6 shows pyridine extractability after soaking in the mixed solvent. A synergetic effect on solvation was found. This presumably results from the effects of electron acceptor (phenol) and donor (butylamine). The synergetic effect cannot be explained by a chemical reaction during soaking at 200°C, therefore, this result supports the proposed solvation mechanism to break the coal-coal charge transfer complexes.

Figure 3.4 Retention of phenol on various ranks of raw coals after soaking at 200°C

Figure 3.5 Pyridine extraction yields and solvent retention after soaking in various solvents with and without TCNQ at 200°C for DECS-16 coal

Figure 3.6 Pyridine extraction yields of DECS-16 coal after soaking in phenol and *n*-butylamine mixed solvent at 200°C

4. The Association Model of Coal Structure

Introduction

The solvent-induced association of high-volatile bituminous coal^{7,8} is a consequence of relatively strong interactions. This association suggests an irreversibility of solvent swelling of coal since coal molecules tend to dissociate, rearrange and reassociate in the lower free energy conformation during soaking. The conventional procedure for determining volumetric swelling was carefully applied to evaluate the potential reversibility of coal swelling¹⁵. Irreversibility of solvent swelling was observed, in contrast with that previously reported. Two different ranks of coal showed distinctly different responses.

As discussed in the previous section, swelling ratios of coal and its pyridine insolubles (PI) are highly dependent on coal concentration. The intrinsic swelling ratio $[Q]$, independent of coal concentration, was consistently more than two times larger than the conventional value Q .

Relatively strong interactions must also be considered as probable 'cross-links'. Since disruption energies of physical associations and covalent bonds generally differ by one to two orders of magnitude, a clear distinction between the covalently bonded (chemical) cross-links and relatively strong secondary interactions (physical cross-links) is necessary for effective coal utilization. Physical and chemical cross-links can be estimated by the dependence of coal concentration on the swelling of fractionated samples. Pyridine solubles (PS) swell in a poorer solvent than pyridine, indicating that associated sites in PS behave as physical cross-links. Physical cross-links show dissociative equilibria under certain conditions. Since it is thought that associated sites partially dissociate at lower coal concentrations, enormous numbers of equilibrium states are possible for the PS. If the PI is cross-linked both physically and chemically, the PI should exhibit dissociative equilibria. Possible equilibrium states, however, are much fewer than those of the PS extract. This means that swelling of the PI is enhanced at low sample concentrations, but the enhancement is less than that of the PS.

Physical cross-links are solvated to some extent under certain conditions, but molecular size must be considered as an important factor for solubilization. Since the average molecular size of the PI is larger than that of the PS, apparent molecular weight between crosslinks in the

Table 4.1 Comparison of predicted solvent swelling behavior for the network and the associated models of coal.

Solvent swelling behavior	network	associated model
1 Reswelling	reversible	irreversible
2 Dependence of coal concentration	none or small	significant
3 Dependence of coal concentration for fractionated samples	significantly different	similar
4 Dependence of fractionation on swelling ratio (Q)	$Q_{\text{solubles}} > Q_{\text{insolubles}}$	$Q_{\text{solubles}} < Q_{\text{insolubles}}$
5 Dependence on solvent for fractionated samples	larger for solubles than insolubles	larger for insolubles than solubles

PI is greater than that in the PS. Therefore, it can be confidently predicted that the swelling value of the PI is larger than that of the PS.

A better solvent can disrupt more physical cross-links than a poorer solvent. Therefore, the swelling ratio of the PI is consistently larger than that of the PS when a better solvent is used. The differences in swelling between the network and associated models are compared in *Table 4.1*¹⁶. All results¹⁴⁻¹⁶ support the importance of relatively strong interactions in coal projected by the associated model.

If significant portions of coal molecules are physically associated, coal should be solubilized under proper conditions. As shown in the previous section, extraction or solubilization of associated high-volatile bituminous coal has been studied. Assuming strong interactions among the molecules, temperatures of $> 200^{\circ}\text{C}$ was selected for soaking to solvate the complexes. Although a high degree of extractability was shown, significant amounts of the solvents used for soaking were physically incorporated. These results support the proposition that coal-coal complexes with charge-transfer interactions are solvated by replacement with coal-solvent complexes. If the procedure is a physical process, associative/dissociative equilibria should be observed using the same soaking procedure. To corroborate this assumption, associative/dissociative equilibria during soaking was studied in this section.

Experimental

DECS-16 coal was obtained from the DOE Coal Bank at the Pennsylvania State University. Its ultimate analyses was shown in *Table 3.1*. All reagents and solvents were obtained from Aldrich Chemical Co. (Milwaukee, WI) and Fisher Scientific (Pittsburgh, PA), and HPLC-grade solvents used without further purification.

Coal samples and solvents (50 ml) were charged to a 250 ml autoclave (Model 4576; Parr Instrument Co., Moline, IL), and purged with N₂ (100 psi, @25°C). The autoclave was heated at desired temperatures for 24 h, while the contents were stirred at 500 rpm. After soaking, the contents of the reactor were washed with the same solvent into a beaker and filtered through a preweighed thimble. The residues were Soxhlet-extracted with pyridine for 24 h. The solvent was largely removed with a rotary evaporator then in a dish heated on a hot plate at 130°C. Purging was accomplished with air when phenol was used for treatment. Residues and extracts were dried at 95°C overnight. Detailed treatment procedures are shown in *Table 4.2*.

