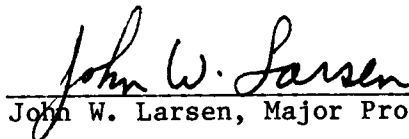
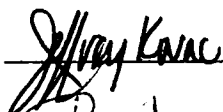
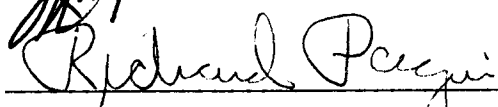
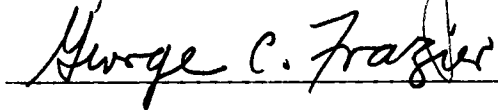


To the Graduate Council:

I am submitting herewith a dissertation written by Thomas K. Green entitled "The Macromolecular Structure of Coal." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.


John W. Larsen, Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:


The Graduate School

THE MACROMOLECULAR STRUCTURE OF COAL

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Thomas K. Green

June 1984

DEDICATION

To my Father and Mother.

ACKNOWLEDGMENT

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This work is dedicated to my family, especially my father and mother.

ABSTRACT

Coals are considered to be three-dimensionally covalently crosslinked macromolecular networks. Solvent swelling techniques, modern polymer theories, and regular solution theory are applied to two bituminous coals in an effort to estimate their crosslink densities. The coals are observed to be extensively, internally hydrogen bonded. The hydrogen bonds serve as crosslinks between the macromolecular chains and contribute substantially to the structural integrity of the coals. Both coals obey the predictions of regular solution theory and their nonpolar solubility parameters (δ) are estimated to be $9.5 \text{ (cal/cm}^3)^{1/2}$. Flory interaction parameters (χ) were calculated for a series of nonpolar solvent-coal pairs. The Flory-Rehner and Kovac equations were then applied to the available data to estimate the crosslink densities of the coals.

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CHAPTER I

INTRODUCTION

Coal chemistry can be divided roughly into three areas: (1) development of conversion processes, (2) studies of the chemistry of these processes, and (3) determination of coal structure. This dissertation falls into the last category. Specifically, this is an investigation of the macromolecular structure of coal. Before expanding on this subject, it is appropriate to provide a brief historical perspective on this important natural resource.

Coal is the most abundant fossil fuel in the United States, comprising 75% of our total reserves.¹ During the nineteenth century coal consumption increased dramatically in this country with a corresponding decrease in wood consumption. After the turn of the century, however, coal consumption exhibited a marked decline, the major reason for this being the increased availability of cheap, convenient, fluid fuels such as petroleum and natural gas.

In the future, however, foreign suppliers of fluid fuels may become less reliable. Discovery and extraction of these fuels in this country were expected to become more difficult and, ultimately, the world will run out of fluid fuel. For these reasons, coal may again become the major source of energy. In fact, the United States is expected to derive 34% of its energy needs from coal by the year 2000 compared with only 18% in 1977.² If this prediction is accurate, it is imperative that further research aimed at more efficient and environmentally sound utilization of our coal reserves be conducted.

From a chemist's viewpoint, coal is a very complex material. Much of its chemical and physical structure has not been elucidated. Although it seems likely that a better understanding of the nature of coal would lead to its more efficient utilization, it can be argued that conversion processes have been successfully developed with little understanding of the operative chemistry. This, however, does not necessarily diminish the significance of fundamental coal research. Optimization of any process will be difficult if the chemistry of that process is not well understood. This could lead to much time and effort being wasted trying to improve a process that cannot, in principle, be improved. Thus, further research on coal structure is justified based on the practical requirements for the utilization of this resource.

The intellectual challenge of a very difficult, complex problem is another justification for investigating coal structure. The simple desire to understand the world we live in, in this case to understand the nature of coal, provides a strong driving force for this research.

In this dissertation we attacked the problem of coal structure with the premise that coals are covalently crosslinked macromolecular networks. The nature of the network will govern its mechanical properties, diffusion of reagents through coal, coal swelling, and some aspects of coal reactivity. Thus, any information gained about the nature of the network will be useful in predicting its behavior. One of the most important structural characteristics of the network is the extent of crosslinking. Are the crosslinks frequent, giving a tight, nonflexible network; or are they far apart, giving a relatively

flexible network? Classical polymer techniques provide an approach to solving this problem.

The principal experimental technique used in this study was solvent swelling. The insoluble portion of the coal was exposed to pure solvent and allowed to swell. The amount of solvent absorbed by the coal at equilibrium was measured. The theories of rubber elasticity, polymer solutions and regular solutions were then applied to the swelling data in an effort to estimate the extent of crosslinking of the coal. Although there are inherent limitations in the application of these theories to coals, we believe the effort to be surprisingly successful.

CHAPTER II

COAL STRUCTURES

A. Overview

Coal is an organic rock originating from a variety of plants and minerals.³⁻⁵ This complex mix of organic and inorganic constituents was deposited in swamps, subjected to microbial decomposition, and eventually buried. As the depth of burial increased, so did the temperature and pressure. This resulted in further chemical and physical changes, most notably a decrease in moisture content and an increase in the carbon content. This process is termed coalification. The organic substances derived from the different plant tissues are termed macerals. Since each maceral originated from chemically dissimilar materials, each responded to coalification differently. Complicating the picture even more is the presence of the inorganic substances or minerals that entered the swamp either as particulate matter or dissolved ions.

Coals are enormously complex, and this dissertation will not deal with all aspects of coal structure. The concern is with the organic portion of coals. Furthermore, the discussion is limited to high vitrinite coals since most coals contain more than 50% of this maceral (commonly 75-80%).³ Vitrinite is thought to originate from the higher plant components lignin and cellulose. The use of vitrinite coals will also simplify the interpretation of the results since the material studied will be much more homogeneous. The major elements in

vitritinite are carbon, hydrogen, and oxygen, with lesser amounts of sulfur and nitrogen.

Coal is a macromolecular solid.⁶⁻⁸ Even degraded coals have enormous molecular weights, often on the order of 10^5 .⁹ Coal is not an ordinary polymer in the sense that there exists a structural repeating unit. However, the existence of largely aromatic and hydroaromatic condensed ring structures as suggested by x-ray and degradation studies is accepted.¹⁰ The molecular weights of the clusters, linked together by aliphatic bridges and occasional ether bridges, are thought to be in the lower hundreds. Several "average" structures of coal molecules, derived from a considerable amount of physical and chemical data too numerous to outline here, have been published. The most popular models have been the Given Model¹¹ (Figure 1) and the Wiser Model¹² (Figure 2). A more recent model has been proposed by Heredy and Wender.¹³ It should be emphasized that these models do not represent coal structure per se. They are collections of the types of structures thought to be present in coals arranged in such a way as to satisfy the physical and chemical data that has been accumulated.

There is evidence that the macromolecules in coals are three-dimensionally crosslinked. For example, coals exhibit elastic properties.^{6,14-17} When subjected to a stress, a coal will stretch for a time and then remain at constant length. When the stress is removed, the coal will return to its original length. This type of behavior is consistent with a three-dimensionally crosslinked macromolecular solid.¹⁸ Coal will also swell in organic solvents without dissolving.¹⁹ Pyridine, a good solvent for coals, will extract at

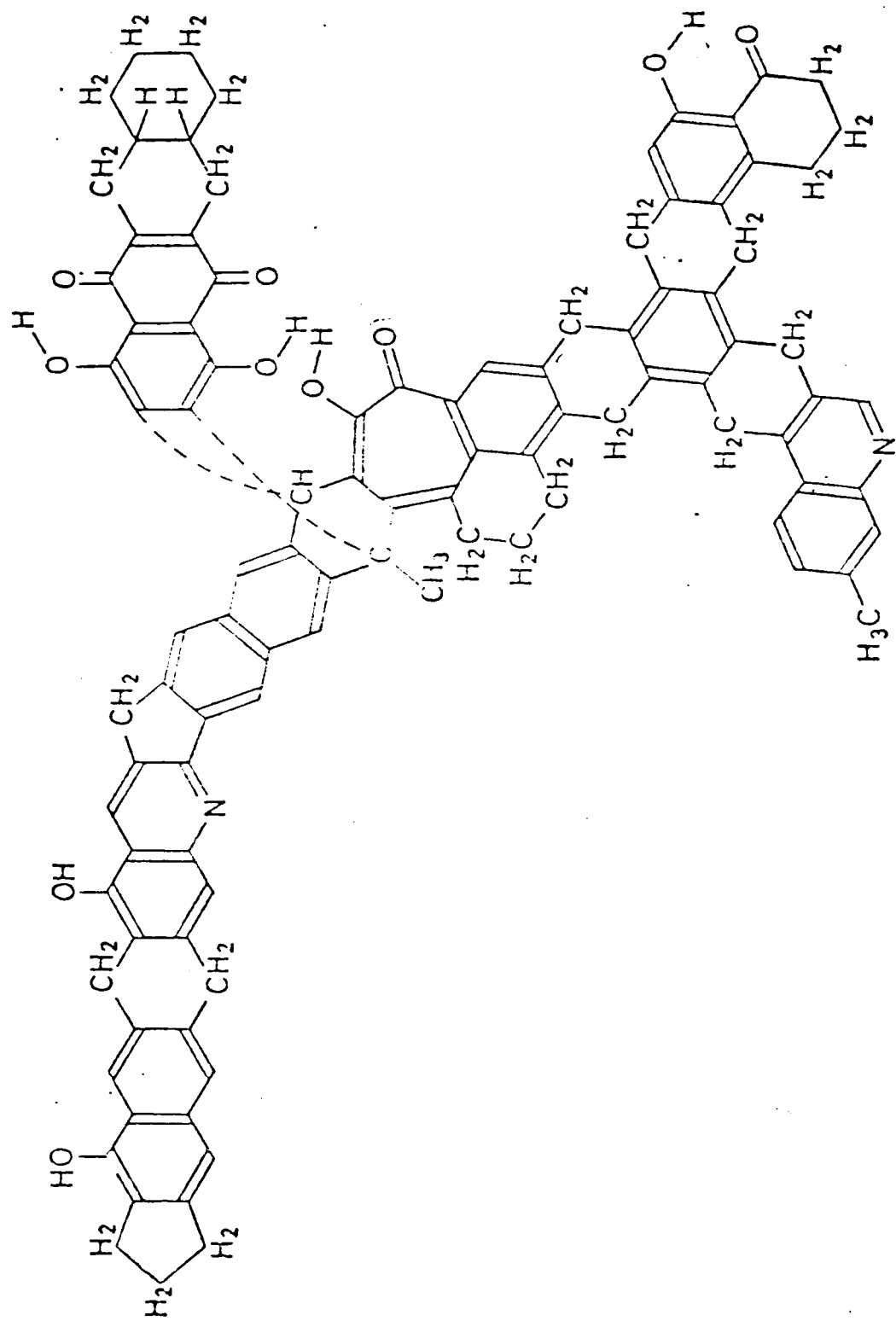


Figure 1. Given Model of Coal Structure.11

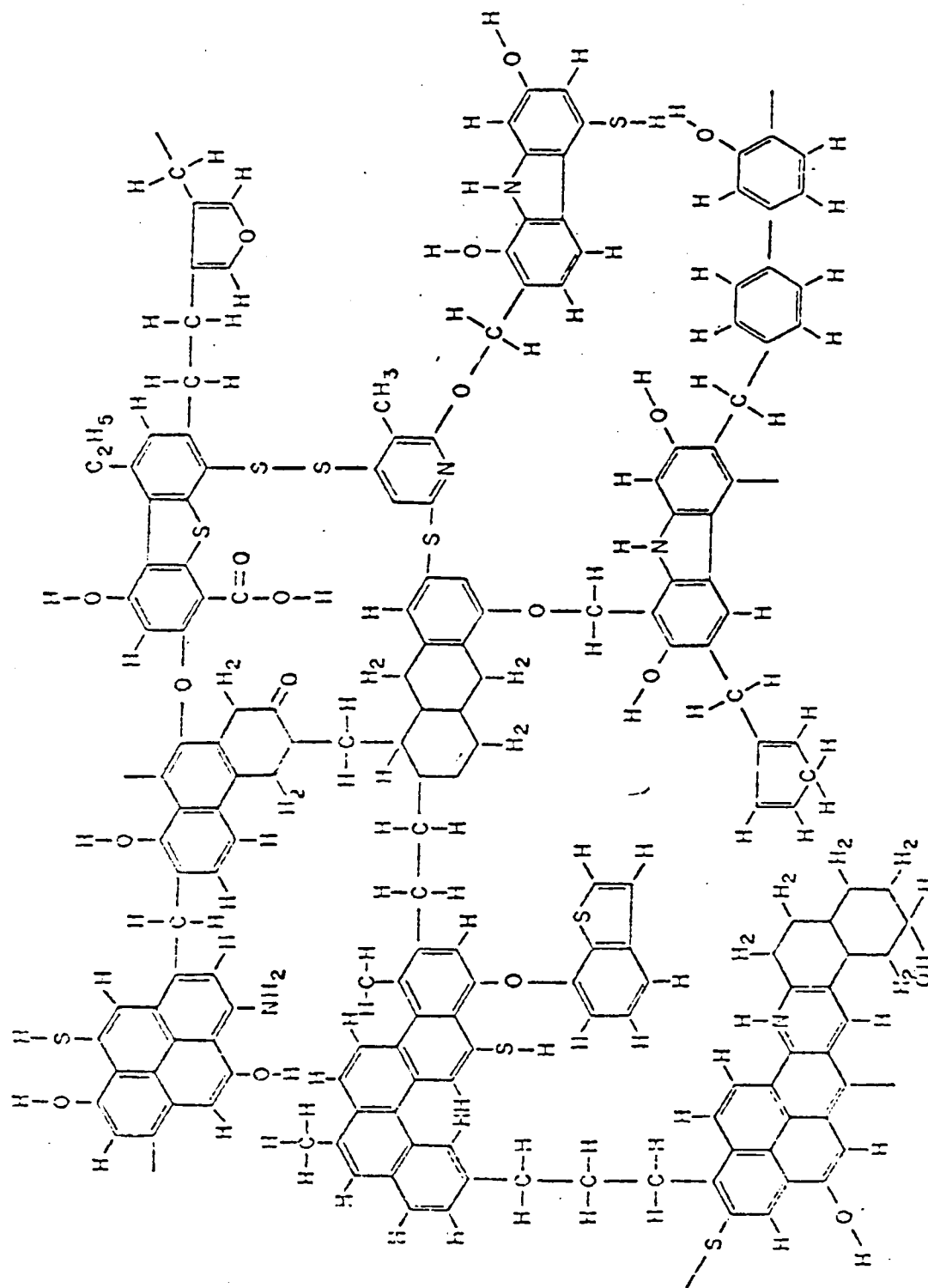


Figure 2. Wisner Model of Coal Structure.

most about 20% of coal while swelling them to more than double their original volume. Clearly, there are strong associative forces holding the macromolecules together. The view adopted in this dissertation is that the macromolecules are covalently crosslinked. Hydrogen bonds, π - π interactions and entanglements may be present as well.

Several macromolecular structural models have been described in the literature. We will describe four models that have been most popular.²⁰ They differ in many aspects, the most important for present purposes being the nature of the forces that hold the macromolecules together. The models are (1) the micelle model, (2) the Sternberg model, (3) the entanglement model, and (4) the three-dimensionally crosslinked macromolecular model. The experimental evidence for the formulation of these models will be discussed and reviewed.

B. The Micelle Model

Historically, micelle models for coal evolved from extraction studies. Early investigators believed that the solutions obtained from these low temperature extractions were colloidal in nature, although recent work has cast doubt on some of these beliefs. The intrinsic viscosity measurements of Boas-Traube and Dryden on ethylenediamine extracts indicated more or less spherical particles of colloidal dimensions.²¹ Kann, using microscopic and light-scattering measurements, estimated these particles to be 200 Å to 700 Å in diameter.²² Evidence for a striking similarity in chemical composition between the solubles and the parent coal exists.²³⁻²⁸ This led to the general

hypothesis among several investigators that the insoluble coal matrix also consisted of micellar units.

Kreulen was perhaps the first to discuss solutions containing coal extracts from the standpoint of colloid chemistry.⁹ He called these solutions organosols, which consisted of a dispersion medium and a micelle phase. The dispersion medium was thought to consist of the solvent along with the molecularly dissolved portion of the coal (oily bitumen). The micelle phase includes an oleophobic nucleus consisting of humins and an oleophilic protective body consisting of bitumen. There is an intimate coherence between the protective bodies and the nucleus. The stability of such a system, Kreulen believed, is governed by the micelle-medium interfacial tension. The yield of extract then should increase with increasing surface tension of the extraction solvent. Kreulen's own extraction studies with xylene, monochlorobenzene, nitrobenzene, and dioxane were in accordance with this view. Furthermore, flocculation of the dispersed micelle phase should occur upon addition of a solvent of surface tension lower than that of the extractor medium. Kreulen points to Wheeler's extraction scheme to verify this conclusion.³⁰

Probably the most striking conclusion of Kreulen's studies is that the bitumens were derived from humic acids after the coal stage had been reached. This is supported by his own successful transformation of Dopplerite, considered to be pure humic acids, into bitumens. This transformation was accomplished by simply heating the Dopplerite in the presence of benzene to high temperature (~300°C) in an autoclave. As he states, coal may be looked upon "as a closed system

of more or less bitumenised humics."²⁹ This statement implies that Kreulen believed coals can be viewed as micellar structures in which the micelles are dispersed in an oily medium.

Bangham, assuming spherical micelles as the basic structural units of coal, derived a simple model that reproduces some physical properties of bright bituminous coals.³¹ He cites evidence that suggests that extracts in pyridine are dispersions of particles on the order of 10^{-10} Å in diameter.³²⁻³⁴ Electron micrographs of humic acids from oxidation of coal also suggest the existence of structural units on the order of 100 Å in diameter. From heats of wetting experiments with methanol, Bangham calculates surface area to volume ratios for coal. Assuming micelles of equal size and shape (spherical), he obtains a unit size of 230 Å. Units of this size pack together to leave an accessible surface area equal to that calculated in the methanol absorption data. Since grinding experiments failed to yield a particle with a smaller diameter, the micelles were considered to be highly stable. As rank increases, compaction of the micelle increases. This is used as a rationale to explain a decrease in the heat of wetting with methanol as rank goes up (accessible surface area goes down).

Based on this model, Bangham derives theoretical porosities, internal surface areas and pore constriction diameters for varying degrees of compaction. He compares these with experimental data for three coals of different ranks. Calculated values of porosity and internal surface area generally agree with the ranges found experimentally for coals. Calculated pore size constrictions approach

molecular sizes at high degrees of compaction, in agreement with observations that coals can function as molecular sieves.

Bangham's premise that there is an "orderliness of structures which alone can account for the remarkable consistency of its physical properties"³¹ leads him to presuppose a basic structural unit in coals. This approach is probably too simplistic since chemical changes during coalification are ignored. Variations in heats of wetting could be due in part to changes in chemical composition rather than degree of compaction of micelle units. For example, the population and distribution of oxygen containing functional groups will play a very important role in the heats of wetting by methanol. Thus, any estimation of micelle unit size from these data could be grossly in error.

Bangham's micellar model for coal is clearly described by Bangham and Berkowitz in a paper that reports that coal particles placed under pressure under a microscope slide deform and aggregate.³⁵ This behavior is ascribed to flow caused by shearing along the boundaries between micelles, which are associated only by van der Waals forces. This is a reasonable explanation, if one believes the micellar structure. But, as pointed out by Bangham, metals, ionic lattices, molecular crystals and fibers show this behavior. Thus the existence of this behavior cannot be taken as evidence for a micellar structure. It is just as valid for an ionic structure as it is for a micellar structure. Berkowitz has used the micellar model to explain the coking of coals.^{36,37} He suggested that softening is due to increasing mobility of micelles with increasing temperature and swelling due to the effect of trapped gases. It is hard to visualize any van der Waals

forces strong enough to remain an effective associative force at temperatures above 350°C. Why, when thermal energy is much much greater than the associative forces between micelles, do coals not lose all cohesion between the tiny (200 Å) micelles and flow? Only molecules held together by covalent bonds will maintain their structural integrity as well as coals do at high temperatures.

Dryden's coal model includes an insoluble matrix consisting of large and strongly linked micelles in intimate association with smaller, less strongly linked micelles.³⁸ The smaller micelles can only be extracted if the coal matrix is first swollen by an appropriate solvent. The extraction process then involves the diffusion of the individual micelles through the swollen pores of the matrix. Evidence for such a model comes from extraction studies of coal with the specific amine solvent, ethylenediamine.³⁹ Dryden found a proportionality between the amount of imbibed (absorbed) solvent and the extraction yield at room temperature. This can be qualitatively explained if it is assumed that solvent is imbibed between larger units that constitute the insoluble residue. The size of the spaces between the larger units increases with the degree of imbibition and the smaller units escape from the matrix. If a continuous distribution of unit sizes is postulated, then the gradual increase in yield due to increases in temperature or the use of a more powerful solvent can be qualitatively explained.

Fundamental to Dryden's model is the evidence that ethylenediamine solutions are colloidal in nature.²⁵ Several experiments, including precipitation by non-solvent, dialysis, chromatography, and

electrophoresis, lend support to this conclusion. Plots of the amount of extract precipitated versus the volume of non-solvent added, if interpreted in terms of the theoretical expressions of Schulz for polymers,⁴⁰ suggest a continuous size distribution of comparatively homogeneous material. Dialysis experiments indicate that not more than about 10% of the extract passes through a cellophane membrane, indicating a high proportion of large molecules or micelles. Strong adsorption of extracts on chromatographic columns, their tendency to elute without separating into discrete bands, and their low mobility in electrophoresis experiments indicate a wide and fairly continuous distribution of micellar sizes. Circumstantial evidence is provided that indicates the dimilarity between residues and extract.²⁵ The heats of wetting of solid coal extract and the undissolved residue show that their surface areas, and therefore probably their ultrafine physical structure, are very similar. This is important to Dryden's model; for if the extraction process separates coal units on the basis of size, rather than kind, the extracts and residues would be expected to be similar in type.

Dryden's work with ethylenediamine as extraction solvent raises an important question. Why are the extracts colloidal in nature? There is recent evidence that ethylenediamine cleaves bonds in coal.⁴¹ If this is true, then the colloidal material may simply be large coal molecules that have been cleaved from the parent structure.

Brown and Waters believed that micelles in the solid state were interlinked by hydrogen bonds and weaker van der Waals forces.⁴² The hydrogen bonding is superseded by van der Waals forces as rank

increases because oxygen containing groups are progressively eliminated during coalification. The micelles of the lower rank coals are therefore held together in a relatively open structure. With increasing rank, crosslinking is less extensive, permitting greater freedom of movement of the micelles; the rigid gel structure degenerates into a sol type of structure accompanied by better packing of micelles. This model is used to explain the mechanism of thermal softening among numerous other properties of coal.

The Brown and Waters model is similar to that of Kreulen's.²⁹ The essential feature includes (1) oily and solid bitumens, (2) humins of colloidal dimensions (MW ~600), and (3) humins of macromolecular size representing the insoluble portion. They suggest the following mechanism for thermal softening. The bitumens, when sufficiently mobile, solvate the humins, thereby weakening the intermicellar bonds and permitting greater movement of the micelles. Above 300°C, the heat and solvent effect of the bitumens cause the humins of colloidal dimension to dissociate from the matrix. At 350°C, corresponding to the "gel point," the larger micelles are dispersed in or superseded by the smaller micelles and bitumens. The gel matrix disintegrates into a sol and the whole coal exhibits fluid properties.

Neavel⁴³ has derived a model of coal plasticity incorporating much of the Brown and Waters model. There is one important difference however; the Neavel model includes as a necessary step for plastic development the thermal rupture of covalent bonds between bridged stable molecular units. Removal of these bitumens reduces plastic capability because repolymerization becomes the dominant fate of free

radicals in the absence of the hydrogen donor. A close relationship between the plasticity mechanism and the liquefaction of coals is clearly recognized.

The existence of covalent crosslinks in coals also helps to explain coal solubility. If hydrogen bonds and van der Waals forces were the sole associative forces between the micelles, any solvent whose energetics rival the coal-coal interactions should dissolve them. It is hard to visualize hydrogen bonds as a significant associative force between coal molecules in the presence of pyridine, an excellent hydrogen bond accepting solvent.^{44,45} It is likely that covalent crosslinks ultimately prevent dissolution of the coal molecules.

C. The Sternberg Model

Sternberg thought coal consisted largely of a mixture of macromolecules with a broad range of sizes held together by dispersion forces and hydrogen bonds.⁴⁶⁻⁴⁹ The model was derived from studies on the solubility characteristics of a reductively alkylated coals.^{46,47} This reaction introduces alkyl groups onto the aromatic portion of coals. The procedure involved treating the coal with an alkali metal forming the "coal anion" followed by alkylation of the anion by an alkyl halide. The reaction dramatically increased the benzene solubility of the coal. The number average molecular weight of the benzene-soluble portion was in the lower thousands with practically no material above 20,000. Sternberg felt the increase solubility was due primarily to disruption of the stacking interactions of the

aromatic clusters by the bulky alkyl substituents. Any hydrogen bond interactions would also be disrupted since the phenolic hydroxyl groups were O-alkylated as well. Thus the soluble products were thought to be representative of the original coal molecules.

Sternberg recognized that extensive ether cleavage was occurring as well, but he did not believe that ether cleavage alone was sufficient to produce a benzene soluble product. In support of this was the fact that simple protonation of the coal anion by an appropriate donor gave a product only 3% soluble in benzene. By contrast, alkylation of the coal anion yielded a product 95% soluble in benzene. Thus, the alkylation step was necessary to render the coal soluble.

Much more is now known about this reaction and it appears that the chemistry is more complex than originally suggested by Sternberg. Besides cleavage of ether bonds, carbon-carbon bond cleavage and elimination reactions occur as well.⁵⁰⁻⁵² Hence, the increased solubility of the alkylated coal could be due, in part, to cleavage of carbon-carbon bonds. The products would therefore represent molecular fragments and not the original coal molecules.

A separate study on the solubility characteristics of coal-derived asphaltenes led Sternberg to propose the acid-base structure for coals.⁴⁷ Asphaltenes are operationally defined as being soluble in benzene and insoluble in pentane. The asphaltenes were isolated from coal liquefaction by the Synthoill process.⁵³ The asphaltenes could be separated into acidic and basic components. The acidic component contained phenolic and pyrolic hydrogen, whereas the basic component contained ether oxygen and pyridinium nitrogen. Furthermore,

the acidic component contained all of the exchangeable protons and the basic component contained none. This precluded the possibility of the asphaltenes having an amphoteric nature. These results suggested that the original coal may have had an acid-base structure as well and that the acidic and basic functional groups were not randomly distributed in the coal as previously believed. If true, the hydrogen bond complexes might represent an important associative force between coal molecules and would have to be disrupted before they could be rendered soluble.

The experimental work appears to confirm the acid-base nature of the asphaltenes. Extrapolation of the results to coal structure is more risky. The conditions used to produce the asphaltenes were quite harsh. Significant chemical changes in molecular structure probably occurred. However, the results suggest the existence of hydrogen bond complexes in coal and point to a need for further investigations.

D. The Entanglement Model

Hombach argues in a series of papers⁵⁴⁻⁵⁷ that coal is made up of highly entangled linear macromolecules. Evidence for such a model comes from a study of the molecular weight distribution of products from two dissimilar reactions. The molecular weight distributions were determined by ultrafiltration and ultracentrifugation. The reactions were the Friedal-Crafts acylation⁵⁸ and the Sternberg reductive alkylation.⁴⁶ The molecular weight distribution of the products were very similar, with most of them having molecular weights above 10^5 . Hombach proposes that such similar molecular weight distributions from such dissimilar reactions could not originate from chemical change

wrought upon the coal. He thought that the reactions simply solubilized the coal molecules and that the molecular weight distributions observed were those of coal molecules plus added groups. As a result, Hombach concludes that coal is made up of highly entangled linear macromolecules.

This argument is weakened if either of the reactions cleaves bonds in coal. The Sternberg reductive alkylation has been found to cleave ether linkages as well as some carbon-carbon bonds in coals.⁵⁰⁻⁵² Consequently, the observed molecular weight distribution of the soluble products from this reaction is that of a depolymerized coal, not simply that of the parent coal macromolecules plus added groups. Much less is known about the chemistry of the Friedel-Craft acylation of coals.

Berkowitz⁵⁹ claims that some degree of entanglement must exist in coals since coal residues obtained from exhaustive extraction with pyridine continued to be extracted with pyridine when added by ultrasonic vibration. However, these results contradict those of Dryden,³⁹ who found that the rate but not the extent of ethylenediamine extraction of coals was affected by ultrasonics. Finally, Tsuboi and coworkers have recently examined the rate of extraction of a Japanese coal.⁶⁰ They found that the rate of extraction was considerably enhanced with ultrasonic irradiation. Moreover, the ESR, IR, and NMR spectra of the coal extracts indicated cleavage of weak bonds in the coal. As a consequence, any conclusions drawn from ultrasonic experiments about the existence of entanglements in coals must take into account the possibility of covalent bond cleavage.

Given the enormous molecular weights of degraded coals as determined by Hombach,⁹ it seems likely that entanglements surely exist in coals. Whether entanglements alone can account for the general insoluble nature of coals is another matter. Hombach argues that the insoluble nature of coal is not sufficient reason to conclude that coal is a three-dimensionally crosslinked structure since, in the future, it may be possible to find a suitable solvent or solvent mixture that will dissolve coal.⁹ Nevertheless, if coal were principally made up of entangled molecules and not covalently crosslinked, a good solvent, given time, should eventually dissolve it. Pyridine-extracted coal residues exposed to pyridine for one and a half years show no sign of further dissolution.⁶¹ An extraordinarily high degree of entanglement would have to be accepted in order to explain these results.

E. The Three-dimensionally Crosslinked Macromolecular Model

Vahrman sees coal as consisting of both an insoluble three-dimensional matrix of large molecules and potentially soluble portion consisting of smaller molecules.⁶² The smaller molecules are inclusions in a macro-micro pore system that penetrates the coal matrix.⁶³⁻⁶⁴ A large portion of these molecules are adsorbed in pores of molecular size. All molecules are not equally accessible. Rather, some residue in pores of narrow diameter and others lie "loose" in pores of larger diameter. Thus, their relative accessibilities can be defined in terms of their disposition in the macro-micro pore system.

The evidence for such a model was derived initially from prolonged extraction studies of a bituminous coal with ethanol and benzene (250 hr).⁶⁵ The sequence of emergence of different hydrocarbon fractions was determined. Vahrman found that molecular size and preferential solubilities were not the major factors controlling the sequence of emergence. In fact, under mild soxhlet extraction conditions, the majority of the molecules with large critical dimensions emerged early. He rationalized that these molecules must lie in pores of large diameter. The solvent penetrates these pores quite easily and solubilizes the molecule. Molecules extracted with difficulty supposedly lie in narrow pores, to which penetration of the solvent is slow.

Two important ideas concerning coal structure emerge from Vahrman's work. First, coal consists primarily of an insoluble matrix or residue along with a substantial portion of smaller molecules. Second, the smaller molecules lie in the macro-micro pore system of the coal. It appears that much of this material is in pores too narrow to permit easy access by the extraction solvent and cannot be physically separated from the residue under the ordinary mild extraction conditions.

That coal is an insoluble matrix with substantial amounts of smaller molecules is a point of general agreement. It is Vahrman's second conclusion that remains open to question: Do all the smaller molecules necessarily reside in the pore system, or could they be trapped in the coal matrix itself rather than the pores? Wiser,⁶⁶ for example, extracted coals first with benzene and then with

pyridine. The amount of benzene soluble material in the pyridine extract was larger than the amount of benzene extract, yet the compositions of the two benzene-soluble portions were the same. Therefore, benzene alone could not extract all the benzene soluble material. Pyridine swells the coal matrix and allows removal of "trapped" benzene soluble. This is an alternative and more satisfactory mechanism for extraction of the smaller molecules.

van Krevelen uses a three-dimensionally crosslinked macromolecular model in his interpretation of the coalification process.⁶⁷ The coalification process is treated as a polycondensation reaction according to the theory worked out by Flory.⁶⁸ van Krevelen starts by assuming that the peat stage involved decomposition of vegetable matter with the formation of reactive, soluble "monomers." At the lignite stage a three-dimensionally crosslinked gel has started to form with a corresponding decrease in the soluble material. The degree of coalification can be determined from the ultimate extraction yields of the coals. The molecular weight distribution of the soluble material at any degree of coalification can be predicted if one assumes a specific number of reactive functional groups on the monomer. Accordingly, van Krevelen measures the molecular weight distribution of four coal extracts and compares the results to those predicted by theory assuming the condensation of two trifunctional monomers with the functional groups of equal reactivity. Obviously this does not describe the real situation but is a grossly oversimplified model. However, he finds good agreement between the observed and predicted molecular weight distribution for all coals studied.

van Krevelen has successfully modeled the coalification process as a condensation polymerization with gel formation. The model is obviously oversimplified but it works. Unaccountably, no studies following up on these observations have been published. Certainly this picture is totally consistent with the view that coals are three-dimensionally crosslinked macromolecular gels.

Larsen and Kovac⁶ point out that the bulk mechanical properties of coals are consistent with a three-dimensionally crosslinked macromolecular structure. They direct attention principally to the study conducted by Morgans and Terry¹⁴ in which the time dependence of strain (elongation) at constant stress (force) of a bituminous coal was measured. Consistent with a crosslinked polymer network, the strain initially increased but eventually became constant. Furthermore, the strain was almost totally recoverable. This is consistent with a crosslinked structure. If the macromolecules were held together by purely entanglements or hydrogen bonds and weaker van der Waals forces, there would be no limit to the flow and the strain would not be totally recoverable.

Brenner recently provided strong evidence in support of a covalently crosslinked structure for coals.¹⁷ He exposed a homogeneous thin section of Illinois No. 6 coal (10-20 microns thick) to vapors of n-propyl amine. The sample approximately doubled in size after exposure for 2.5 minutes. The sample was allowed to dry by exposing it to the atmosphere; within 30 seconds it shrank to its original size and nearly the original shape. After exposure and drying a second time, the sample was nearly identical to the first shrunken

sample. Brenner also observed that the swollen sample was substantially more flexible than the original sample or the sample after drying.

Brenner concluded that this rapid, highly reversible swelling behavior of coal was consistent with a covalently crosslinked macromolecular gel wherein chains are able to reorient and extend themselves during the swelling process. The flexibility of the swollen coal is attributed primarily to the solvation (breaking) of interchain hydrogen bonds that occurs during the swelling process. The chain length between the crosslink in the swollen coal is substantially greater than that in the dry coal and therefore the coal exhibits greater flexibility.

This concludes the discussion of the various models of coal structure. For reasons discussed above, we promote the view that coal is best described as a covalently crosslinked macromolecular structure. A goal of this research was to develop a method for determining the degree of crosslinking of coals. The motivation and approach for the determination of this parameter will be discussed in the next section.

CHAPTER III

ESTIMATION OF CROSSLINK DENSITY

A. Motivation

A requirement of any coal model is that it be able to explain and predict coal properties. The question can be asked: what impact does the macromolecular structure of coal have on coal properties? This question has been thoroughly addressed by Larsen.¹⁷ He demonstrated that many properties show a distinct change at about 85% carbon. He tentatively attributes this to a minimum in crosslink density which occurs with coals having ~86% carbon. This observed minimum is rationalized as follows. From about 75% to 85% carbon the principal change that occurs is deoxygenation. It is speculated that the ether linkages are lost and not fully replaced by other carbon-based linkages. This results in a decrease in crosslink density. Somewhat beyond 86% carbon, dehydrogenation becomes dominant. The loss of hydrogen, as methane, results in a rapid increase in the crosslink density.

Larsen points out that the crosslink density of a coal should be expected to influence strongly its chemical reactivity. Consider two coals, for example, which differ only in their crosslink density. If they are subjected to a depolymerization reaction in which the reactive sites are crosslinks, clearly a more tightly crosslinked coal will give soluble products more slowly than a loosely crosslinked coal. Such structure-reactivity relationships will not be observed under vigorous

reaction conditions, such as most conversion processes, he points out, because the conditions are so harsh and reaction times are so long that the effects of crosslink density are likely to be masked. Rather, depolymerization reactions under mild condition would be a better place to look for such relationships.

Larsen points to one such reaction: a depolymerization of coals heated in quinoline for 4 hours at 350°C.⁶⁹ This reaction is capable of solubilizing 95% of some coals in quinoline and 70% of some coals in pyridine. A plot of extraction yield versus % carbon shows a maximum at about 86% carbon. If a minimum in crosslink density occurs at 86% carbon then the observed maximum in reactivity is expected. Numerous other examples of coal behavior consistent with a minimum in the crosslink density at ~86% carbon are given.

One need not limit the discussion to depolymerization reactions. Suppose the site in the coal is not a crosslink but some other functional group, e.g. a phenolic hydroxyl group. In order for the hydroxyl group to react, the reagent must reach it. Suppose the solvent swells the coal and expands the matrix thus allowing the reagent access to the reactive site. The reaction might occur faster in a good swelling solvent because it allows easier access to the reactive site. Indeed, Larsen and coworkers point out that the reactions of hydroxyl group in coals are orders of magnitude slower than solution hydroxyl reactions,⁷⁰ implying that reagent access is an important consideration that should not be overlooked by coal chemists.

Thus it appears that crosslink density may be an important parameter controlling the reactivity of coals. At the same time, there is very little published work dealing with it. The minimum in crosslink density at 86% carbon has not been unequivocally verified, although there is evidence suggesting its existence. In light of this, further investigations aimed at determining crosslink densities are justified. First, reliable methods for its determination must be developed. It was with this motivation that this work was undertaken.

B. Approach

1. Coal as an Elastomer

As demonstrated by Brenner, coals absorb their own volume of solvents without dissolving and, upon removal of the solvent, the coal shrinks to its original size and nearly its original shape.¹⁷ Solvent swelling is simply elastic expansion of the coal network. Other materials exhibit similar behavior upon exposure to solvents, most notably, crosslinked rubbers. The theory of rubber elasticity was developed by Kuhn,⁷¹ Flory and Rehner,⁷² James and Guth⁷³ and Treloar⁷⁴ to account for this kind of behavior. An important outcome of the theory is the so-called Flory-Rehner equation which can be used to calculate crosslink densities of rubber-like materials using solvent swelling techniques. Thus, the theory provides an intellectual basis for the interpretation of solvent swelling of coal as well. For this reason, solvent swelling was chosen as the principal investigative technique of this work.

Attempts to apply the simple theories of rubber elasticity to coal raises some serious questions. The differences between the two materials are substantial. Crosslinked natural rubber, for example, consists of repeating isoprene units with sulfide crosslinks. It is capable of sustaining large deformations without rupture; elongations of five to ten times are common. One reason for the high degree of flexibility is the presence of long polymer chains, each comprising a hundred or more single bonds between crosslinks. The system also possesses a high internal mobility due to the rotatable carbon-carbon single bonds. This allows rearrangements of the chains during the deformation.

Coal, on the other hand, exhibits a lower degree of flexibility. This is probably due, in part, to a shorter molecular chain length between crosslinks. Furthermore, the hydrocarbon skeleton consists largely of aromatic/hydroaromatic condensed rings. This type of structure would impart a stiffness to the coal network. On a qualitative level, differences in the elastic behavior of the two materials are expected. The theory has been modified to account for these differences by Kovac⁷⁵ and Peppas.⁸ This will be more fully discussed in the next section which concerns the thermodynamics of solvent swelling.

2. Thermodynamics of Solvent Swelling

Swelling of a crosslinked elastomer involves the mixing of two pure components: (1) the solid elastomer and (2) the liquid solvent.^{76,77} Since the elastomer is crosslinked it is necessarily insoluble. The amount of solvent absorbed is set by the following two factors: (1) the elastic properties of the network and (2) the free

energy of mixing of the solvent and the network. A lightly crosslinked elastomer will swell more than one extensively crosslinked, providing they are of the same chemical composition.

For the purposes of thermodynamic analysis, swelling is divided into two simultaneous processes. First, there is a mixing of the chain network with the solvent molecules, resulting in an increase in the entropy of the system. There is a heat of mixing as well but this is often relatively small. The change in free energy upon mixing, ΔG_{mix} , is therefore negative with the principal driving force being the increase in entropy. The other thermodynamic consideration involves elastic expansion of the network. As the solvent is absorbed, the chains are extended. This results in a decrease in entropy of the network since extended chains are in a more ordered state. In synthetic elastomers there is usually no significant change in the enthalpy upon expansion. The change in free energy, ΔG_e , is positive, with the principal restoring force being entropic in nature.

When the above two forces are exactly balanced, a state of equilibrium exists and the swelling ceases. The sum of the free energy changes is zero.

$$\Delta G_{\text{total}} = \Delta G_{\text{mix}} + \Delta G_e = 0 \quad (1)$$

An expression for ΔG_{mix} has been derived by Flory⁷⁸ and Huggins⁷⁹ using a statistical treatment of polymer solutions. The entropy of mixing is derived using a lattice model. A site on the three-dimensional lattice is occupied by either a solvent molecule or a polymer segment. This treatment leads to the expression for the entropy of mixing, ΔS_{mix} ,

$$\Delta S_{\text{mix}} = k(n_1 \ln v_1 + n_2 \ln v_2) \quad (2)$$

where n_1 is the number of moles of solvent or polymer and v_1 is the volume fraction. This expression amounts to an extension of the ideal solution concept to polymer solutions.

The expression for the heat of mixing, ΔH_{mix} , is introduced on a semi-empirical basis. The heat of mixing is considered to originate from first neighbor interactions between solvent molecules and polymer segments.

$$\Delta H_{\text{mix}} = kT\chi n_1 v_2 \quad (3)$$

where χ is the Flory interaction parameter, a dimensionless parameter characterizing the interaction energy between the solvent molecule and polymer segment. Originally χ was associated only with the heat of mixing; but, as Flory point out,⁷⁷ there is no reason for dismissing the possibility of a contribution to the entropy from first neighbor interactions as well. Thus, χ can be defined as the sum of an entropic contribution, χ_s , and an enthalpic contribution, χ_H .

$$\chi = \chi_H + \chi_s \quad (4)$$

Combining Equations 2 and 3 followed by differentiation with respect to the number of solvent molecules, n_1 , the change in free energy of dilution is obtained.

$$\Delta G_{\text{mix}} = RT[\ln(1 - v_2) + v_2 + \chi v_2^2] \quad (5)$$

The change in free energy upon elastic expansion comes from the Gaussian network theory derived by Kuhn⁷¹ and others.⁷²⁻⁷³ It gives as the free energy upon elastic expansion

$$\Delta G_e = \frac{\rho_2 RT}{\bar{M}_c} V_1 v_2^{1/3} \quad (6)$$

where V_1 is the molar volume of the solvent, ρ_2 is the density of the elastomer, and $\bar{M}_c$ is the number average molecular weight per cross-link. Combining Equations 5 and 6 gives the Flory-Rehner equation⁷²

$$\bar{M}_c = \frac{\rho_2 V_1 v_2^{1/3}}{-[\ln(1 - v_2) + v_2 + \chi v_2^2]} \quad (7)$$

$\bar{M}_c$ is related to the crosslink density of ρ_x , expressed as the moles of crosslinks per unit volume, by the following equation.

$$\rho_x = \frac{1}{\bar{V} \bar{M}_c} \quad (8)$$

where $\bar{V}$ is the specific volume of the elastomer.

Equation 7 can be used to calculate the degree of crosslinking for a network whose chains obey Gaussian statistics, that is, where the spatial configuration of the chains upon deformation can be defined by a Gaussian distribution. This Gaussian assumption has been known to fail for short chains and large deformations. It has been postulated that the macromolecular chains in bituminous coals do not obey Gaussian statistics.^{6,8,75} The large planar aromatic and hydroaromatic arrays that make up the chains are not expected to respond as a more flexible

and mobile aliphatic chain. Kovac⁷⁵ and Peppas,⁸ in order to incorporate non-Gaussian effects, have derived expressions that can be used to interpret solvent swelling of coals. The Kovac expression is presented here since it will be used in this work.

$$\bar{M}_c = \frac{\rho_2 V_1 v_2^{1/3} + \rho_2 v_1 / N v_2^{1/3}}{-[\ln(1 - v_2) + v_2 + \chi v_2^2]} \quad (9)$$

This equation contains the additional parameter N which expresses the number of repeating units between crosslinks in the short chain model. It can be defined as the ratio of number average molecular weight per crosslink, $\bar{M}_c$, to the average molecular weight of the clusters, M_o .

$$N = \frac{\bar{M}_c}{\bar{M}_o} \quad (10)$$

It describes the deviation from Gaussian behavior. The Gaussian limit is obtained when N becomes infinite since the Kovac equation then reduces to the Flory-Rehner equation.

Differences in the swelling behavior of a given elastomer in different solvents can be attributed to differences in the χ value of the elastomer-solvent pair. A more negative value of χ means the solvent has a greater affinity for the polymer. Interestingly, many systems actually have relatively small positive χ values associated with them, i.e. the heat of mixing is endothermic. In this case, the heat of mixing tends to slightly oppose the swelling process. Not all χ values will be positive; if there is a specific interaction between the elastomer and solvent such as hydrogen bonding (e.g. cellulose and

water), χ might be large and negative. The heat of mixing would be a significant driving force for the swelling process in this case.

In order to calculate $\bar{M}_c$ using Equation 7 or 9, it is necessary to make two experimental measurements. First, the elastomer is swollen and the volume fraction of the elastomer in the equilibrium state, v_2 is measured. The Flory interaction parameter, χ , must also be measured. There are several different methods developed for measuring χ that are discussed in a good review by Orwoll.⁸⁰ In this dissertation the theory of regular solutions was used to measure χ for coal-solvent systems.⁸¹ The Flory-Huggins theory of polymer solutions^{78,79} discussed above is a variant of the regular solution theory. The main difference is in the expression for the ideal entropy of mixing. Some background on regular solution theory now follows.

3. Hildebrand-Scatchard Theory of Regular Solutions

Hildebrand defined a regular solution as follows: "A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged."⁸² Put in another way, a regular solution is one in which the mixing is virtually random in spite of the nonideal enthalpy of mixing. Hildebrand⁸³ and Scatchard⁸⁴ derived an equation for the internal energy of mixing.

$$\Delta E^{\text{mix}} = (x_1 v_1 + x_2 v_2)(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (11)$$

where x_i is the mole fraction, ϕ_i is the volume fraction and δ_i is the solubility parameter. The solubility parameter is defined as the

square root of the cohesive energy density, c , which is approximated as the molar heat of vaporization divided by the molar volume.

$$\delta^2 = c \approx \left(\frac{\Delta U_1^g}{V_1} \right) \approx \left(\frac{\Delta H_1^g - RT}{V_1} \right) \quad (12)$$

Two assumptions in the derivation of the Hildebrand-Scatchard equation, among others, should be noted. The first assumption is that the mutual energy of the two molecules depends upon the distance between them. Thus, the geometric mean assumption is used in describing the internal energy of the mixing. This gives rise to the $(\delta_1 - \delta_2)^2$ term. Second, the mixing is assumed to be totally random. This would be valid only in the absence of polar and other specific effects (i.e., nonpolar systems). For example, systems which form 1:1 complexes will not have the entropy of mixing calculated for an ideal or regular solution and are not expected to obey the predictions of regular solution theory.

If it is assumed that the Hildebrand-Scatchard equation gives the enthalpy of mixing then it can be shown that

$$\chi_H = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (13)$$

and then

$$\chi = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 + \chi_s \quad (14)$$

Note that Equation 13 only allows for athermal or positive heats of mixing. χ is minimized when the solubility parameters of the two components are equal. Thus, the old rule "like dissolves like" is pertinent here.

Attempts have been made to extend regular solution theory to polar systems. Blanks and Prausnitz introduced the idea of the two-component solubility parameter in their work with polymer-solvent systems.⁸⁵ The total solubility parameter is considered to consist of a nonpolar component, λ , and a polar component, τ .

$$\delta^2 = \lambda^2 + \tau^2 \quad (15)$$

The polar component of the solubility parameter is evaluated by invoking the homomorph concept of Brown.⁸⁶ The homomorph of a polar molecule is a nonpolar molecule having a similar size and shape. The polar energy of vaporization is simply the difference between the experimentally-determined energy of vaporization of the polar molecule and that of the nonpolar homomorph at the same reduced temperature. Application of the Hildebrand-Scatchard equation to polar systems is complicated by the fact that the geometric mean assumption is unlikely to apply when polar forces are operating. Nevertheless, modification of the equation was made in order to incorporate polar effects.

In order to treat polar-polar polymeric systems (e.g. polymethylmethacrylate and polar solvents), Blanks and Prausnitz used the following equation to calculate the enthalpic contribution to χ .

$$\chi_H = \frac{V_1}{RT} \left[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 \right] \quad (16)$$

The respective nonpolar and polar solubility parameters of the polymer and solvent must be known. An evaluation of the entropic contribution, χ_S , was made using three nonpolar systems and a large number of

nonpolar solvents. For these systems, values of χ were experimentally determined by other methods. χ_H values were then calculated from a knowledge of the solubility parameters. From 23 calculations, an average value of 0.34 was found for χ_S , with a standard deviation from the mean being 0.08. For 19 polar-polar systems the average difference between calculated and experimental χ value was 0.07. The results are surprisingly good considering the assumptions of the theory.

Questions have been raised concerning the use of a constant entropic contribution.⁸⁷ Since χ_S should depend upon the size and shape of the solvent molecule as well as the polymer groups, there is no reason it should remain constant from one system to another. Guillet and Ito evaluated χ_S for several olefin polymers and hydrocarbon solvents using inverse gas chromatography and found that it was not constant.⁸⁷ However, it ranged from 0.20 to 0.41 with an average value of 0.33. They concluded that the use of the average value should give a reasonable approximation of χ parameters for the systems studied.

As mentioned earlier, the solubility parameter of an organic solvent can be evaluated from a knowledge of its molar heat of vaporization and its molar volume. Extensive lists of solubility parameters of organic solvents can be found in the literature.^{88,89} Estimation of the solubility parameter of a crosslinked elastomer is more difficult. Quite often the elastomer is exposed to solvents with a range of solubility parameters.^{90,91} The solubility parameter of the solvent which swells the elastomer the most is assigned to the elastomer (see

Figure 3). This allows a calculation of the enthalpic contribution to χ using Equation 13 (nonpolar system) or 16 (polar system).

Thus, if the solubility parameter of a coal network can be estimated from a plot similar to Figure 3, then χ may be calculated for the particular solvent-coal system. A knowledge of the volume fraction of coal, v_2 , along with χ allows a calculation of the molecular weight per crosslink, $\bar{M}_c$, using equation 7 or 9.

C. Literature Survey

Sanada and Honda were the first to use solvent swelling and the Flory-Rehner equation to estimate crosslink densities of coal.¹⁹ (There are earlier studies of the swelling of coal by solvents but they were not guided by an understanding of the physical chemistry of the system studied.)⁹²⁻⁹⁴ The swelling solvent was pyridine. The measurements were made gravimetrically at 25°C on a series of coals ranging from 65 to 93% carbon. All coals were exhaustively extracted with pyridine before swelling since equilibrium could not be reached if a substantial portion of the pyridine-soluble material was present in the coal. χ values were estimated from the concentration dependence of osmotic pressure in pyridine solution of coal extracts.⁹⁵ $\bar{M}_c$ was calculated using the Flory-Rehner equation (Equation 7). Unfortunately, the molar volume of pyridine was left out of the calculations which resulted in low values of $\bar{M}_c$ (<200). A recalculation gives more reasonable $\bar{M}_c$ values, ranging from 700 to 15,000. However, the error does not affect the qualitative conclusion that a maximum in $\bar{M}_c$ occurred at ca 85% carbon. Sanada and Honda point to other properties

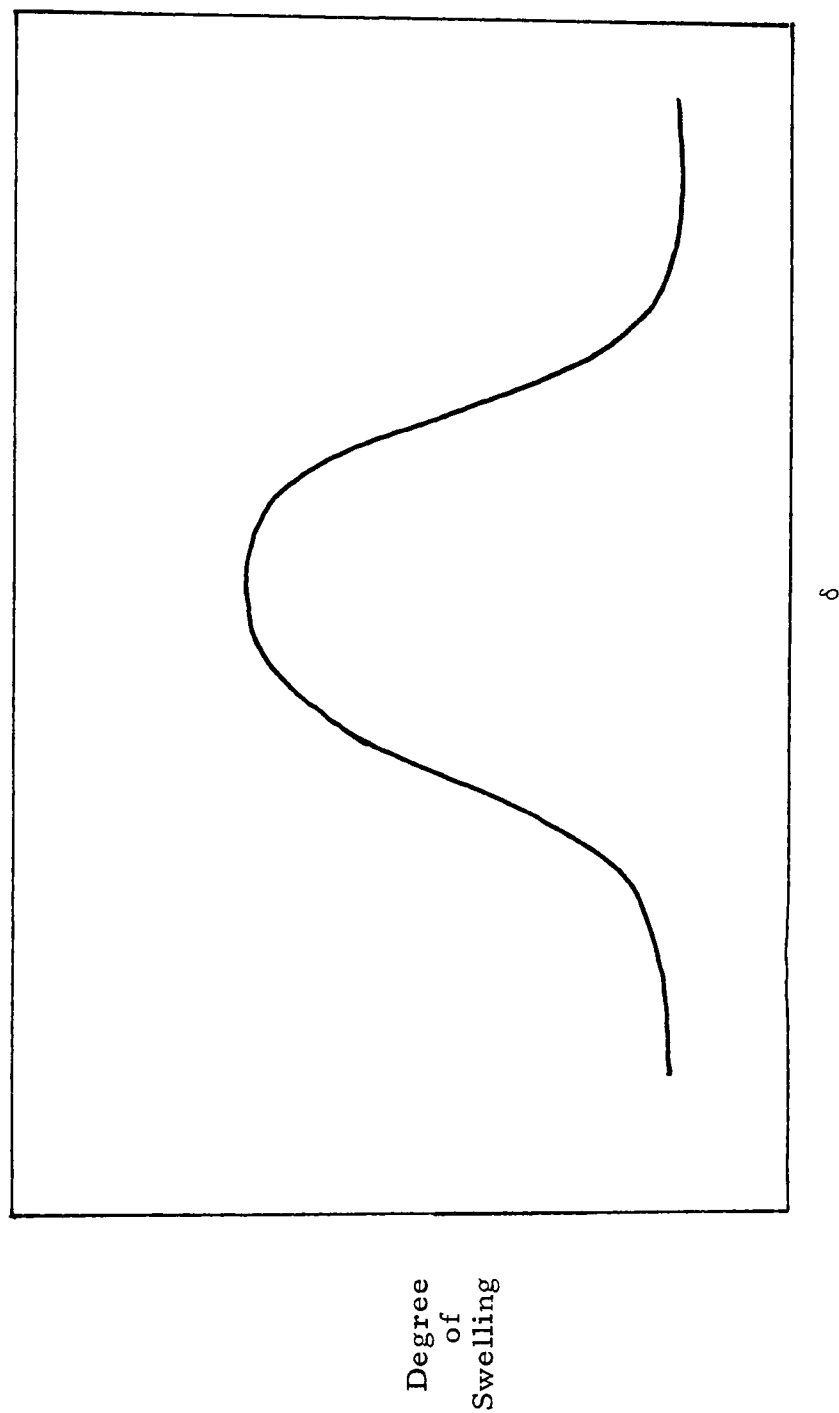


Figure 3. Plot of Degree of Swelling Versus Solubility Parameter of Solvent for a Synthetic Elastomer.

that correlate with this observation. Creep compliance measured at 350°C and the maximum fluidity of coals measured by a Geisler plastometer showed maximum at ca 85% carbon as well.

The swelling measurements of Sanada and Honda were not corrected for pore volume. Any gravimetric measurement measures the weight of solvent absorbed into pores as well as that absorbed into the coal matrix itself. Some coals exhibit as much as 20% pore volume.⁹⁶ Therefore, considerable error in the swelling measurements may exist. Also, the χ values for the coal-pyridine systems were not measured on the same coals used in the study but were measured on coal extracts in a separate, earlier study.⁹⁵ For this reason, the χ values are questionable.

Sanada and Honda also attempted to determine solubility parameters of coals both by solvent swelling⁹⁷ and solvent extraction.⁹⁸ In the swelling study, a lignite and bituminous coal exhibited maximum swelling at a δ of 10.8 (cal/cm³)^{1/2}, that of pyridine. No effort was made to evaluate χ values for the coal-solvent systems. In the solvent extraction study, two coals were Soxhlet-extracted with fourteen solvents at their boiling points. A plot of extraction yield versus the solubility parameter of the solvent at its boiling point, δ_b , gave a smooth curve for both coals, with a maximum in yield at a δ_b value of 10.0 (cal/cm³)^{1/2}.

Kirov and coworkers used solvent swelling and the theory of regular solutions to calculate crosslink densities of three Australian coals.⁹⁹ Seventeen solvents were used to determine the solubility parameters of coals and χ was calculated using Equation 14, with a

value of 0.30 for χ_s . Interestingly, in contrast to the Sanada and Honda study, $\bar{M}_c$ was found to decrease with rank. However, $\bar{M}_c$'s derived from the data of both papers are consistent, lending credence to the technique.

Both Sanada and Honda⁹⁷ and Kirov and coworkers⁹⁹ found that maximum swelling was induced by amine solvents. This is not surprising since it has long been recognized that many solvents possessing an unshared pair of electrons interact strongly with coals.^{93,100,101} However, there are theoretical objections to applying regular solution theory to systems where specific interactions are present. The existence of 1:1 hydrogen-bonded complexes between acid sites in the coal and pyridine, for example, would make the application of the Flory-Rehner equation or regular solution theory to the system very risky because the assumption of random mixing would not be obeyed.

van Krevelen⁶⁷ has calculated solubility parameters of coal based on Small's group contribution method.¹⁰² Briefly, Small showed that quantity δV_m , where V_m is the molar volume of an atom group, is additive. Thus

$$\delta = \sum_i F_i / V_m \quad (17)$$

where F_i is the contribution of the atom group to the solubility parameter. The value of F_i derived by Small, however, could not be used for coals since the identity and population of the various groups in coal were not sufficiently known. Instead, van Krevelen derived F_i values for single atoms from available data on pure compounds. From the elemental analysis and the aromaticity of the coal, the

solubility parameters as a function of rank were calculated. The results indicate a distinct minimum in δ at ~88% carbon. The range of δ from 70 to 95% carbon was ~11 to 15 (cal/cm³)^{1/2}. An interesting conclusion is that solvents such as benzene and tetralin, although aromatic, have δ values that lie outside this range and therefore are to be considered as poor solvents for all coals regardless of the carbon content.

van Krevelen's values of solubility parameters can only be considered as rough estimates since the population and distribution of the various functional groups were not known. There was also considerable uncertainty in the aromaticity values of the coal. Although van Krevelen points to examples that appear to verify the approach, the accuracy of the calculations remains in question since the results have not been experimentally verified. The approach fails to consider hydrogen bonding and polar effects which may have considerable influence on coal solubility.

Mixed solvent systems have been used to determine solubility parameters for coals.^{103,104} Hombach, for example, swelled several coals with binary mixtures of tertiary amines and alcohols of different composition. The solubility parameter of the binary mixture can be defined as follows:

$$\delta_{\text{mix}}^2 = v_1 \delta_1^2 + v_2 \delta_2^2 \quad (18)$$

where v_1 is the volume fraction of the solvent. A plot of swelling degree versus δ_{mix} using a series of mixtures showed a maximum. The δ_{mix} value at which this maximum occurred was assigned as the δ value

of the coal. As an alternative to measuring the degree of swelling, Hombach also measured the limiting wavelength of the extractable material at 1% transmission in the UV-visible spectrum. A plot of the limiting wavelength versus δ_{mix} exhibited a maximum as well. In this manner, Hombach estimated a solubility parameter range for a series of coals of different rank. His results are in qualitative agreement with van Krevelen's calculations,⁶⁷ with a minimum in δ observed at ca 90% carbon. Weinberg and Yen have used a similar approach for estimating solubility parameters of coals and coal liquefaction products.¹⁰⁴

The use of mixed solvents to determine solubility parameters of coals assumes that the solvent mixture absorbed by the coal is of the same composition as the original solvent mixture, i.e. the coals are not selective sorbents. Because solvents capable of hydrogen bond interactions with coals were used in these studies, the possibility of selective absorption by the coal exists so the results discussed above must be viewed with caution.