Elemental analyses of treated coals were conducted by Geochemical Testing (Somerset, PA).

Table 4.2 Change in extractability of DECS-16 coal by soaking with phenol and toluene

(1) (See Figure 4.1)

(2) (See Figure 4.2)

(3) (See Figure 4.3)

Key: PS; pyridine solubles, PI; pyridine insolubles

Results and Discussion

In the previous section, it was shown that a significant amount of phenol was physically incorporated after soaking at 200-250°C, and that some of the retained phenol was recovered by washing with methanol. The following mechanism was proposed: Coal-coal complexes with charge-transfer interactions are solvated by replacement with coal-solvent complexes. Therefore, if phenol is removed with methanol, a portion of the coal-phenol complexes originally soluble in pyridine may become insoluble.

The DECS-16 coal was soaked in phenol at 200°C for 24 h then extracted with pyridine. The dried pyridine solubles (PS-1) obtained from extraction were Soxhlet-extracted with methanol for 5 days and then with pyridine for 24 h (see *Table 4.2 (1)* and *Figure 4.1*). Some pyridine insolubles (PI-2; 8 wt%) were observed. All of the PS-1 fraction was easily extractable with pyridine before the washing step, therefore, the amount of insolubles after treatment is small but significant. This demonstrates associative/dissociative equilibria and supports the proposed mechanism.

Figure 4.1 Change in a soluble portion by rinsing with methanol for pyridine extract from DECS-16 coal soaked in phenol at 200°C

Two additional experiments have been conducted to evaluate associative/dissociative equilibria. As shown in the previous section, a large portion (70 wt%) of the DECS-16 coal was extractable with pyridine after soaking in phenol at 250°C. The pyridine solubles (PS-1, see *Table 4.2* (2)) obtained from this treatment were soaked in toluene under the same conditions used for phenol soaking. Approximately 60 wt% of these pyridine solubles changed to pyridine insolubles by soaking in toluene. The amount of pyridine solubles (PS-2) was nearly equal to that of the raw coal (*Figure 4.2*). We conclude that a portion of the retained phenol has been released from phenol-coal complexes during soaking in toluene, and that the solubilized part (forming phenol-coal complexes) has become insoluble. The mixture of PS-2 and PI-2 was again soaked in phenol under the same conditions. Most (~90 wt%) of this mixture became soluble again. A small portion of the mixture was not solubilized, presumably due to difficult resolubilization characteristic of solvent-induced associates^{7,8}.

In another test, the coal was recovered by precipitation in methanol after soaking in phenol due to problems involving isolation of coal from the mixture. The recovered coal (Coal-2, see *Table 4.2* (3)) was then soaked in the same fashion in toluene. The treated coal was recovered by precipitation in methanol (Coal-3). The coal treated with toluene was once more soaked in phenol under the same condition, and Coal-4 was recovered. Pyridine extractability of these coal samples was measured with results shown in *Figure 4.3*. Methanol solubles during precipitation in methanol were not determined. Again, the coal was largely solubilized by soaking in phenol and insolubilized by soaking in toluene. The difference in pyridine extractability between the above and these latest experiments (*Figures 4.2* and *4.3*) stems from the small retention of phenol and the quantity of methanol solubles in the latter experiment. Coal-3 was less solubilized than the mixture of PS-2 and PI-2 (*Figure 4.2*) under the same treatment. Coal occludes associates by soaking in poor solvents (solvent-induced association). The average molecular weights of the associates are larger for Coal-3 than the mixture of PS-2 and PI-2, since average molecular weights of pyridine insolubles are larger than those of pyridine solubles. This would make solubilization difficult, although coal-phenol complexes are partially replaced by coal-coal complexes during soaking in phenol. *Table 4.3* shows elemental analyses of these samples from Coal-1 to Coal 4. Incorporation of phenol in Coal-2 is apparently larger than that for other samples, because of the higher quantity of oxygen. If this is accepted, aromaticity and quantities of other elements are similar among samples Coal-2, Coal-3, and Coal-4.

Figure 4.2 Associative equilibria in toluene and phenol at 250°C for pyridine solubles from DECS-16 coal

Figure 4.3 Associative equilibria in toluene and phenol at 250°C for DECS-16 coal

Table 4.3 Elemental analysis of samples from treatment (2) in *Table 4.1*

Sample	Element wt% (daf)					H/C
	C	H	N	S	O (diff) atom/atom	
Coal-1	80.7	6.1	1.5	0.5	11.2	0.91
Coal-2	76.6	5.0	1.6	0.5	16.3	0.78
Coal-3	81.8	4.6	1.6	0.4	11.6	0.67
Coal-4	81.3	4.7	1.7	0.7	11.7	0.69

Conclusion

The above results support associative/dissociative equilibria during soaking under the condition used in this study. Therefore, the proposed mechanism of associative/dissociative equilibria and high extractability (up to 70 wt%) observed are consistent with the associated model of coal.

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