Nelson has used an isopiestic method to estimate $\bar{M}_c$ values for coal.¹⁰⁵ Evaluation of the χ parameters was made by measuring the equilibrium swelling in methanol of a lignite and a subbituminous coal at several relative vapor pressures. The χ values were calculated from the equation

$$\ln \frac{P}{P_0} = \ln v_1 - v_2 - \chi v_2^2 \quad (19)$$

where P is the vapor pressure of the swelling solvent under the experimental conditions, P_0 is the vapor pressure of the solvent at one atmosphere, and v_1 and v_2 are the equilibrium volume fractions of

the solvent and coal, respectively. Using the methods of Rogers,¹⁰⁶ $\bar{M}_C$ was plotted against corresponding values of $V_1\rho_2v_2(v_2^{1/3} - v_2/2)$. The slope of the plot is equal to $1/\bar{M}_C$. The experimental $\bar{M}_C$ values for both coals was 70. It was suggested that the low values reflect the stiffness of the chain segments of the coal and that the use of a stronger swelling agent may provide more realistic $\bar{M}_C$ values.

The swelling measurements in the Nelson study were conducted on coals that were not exhaustively extracted prior to swelling. Although the solvents (benzene, tetralin, methanol) probably dissolve little, if any, of the smaller molecules, it is not clear that material was not dissolved during the swelling process. If this occurred, the dissolved material would lower the chemical potential of the system and solvent vapor would continue to condense. Under the condition, equilibrium would not be reached in a finite time.

Finally, Peppas and Lucht have estimated $\bar{M}_C$ values for seven coals ranging from a lignite to an anthracite.¹⁰⁷ The coals were exhaustively extracted with pyridine was the swelling agent as well. The appropriate corrections were made to account for the porous nature of coals. The χ values were calculated from Equation 20, which presents a linear relationship between χ and the carbon content of the coal.

$$\chi = 0.012(\%C - 0.049) \quad (20)$$

This empirical relationship is based on the work of Korov and coworkers.⁹⁹ As pointed out by Peppas, the validity of this equation remains to be realized.

Calculation of $\bar{M}_c$ values by Peppas was made using an expression similar to the Kovac expression for a modified Gaussian network.⁷⁵ The parameter N, which expresses the number of links between crosslinks (Equation 10), was adjusted so that an average molecular weight of 150 was obtained. Interestingly, the degree of swelling exhibited no rank dependence. Likewise, $\bar{M}_c$ values were nearly constant at 400. Thus, with molecular weight of 150 for the average cluster size, approximately three clusters were estimated to be between the multifunctional crosslinks.

The use of an average molecular weight of 150 for the molecular units in coals is probably too low. van Krevelen, in successfully modelling the coalification process with gel formation, estimated the average molecular weight of the structural units in coals to be ~400.⁶⁷ Whitehurst and coworkers, in short-time liquefaction studies of an Illinois No. 6 and Wyodak coal, determined the average molecular weights of the products to be 430 and 600, respectively.¹⁰⁸ Since it was shown that neither destruction of polycyclic saturated structures or hydrogenation of polycyclic aromatic structures took place during reaction, these structures were thought to exist in the original coal as well. Ignasiak and Gawlak measured the molecular weight distribution of the products of reductively alkylated coals.⁵⁰ They concluded that a bituminous coal and a lignite were made up of units with number average molecular weights of 670 and 500, respectively. Finally, Heredy and Wender have derived a model molecule for bituminous coals based on an enormous amount of physical and chemical data.¹³ The

model contained five condensed aromatic/hydroaromatic structures linked together, giving an average molecular weight of 300 per cluster.

The amount of pyridine absorbed by the coals in the Peppas study is unusually low. The coal that swelled the most absorbed only 0.22 ml of solvent per 1 ml of coal. This is in contrast to the measurements of Sanada and Honda¹⁹ and the ones repeated in this dissertation, which indicate nearly a doubling in volume of most coals with pyridine. Only high rank coals exhibited such poor swelling behavior. If Peppas's coals had not reached equilibrium, erroneously low values of $\bar{M}_c$ are expected.

CHAPTER IV

EXPERIMENTAL PROCEDURES

A. Swelling Measurements

1. Gravimetric Measurements

The elemental analysis of the coals used in this study are listed in Table I. Two different Illinois No. 6 coals were used and these are designated as (1) and (2).

All coals were ground under dry N_2 using a ball mill and sieved to -100 Tyler mesh. The coals were then exhaustively Soxhlet-extracted with pyridine prior to swelling, dried in a vacuum oven at 105°C for 24 hrs, and resieved to -100 Tyler mesh. Approximately 100 to 300 mg of the coal was weighed into a previously weighed glass bottle and cap. The bottle was suspended in a vacuum dessicator that contained a pool of purified solvent (~50 ml). All solvents were purified according to standard methods.¹⁰⁹ The solvent was cooled to dry ice/isopropanol temperatures (-78°C) and the dessicator was evacuated to less than 1 mm Hg. The solvent was then warmed to room temperature. The cooling-evacuation-warming cycle was repeated an additional two times to remove as much air as possible. After a period of time, the dessicator was opened to the atmosphere and the bottle was immediately capped and weighed. To establish when a equilibrium weight was reached, several samples of the coal were exposed to solvent vapors for different times until a constant weight was obtained. The time to equilibrium was found to depend significantly on the presence of air. For example, a plot of time versus weight increase of the Illinois No.

TABLE I
ELEMENTAL ANALYSIS (WT PERCENT) OF UNEXTRACTED
AND PYRIDINE-EXTRACTED COALS^a

Coal	%C	%H	%N	%S	%O ^b	%MM ^c
Bruceton						
Unextracted	83.14	5.27	1.62	1.22	8.76	5.43
Extracted	82.57	5.20	2.41	0.98	8.84	5.27
Illinois No. 6(1)						
Unextracted	79.81	5.11	1.85	2.05	11.18	7.03
Extracted	78.80	5.03	2.45	1.95	11.85	7.73
Illinois No. 6(2)						
Unextracted	79.07	6.05	1.46	5.06	8.37	13.49
Extracted	76.35	5.71	2.45	5.12	10.38	15.26
Wyodak (Rawhide)						
Unextracted	72.24	5.19	0.95	0.51	21.10	8.36
Extracted	70.57	5.01	2.41	0.57	21.62	10.80
Big Brown Lignite						
Unextracted	67.54	5.35	1.29	1.15	24.67	7.13
Extracted	69.45	5.62	2.70	1.14	21.09	12.13
North Dakota Lignite						
Unextracted	70.34	5.23	1.09	0.76	22.58	8.16
Extracted	69.16	5.31	0.99	0.61	23.93	9.39

^aDry, mineral matter free basis (dmmf).

^bBy difference.

^cCalculated according to the equation $1.08 \text{ Ash} + 0.55\text{S}$.

6(1) coal using pyridine as the solvent is shown in Figure 4. When the system was evacuated to 0.5 mm Hg, equilibrium was reached in approximately 8 hours. However, when the system was not evacuated, equilibrium was reached in approximately 5 days. Thus, the rate of sorption, but not the extent, was affected by the presence of air. The weight ratio on a dry basis, W_{dry} , is defined as

$$W_{\text{dry}} = \frac{\text{wt of swollen coal}}{\text{wt of dry coal}} = \frac{w_s + w_{c,\text{dry}}}{w_{c,\text{dry}}} \quad (21)$$

where w_s is the equilibrium weight of solvent sorbed by a unit weight of dry coal, $w_{c,\text{dry}}$.

2. Volumetric Measurements

Approximately 400-600 mg of coal (-100 Tyler mesh) was placed in a 8 mm o.d. Pyrex tube and centrifuge for five minutes in a Fischer centrifuge at 1725 rpm. The height of coal was measured as h_1 . Excess solvent (3-4 ml) was added and the tube was vigorously shaken to insure complete mixing. The coal was again centrifuged and the height was measured. The mixing and centrifuging was repeated until a constant height of coal, h_2 , was reached. The volumetric swelling ratio on a dry basis, $Q_{v,\text{dry}}$, is defined as

$$Q_{v,\text{dry}} = \frac{h_2}{h_1} = \frac{v_{c,\text{dry}} + v_s}{v_{c,\text{dry}}} \quad (22)$$

where v_s is the volume of solvent absorbed by a unit volume of dry coal, $v_{c,\text{dry}}$.

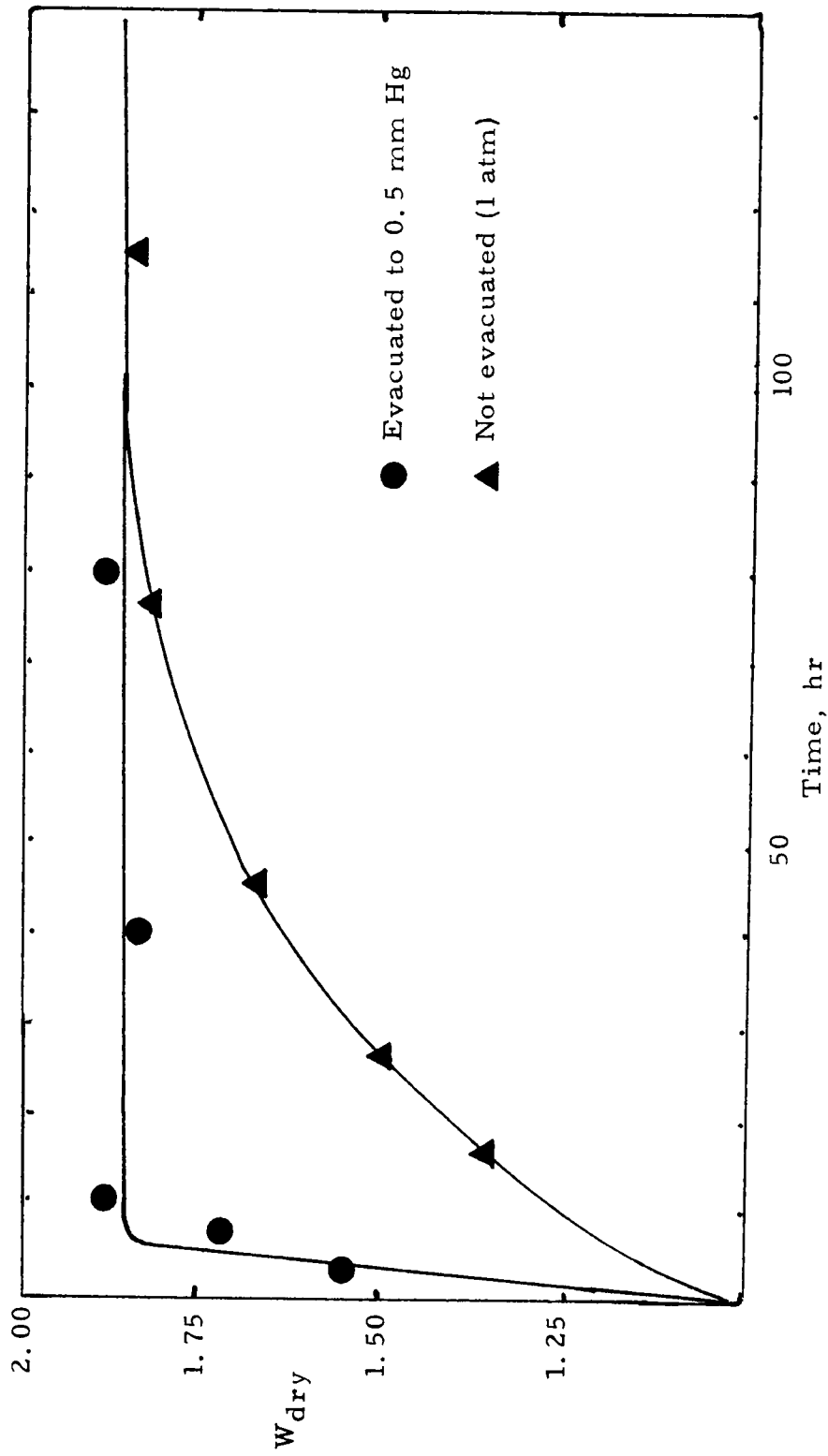


Figure 4. Plot of Time Versus Weight Increase for the Pyridine-Extracted Illinois No. 6(2) Coal.

B. Solvent Mixtures and Coal

1. Alcohol/Amine Mixture

600 mg of an unextracted or pyridine-extracted Bruceton coal was placed in a 8 mm o.d. Pyrex tube. 1.50 ml of the appropriate alcohol/N,N-dimethylaniline mixture was pipetted onto the coal, the alcohol being either methanol, ethanol, 2-propanol, or t-butanol. The tube was sealed and the mixture was shaken vigorously every few hours for approximately three days. This was sufficient time for swelling equilibrium to be reached as judged by constant height of the coal.

After swelling, the supernatants were analyzed by g.c. to determine if selective absorption by the coal had occurred. A Hewlett-Packard 5880 A Series gas chromatograph equipped with a glass capillary column and FID detector was used for the analysis. For all but the methanol/amine systems, 1.00 ml of an internal standard, methylcyclohexane, was added to the tube prior to the analysis. Since methylcyclohexane did not swell the coal appreciably by itself, it was assumed that its volume in the supernatant was 1.00 ml. The absolute volumes of the alcohol and amine in the supernatants, $V_{i,super}$, were calculated by the following equation:

$$V_{i,super} = (A_i/A_{IS})_{super} (A_{IS}/A_i)_{orig} V_{i, total} \quad (23)$$

where A_i is the g.c. peak area of component i, A_{IS} is the g.c. peak area of the internal standard, and $V_{i,total}$ is the total volume of component i in the mixture. The volume of component i absorbed by the coal, $V_{i,abs}$, is simply

$$V_{i,abs} = V_{i,total} - V_{i,super} \quad (24)$$

A swelling ratio, Q_{calc} , could be calculated if the respective volumes of each component absorbed by the coal were known.

$$Q_{calc} = (V_{1,abs} + V_{2,abs}) / (w_{c,dry} / \rho_{c,dry}) + 1 \quad (25)$$

where $w_{c,dry}$ is the weight of dry coal and $\rho_{c,dry}$ is the apparent density of dry coal in cyclohexane.

The internal standard, methylcyclohexane, was not soluble in the methanol/N,N-dimethylaniline mixtures. For this reason, the volumes of the components absorbed by the coal could not be directly calculated from the g.c. analysis using Equations 23 and 24. However, an indirect calculation could be made from the available swelling data. The swelling ratio, $Q_{v,dry}$, is a measure of the total volume of solvent absorbed per ml of dry coal. The volume absorbed in the experiment, V_{abs} , is therefore

$$V_{abs} = (Q_{v,dry} - 1)w_{c,dry} / \rho_{c,dry} \quad (26)$$

The total volume in the supernatant is then

$$V_{super} = V_{total} - V_{abs} \quad (27)$$

The relative volumes of the components in the supernatant were known from the g.c. analysis. Hence,

$$V_{i,super} = x_i V_{super} \quad (28)$$

where x_i is the volume fraction of component i in the supernatant.

Since the total volume of i is known, then $V_{i,abs}$ is known.

$$V_{i,abs} = V_{i,total} - V_{i,super} \quad (29)$$

In this manner, the absolute volumes of the solvent components absorbed by the coal could be calculated without the use of the internal standard.

2. Chlorobenzene/Pyridine Mixture

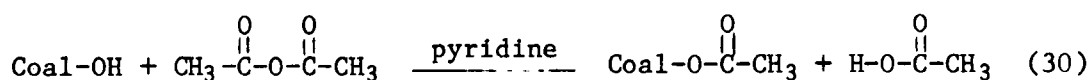
400 mg of a pyridine-extracted Illinois No. 6(2) coal was placed in a 8 mm o.d. Pyrex tube. The coal was centrifuged for five minutes and the height was measured. The tube was partially submerged in a liquid nitrogen bath and 2.00 ml of the appropriate solvent mixture was pipetted onto the coal. The tube was evacuated to better than 1 mm Hg, sealed off, shaken vigorously, and attached to a mechanical shaker for 24 hrs. After this time, the coal was centrifuged and the height was measured. After two more days of shaking, the height of coal in the tube had not changed, indicating equilibrium had been obtained. The tubes were broken open and the supernatants were analyzed by g.c. The absolute volumes of the components absorbed by the coal were calculated as in the methanol/*N,N*-dimethylaniline system (Equations 26-29).

C. Acetylation of Hydroxyl Groups

1. Preparation of Coals for Swelling

The Illinois No. 6(2) and Bruceton coals were acetylated by the standard method of Blom.¹¹⁰ This method consists of acetylating the

hydroxyl groups with acetic anhydride in the presence of pyridine.



Approximately 10 g of dry coal was weighed into a 250 ml round bottom flask. 200 ml of a mixture of acetic anhydride and pyridine (1:2 by volume) was added and the mixture was refluxed with stirring for 24 hrs. After cooling, the mixture was placed in a 2000 ml erlenmeyer flask and 500 ml of distilled water was added. The coal was filtered through a medium-porosity Whatman filter using a Buchner funnel, washed free of acid with distilled water, placed in a vacuum oven for 24 hrs at 105°C to dry, and weighed. An FTIR spectrum of the sample was obtained in order to determine if all the hydroxyl groups had been acetylated (see Section IV.C.3 for the procedure).

2. Determination of the Number of Hydroxyl Groups

Approximately 1.2 g of the Illinois No. 6(2) coal was refluxed in 25 ml of an acetic anhydride/pyridine mixture (1:2 by vol) for 24 hrs. 50 ml of distilled water was added and the mixture was filtered and washed free of acid. The acetylated coal was transferred to a 250 ml round bottom flask. 70 ml of distilled water and 3 g of barium hydroxide were added. The mixture was refluxed for 12 hrs and, upon cooling, 2 ml of phosphoric acid (85% by wt) was added. The mixture was distilled with 25 ml portions of distillate being collected in a 25 ml volumetric flask. After each collection, 25 ml of distilled water was added to the distillate flask through a dropping funnel. Each 25 ml portion collected was titrated to its phenolphthalein end-point with a standard .01 N NaOH solution. The distillation was continued until a

constant volume of titrant neutralized 25 ml of distillate. The meq of OH per g of dry coal was calculated from Equation 31.

$$\text{meq OH/g dry coal} = [v_1 + v_2 \dots v_n] - nv_0 \text{]} N_B / w_{c,\text{dry}} \quad (31)$$

where v_1 through v_n are the volumes of titrant need for each titration, n is the number of titrations, v_0 is the volume of titrant needed for neutralization of the phosphoric acid, and N_B is the normality of the titrant.

3. FTIR Procedure

The coals were dried for 24 hrs in a vacuum oven at 105°C. The KBr used was baked at 450°C for 24 hrs. Both coal and KBr were transferred to an Atmosphere's glove box and combined in the proper proportion (20 mg coal/1 g KBr) in a WIG-L-BUG shaker. After shaking for 3 min., 100 mg of the resulting powder were transferred to a bolt KBr pellet press and the nuts were tightened by hand. The KBr-coal pellet was transferred under nitrogen to a Digilab Model 20 C/V FTIR and the transmission spectrum was recorded.

D. Kinetics of Swelling

Approximately 400 to 600 mg of coal was placed in a 8 mm o.d. tube. The coal was centrifuged for 5 minutes and the height was measured. Excess solvent (3-4 ml) was added and the mixture was shaken vigorously. This was time zero. After approximately five minutes, the mixture was centrifuged for exactly one minute, the height was measured, and the time recorded. The mixture was immediately shaken

again. This procedure was followed until equilibrium swelling was reached.

E. Cyclohexane Densities

The density measurements were carried out in a pycnometer with a total volume of about 15 ml. 3 to 4 g of dry coal was weighed out in the previously weighed pycnometer. The pycnometer was then connected to the apparatus shown in Figure 5 for evacuation of air. The joint and vacuum stopcocks were greased with Dupont high vacuum silicon grease. S1 was closed off and S2 was opened. After a vacuum of better than 1 mm Hg was obtained, S1 was slowly opened to allow removal of the air pocket between the solvent and S1. When the solvent reached S1, the stopcock was closed. After a vacuum of better than 1 mm Hg was again attained, S2 was closed. S1 was then slowly opened to allow addition of cyclohexane. The pycnometer was removed and the grease was carefully removed with diethylether. It was then placed in a stirred constant-temperature water bath maintained at $30.00 \pm 0.02^\circ\text{C}$. After thermal equilibrium was reached, the pycnometer was weighed. The weighings were continued for several days until a constant weight was obtained. The density of the dry coal, $\rho_{c,dry}$, was calculated from Equation 32.

$$\rho_{c,dry} = w_{c,dry} / (w_t - w_p - w_{c,dry}) \quad (32)$$

where w_t is the total weight of the pycnometer, coal, and cyclohexane, w_p is the weight of the pycnometer, V_p is the volume of the pycnometer, and ρ_1 is the density of cyclohexane at 30°C (0.7692 g/ml).

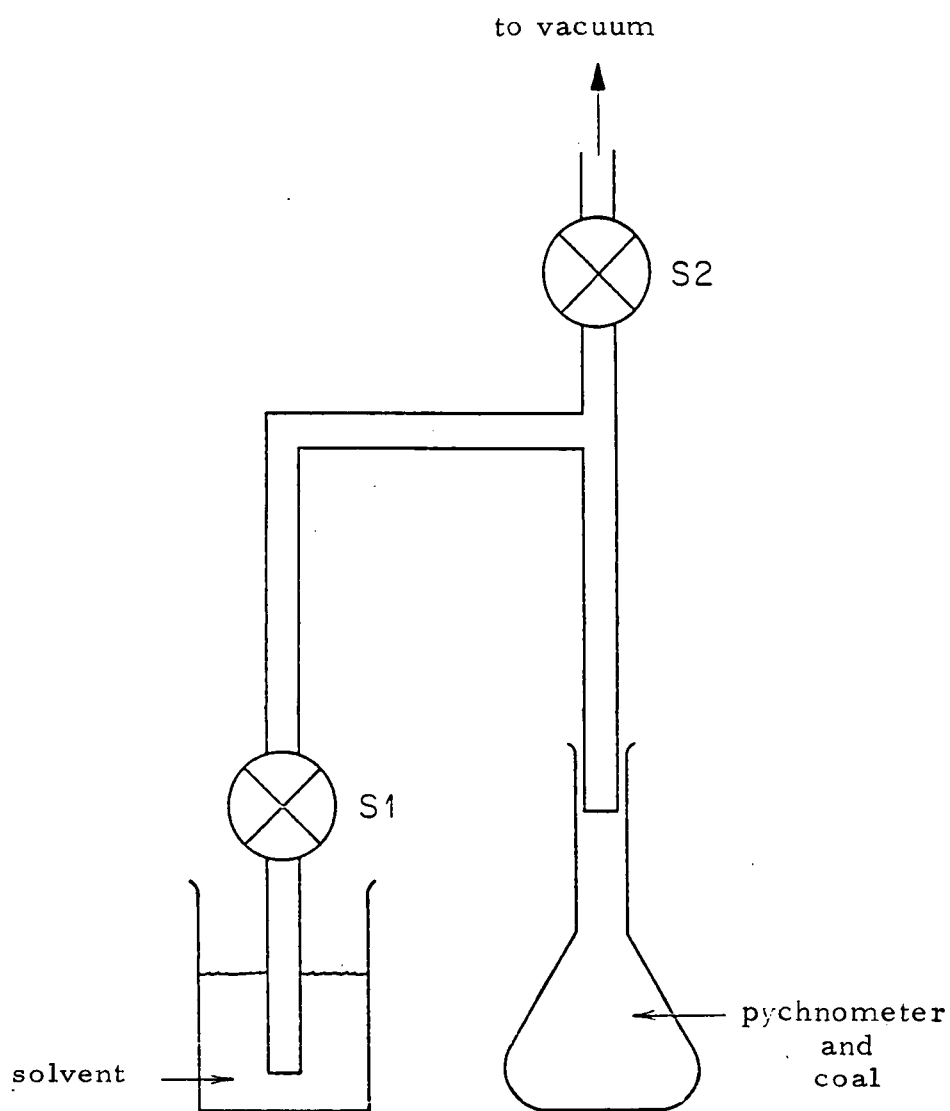


Figure 5. Apparatus for Measuring Cyclohexane Densities of Coals.

CHAPTER V

RESULTS AND DISCUSSION

A. Swelling Measurements

1. Gravimetric Measurements

Vapor-phase gravimetric swelling measurements were performed on coals that were exhaustively Soxhlet-extracted with pyridine. The extraction data are contained in Table II. The coals were exposed to pure solvent vapor at room temperature inside a dessicator until equilibrium was reached as judged by constant weight. Prior extraction with pyridine was necessary since any extractable material present during the swelling process prevents equilibrium from being reached in a finite time. The swelling data are contained in Table III. The weight ratio on a dry basis, W_{dry} , is defined as

$$W_{\text{dry}} = \frac{w_s + w_{c,\text{dry}}}{w_{c,\text{dry}}} = \frac{\text{wt of swollen coals}}{\text{wt of dry coal}} \quad (21)$$

where w_s is the weight of solvent sorbed by a unit weight of dry coal, $w_{c,\text{dry}}$. When the ratio is 1.0, the coal has sorbed no solvent. On some samples, more than one measurements was made and the reproducibility was good. The average of five weight ratios using the Bruceton coal and 2-propanol, for example, was 1.41 ± 0.04 (r.s.d.). Thus although high vacua were not attained in the sorption chamber (~ 1 mm Hg) and the temperature was not precisely controlled, the reproducibility of the measurement, in most cases, was on the order of 2-3%.

TABLE II

WT PERCENT OF COAL EXTRACTED BY EXHAUSTIVE
SOXHLET EXTRACTION WITH PYRIDINE^a

Coal	Extractability
Bruceton	21.2
Illinois No. 6(1)	18.7
Illinois No. 6(2)	19.9
Wyodak (Rawhide)	10.8
North Dakota Lignite	7.5
Big Brown Lignite	8.5

^aEach value based on the average of at least three extractions.

TABLE III

GRAVIMETRIC SWELLING RATIOS W_{dry} , OF PYRIDINE-EXTRACTED COALS

Solvent	Bruceton	Illinois No. (1)	North Dakota Lig.	Wyodak
Pentane	----	1.14	1.19	----
Cyclohexane	1.16	1.15	1.32	1.23
	1.16	1.08	----	1.23
	1.09	1.09	----	----
Toluene	1.39	1.44	1.20	1.33
	1.43	1.44	1.16	1.32
	1.40	1.40	----	----
	1.40	1.33	----	----
Benzene	1.45	1.42	1.42	----
	1.44	1.34	----	----
Carbon tetrachloride	1.46	1.34	1.34	----
Carbon disulfide	1.53	1.46	----	----
1,4-Dioxane	1.90	1.64	1.78	1.71
	----	----	1.78	1.74
Pyridine	2.03	1.85	2.04	2.16
	2.04	1.89	----	2.08
Methanol	1.27	1.24	1.31	1.34
	1.28	1.30	1.25	1.26
	1.41	1.31	----	----
Ethanol	1.39	1.41	1.35	1.43
	1.41	1.46	1.38	1.48
	1.42	1.35	----	----
	----	1.36	----	----
Acetone	1.46	1.54	1.44	1.54
Nitromethane	1.43	----	1.44	1.34

TABLE III (Continued)

Solvent	Bruceton	Illinois No. (1)	North Dakota Lig.	Wyodak
2-Propanol	1.42	1.43	1.42	1.35
	1.38	1.42	1.54	1.23
	1.35	1.43	1.43	---
	1.44	1.54	1.41	---
	---	1.43	---	---
Methylene Chloride	1.84	1.60	1.94	1.64
Chloroform	2.00	2.21	2.21	1.74
Nitrobenzene	1.66	1.71	1.71	1.41
	1.57	1.63	1.63	1.42
Formamide	1.16	1.26	1.26	1.26
Aniline	1.96	---	2.31	2.00
Acetonitrile	1.25	1.33	1.33	1.27
	1.27	1.33	1.33	---
	1.34	1.32	1.32	---
	---	1.37	---	---
2,6-Lutidine	1.90	1.79	1.79	1.35
Chlorobenzene	1.72	1.46	1.46	1.35
	---	1.47	---	---
	---	1.46	---	---
	---	1.54	---	---
	---	1.47	---	---
o-Dichlorobenzene	1.72	1.61	1.61	---
	---	1.58	---	---

The weight ratio, W_{dry} , is a measure of the amount of solvent that fills pores as well as that amount that swells the coal. Coals are highly porous materials.⁹⁶ The total porosity of an Illinois No. 6 coal (<2300 Å diameter) is 23% whereas the microporosity (<18 Å diameter) is 9.8%.¹¹¹ Failure to correct the weight ratio for occluded solvent may lead to significant errors in the swelling measurements. A correction requires a knowledge of the pore volume accessible to the solvent. Nelson and coworkers have developed a method for making this correction.¹¹² Corrections were not applied to the gravimetric data here because the accessible pore volumes were not known.

Some W_{dry} values were converted to swelling ratios on a dry mineral matter free (dmmf) basis, $Q_{v,\text{dmmf}}$. These values are compared with swelling ratios obtained by a volumetric technique discussed later. $Q_{w,\text{dmmf}}$ is a measure of the degree of expansion by volume of the coal network (ignoring pore volume) and is defined as

$$Q_{w,\text{dmmf}} = \frac{v_s + v_{c,\text{dmmf}}}{v_{c,\text{dmmf}}} = \frac{\text{vol of swollen dmmf coal}}{\text{vol of dmmf coal}} \quad (33)$$

The conversion was made as follows; if x is the weight fraction of mineral matter, then the volume per gram of dmmf coal is $(1 - x)/\rho_{c,\text{dmmf}}$, where $\rho_{c,\text{dmmf}}$ is the apparent density of the dmmf coal in cyclohexane at 30°C. The densities of the coals were measured in cyclohexane because it was shown to be a poor swelling solvent and therefore leaves the coal structure unperturbed. The volume of solvent that is sorbed by the coal is $(W_{\text{dry}} - 1)/\rho_s$, where ρ_s is the

density of the solvent at 25°C. This gives for the swelling ratio:

$$Q_{w,dmmf} = \frac{(W_{dry} - 1)/\rho_s + (1 - x)/\rho_{c,dmmf}}{(1 - x)/\rho_{c,dmmf}} \quad (34)$$

Simplifying gives

$$Q_{w,dmmf} = \frac{(W_{dry} - 1)/\rho_{c,dmmf}}{\rho_s (1 - x)} + 1 \quad (35)$$

Equation 35 was used to calculate swelling ratios on a dmmf basis from the experimentally determined weight ratios.

2. Volumetric Measurements

Liquid-phase volumetric measurements were performed on several pyridine-extracted and unextracted coals using a technique developed by Liotta.¹¹³ Measurements were also performed on some O-acetylated and O-methylated coals. The data are contained in Tables IV-VI. The technique measures the volume of solvent absorbed by a unit volume of dry coal. The coal was placed in a narrow Pyrex tube and the height of coal was measured as h_1 . Excess solvent was added and after the height reached a constant value, it was measured as h_2 . The swelling ratio, $Q_{v,dry}$, is defined as

$$Q_{v,dry} = \frac{v_s + v_{c,dry}}{h_1} = \frac{h_2}{h_1} \quad (22)$$

where v_s is the volume of solvent absorbed by a unit volume of dry coal, $v_{c,dry}$. The measurements were made at room temperature except

TABLE IV

EQUILIBRIUM VOLUMETRIC SWELLING RATIOS OF PYRIDINE-EXTRACTED COALS

Solvent	Bruceton	$Q_{v,dry}$		Big Brown Lignite
		Ill. No. 6(1)	Ill. No. 6(2)	
Biphenyl ^a	1.15	----	1.11	----
	----	----	1.10	----
1,4-Dioxane	2.07	1.73	2.00	----
	----	----	2.00	----
	----	----	2.00	----
Pyridine	2.32	1.94	2.29	2.03
	----	----	2.62	----
	----	----	2.44	----
	----	----	2.25	----
	----	----	2.21	----
Cyclohexane	1.13	1.00	1.00	----
	1.07	----	----	----
	1.10	----	----	----
	1.09	----	----	----
	1.07	----	----	----
	1.07	----	----	----
Methanol	----	----	----	1.57
Ethanol	1.45	1.44	----	1.58
	1.44	----	----	----
Carbon Disulfide	1.52	----	1.40	----
	1.47	----	1.42	----
	1.38	----	----	----
	1.38	----	----	----
Benzene	1.62	1.40	1.51	----
	1.58	1.37	1.53	1.29
	1.60	1.38	----	----
	1.53	1.38	----	----
	1.58	----	----	----
Ethylenediamine	2.03	----	----	1.97
o-Xylene	1.51	----	1.41	----
N,N-Dimethylaniline	1.78	----	----	----
	1.87	----	----	----
Tetralin	1.65	----	1.50	----
	----	----	1.53	----
n-Heptane	1.16	----	1.00	----
Methylcyclohexane	1.08	----	1.03	----
Diethylether	1.54	----	1.60	----
Dimethylsulfoxide	2.21	----	2.21	----
	----	----	2.06	----
	----	----	2.17	----

TABLE IV (CONTINUED)

Solvent	Bruceton	$Q_{v,dry}$		Big Brown Lignite
		Ill. No. 6(1)	Ill. No. 6(2)	
Tetrahydrofuran	2.07	----	2.17	----
	----	----	2.10	----
	----	----	2.06	----
	----	----	2.13	----
Toluene	1.57	1.47	1.46	1.23
	1.56	1.40	1.45	----
	1.55	1.40	----	----
	1.53	1.38	----	----
	----	1.38	----	----
	----	1.33	----	----
Acetone	1.63	----	1.65	----
	----	----	1.73	----
	----	----	1.66	----
2-Propanol	----	1.52	----	1.53
Methylene Chloride	1.65	1.48	1.51	1.45
Nitrobenzene	----	----	1.85	----
Aniline	2.20	1.82	----	----
	2.23	----	----	----
Acetonitrile	1.45	1.38	1.4	1.38
	1.45	1.40	----	----
	1.40	----	----	----
Naphthalene ^a	1.58	----	1.43	----
n-Pentane	1.17	----	1.00	----
Chlorobenzene	1.73	1.52	1.59	----
	1.85	----	1.56	----
	1.78	----	1.60	----
	1.87	----	1.53	----
	1.80	----	1.61	----
Phenol ^a	----	----	2.05	----

^a Measured at 100°C.

TABLE V

EQUILIBRIUM VOLUMETRIC SWELLING RATIOS OF UNEXTRACTED COALS

Solvent	Ill. No. 6(1)	Ill. No. 6(2)	Bruceton
Benzenedrofurane	1.00	1.13	1.21
N,N-Dimethylaniline	1.05	----	----
1,4-dioxane	1.36	1.45	----
Aniline	1.64	----	----
2-Propanol	1.09	----	----
Acetonitrile	1.05	1.10	----
Ethanol	1.19	----	----
Methanol	1.13	----	----
n-Pentane	----	1.00	1.05
n-Heptane	----	1.00	----
Cyclohexane	----	1.00	1.05
Toluene	----	1.08	1.20
Chlorobenzene	----	1.23	----
Carbon Disulfide	----	1.09	1.15
Diethylether	----	1.21	----
Acetone	----	1.35	----
Dimethylsulfoxide	----	2.28	----
Pyridine	2.00	2.61	----
Tetrahydrofuran	----	1.90	----
Biphenyl ^a	----	1.00	1.03
Nitrobenzene	----	1.56	----
Benzonitrile	----	1.49	----

^a Measured at 100°C.

TABLE VI

EQUILIBRIUM SWELLING RATIOS OF O-ACETYLATED AND O-METHYLATED COALS

Solvent	$Q_{v,dry}$		
	Illinois No. 6(2)		O-Acetylated
	O-Acetylated	O-Methylated ^a	
Pentane	1.07	----	----
Cyclohexane	1.05	1.15	1.65
Toluene	1.72	1.62	2.21
Benzene	1.83	1.71	2.28
Chlorobenzene	2.10	----	2.44
Carbon disulfide	1.74	1.62	2.05
Diethylether	1.44	1.38	----
Acetone	1.69	1.50	----
Acetonitrile	1.53	1.38	----
Dimethylsulfoxide	2.57	----	----
Pyridine	2.80	2.25	2.49
1,4-Dioxane	2.35	----	2.34
Tetrahydrofuran	2.52	1.93	----
Tetralin	1.87	1.80	----
Nitrobenzene	2.86	----	----
Benzonitrile	2.50	----	----

^aSample supplied by Ron Liotta, Exxon Corporate Research Laboratories, Linden, New Jersey

when using phenol, biphenyl, and naphthalene which are solids at room temperature. In these cases the measurements were made at 100°C. Equilibrium was reached rapidly with most solvents, generally requiring only a few minutes. A few hours were required with some solvents, e.g., quinoline.

Inefficient packing of coal particles will lead to errors in the "true" swelling ratio. To minimize this effect, all coals were ground to -100 Tyler mesh before swelling. The reproducibility of the measurements was good. The average of five measurements using the pyridine-extracted Bruceton coal and benzene, for example, was 1.58 ± 0.03 (r.s.d.). The swelling ratio did not depend on the amount of coal which was typically 400-600 mg.

The volumetric techniques has two distinct advantages over the gravimetric technique: (1) the volumetric techniques is much more rapid and (2) it is insensitive to solvent that fills pores and, hence, no correction is required to obtain the "true" swelling ratio.

The swelling ratio, $Q_{v,dry}$, must be corrected for mineral matter in order to compare it with the gravimetrically obtained swelling ratio, $Q_{w,dmmf}$. Although the mineral matter is not expected to swell, it occupies a volume. The volume of dmmf coal per unit volume of dry coal is $(1 - x/\rho_{mm})$, where x is the weight fraction of mineral matter of density ρ_{mm} . A value of 2.7 g/ml was chosen for ρ_{mm} , a commonly accepted value. The volume of solvent absorbed per unit volume of dry coal is $(Q_{v,dry} - 1)$. The swelling ratio, $Q_{v,dmmf}$, is therefore

$$Q_{v,dmmf} = \frac{(Q_{v,dry} - 1) + (1 - x/\rho_{mm})}{(1 - x/\rho_{mm})} \quad (36)$$

Simplifying gives

$$Q_{v,dmmf} = \frac{Q_{v,dry} - x/\rho_{mm}}{1 - x/\rho_{mm}} \quad (37)$$

Equation 37 was used to convert the experimental swelling ratios, $Q_{v,dry}$, to a dmmf basis.

3. Comparison of Swelling Measurements

The two independently-measured swelling ratios, $Q_{w,dmmf}$ and $Q_{v,dmmf}$ were compared for the pyridine-extracted Bruceton and Illinois No. 6(1) coals using a variety of swelling solvents. The data are contained in Table VII. $Q_{w,dmf}$ is larger than $Q_{v,dmmf}$ in all cases. This is expected since $Q_{w,dmmf}$ is a measure of accessible pore volume as well as the amount of swelling. A plot of $Q_{v,dmmf}$ against $Q_{w,dmmf}$ is nearly linear for both coals (Figure 6 and 7). For the Bruceton coal and ten solvents, a regression analysis yields the equation

$$Q_{w,dmmf} = 0.928 Q_{v,dmmf} + 0.27 \quad (38)$$

with correlation coefficient of 0.98. For the Illinois No. 6(1) coal and ten solvents, the analysis yields the equation

$$Q_{w,dmmf} = 1.01 Q_{v,dmmf} + 0.18 \quad (39)$$

with a correlation coefficient of 0.97.

TABLE VII

COMPARISON OF GRAVIMETRIC AND VOLUMETRIC SWELLING RATIOS
ON A DRY, MINERAL MATTER FREE BASIS

Solvent	Illinois No. 6(1)		Bructon	
	$Q_{w,dmmf}$	$Q_{v,dmmf}$	$Q_{w,dmmf}$	$Q_{v,dmmf}$
1,4-Dioxane	1.87	1.75	2.20	2.09
Pyridine	2.25	1.97	2.46	2.35
Cyclohexane	1.20	1.00	1.25	1.09
Ethanol	1.71	1.45	1.71	1.45
Toluene	1.60	1.40	1.65	1.56
2-Propanol	1.71	1.54	----	----
Methylene Chloride	1.64	1.49	1.88	1.66
Acetonitrile	1.61	1.40	1.57	1.44
Benzene	1.61	1.39	1.68	1.59
Chlorobenzene	1.67	1.54	1.90	1.83
Acetone	----	----	1.81	1.64

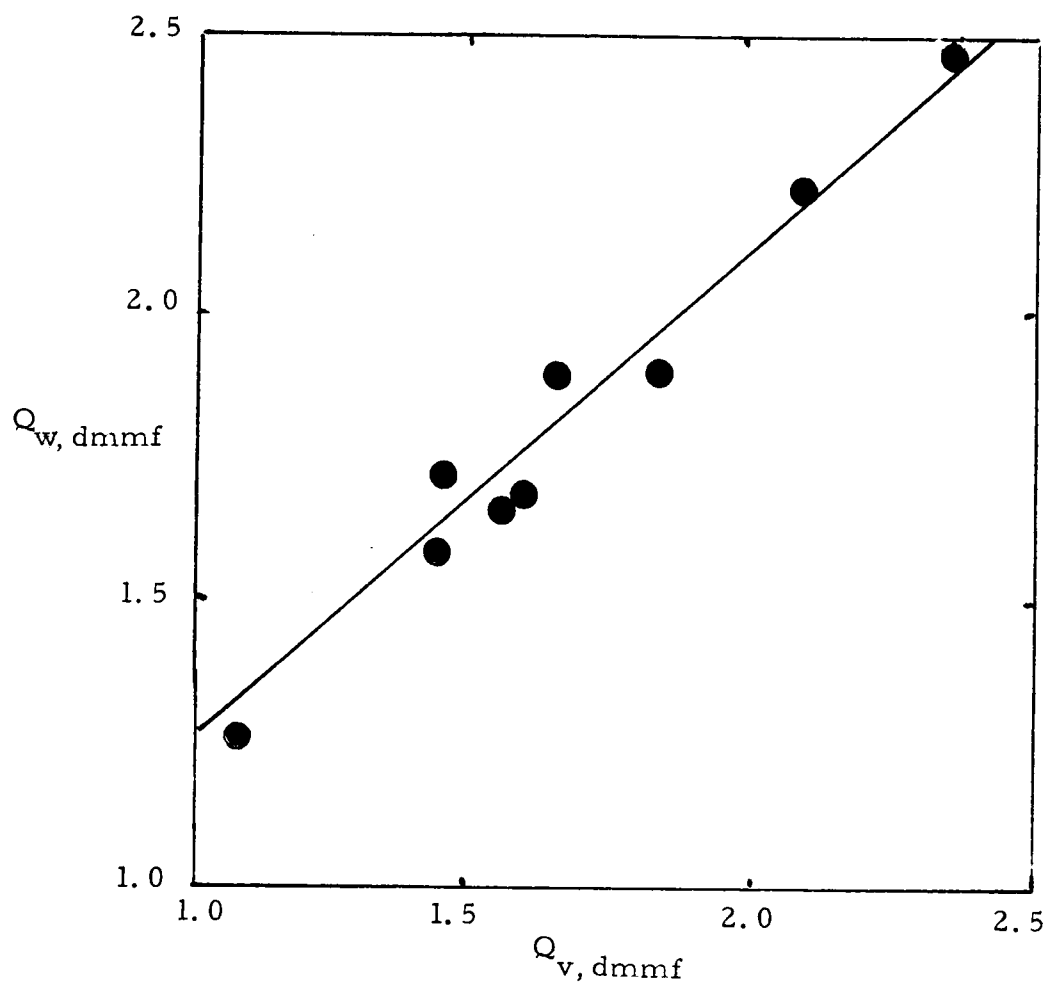


Figure 6. Plot of Q_v, dmmf Versus Q_w, dmmf for Pyridine-Extracted Bruceton Coal.

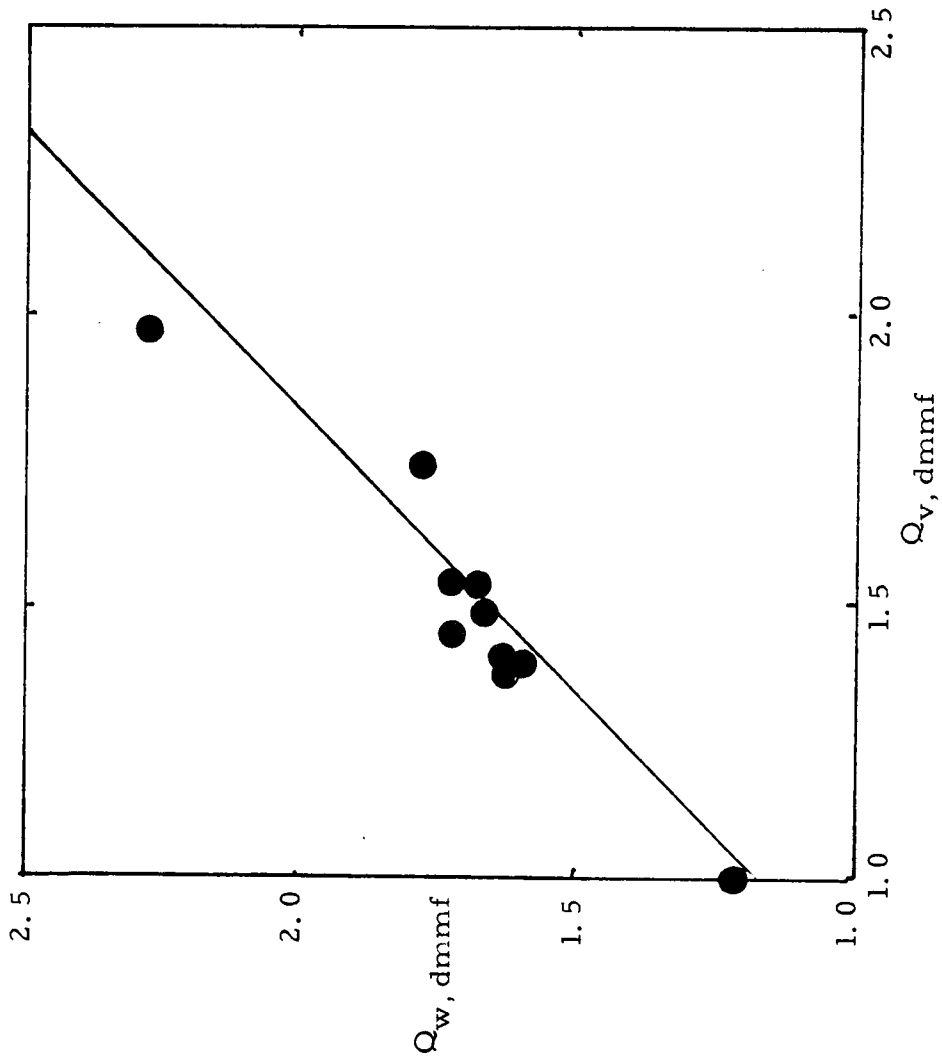


Figure 7. Plot of Q_v, dmmf Versus Q_w, dmmf for the Pyridine-Extracted Illinois No. 6(1) coal.

The accessible pore volume per ml of dmmf coal, V_p , will depend on several factors:¹¹⁴ (1) surface tension of the solvent in equilibrium with its vapor, (2) the contact angle between the absorbed solvent vapor and the solid coal, and (3) the degree of swelling. If the overall effect of these factors on V_p is large, then V_p may vary significantly from one solvent to the next. However, if the effect of these factors is small, then V_p is virtually cast. If V_p is cast, then a linear relationship between $Q_{w,dmmf}$ and $Q_{v,dmmf}$ with a slope of 1.00 is expected.

$$Q_{w,dmmf} = Q_{v,dmmf} + V_p \quad (40)$$

The plots of $Q_{w,dmmf}$ against $Q_{v,dmmf}$ for both coals yield slopes very close to 1.00. Therefore, the effect of surface tension, contact angle, and degree of swelling appear to have little effect on the total accessible pore volume of the coals. Accordingly, the intercept should be a good estimate of V_p .

V_p values for the pyridine-extracted Bruceton and Illinois No. 6(1) coals are estimated as 0.27 ml and 0.18 ml per ml of dmmf coal, respectively. The % total accessible pore volume is $(0.27/1.27) 100 = 21\%$ for Bruceton coal and $(0.18/1.18) 100 = 15\%$ for the Illinois No. 6(1) coal. These values fall within the range of pore volumes accessible to helium of several American coals as measured by Nandi and Walker.⁹⁶ The coals varied widely in % pore volume, ranging from 4 to 23%. Thus, the pore volumes estimated for these two coals are consistent with other studies on coal porosity, giving credence to both swelling techniques.

B. Solubility Parameters of Coals

The volumetric swelling technique was employed to measure the solubility parameters of the pyridine-extracted Bruceton and Illinois No. 6(2) coals. This method was shown to be rapid, reliable and insensitive to solvent that fills pores. The solubility parameters of the swelling solvents were taken from the review articles of Barton⁸⁸ or Hansen.⁸⁹ Five different solubility parameters are given for each solvent. The symbol δ represents the thermodynamically-determined parameter defined by Equation 12. This parameter has proved useful for regular solutions, i.e. nonpolar systems. For nonregular solutions, the total solubility parameter, δ_o , has been useful, and is defined by the equation

$$\delta_o = (\sum \delta_i)^{1/2} \quad (41)$$

where δ_i are the empirical estimates of the various contributions from dispersion forces, δ_D , polar forces, δ_P , and hydrogen bonding, δ_H . δ and δ_o may be compared but in general are not expected to be equal since δ is a thermodynamic quantity and δ_o is an empirical quantity. Often, the associated interactions are collectively described by the equation

$$\tau = (\delta_H^2 + \delta_P^2)^{1/2} \quad (42)$$

where τ is the polar solubility parameter of Blanks and Prausnitz.⁸⁶

The measurement of a solubility parameter of a crosslinked elastomer involves plotting the solubility parameter of the solvent

against the degree of swelling of the elastomer caused by that solvent. The solubility parameter of the solvent that swells the elastomer the most is assigned as the solubility parameter of the elastomer (see Figure 3). Therefore we plotted the thermodynamic solubility parameters, δ , of the swelling solvents used in this study against the respective swelling ratios, $Q_{v,dry}$, for the pyridine-extracted Bruceton and Illinois No. 6(2) coals. The results are shown in Figures 8 and 9. Clearly, no correlation is observed. The points appear randomly scattered.

The failure of this treatment to yield a solubility parameter for the coals is not surprising: regular solution theory applies only to solutions in which the mixing is virtually random. Many of these solvents are capable of forming hydrogen bond complexes with acid sites in the coal. This effect is particularly striking for pyridine and biphenyl, which have similar δ values of 10.7 and 10.6 (cal/cm³)^{1/2} and therefore might be expected to be equally effective swelling solvents based on their δ values alone. However, pyridine swells the Bruceton coal to more than double its own volume ($Q_{v,dry} = 2.32$) whereas biphenyl is a poor swelling solvent ($Q_{v,dry} = 1.15$). We will demonstrate later that this difference can be largely attributed to the ability of pyridine to hydrogen bond to the coal network. The point here is that regular solution theory will not apply to systems in which highly specific interactions are operating, and the failure of the treatment under these circumstances is expected.

Since mixing is expected to be random only in nonpolar systems, we plotted the δ values of the nonpolar solvents against $Q_{v,dry}$ for

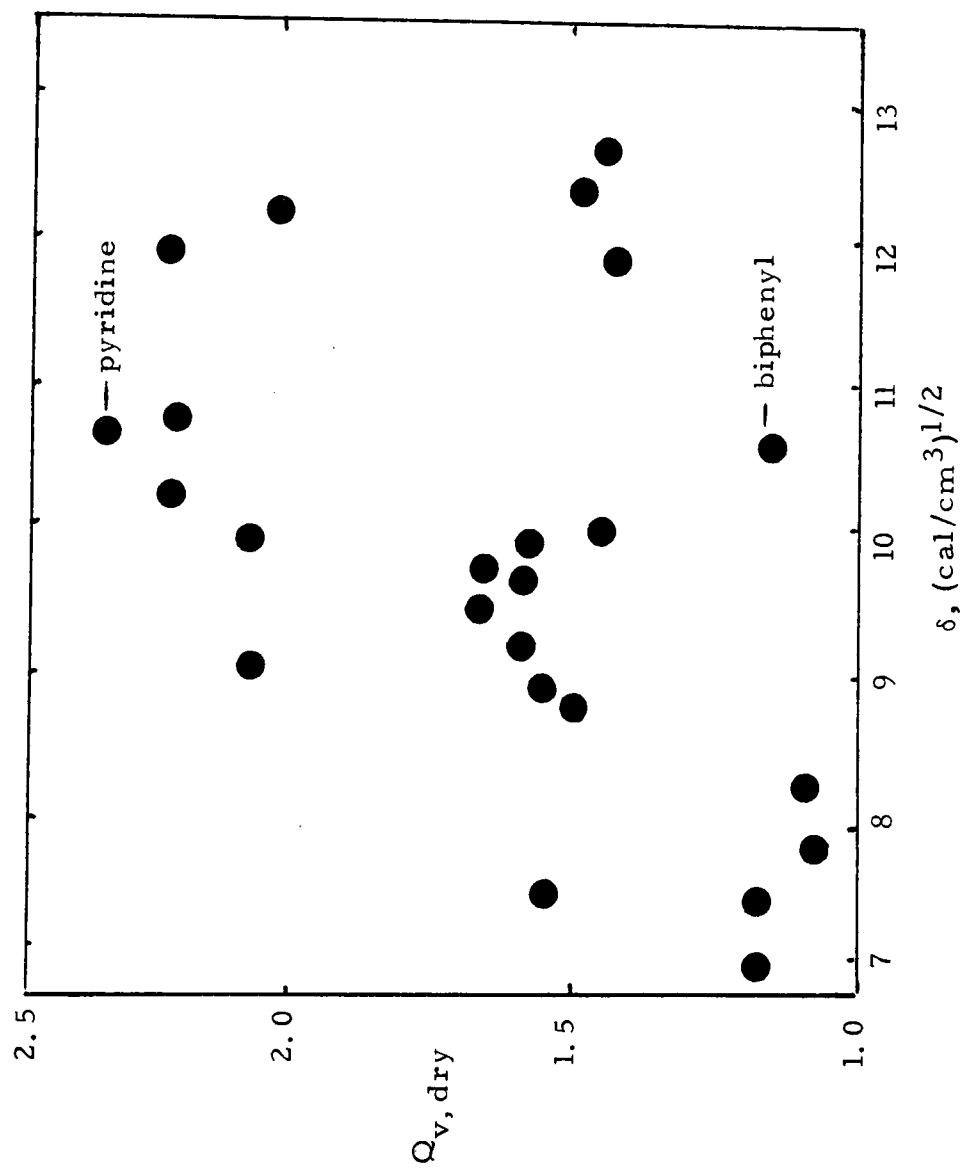


Figure 8. Plot of δ of Solvent Versus $Q_{v,dry}$ for the Pyridine-Extracted Bruceton Coal.

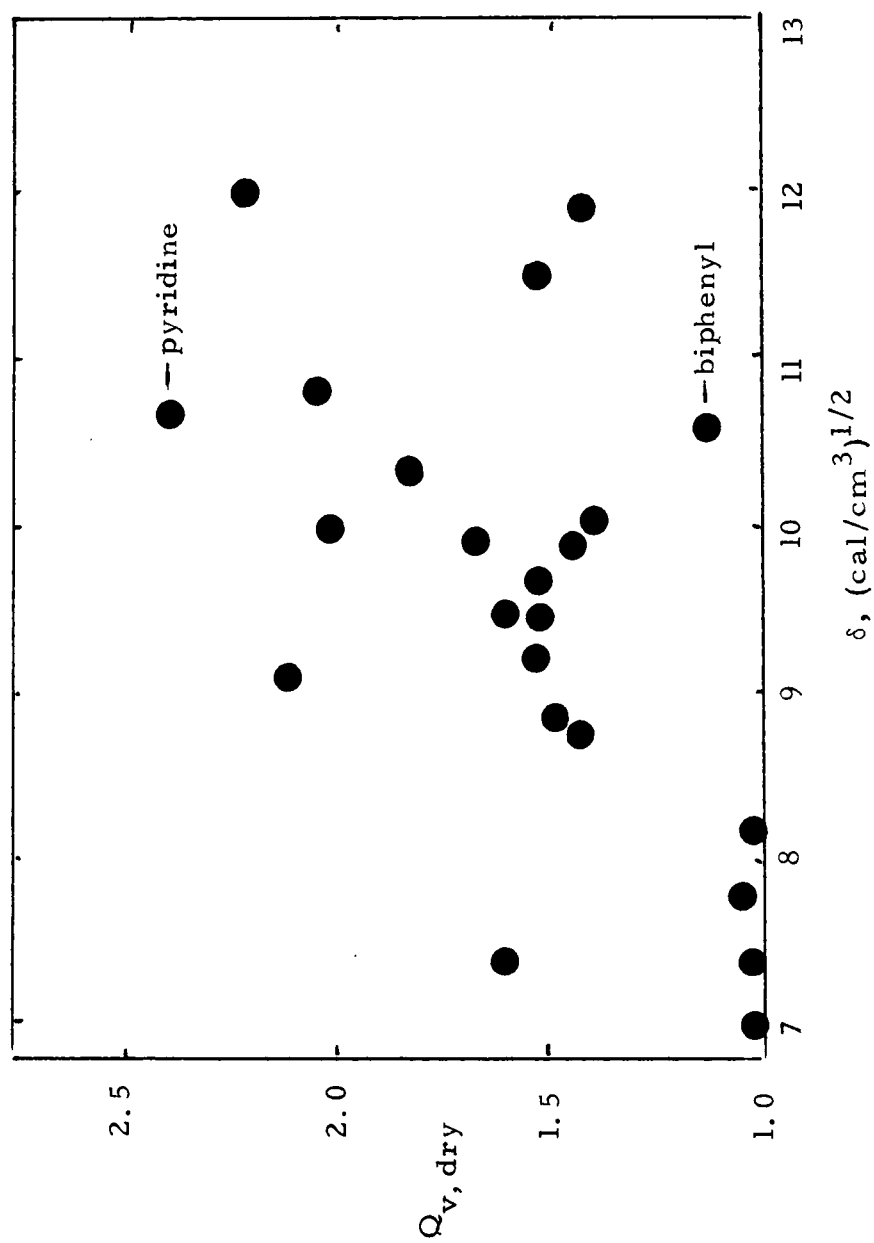


Figure 9. Plot of δ of Solvent Versus $Q_{v,dry}$ for the Pyridine-Extracted Illinois No. 6(2) Coal.

these two coals. The results are shown in Figures 10 and 11. In accord with the predictions of regular solution theory, a good correlation is observed, resulting in a maximum in $Q_{v,dry}$ at a δ value of $9.5 \text{ (cal/cm}^3\text{)}^{1/2}$ for each coal. Hence, this δ value is assigned to the coals. The curves are remarkably symmetrical, demonstrating that the coals, in spite of their enormous complexity, are surprisingly well-behaved. Moreover, because random mixing is expected in these systems, χ values for each coal-solvent pair and ultimately, the average molecular weight per crosslink, $\bar{M}_c$, can be calculated using Equations 7, 9 and 14. The results of these calculations are presented in Section V.D.

C. Evidence for Hydrogen Bond Crosslinks

Larsen and coworkers argued that most hydroxyl groups in solid coals are hydrogen bonded.¹¹⁵ In this elegant study, the hydroxyl groups were converted to their $-\text{OSnBu}_3$ derivatives. The Sn Mossbauer spectra of the derivatized coals revealed that most of the tin was in a trigonal bipyramidal configuration, which required the nearby presence of another heteroatom. Thus, the hydroxyl groups in the parent coals were probably paired with heteroatoms as well. Clearly, the IR spectra of coals indicate that extensive internal hydrogen bonding occurs.¹¹⁵

A relevant question in regard to the above results is this: Are the hydrogen bonds in coals formed between two different clusters that make up the macromolecular chains, termed intercluster, or are they confined to a single cluster, termed intracluster? If they are inter-cluster hydrogen bonds, then they will act as crosslinks between the

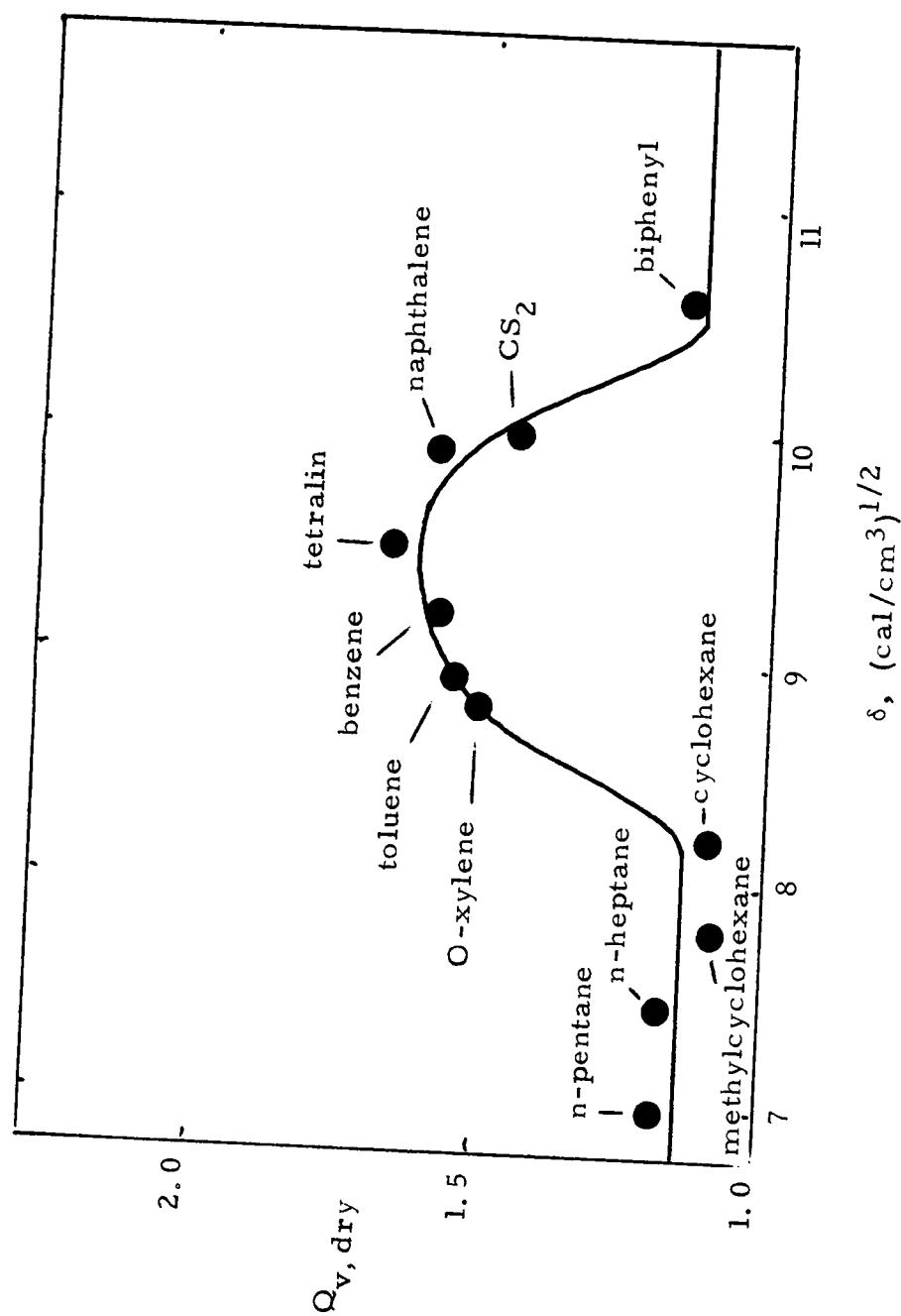


Figure 10. Plot of δ of Nonpolar Solvent Versus $Q_{v,dry}$ for Pyridine-Extracted Bruceton Coal.

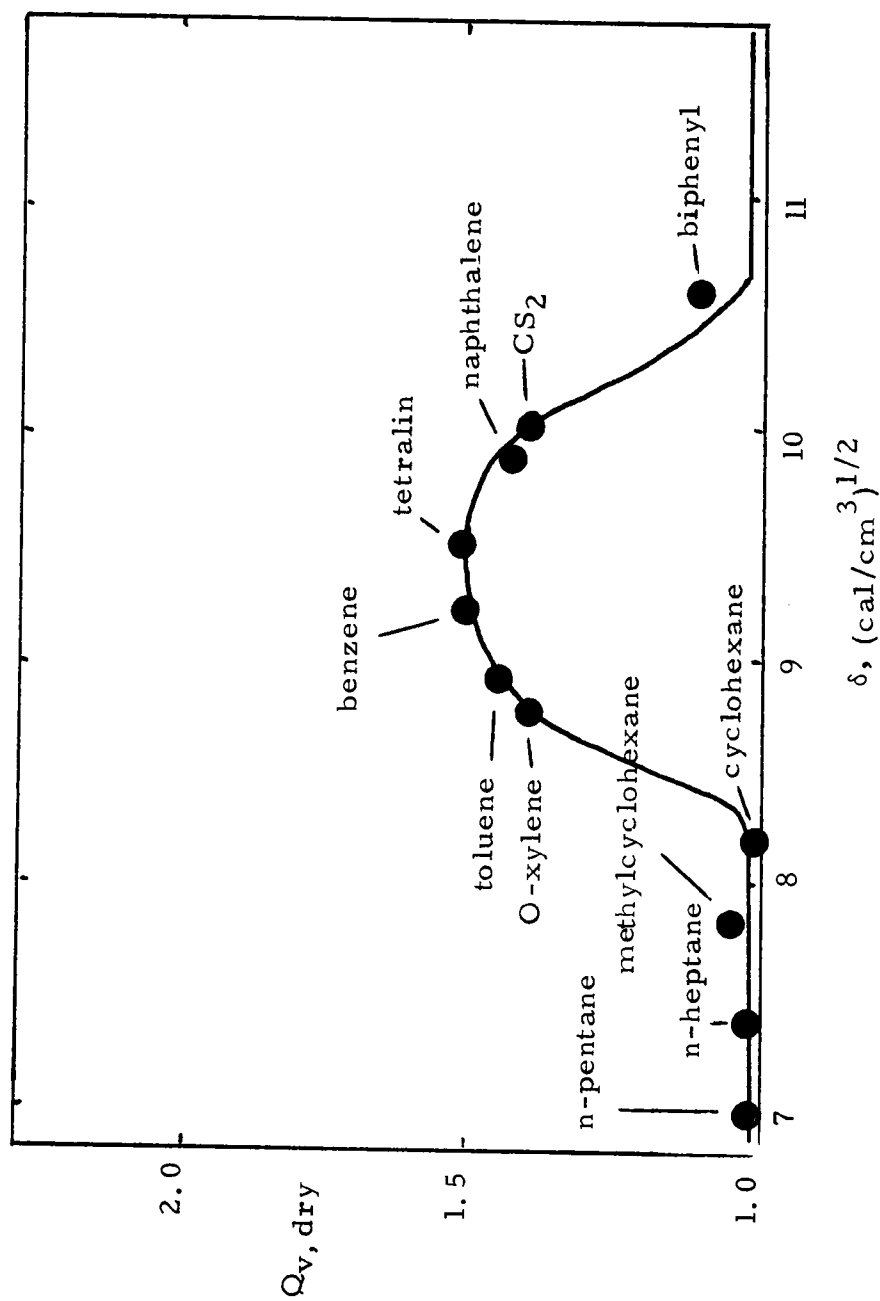
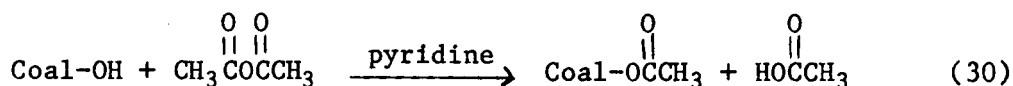


Figure 11. Plot of δ of Nonpolar Solvent Versus $Q_{v,dry}$ for Pyridine-Extracted Illinois No. 6(2) Coal.

chains, and may have considerable impact on the structural integrity of the coal. However, if they are intracluster hydrogen bonds, they do not act as crosslinks between chains, and therefore they will have little or no impact on the structural integrity of the coal.

To investigate this question, we studied the swelling behavior of the coals in nonpolar solvents with and without the hydrogen bond network. The network was removed by O-acetylation of the hydroxyl groups in the coal. This reaction, an established method for counting hydroxyl groups in coal,¹¹⁰ consists of refluxing the coal in pyridine in the presence of acetic anhydride.



The O-acetylated coals were exhaustively extracted with pyridine prior to swelling. Nonpolar solvents were chosen as the swelling agents because of their inability to perturb the hydrogen bond network. Hence, if the hydrogen bonds serve as crosslinks, then a given nonpolar solvent should swell the O-acetylated coal more than the unextracted coal simply because the O-acetylated coal has a lower crosslink density. If the bonds do not serve as crosslinks, no difference in swelling behavior is expected.

The swelling ratios, $Q_{v,\text{dry}}$, were measured on the unextracted, pyridine-extracted, and O-acetylated Bruceton and Illinois No. 6(2) coals using nonpolar solvents that cover a wide range of δ values. The δ values were then plotted against $Q_{v,\text{dry}}$ for each coal. The results are shown in Figures 12 and 13. Three distinctly different curves are observed for each coal. The degree of swelling in the good nonpolar

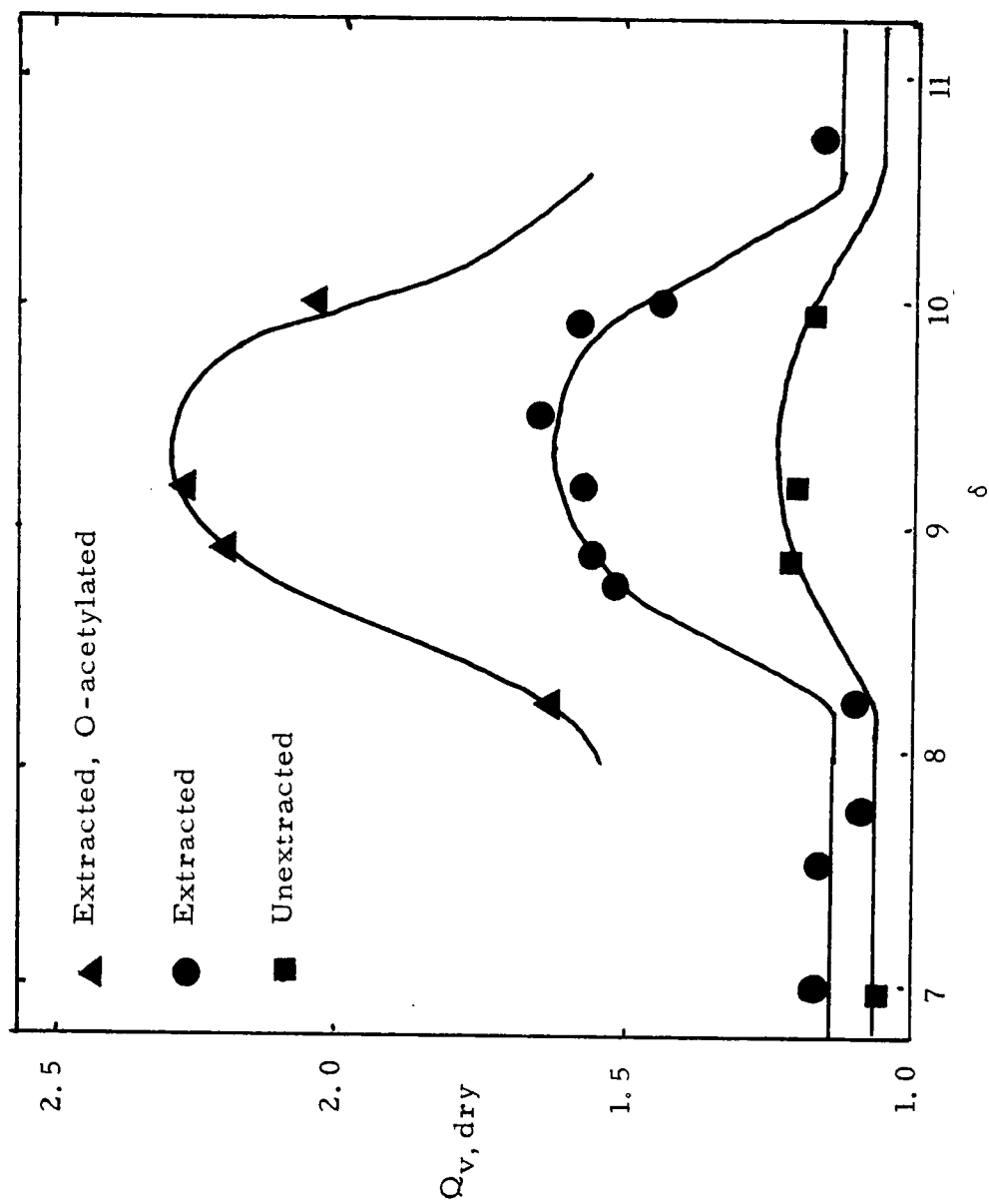


Figure 12. Plot of δ Nonpolar Solvent Versus $Q_{v,dry}$ for the Bruceton Coals.

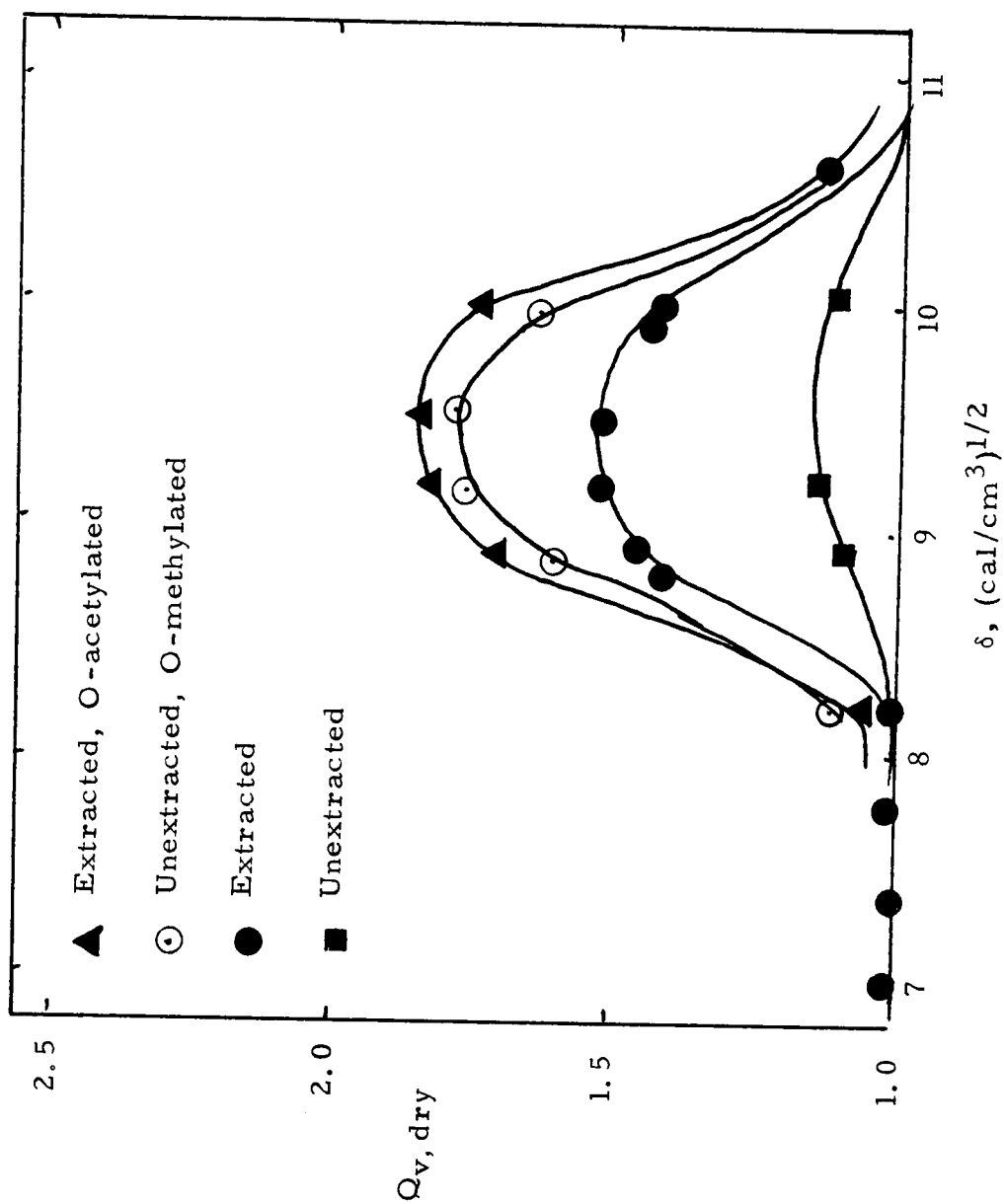


Figure 13. Plot of δ of Nonpolar Solvent Versus $Q_{v,dry}$ for the Illinois No. 6(2) Coals.

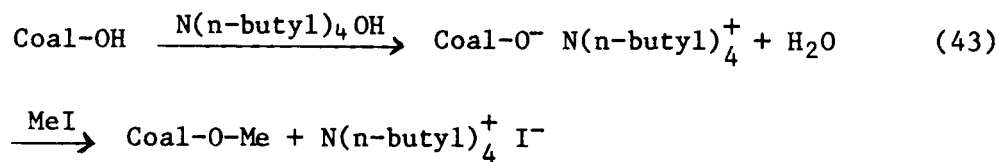
solvents, roughly in the range of 9 to 10 δ , increases in the order unextracted < extracted < O-acetylated coal. If hydrogen bonds serve as crosslinks, the O-acetylated coal, because of its lower crosslink density, is expected to swell the most. This is observed. The extraction with pyridine only partially disrupts the hydrogen bond crosslinks since the extracted coals swell more than the unextracted coals but less than the O-acetylated coals.

Before accepting these conclusions, it is worthwhile to briefly examine some alternative explanations that may account for the observed behavior. These include: (1) the chemical nature of the O-acetylated, extracted, and unextracted coals differ significantly and this accounts for different swelling behavior, and/or (2) the extraction process loosens the coal network by removing noncomplexed material, allowing it to swell more in a good solvent.

With regard to explanation (1), there is existing evidence that coal extracts and residues are similar in chemical nature.²³⁻²⁸ The elemental analysis of the unextracted and extracted coals are similar as well (see Table I, p 46). Thus, the different swelling behavior of the unextracted and extracted coals is probably not due to differences in their chemical nature. It might be argued that the O-acetylation reaction makes the coal less polar, allowing it to swell more in nonpolar solvents. Roughly, this amounts to a consideration of the difference in the polarities of phenol and phenyl acetate in nonpolar solvents. These molecules have similar solution dipole moments (measured in benzene) of 1.6 and 1.69 D, respectively.^{116,117} Hence,

it is unlikely that the O-acetylated coal is less polar than the unextracted or extracted coal.

The extracted coal network may be more flexible than the unextracted coal network simply because noncomplexed material hinders extension of the network (Explanation 2). To investigate this question, we acquired an Illinois No. 6(2) coal that was O-methylated but left unextracted. The O-methylation was carried out according to Liotta's method,¹¹¹ which consists of reacting the coal in an aqueous methanol solution of tetra-n-butyl ammonium hydroxide, followed by addition of methyl iodide.



The O-acetylation reaction employs pyridine at its boiling point as the solvent and therefore considerable material is extracted from the coal. However, the O-methylation method employs aqueous methanol at room temperature as the solvent. Under these conditions, virtually no material is extracted from the coal. Hence, this coal is O-methylated and unextracted.

The results of swelling the coal with the set of nonpolar solvents is shown in Figure 13. Note that this coal, although unextracted, swells considerably more than the extracted coal. It swells somewhat less than the O-acetylated coal.

The results demonstrate that it is not merely the removal of extractable material that allows the coal to swell more in a given

nonpolar solvent. If this were true, the unextracted, O-methylated coal would swell less than the extracted coal, not more. The most likely explanation for the observed behavior is that the hydroxyl groups are involved in intercluster hydrogen bonding and serve as crosslinks in the presence of a nonhydrogen bonding (nonpolar) solvent. The O-methylation reaction eliminates these interactions and allows the coal to expand more to contain the solvent.

There are two possible mechanisms that can explain how the pyridine-extraction partially disrupts the hydrogen bond crosslinks. First, a hydrogen bond complex may exist directly between two otherwise independent chain sections in the network. Pyridine, a good hydrogen bond acceptor, solvates this complex and swells the coal, which displaces the two functional groups that originally formed the complex. It seems unlikely that all of the complexes reform upon removal of the pyridine. Apparently some do reform (or alternatively were never disrupted) because the extracted coals swell less than O-acetylated coals. Second, it is possible that the extractable material, by forming complexes with the insoluble network, stiffens it by tying otherwise independent chain sections together. Removal of this material would loosen the network. Both of these explanations are plausible and have the overall effect of decreasing the noncovalent crosslink densities of the unextracted coals. We make no attempt here to distinguish between the two mechanisms.

The results presented thus far demonstrates that (1) the swelling behavior of the Bruceton and Illinois No. 6(2) coals in nonpolar solvents can be dealt with quantitatively and (2) hydrogen bonds play a

very important structural role in the coals. From these conclusions, we hypothesized that the swelling behavior of the coals in polar solvents might be related to the solvent's ability to form hydrogen bonds with the coal network, and that this might be dealt with quantitatively as well.

Recall that the empirical solubility parameter of a polar molecule, δ_o , can be separated into its respective components due to dispersion forces, polar forces and hydrogen bonding (Equation 44). The component due to dispersion forces, δ_D , is a nonpolar solubility parameter. Pyridine, for example, has a δ_D value of 9.3, which is very close to the optimum nonpolar δ value of 9.5 assigned to the Bruceton and Illinois No. 6(2) coals in this study. Based on this criterion, pyridine is expected to have a strong affinity for the hydrocarbon portion of the coals. However, pyridine swells the coals more than even the best nonpolar solvent. For example, pyridine swells the extracted Bruceton coal to double its own volume ($Q_{v,dry} = 2.32$), whereas tetralin, the best nonpolar solvent for the coal, swells it about half that much ($Q_{v,dry} = 1.65$). This "excess" swelling might be attributed to the ability of pyridine to disrupt the hydrogen bond crosslinks, thus allowing the coal to expand to contain it.

To test this hypothesis, we plotted the swelling ratios, $Q_{v,dry}$, of several polar solvents against their nonpolar solubility parameters using the extracted Bruceton and Illinois No. 6(2) coals. The results are shown in Figures 14 and 15. None of the solvents chosen for this analysis are capable of hydrogen bonding with themselves. This therefore simplifies the interpretation of the results.

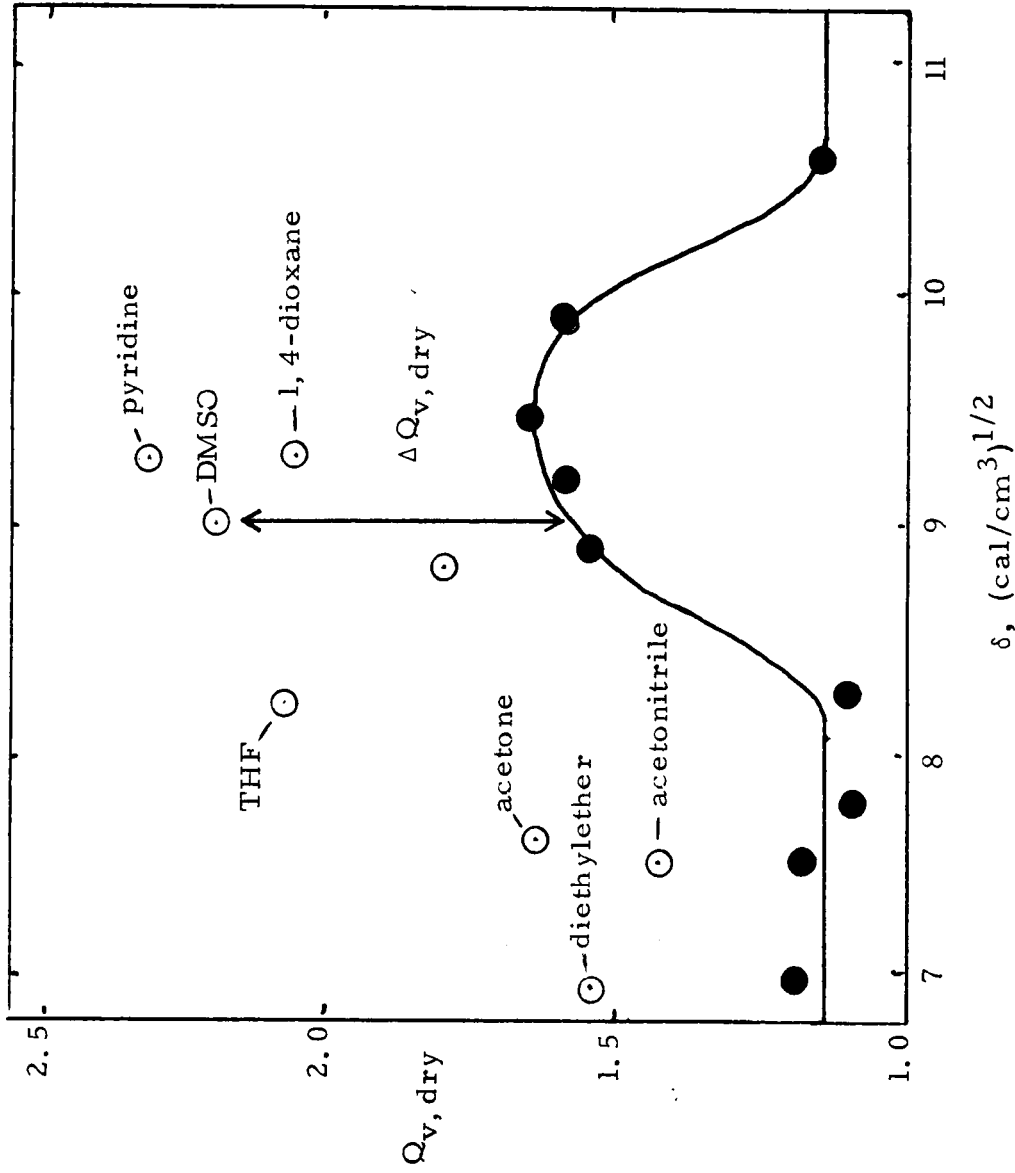


Figure 14. Plot of Nonpolar δ of Polar Solvents Versus $Q_{v,dry}$ for the Extracted Bruce-ton Coal.

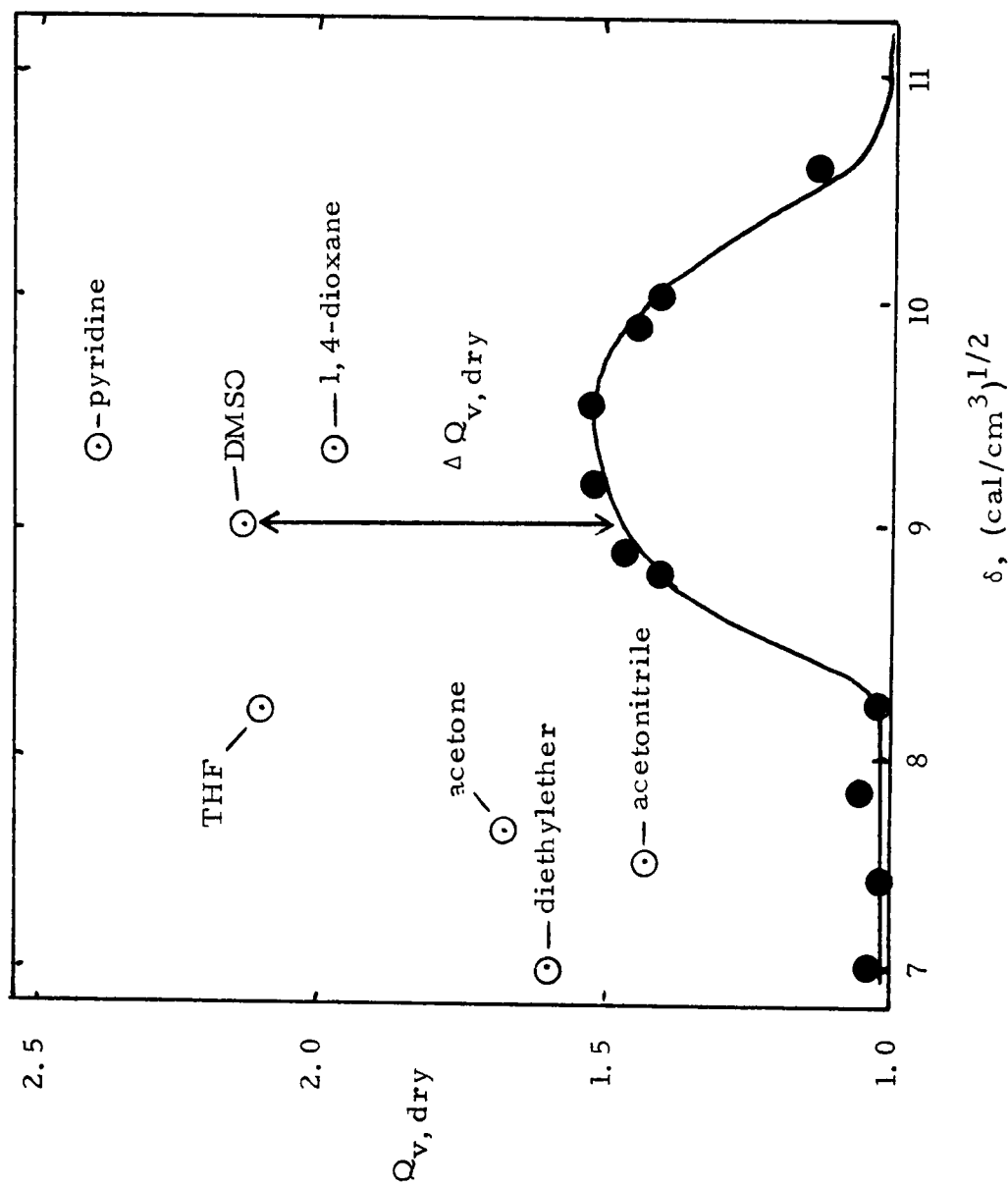


Figure 15. Plot of Nonpolar δ of Polar Solvents Versus $Q_{v,dry}$ for the Extracted Illinois No. 6(2) Coal

Also shown in the figures are the curves resulting from the analysis of the nonpolar solvents. The difference in $Q_{v,dry}$ of the polar solvent and the corresponding value on the curve is designated as $\Delta Q_{v,dry}$. $\Delta Q_{v,dry}$ is the excess swelling due to the polar nature of the solvent.

We plotted these $\Delta Q_{v,dry}$ values against the hydrogen bond enthalpies for the interaction with p-fluorophenol, ΔH_f^O , with these solvents. These quantities, determined calorimetrically by Arnett and coworkers,^{44,45} are a measure of the ability of the solvent to accept a hydrogen bond from p-fluorophenol. The phenol is a suitable model for this analysis since phenolic hydroxyl groups are the principal functional groups in coals that are capable of donating a hydrogen bond to these swelling solvents. The results are shown in Figures 16 and 17. With the exception of tetrahydrofuran, a good linear correlation is observed for both coals. Disregarding the THF data, a least-squares equation for the data on the Bruceton coal is

$$\Delta Q_{v,dry} = 0.127 \Delta H_f^O - 0.220 \quad (44)$$

with a correlation coefficient of 0.96. The same analysis on the Illinois No. 6(2) data yields the equation

$$\Delta Q_{v,dry} = 0.14 \Delta H_f^O - 0.178 \quad (45)$$

with a somewhat less satisfactory correlation coefficient of 0.90.

The standard deviation of the ΔH_f^O values is approximately 0.1 kcal/mol whereas the standard deviation of the $\Delta Q_{v,dry}$ values is

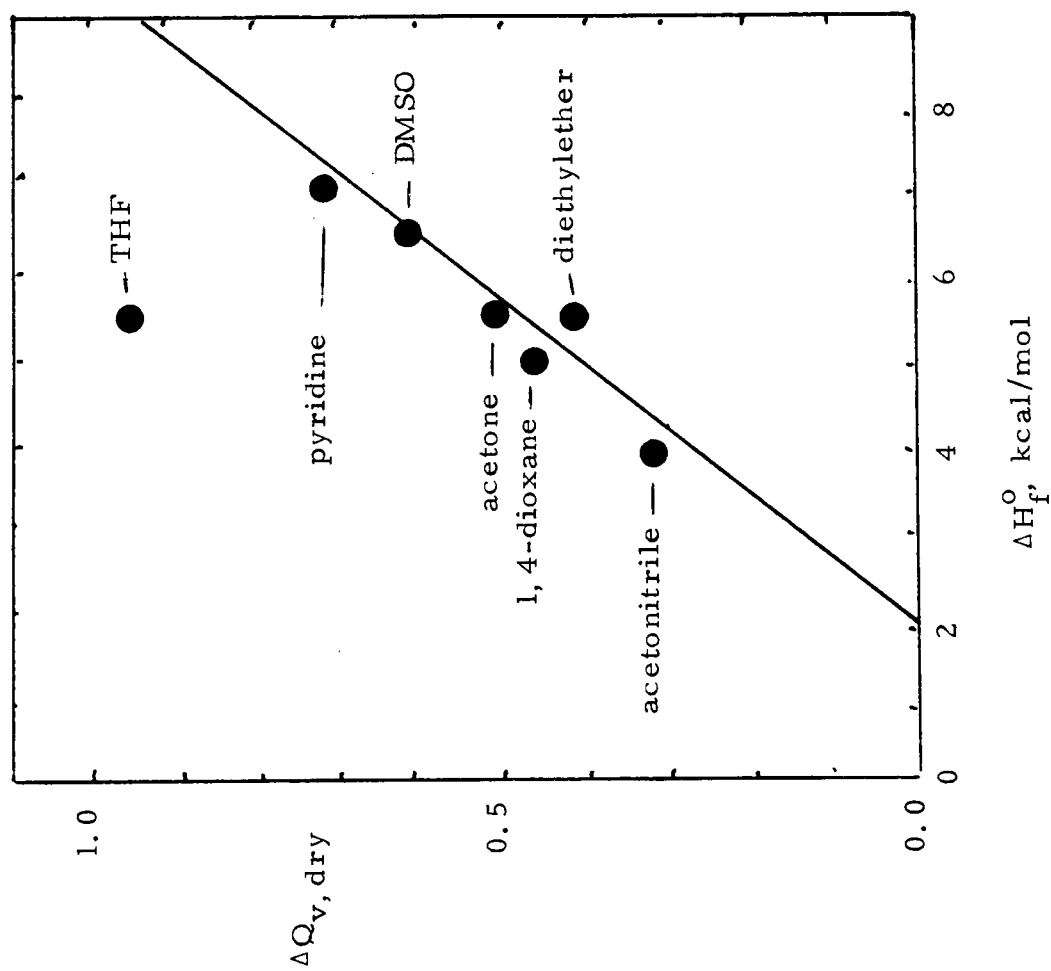


Figure 16. Plot of ΔH_f° of Polar Solvent Versus $\Delta Q_{v,dry}$ for the Extracted Bruceton Coal.

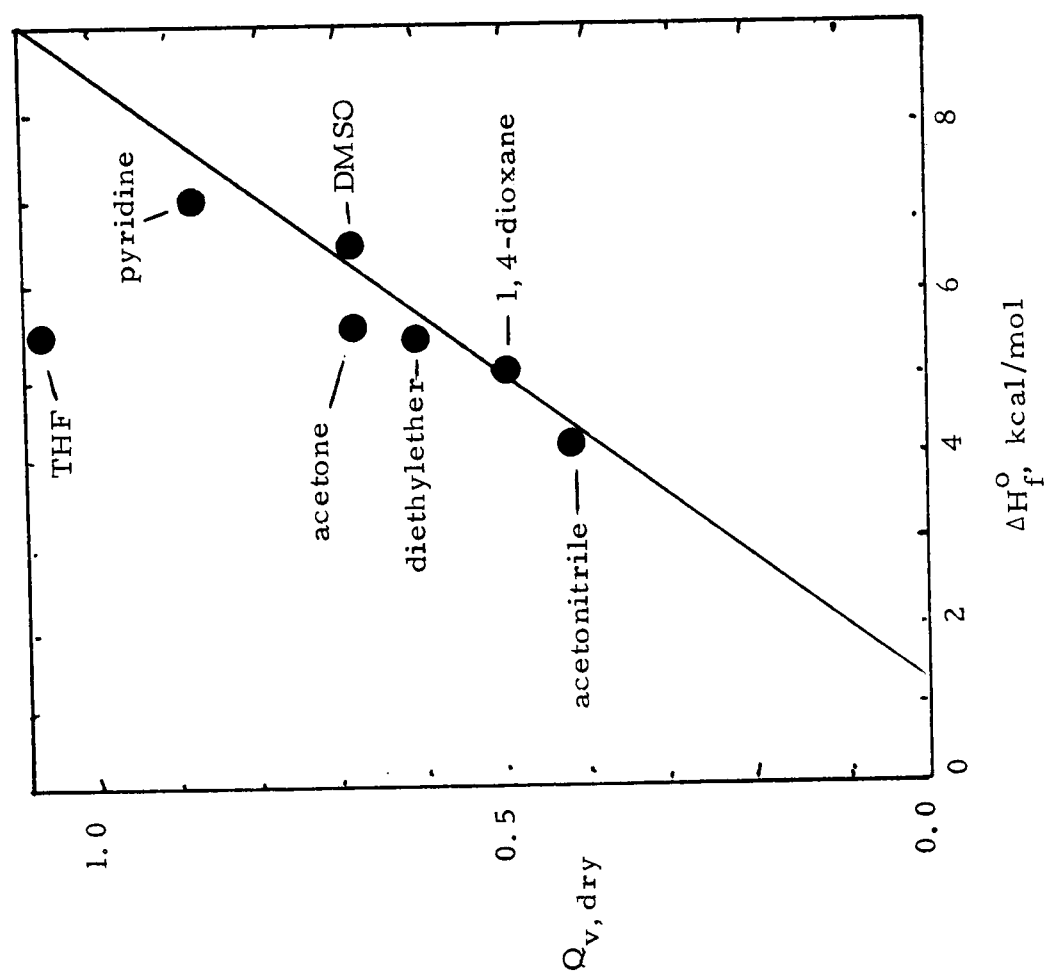


Figure 17. Plot of ΔH_f° of Polar Solvent Versus $\Delta Q_{v,dry}$ for the Extracted Illinois No. 6(2) Coal.

generally 0.06 to 0.10. Thus, the relative error of the $\Delta Q_{v,dry}$ values is substantially greater than that of the ΔH_f^O values. In some instances, only one swelling measurement was made and therefore the uncertainty is not known. In light of this and the fact that these solvents represent several chemical families, the correlation is surprisingly good. The peculiar behavior of THF will be discussed later.

These results demonstrate that the degree of swelling of the coals in polar solvents correlates well with the ability of the solvent to accept a hydrogen bond, providing that the affinity of the solvent for the hydrocarbon portion of the coal is taken into account. The inference is clear; the degree of swelling of the coals in polar solvents is a direct consequence of the disruption of the hydrogen bond crosslinks in the coal. The solvents that form the strongest hydrogen bonds with the coal will disrupt more of the crosslinks, and therefore the coal will expand more to contain it. Since it is clear that hydrogen bonds contribute significantly to the structural integrity of the coals, this is a reasonable explanation. Moreover, this interpretation accounts for much of the swelling behavior of the coals that was previously bewildering.

We also present the results of a similar analysis on the unextracted Illinois No. 6(2) coal. The $\Delta Q_{v,dry}$ versus ΔH_f^O plot is shown in Figure 18. No ΔH_f^O values were available for nitrobenzene and benzonitrile. However, Arnett and coworkers^{44,45} have found a reasonably good correlation between ΔH_f^O and the so-called Gutman's "donor numbers", DN, which are known for these solvents.¹¹⁸ The DN

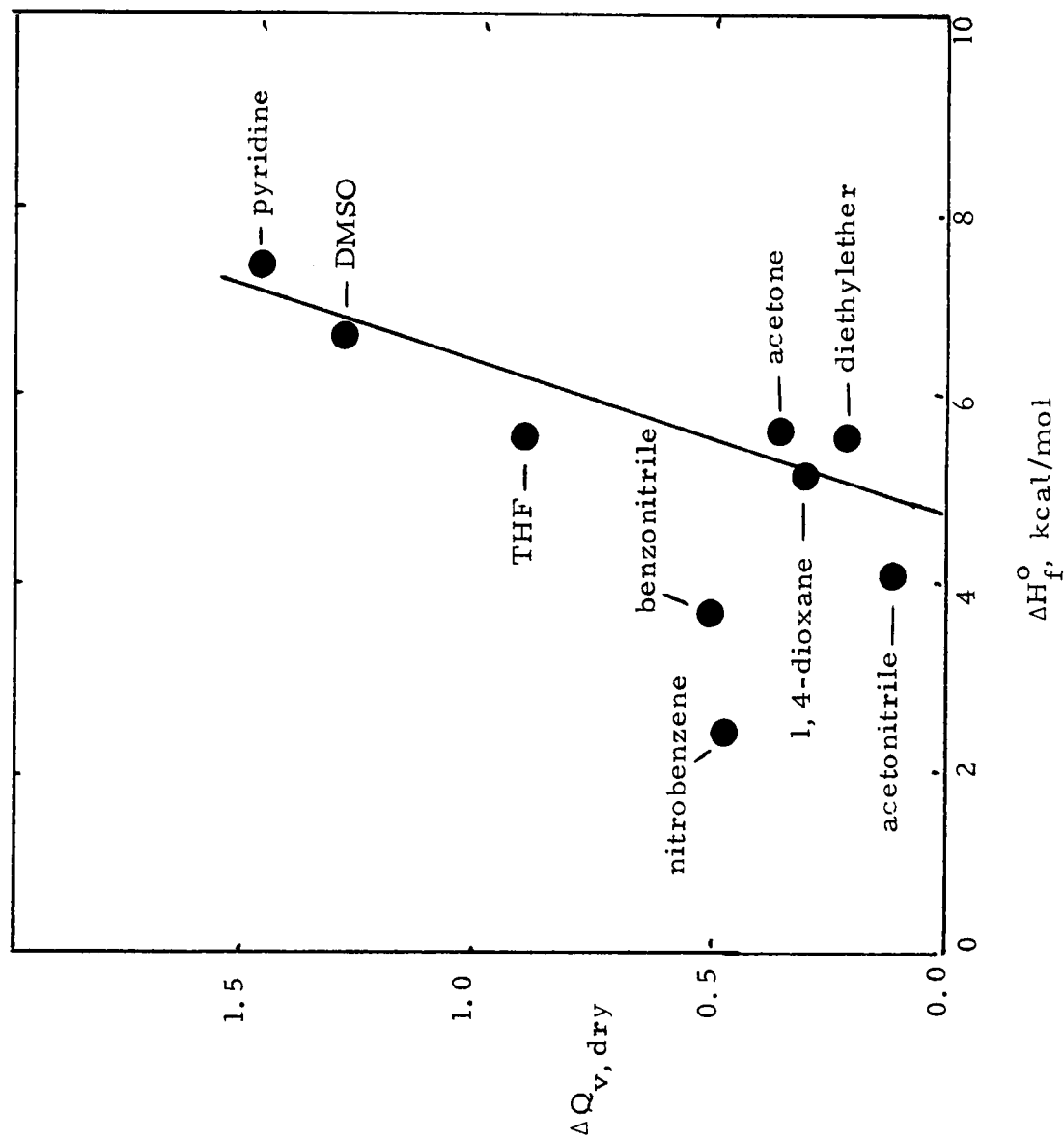


Figure 18. Plot of ΔH_f^0 of Polar Solvent Versus $\Delta Q_{v, \text{dry}}$ for the Unextracted Illinois No. 6(2) Coal.

of a base is simply the calorimetrically-determined enthalpy of adduct formation between the base and antimony pentachloride (SbCl_5). The straight line relationship between ΔH_f^0 and DN that Arnett and coworkers obtained correspond to the equation

$$-\Delta H_f = 0.182 \text{ DN}_{\text{SbCl}_5} + 1.68 \quad (46)$$

We used this equation to calculate ΔH_f values for nitrobenzene and benzonitrile.

The plot of ΔH_f^0 versus $\Delta Q_{v,\text{dry}}$ for the unextracted Illinois No. 6(2) coal in Figure 18 shows considerable scatter. Certainly there is no good linear correlation between ΔH_f^0 and $\Delta Q_{v,\text{dry}}$, although there appears to be a general increase in $\Delta Q_{v,\text{dry}}$ with increasing hydrogen bond strength of the solvent. However, the six polar solvents that yielded a good straight line correlation for the extracted coal (see Figure 17) yield a good correlation here as well. For the purposes of this discussion, and for reasons that will become evident later, we drew a curve through this group of points. Note that the points that correspond to nitrobenzene and benzonitrile lie above this curve. We will return to this point momentarily.

Finally, we consider the deviations of the polar solvents from regular solution behavior for the O-acetylated Illinois No. 6 coal. If the deviations from $Q_{v,\text{dry}}$ versus δ plots ($\Delta Q_{v,\text{dry}}$) for the underivatized coals are due solely to hydrogen bonding interactions, then all solvents, polar and nonpolar, should lie on the same $Q_{v,\text{dry}}$ versus δ curve for the O-acetylated coals, since hydrogen bond interactions are absent in these systems.

The $Q_{v,dry}$ versus δ curve for the O-acetylated Illinois No 6(2) coal and the points corresponding to ten polar solvents are shown in Figure 19. Clearly, the deviations of many of these polar solvents from regular solution behavior are substantial. There must be some other explanation other than hydrogen bonding to account for such large deviations.

One possible explanation is that the O-acetylation reaction significantly changes the chemical nature of the coal by introducing a number of carbonyl groups into the coal (~5 per 100 C atoms). This may give rise to new types of coal-solvent interactions that are nonexistent in the underivatized coal-solvent systems. However, some of these polar solvents also deviate significantly from regular solution behavior for the O-methylated Illinois No. 6(2) coal as shown in Figure 20. No carbonyl groups were introduced into this coal. Hence, this explanation is inadequate in explaining the deviation of the polar solvents from regular solution behavior for the O-acetylated Illinois No. 6(2) coal.

Another possible explanation is that the deviation of the polar solvents for the O-methylated and O-acetylated coals are residual polar effects that are linear in hydrogen bond strengths. This would explain the good correlations observed between ΔH_f^O and $\Delta Q_{v,dry}$ for the extracted coals. The $\Delta Q_{v,dry}$ versus ΔH_f^O plot for the polar solvents and the O-acetylated coal is shown in Figure 21. Considerable scatter among the solvents is observed. Certainly there is no single general correlation between $\Delta Q_{v,dry}$ and ΔH_f^O . However, the plot can be resolved

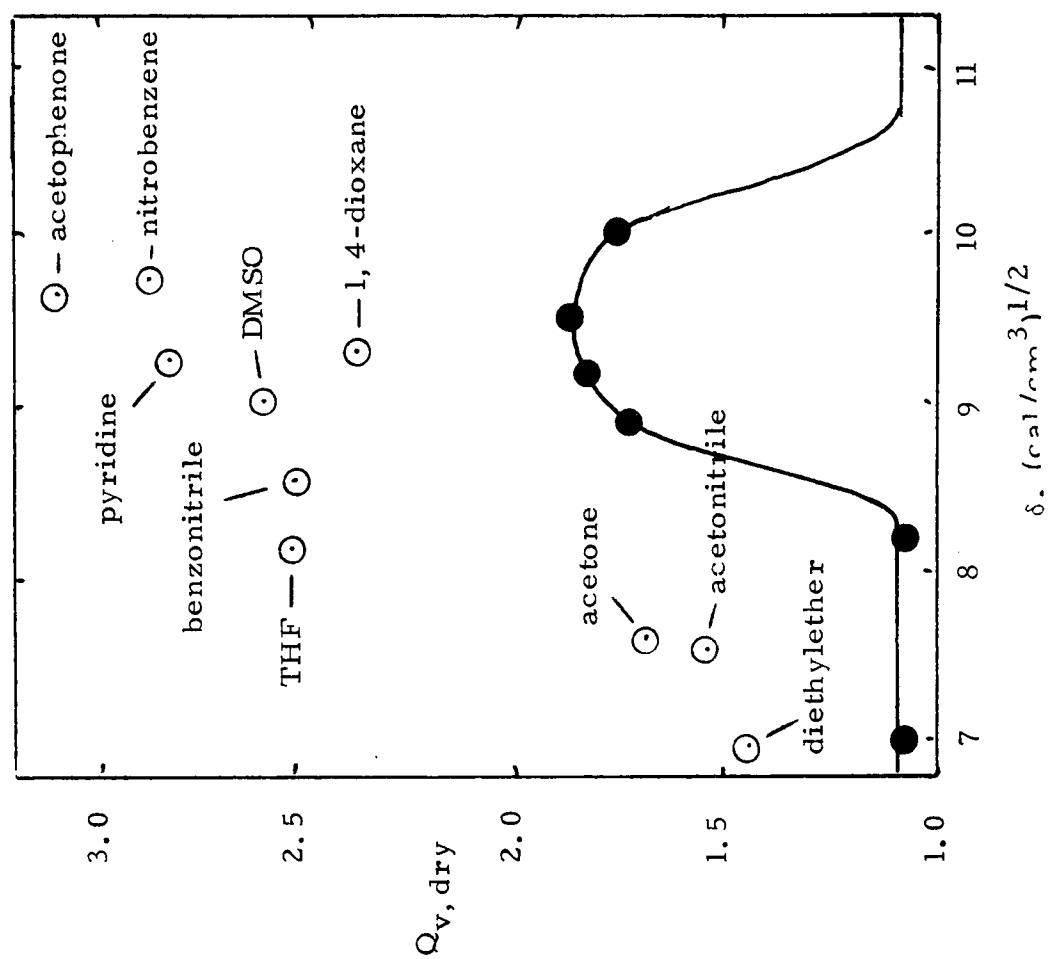


Figure 19. Plot of Nonpolar δ of Polar Solvent Versus $Q_{v,dry}$ for the O-acetylated Illinois No. 6(2) Coal.

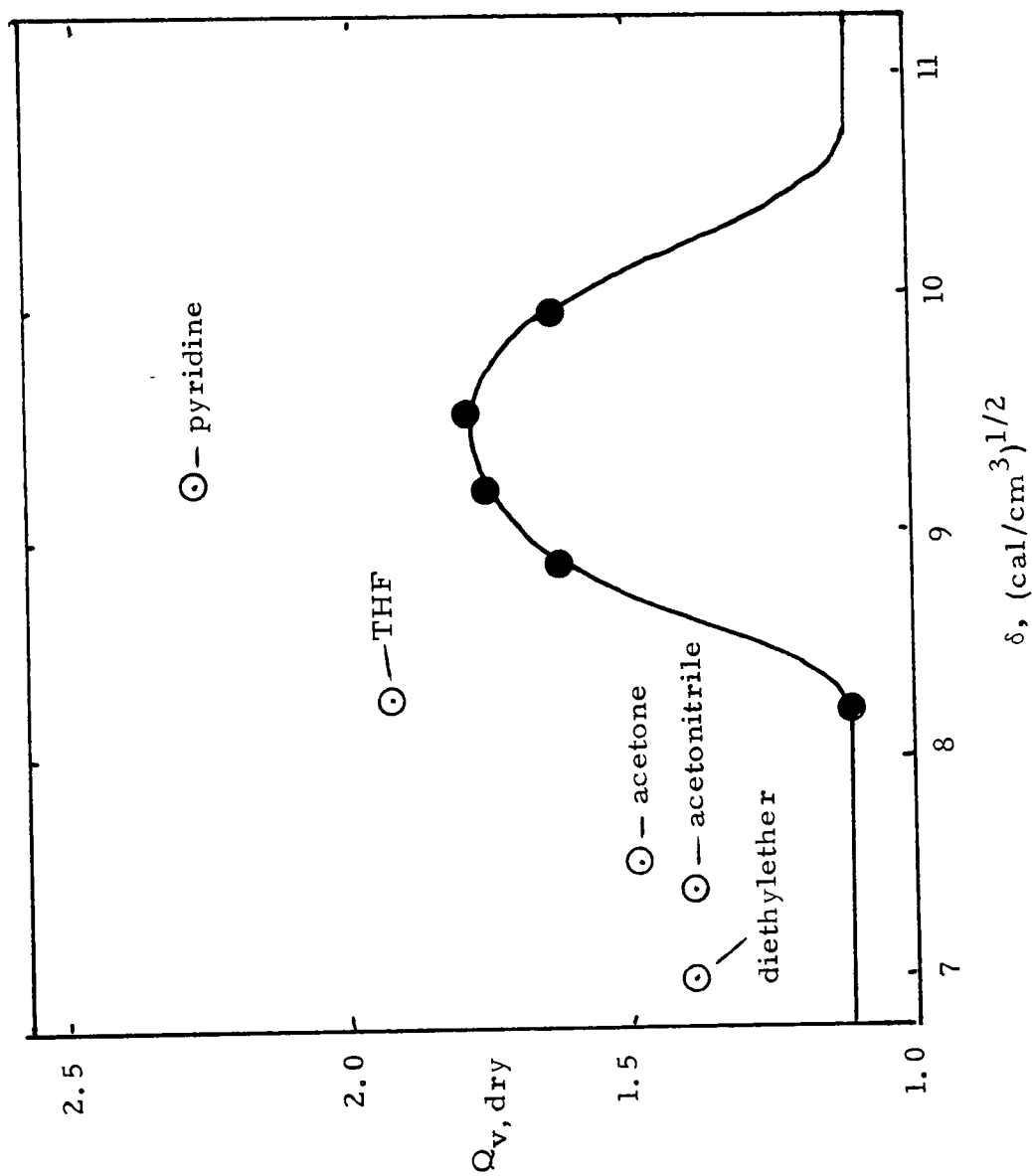


Figure 20. Plot of Nonpolar δ of Polar Solvent Versus $Q_{v,dry}$ for the O-Methylated Illinois No. 6(2) Coal.

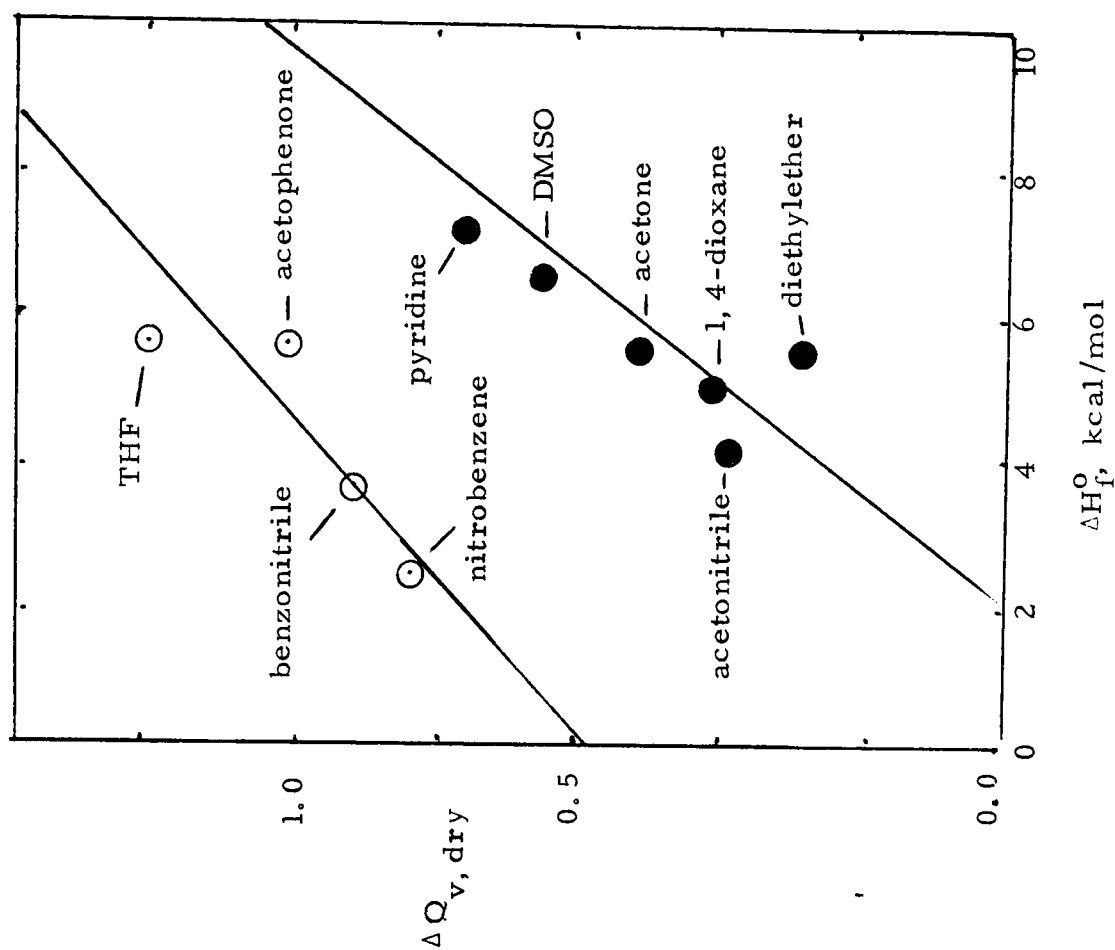


Figure 21. Plot of ΔH_f^o of Polar Solvent Versus $\Delta Q_{v, \text{dry}}$ for the O-acetylated Illinois No. 6(2) Coal.

into a pair of nearly parallel straight lines. The lines that are drawn are least-squares fits of the data.

The lower curve in the figure is very similar to the corresponding curve for the extracted Illinois No. 6(2) coal (see Figure 17, p 90) and includes the same solvents. Thus, the deviations of these polar solvents appear to be residual polar effects that are linear in hydrogen bond strengths. This explains why good correlations between $\Delta Q_{v,dry}$ and ΔH_f^0 are observed for this set of solvents and the underivatized coals.

THF, benzonitrile, nitrobenzene, and acetophenone deviate substantially from the lower curve in Figure 21. Recall that two of these solvents exhibited similar behavior towards the unextracted Illinois No. 6(2) coal (see Figure 18). Benzonitrile and nitrobenzene, in fact, show substantial and unusual shifts in their swelling capability upon derivatization of the coal. $Q_{v,dry}$ for nitrobenzene increases from 1.56 (unextracted coal) to 2.86 (O-acetylated coal) upon derivatization. In a similar manner, $Q_{v,dry}$ for benzonitrile increases from 1.49 to 2.50. No other polar solvents show such dramatic shifts in $Q_{v,dry}$ upon derivatization of the coal.

The questions arise: Do the polar solvents in the upper curve in Figure 21 possess a unique solvent property that the solvents in the lower curve lack and, if so, can the "excess" swelling of the derivatized coal by these solvents compared to those that define the lower curve be rationalized in terms of this solvent property?

Three of the four solvents in the upper curve in Figure 21 are unique in the sense that they are aromatic solvents with

electron-attracting groups directly attached to the ring. These groups will withdraw the mobile π electrons in the aromatic ring, making the aromatic ring electron-deficient. Thus, these solvents possess electron-acceptor properties and could possibly participate in donor-acceptor complexes with any electron-donating groups that may exist in the coal. For example, these solvents may be accepting π electrons from some aromatic structure in the coal, thus forming π - π donor-acceptor complexes. This explanation would account for the greater swelling at the O-acetylated coal by these solvents compared to the other polar solvents in the lower curve in Figure 21.

Admittedly, these solvents are, at very best, weak acceptors. Certainly, any electron-donating structures in the coal must be of significant basicity before participating in donor-acceptor complexes with these solvents. Nevertheless, the data suggest the existence of such complexes and point to a need for further investigations.

The above explanation does not account for the behavior of THF. THF might be expected to act as a so-called "n-donor" since it possesses lone pairs of electrons in the atomic orbital of oxygen. Thus, THF may be forming specific complexes with electron-accepting structures in the coal.

This discussion, of course, raises the question of whether donor-acceptor complexes exists in coals and, if so, what kinds of structures are involved? Also, do the complexes constitute an important associative force between the macromolecular chains much like the hydrogen bonds do? We presently have no answers to these questions. Certainly this is an area of study that deserves further attention.

Finally, we point out that all the solvents in the upper curve in Figure 21 possess a polar solubility parameter, τ , of about $4.7 \text{ (cal/cm}^3\text{)}^{1/2}$ (see Table VIII). Recall that τ is the polar solubility parameter as introduced by Blanks and Prausnitz, and is described by the equation

$$\tau = (\delta_H^2 + \delta_P^2)^{1/2} \quad (42)$$

where δ_H and δ_P are the empirical estimates due to hydrogen bonding and polar forces, respectively. Note in Table VIII that none of the polar solvents that define the lower curve possess a τ value close to $4.7 \text{ (cal/cm}^3\text{)}^{1/2}$. It is not clear whether this fact has any physical or chemical meaning with regard to the interaction of these solvents with the O-acetylated coal. It does suggest, however, that these solvents are engaging in some specific polar interaction with the coal.

To conclude this section, we demonstrate that the strengths of the hydrogen bonds in the coal network can be estimated by comparing the swelling behavior of the O-acetylated and unextracted coals in the various solvents. For example, consider pyridine and the Illinois No. 6(2) coal. $Q_{v,dry}$ for the O-acetylated coal is 2.80, whereas it is 2.61 for the unextracted coal. This means that the unextracted coal absorbs $(1.61/1.80) \times 100 = 89\%$ of the volume of pyridine absorbed by the O-acetylated coal. Clearly, the pyridine is disrupting most of the hydrogen bonds in the unextracted coal. We performed this analysis on ten other polar solvents and then plotted the results against ΔH_f^O for each solvent. The results are shown in Figure 22. There is a distinct break in the curve at a ΔH_f^O value of $\sim 5 \text{ kcal/mol}$. This result means

TABLE VIII
POLAR SOLUBILITY PARAMETERS OF POLAR SOLVENTS

Solvent	$\tau, (\text{cal}/\text{cm}^3)^{1/2^a}$
Acetophenone	4.6
Tetrahydrofuran	4.8
Nitrobenzene	4.6
Benzonitrile	4.7
Pyridine	5.2
DMSO	9.4
Acetone	6.1
1,4-Dioxane	3.7
Diethylether	2.9
Acetonitrile	9.3

^aCalculated from Equation 42; δ_P and δ_H taken from Barton's review article.

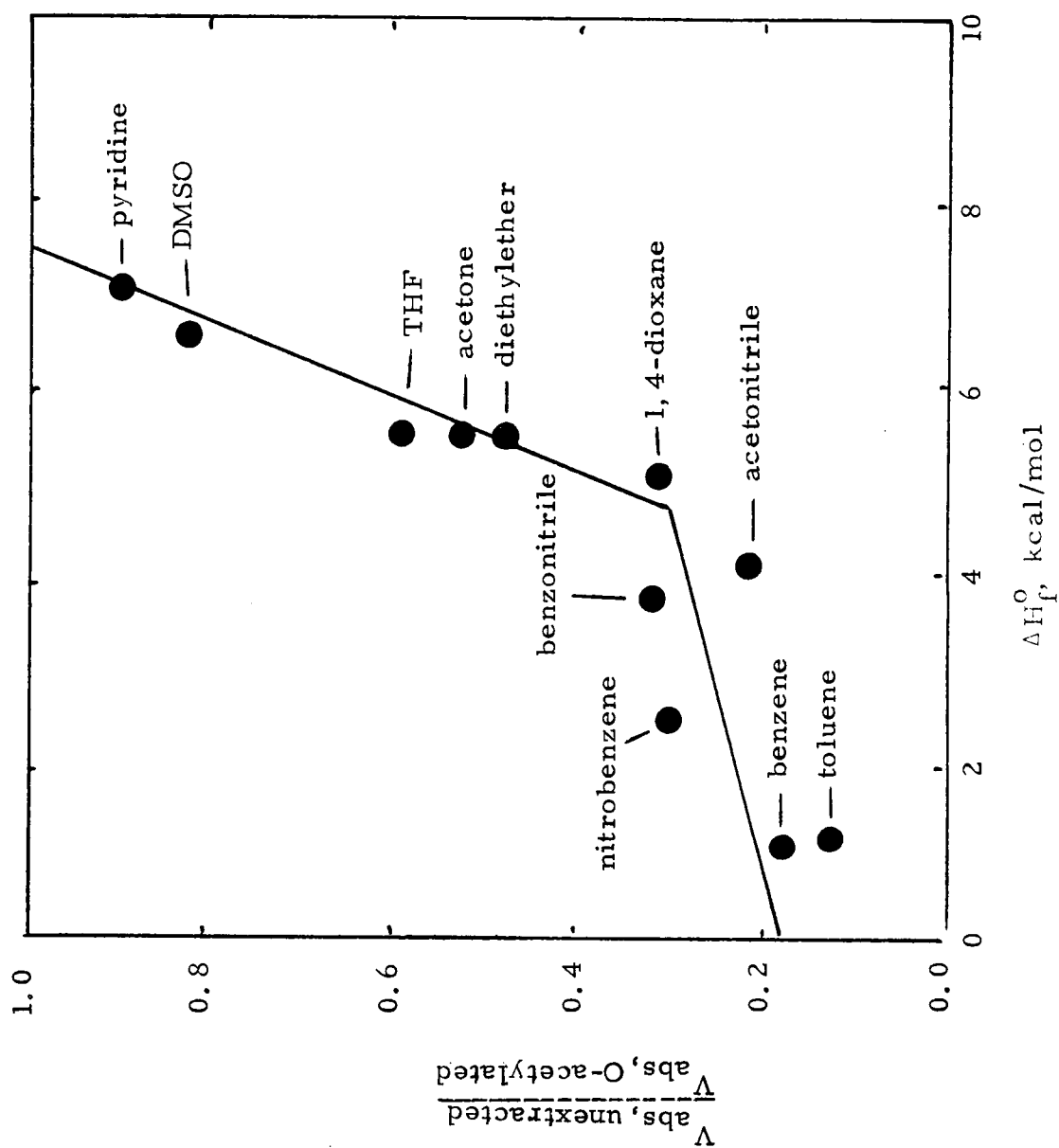


Figure 22. Plot of ΔH_f^O of Polar Solvent Versus $V_{\text{abs, Unextracted}}/V_{\text{abs, O-acetylated}}$ for the Illinois No. 6(2) Coal.

that the coal-solvent hydrogen bond strength must exceed about 5 kcal/mol before the coal-coal hydrogen bond will be disrupted. Hence, the strengths of the hydrogen bonds in the Illinois No. 6(2) coal range from roughly 5 to 7.5 kcal/mol.

We demonstrated in this section that coal solubility in polar and nonpolar solvents can be treated quantitatively. The best swelling solvents will possess both (1) a high affinity for the hydrocarbon portion of the coals, that is, a nonpolar solubility parameter in the range of 9 to 10 δ and (2) an ability to disrupt the hydrogen bond crosslinks of the coal. The hydrogen bond enthalpies for the interaction of p-fluorophenol with the solvents are reasonable quantitative indicators for assessing this ability. The other polar effects may be important as well, and these effects appear to be linear in hydrogen bond strengths based on the analysis of the o-acetylated Illinois No. 6(2) coal. The existence of donor-acceptor complexes in coals have also been implicated, although no firm proof of their existence has been demonstrated.

D. χ Parameters and Crosslink Densities

The solubility parameters of the Illinois No. 6(2) and Bruceton coal were measured as $9.5 (\text{cal/cm}^3)^{1/2}$ in nonpolar solvents (see Figures 12 and 13, p 80 and 81). Since random mixing is expected in these systems, χ parameters for the coal-solvent pairs can be calculated from Equation 14. The results are presented in Table IX. Solvents whose solubility parameters lie outside the 8.5 to 10.5 δ range were not considered since these solvents swell the coals very little. A

TABLE IX

χ PARAMETERS FOR THE NONPOLAR SOLVENTS AND THE BRUCETON
AND ILLINOIS NO. 6(2) COALS

Solvent	$\delta_1 (\text{cm}^3/\text{cal})^{1/2}$	$V_1 (\text{cm}^3/\text{mol})^a$	χ_H^b	χ^c
o-xylene	8.8	121.4	0.100	0.400
Toluene	8.9	106.8	0.065	0.365
Tetralin	9.5	136.0	0.000	0.300
Naphthalene	9.9	111.5	0.030	0.330
CS ₂	10.0	60.0	0.025	0.325

^aAt 25°C.

^bCalculated from Equation 13; the δ value of both coals estimated to be $9.5 (\text{cal}/\text{cm}^3)^{1/2}$.

^cCalculated from Equation 4; χ_s equal to 0.30.

value of 0.30 was chosen for the entropic contribution, χ_s . This choice is somewhat arbitrary since χ_s for a given polymer should depend on both the size and shape of the swelling solvent. However, the mean value of χ_s for other polymer-solvent systems was found to be near 0.30, so the choice is reasonable.^{85,87}

The number average molecular weight per crosslink, $\bar{M}_c$, was calculated from the Flory-Rehner equation (Equation 7). The results are presented in Table X. A density of 1.3 g/ml for the coals was used in all calculations. The volume fraction of coal in the swollen state, v_2 , is equal to $1/Q_{v,dry}$.

In theory, $\bar{M}_c$ for a given coal should be independent of the swelling solvent. The results in Table X do not reveal this. For example, $\bar{M}_c$ range from 190 to 540 for the extracted Illinois No. 6(2) coal. In spite of the inconsistencies, the averages clearly indicate that $\bar{M}_c$ increase in the order unextracted < extracted < o-acetylated. This result is expected since the number of hydrogen bond crosslinks decreases in this order, which results in an increase in the chain length between crosslinks (greater $\bar{M}_c$).

The $\bar{M}_c$'s for the unextracted coals are in the 100-200 range for both coals. Since the molecular weights of the aromatic/hydroaromatic clusters in bituminous coals are thought to cover the lower hundreds (300-700), the $\bar{M}_c$'s appear to be too low, since this would require several crosslinks per cluster. However, the results reveal the trends expected in $\bar{M}_c$ for each set of coals and may be good estimates in a relative sense.

TABLE X
THE NUMBER AVERAGE MOLECULAR WEIGHT PER CROSSLINK OF THE BRUCETON
AND ILLINOIS NO. 6(2) COALS USING THE FLORY-REHNER EQUATION

Solvent	Illinois No. 6(2)			Bruceton		
	Unextracted	Extracted	O-acetylated	Unextracted	Extracted	O-acetylated
o-xylene	---	430	0.709	---	550	---
Toluene	100	0.926	410	0.685	700	0.581
Benzene	110	0.885	360	0.658	630	0.546
Tetralin	---	---	540	0.658	990	0.535
Naphthalene	---	---	380	0.699	---	---
CS ₂	60	0.900	190	0.709	380	0.575
Average	90	390	680	150	480	1040

As stated earlier, the Flory-Rehner equation was derived for materials whose chains are long and flexible. The larger planar aromatic and hydroaromatic arrays that are thought to make up the chains in coals are not expected to respond as a more flexible and mobile chain. Thus, the Flory-Rehner equation is not expected to yield quantitatively realistic $\bar{M}_c$'s for the coals. We therefore applied the Kovac equation (Equation 9) to the systems. The results are presented in Tables XI and XII.

The Kovac equation contains an additional parameter N , which expresses the number of repeating units between crosslinks in the short chain model. N can be defined as the ratio of the number average molecular weight per crosslinks, $\bar{M}_c$, to the number average molecular weight of the cluster, $\bar{M}_0$.

$$N = \bar{M}_c / \bar{M}_0 \quad (10)$$

N describes the derivation from Gaussian behavior. The Gaussian limit is obtained when N becomes infinite since the Kovac equation then reduces to the Flory-Rehner equation. Since the molecular weights of the clusters in bituminous coals are thought to range from 300 to 700, N was varied such the $\bar{M}_0$ covered this range for each coal. The N values were then plotted against $\bar{M}_0$ for each set of coals. The results are shown in Figures 23 and 24 for the Illinois No. 6(2) and Bruceton coals, respectively.

In order to estimate an $\bar{M}_c$ for a coal using the Kovac equation, it is necessary to assume a value for the average molecular weight of the cluster, $\bar{M}_0$. Here we assume a $\bar{M}_0$ of 400 for both coals. With this

TABLE XI

THE NUMBER AVERAGE MOLECULAR WEIGHT PER CROSSLINK OF THE
ILLINOIS NO. 6(2) COAL USING THE KOVAC EQUATION

		$\bar{M}_c$			
Unextracted	N	0.4	0.5	1.0	2.0
Toluene		430	310	200	150
Benzene		400	340	220	170
CS ₂		240	200	130	100
Average		360	280	190	140
$\bar{M}_o$		900	560	190	70
Extracted	N	1.0	1.25	2.0	3.0
o-xylene		980	870	710	620
Toluene		940	830	670	580
Benzene		840	740	600	520
Tetralin		1250	1100	900	780
Naphthalene		860	760	620	540
CS ₂		430	390	310	270
Average		880	780	640	550
$\bar{M}_o$		880	620	320	180
O-acetylated	N	1.5	2.0	3.0	4.0
Toluene		1370	1200	1030	950
Benzene		1260	1110	950	870
Tetralin		1920	1680	1440	1320
CS ₂		740	650	560	510
Average		1320	1160	1000	910
$\bar{M}_o$		880	580	330	230

TABLE XII

THE NUMBER AVERAGE MOLECULAR WEIGHT PER CROSSLINK OF THE
BRUCETON COAL USING THE KOVAC EQUATION

		$\bar{M}_c$			
		0.5	0.75	1.0	2.0
Unextracted	N				
Toluene		630	490	410	300
Benzene		440	330	270	190
CS ₂		370	280	240	180
Average		480	370	300	220
$\bar{M}_o$		960	490	300	110
Extracted	N	1.0	1.5	2.0	3.0
o-xylene		1290	1080	920	800
Toluene		1180	950	840	730
Benzene		970	780	690	600
Tetralin		1650	1330	1170	1020
Naphthalene		1240	1000	880	760
CS ₂		470	380	340	300
Average		1130	920	810	700
$\bar{M}_o$		1130	610	400	230
O-acetylated	N	2.0	3.0	4.0	5.0
Toluene		2630	2230	2030	1910
Benzene		1200	1780	1610	1520
CS ₂		1070	910	830	780
Average		1930	1640	1490	1400
$\bar{M}_o$		970	550	370	280

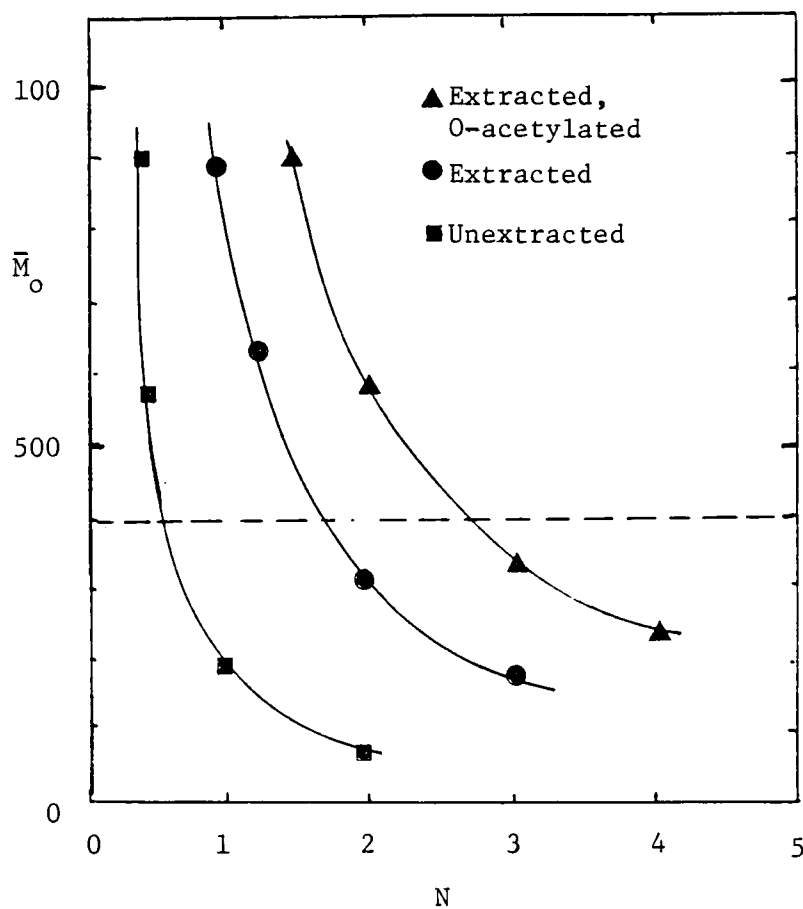


Figure 23. Plot of N Versus $\bar{M}_0$ for Illinois No. 6(2) Coal.

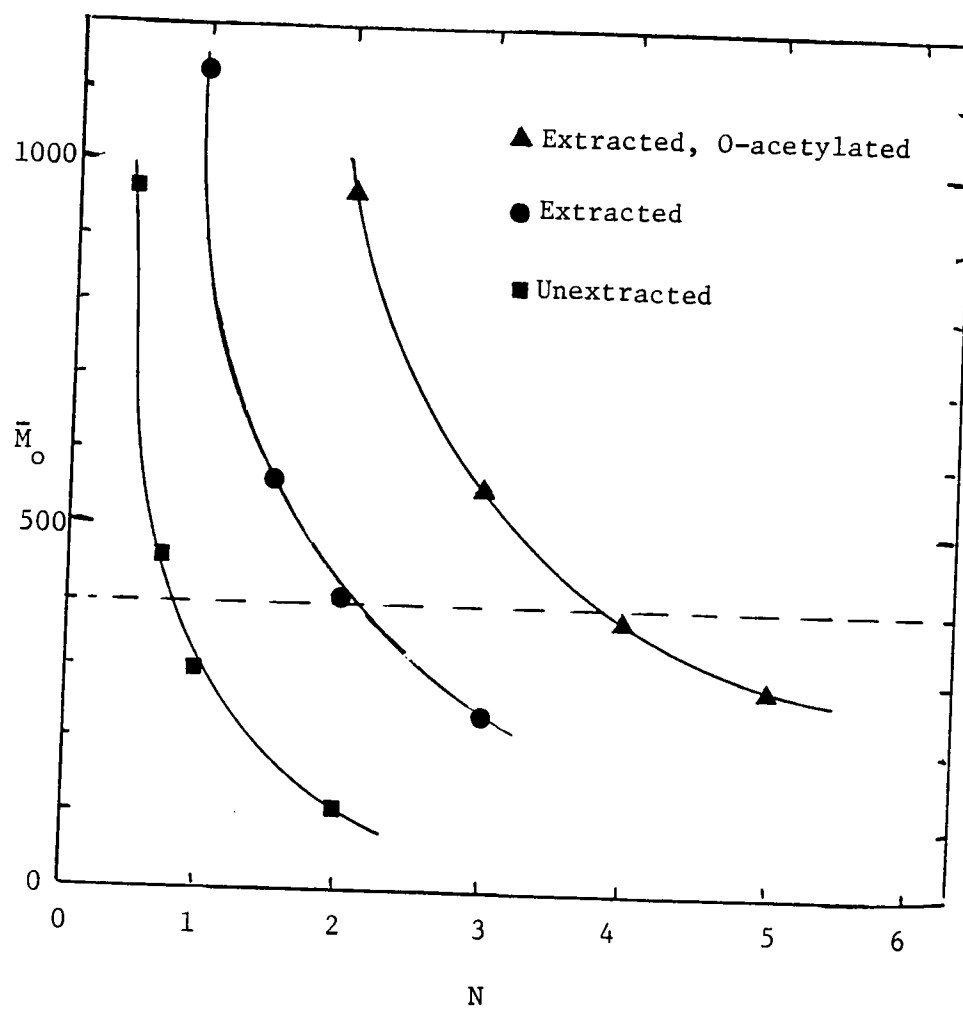


Figure 24. Plot of N Versus $\bar{M}_0$ for Bruceton Coal.

assumption, both N and $\bar{M}_c$ for each coal can be estimated from Figures 23 and 24. The results are presented in Table XIII.

On a qualitative level the results from the Kovac treatment are similar to those of the Flory-Rehner treatment, although the Kovac treatment yields somewhat greater $\bar{M}_c$'s. Interestingly, the Kovac treatment yields N values less than 1.0 for both unextracted coals. This requires that there be more than one crosslink per cluster, a situation that seems improbable. One might attribute this result to a poor choice for $\bar{M}_0$. However, it is clear for Figures 23 and 24 that any choice of $\bar{M}_0$ in the range of 300-700 yields an N of 1.0 or less for the unextracted coals.

Another factor that must be considered here is the low degree of swelling of the unextracted coals. Indeed, all the swelling ratios (Q) are less than or equal to 1.2, reflecting that the coals are very tightly crosslinked by the hydrogen bond network. Clearly, the unextracted coals are very inflexible networks, and the Kovac expression may fail to yield realistic results under these circumstances.

It is convenient to calculate crosslink densities (ρ_x 's) from the $\bar{M}_c$'s using Equation 8 in order to draw comparisons between the different coals and the two treatments. A density of 1.3 g/ml was assumed for all coals. The results are presented in Table XIV.

The results from both treatments indicate that the unextracted coals have several times the crosslink densities of the O-acetylated coals. Recall that the unextracted coals are crosslinked by both covalent bonds and hydrogen bonds. Thus, any ρ_x calculated for an

TABLE XIII

THE NUMBER AVERAGE MOLECULAR WEIGHT PER CROSSLINK OF THE BRUCETON
AND ILLINOIS NO. 6(2) COALS ASSUMING AN $\bar{M}_0$ OF 400

	Unextracted	Extracted	O-acetylated
Bruceton			
$\frac{N}{M_c}$	0.8	2.0	3.8
	320	800	1500
Illinois No. 6(2)			
$\frac{N}{M_c}$	0.6	1.8	2.7
	240	720	1100

TABLE XIV

CROSSLINK DENSITIES OF BRUCETON AND ILLINOIS NO. 6(2) COALS

Coal	ρ_x , mmol/ml of coal		
	Unextracted	Extracted	O-acetylated
Bruceton			
Flory-Rehner	8.7	2.7	1.2
Kovac	4.1	1.6	0.9
Illinois No. 6(2)			
Flory-Rehner	14	3.3	1.9
Kovac	5.4	1.8	1.2

^aCalculated from Equation 8; 1.3 g/ml assumed for density of all coals.

unextracted coal must represent both hydrogen bond and covalent crosslinks. The ρ_x if an O-acetylated coal represents only covalent crosslinks, since all hydrogen bond interactions have been disrupted. Therefore, the hydrogen bond crosslink density of a coal, $\rho_{x,H\text{-bond}}$, is simply the difference in the ρ_x 's of the unextracted coal (covalent plus hydrogen bond crosslinks) and the O-acetylated coal (covalent crosslinks only)

$$\rho_{x,H\text{-bond}} = \rho_{x,\text{unextracted}} - \rho_{x,O\text{-acetylated}} \quad (47)$$

The $\rho_{x,H\text{-bond}}$'s were calculated for both coals using both treatments and are presented in Table XV. The number of hydroxyl groups estimated to be present in the coals are also listed for comparison.

The results from the Flory-Rehner equation indicate that there are roughly two to three times as many hydrogen bond crosslinks as hydroxyl groups in the coals. This would mean that every hydroxyl group serves as two or three crosslinks. Clearly, this is unrealistic and highly improbable. It therefore appears that the Flory-Rehner equation yields unrealistic crosslink densities for the coals.

The number of hydrogen bond crosslinks in the coals calculated from the Kovac equation, however, are remarkably close to the estimated number of hydroxyl groups in the coals. In this regard, the Kovac equation provides more realistic crosslink densities. Moreover, the result indicates that most of the hydroxyl groups are not only hydrogen bonded, but that most serve as crosslinks as well. We presently have no evidence to support this and, indeed, a substantial number of hydrogen bonds may be intra cluster instead of inter cluster in

TABLE XV

COMPARISON OF THE CALCULATED HYDROGEN BOND CROSSLINK DENSITIES
AND THE NUMBER OF HYDROXYL GROUPS IN THE BRUCETON
AND ILLINOIS NO. 6(2) COALS

	<u>Flory-Rehner Equation</u>	<u>Kovac Equation</u>	
	$\rho_{x,H\text{-bonds}}^a$ (mmol/ml)	$\rho_{x,H\text{-bonds}}^a$ (mmol/ml)	OH Content ^b (mmol/ml)
Bruceton	7.5	3.2	2.3
Illinois No. 6	12	4.2	4.3

^a Calculated from Equation 47.

^b Calculated from data in Table XXVI; a density of 1.3 g/ml assumed for both coals.

nature. Nevertheless, the result is a striking one, and suggests that the Kovac model may be providing realistic crosslink densities.

Finally the results from the Kovac treatment indicate that the Bruceton coal has somewhat fewer covalent crosslinks than the Illinois No. 6(2) coal ($0.9/1.2 = 0.75$).

Another aspect of these results that deserves attention is the observed dependency of $\bar{M}_C$ for a given coal on the swelling solvent (see Table X). Theoretically, $\bar{M}_C$ should be constant among a group of solvents, providing that the solvents are nonpolar and therefore do not themselves disrupt hydrogen bond crosslinks. These inconsistencies in $\bar{M}_C$ indicate the existence of either errors in the swelling measurements or in χ . Any errors in the swelling measurements would have to be substantial to account for such large inconsistencies in $\bar{M}_C$. For example, consider the extracted Bruceton coal and the solvents tetralin and CS_2 . Assume that the "true" $\bar{M}_C$ is 690, that calculated from the Flory-Rehner equation using the tetralin data. To obtain an equivalent $\bar{M}_C$ using CS_2 , v_2 would have to be 0.46 ($Q = 2.2$), not 0.69 ($Q = 1.4$). An error of this magnitude seems unlikely since the volumetric and gravimetric measurements gave the same results (corrected for pore volume). Hence, the inconsistencies in $\bar{M}_C$ probably arise from errors in χ .

Interestingly, a good linear relationship exist between the $\bar{M}_C$'s calculated from the Flory-Rehner equation and the molar volumes of the solvents, V_1 . These results are presented in Figures 25 and 26 for the Bruceton and Illinois No. 6(2) coals, respectively. Each line

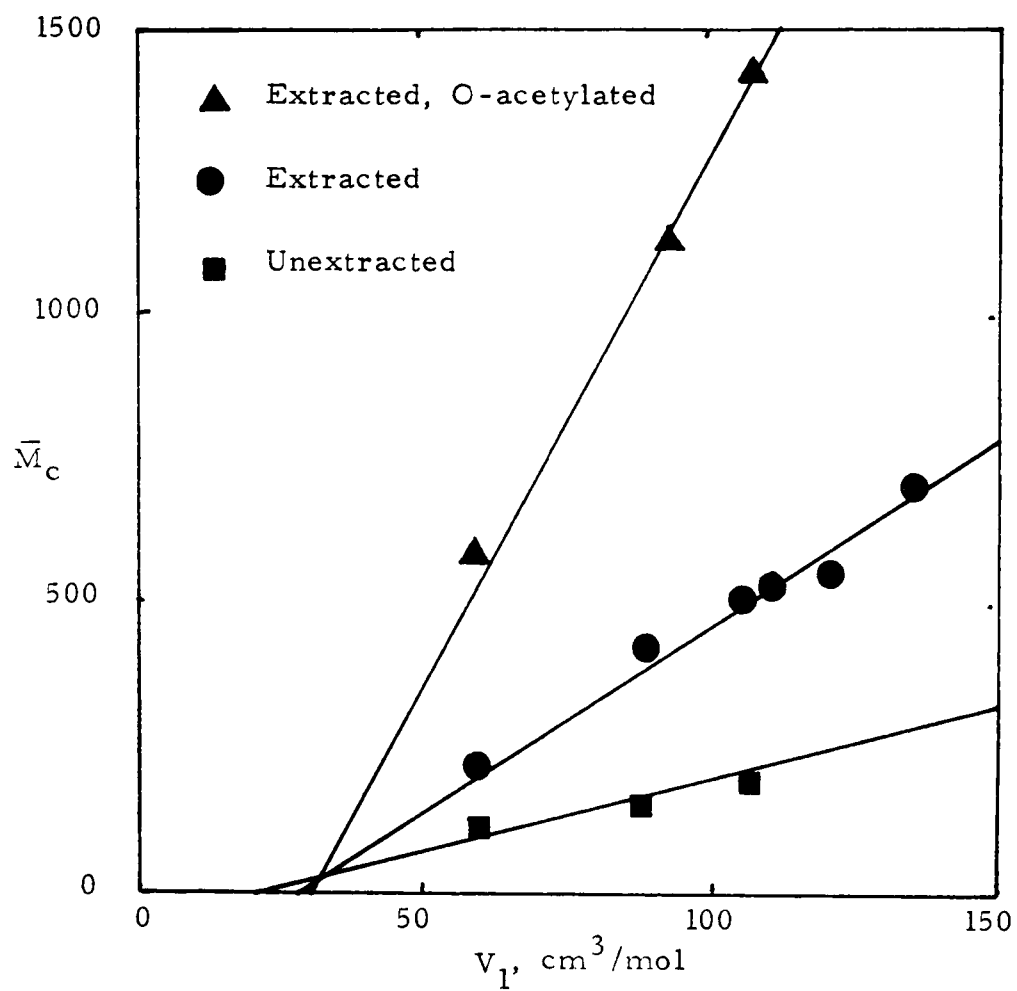


Figure 25. Plot of calculated $\bar{M}_c$ of the Bruceton Coal Versus V_1 of the solvent.

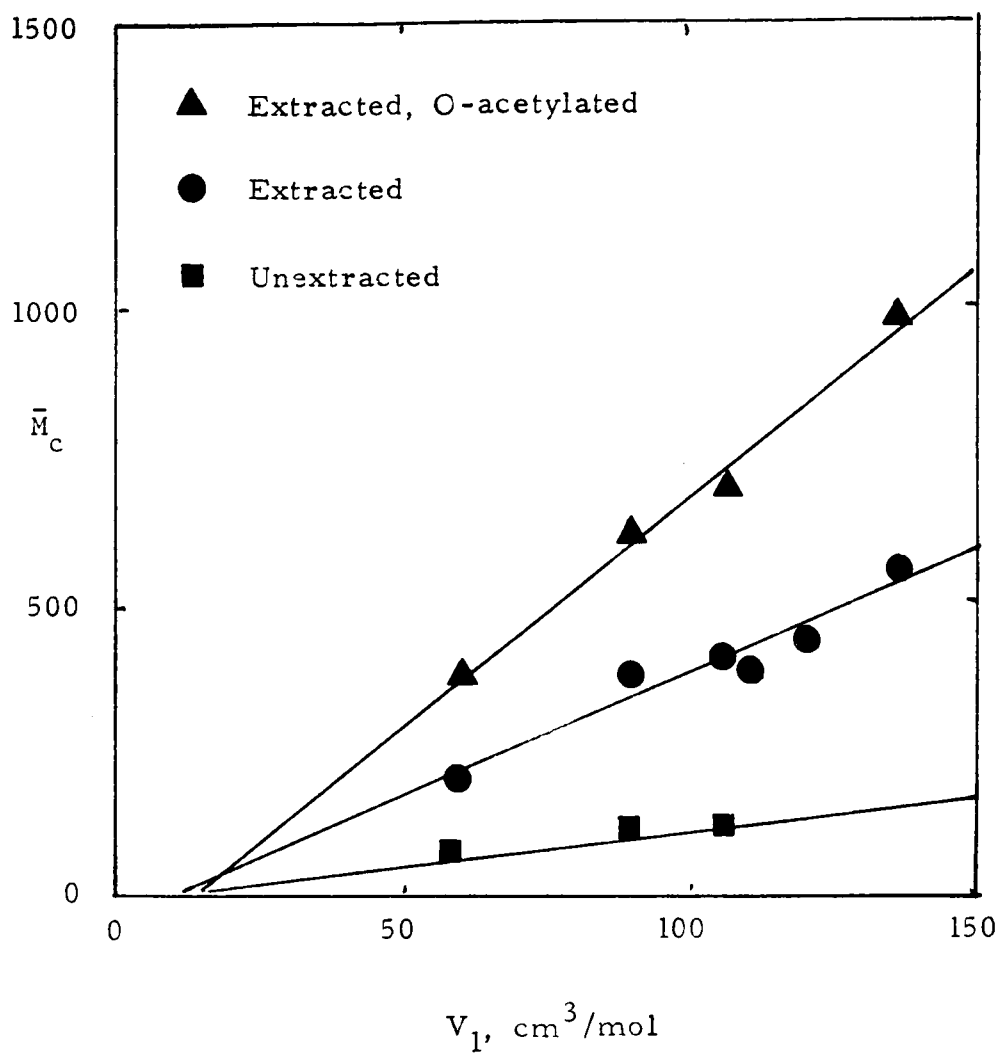


Figure 26. Plot of calculated $\bar{M}_c$ of the Illinois No. 6(2) Coal versus solvent.

drawn is a least squares fit of the data. The lines for each set of coals converge to nearly the same point at $\bar{M}_C$ equal to zero.

Recall that Equation 14 contains both an entropic and an enthalpic contribution to χ . Although there is a strong theoretical justification for the inclusion of the $(\delta_1 - \delta_2)^2$ term in χ (the enthalpic contribution), there is no similar justification for the inclusion of a constant χ_s in χ . If this consumption of a constant χ_s is incorrect, it will lead to errors in χ , and ultimately to inconsistencies in the $\bar{M}_C$'s calculated for a given coal and a set of solvents.

We chose χ_s to be 0.30 in this treatment, irrespective of the swelling solvent. However, χ_s theoretically depends on the size and shape of the solvent as well as the polymer groups.¹¹⁹ It is therefore reasonable to assign this χ_s only to solvents of a particular size. In this instance, we assign a χ_s of 0.30 to solvents with a V_1 of 100 cm³/mol, which is near the mean V_1 of the solvents employed in this study. We next assume that the error in χ for each coal-solvent pair lies in χ_s and treated χ_s as an adjustable parameter.

Consider the extracted Bruceton coal. If χ_s and V_1 are set at 0.30 and 100 cm³/mol, respectively, then $\bar{M}_C$ for this coal is set at about 460 (from Figure 25). We then adjusted χ_s for each solvent to give an $\bar{M}_C$ of 460 using the Flory-Rehner equation. Note that no adjustment was made of χ_H . The adjusted χ_s and χ parameters that resulted from this treatment are given in Table XVI.

Resulting χ parameters were then used to calculate $\bar{M}_C$ for all other coals using the Flory-Rehner equation. The results are presented

TABLE XVI

ADJUSTED χ_s AND χ PARAMETERS FOR THE NON-POLAR SOLVENTS AND THE BRUCETON AND ILLINOIS NO. 6(2) COALS^a

Solvent	χ_x	χ
O-xylene	0.182	0.282
Toluene	0.247	0.312
Benzene	0.366	0.380
Tetralin	0.000	0.000
Naphthalene	0.217	0.247
CS ₂	0.681	0.706

^a χ_s was adjusted to give an $\bar{M}_c$ of 460 for extracted Bruceton coal. $\chi = \chi_H + \chi_s$.

in Table XVII. With the exception of the CS₂-O-acetylated coals pairs, the χ parameters give self-consistent $\bar{M}_c$'s for any given coal. However, the $\bar{M}_c$'s are very similar to the average $\bar{M}_c$'s using the original χ parameters (see Table X).

Finally, we applied the Kovac equation to the adjusted χ parameters and the swelling data. As before, $\bar{M}_0$ was varied to cover the 300-700 range. The results of the calculations are shown in Tables XVIII and XIX. Again, $\bar{M}_c$'s for the CS₂-O-acetylated coal pairs are exceptionally high, but otherwise the results are self-consistent. Plots of $\bar{M}_0$ against N are shown in Figures 27 and 28. Assuming an $\bar{M}_0$ of 400, $\bar{M}_c$'s for all coals were estimated, the results of which are shown in Table XX. These results are also very similar to those generated from the original χ parameters.

By treating χ_s as an adjustable parameter we obtained more consistent $\bar{M}_c$'s for a given coal among a group of solvents. Although the average $\bar{M}_c$'s are not substantially different than those generated from the original χ parameters, the two sets of χ parameters themselves differ considerably. It is not clear which set of χ parameters is more realistic. Other independent methods for measuring χ to coals and nonpolar solvents must be developed so that the χ parameters presented here can be tested.

A goal of this research was to develop a method for measuring the covalent crosslink densities of bituminous coals. Using regular solution theory we estimated $\bar{M}_c$'s for two bituminous coals to lie between 1000 and 2000. Although the certainty of these numbers is in question, they do not seem to be unreasonable estimates at this time.

TABLE XVII

NUMBER AVERAGE MOLECULAR WEIGHT PER CROSSLINK OF THE BRUCETON AND ILLINOIS NO. 6(2) COALS
USING THE FLORY-REHNER EQUATION AND ADJUSTED χ PARAMETERS

Solvent	$\bar{M}_c$				
	Unextracted	O-Acetylated	Unextracted	Extracted	O-acetylated
O-xylene	--	--	--	370	--
Toluene	180	1240	100	380	630
Benzene	160	1340	110	400	730
Tetralin	--	--	--	370	620
Naphthalene	--	--	--	340	--
CS ₂	180	4620	90	410	1370
Average:	170	1290 ^a	100	380	660 ^a

^aExcludes CS₂ data.

TABLE XVIII

THE NUMBER AVERAGE MOLECULAR WEIGHT PER CROSSLINK OF THE ILLINOIS NO.
6(2) COAL USING THE KOVAC EQUATION AND ADJUSTED χ PARAMETERS

		$\bar{M}_c$			
Unextracted	N	0.4	0.5	1.0	2.0
Toluene		350	230	200	150
Benzene		430	360	240	180
CS ₂		330	290	190	140
Average		370	290	210	160
$\bar{M}_o$		920	590	210	80
Extracted	N	1.0	1.25	2.0	3.0
o-xylene		830	740	600	520
Toluene		860	770	620	540
Benzene		940	830	670	580
Tetralin		980	760	620	530
Naphthalene		770	680	550	480
CS ₂		920	820	660	580
Average		880	770	620	540
$\bar{M}_o$		880	620	310	180
O-acetylated	N	1.5	2.0	3.0	4.0
Toluene		1230	1080	930	860
Benzene		1460	1280	1090	1000
Tetralin		1250	1100	940	860
CS ₂		2730	2390	2050	1880
Average ^a		1310	1150	990	910
$\bar{M}_o$		880	580	330	230

^aExcludes CS₂ data.

TABLE XIX

THE NUMBER AVERAGE MOLECULAR WEIGHT PER CROSSLINK OF THE BRUCETON
COAL USING THE KOVAC EQUATION AND ADJUSTED χ PARAMETERS

		$\bar{M}_c$			
		0.5	0.75	1.0	2.0
Unextracted	N				
Toluene		600	460	390	290
Benzene		470	350	290	200
CS ₂		600	460	390	290
Average		550	420	360	260
$\bar{M}_o$		1110	560	360	130
Extracted	N	1.0	1.5	2.0	3.0
o-xylene		1070	860	760	660
Toluene		1080	870	770	670
Benzene		1080	880	780	670
Tetralin		1090	880	780	670
Naphthalene		1090	880	780	670
CS ₂		1050	850	750	750
Average		1080	870	770	680
$\bar{M}_o$		1080	580	380	230
O-acetylated	N	2.0	3.0	4.0	6.0
Toluene		3360	1950	1780	1600
Benzene		3670	2120	1920	1730
CS ₂		8340	7080	6480	5860
Average ^a		3520	2040	1850	1660
$\bar{M}_o$		1760	680	460	280

^aExcludes CS₂ data.

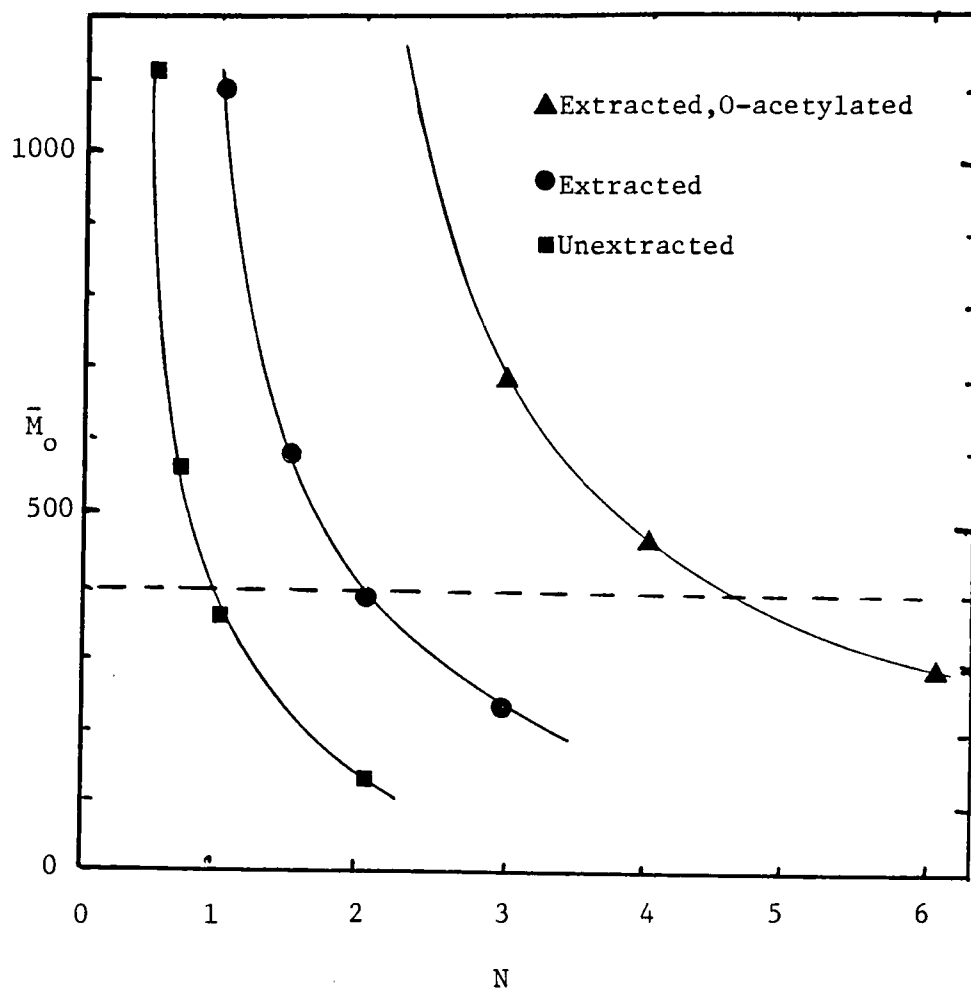


Figure 27. Plot of N Versus $\bar{M}_o$ for Illinois No. 6(2) Coal Using Adjusted χ Parameters.

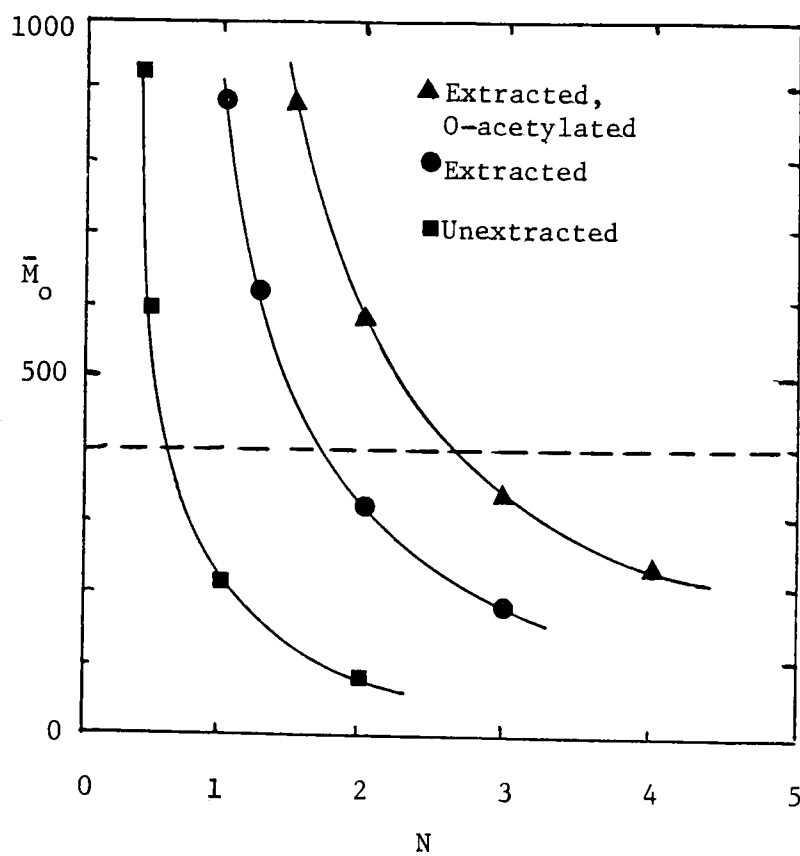


Figure 28. Plot of N Versus $\bar{M}_O$ for Bruceton Coal Using Adjusted χ Parameters.

TABLE XX

THE NUMBER AVERAGE MOLECULAR WEIGHT PER CROSSLINK OF THE BRUCETON AND
ILLINOIS 6(2) COALS USING THE KOVAC EQUATION AND
ADJUSTED χ PARAMETERS ASSUMING AN M_o OF 400

	Unextracted	Extracted	O-acetylated
Bruceton			
$\frac{N}{M_c}$	1.8	2.1	4.6
	400	840	1800
Illinois No. 6(2)			
$\frac{N}{M_c}$	0.6	1.8	2.7
	240	720	1100

We suggest that this technique be exploited more fully using a variety of bituminous coals and that the results be tested against those obtained by other independent methods.

E. Kinetics of Swelling

The diffusion of reagents into solid coals is an important area of study as pointed out by Larsen.⁷⁰ It is important because it may be the rate-limiting step in many coal reactions. For this reason, we found it worthwhile to briefly examine the kinetics of swelling of coals with a few solvents. Since coals have a macromolecular nature, it is useful to analyze the diffusion behavior of coals in terms of the diffusional theories developed for polymers. The details of these theories will not be presented here. However, a few of the basic ideas concerning diffusion in polymers will be briefly sketched.

The diffusion behavior of rubbery polymers generally can be described by the concentration-dependent form of Fick's Law.¹²⁰

$$\partial c / \partial t = \partial (D \partial c / \partial x) / \partial x \quad (48)$$

where c is the solute concentration, x is the direction of diffusion, and D is the solute diffusion coefficient. Many glassy polymers, however exhibit anomalous or non-Fickian behavior, the difference being that rubbery polymers respond much more rapidly to changes in their condition than glassy polymers. Thus, any deviation from Fickian behavior can be considered to originate from the slow relaxation of the polymer structure compared to the rate of diffusion of the penetrant.

Alfrey, Gurnee, and Lloyd proposed a useful classification system:¹²¹

(1) Case I or Fickian diffusion in which the rate of diffusion is much less than that of relaxation.

(2) Case II diffusion, the other extreme in which diffusion is very rapid compared with the relaxation process.

(3) Non-Fickian or anomalous diffusion which occurs when the diffusion and relaxations are comparable.

Case I systems are controlled by the diffusion coefficient which is controlled by several factors. A few of these that are particularly relevant to this discussion are:

(1) Size of the diffusing molecule: the diffusion coefficient decreases as the molecular size increases.

(2) Nature of the polymer: the greater the flexibility of the polymer chains, the higher the diffusion coefficient.

(3) Effect of crosslinking: increasing the degree of crosslinking increases the activation energy and decreases the diffusion coefficient.

In Case II the controlling parameter is the constant velocity of the advancing front of the penetrant that marks the boundary between the swollen gel and the glassy core.

In the amount of penetrant sorbed at time t is defined as

$$M_t = k t^h \quad (49)$$

where k and n are constants, then Case II systems are characterized by $n=1$ and Case I systems by $n=1/2$. Case III lies somewhere in between Case I and II because n takes on an intermediate value between $1/2$ and 1 .

The volumetric method was employed to investigate the kinetics of swelling of the Illinois No. 6(2) and Bruceton coals. Although this method has the disadvantage of packing inefficiencies, it has the advantage of avoiding the complicating effect of the pore structure of coals that accompanies gravimetric measurements. The measurements were not carefully temperature-controlled; they were performed at ambient temperature. In this regard, the kinetic data should be viewed with caution since temperature surely has an effect on the rate of swelling. With some solvents the swelling was so rapid that a meaningful measurement could not be made. For example, 1,4-dioxane swelled the extracted Bruceton coal much more rapidly than did N,N-dimethylaniline or quinoline (Table XXI). The larger molar volumes of quinoline and N,N-dimethylaniline indicate that the size of the molecule determines, in part, the rate of swelling.

The kinetic data for the extracted Bruceton coal and the solvents quinoline and N,N-dimethylaniline are plotted in Figure 29. Equilibrium is reached in approximately 70 min with both solvents.

The swelling ratio, $Q_{v,dry}$, is a measure of the volume of solvent absorbed and is proportional to M_t in Equation 49. If $n=1$, then $Q_{v,dry}$ versus t should give a straight line. Clearly, these systems are not Case II systems. However, when $Q_{v,dry}$ is plotted against $t^{1/2}$ as shown in Figure 30 a straight line is observed. A least-squares analysis on the quinoline data yields the equation

$$Q_{v,dry} = 0.15t^{1/2} + 1.09 \quad (50)$$

TABLE XXI

EQUILIBRIUM TIMES FOR THE SWELLING OF AN EXTRACTED BRUCETON COAL

Solvent	$V_l, \text{cm}^3/\text{mol}$	$Q_{v, \text{dry}}$	Equilibrium time, min
1,4-dioxane	85.7	2.08	~ 10
N,N-dimethylaniline	126.8	1.80	~ 70
Quinoline	118.0	2.20	~ 70

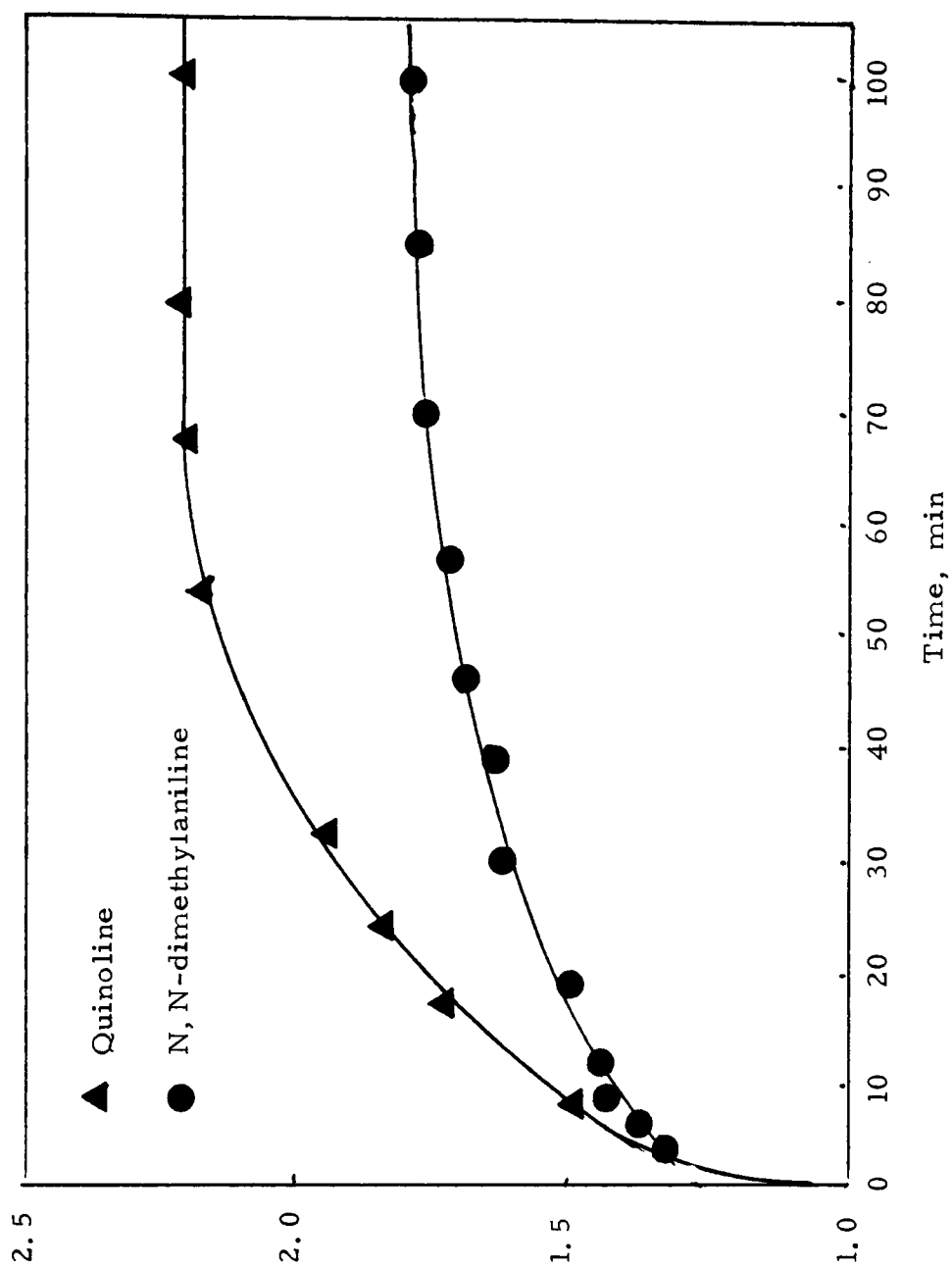


Figure 29. Plot of Time Versus $Q_{v,dry}$ for the Pyridine-Extracted Bruceston Coal Using Quinoline and N,N-dimethylaniline.

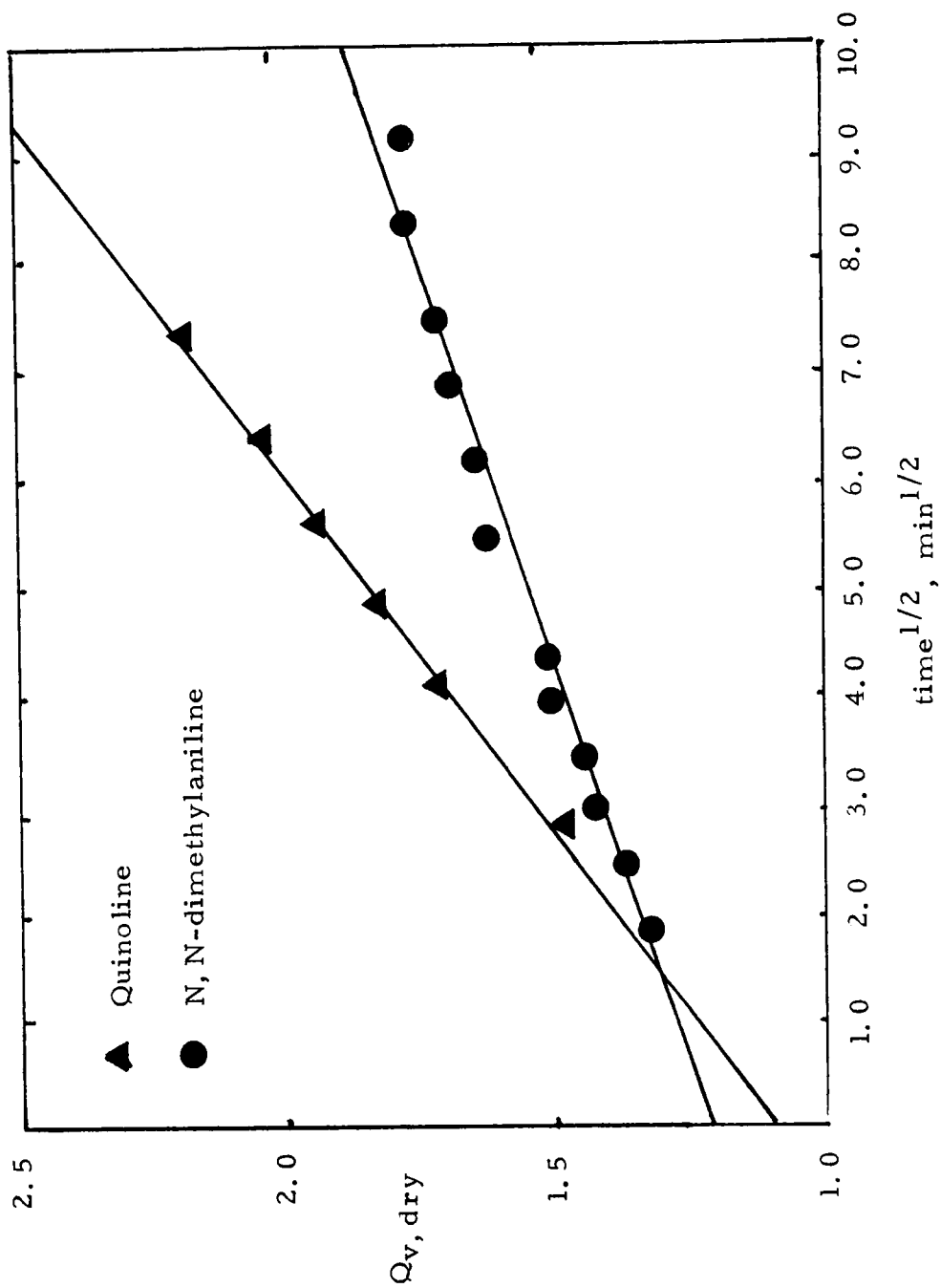


Figure 30. Plot of Square Root of Time Versus $Q_{v,dry}$ for the Pyridine-Extracted Bruceston Coal Using Quinoline and N,N-dimethylaniline.

with a correlation coefficient of 1.00. The same analysis on the N,N-dimethylaniline data yields the equation

$$Q_{v,dry} = 0.68t^{1/2} + 1.21 \quad (51)$$

with a correlation coefficient of 1.00. Interestingly, the lines do not intersect the origin, suggesting a two-stage sorption process; a rapid initial sorption too fast to be measured by the technique employed, followed by a more substantial slower process. Alternatively, this may have resulted from some small systematic error in the swelling measurement.

A substantial portion of the swelling process for the extracted Bruceton coal with these two solvents follows Fickian behavior. This indicates that the rate of relaxation of the coal network is faster than the rate of diffusion of the swelling solvent. Thus, the behavior of the coal is typical of a rubbery polymer.

Since these systems follow Fickian diffusion, the rate of swelling is controlled by the diffusion coefficient. The diffusion coefficient is controlled by several factors, one of which is the degree of crosslinking of the network. According, a coal that is more loosely crosslinked should swell faster than one tightly crosslinked. Since hydrogen bonds serve as crosslinks in the Bruceton and Illinois No. 6(2) coals, the removal of these bonds should increase the rate of swelling in a nonpolar solvent. Therefore we compared the rates of swelling of an extracted and an O-acetylated Illinois No. 6(2) coal in tetralin. The O-acetylated coal has the lower noncovalent crosslink

density and should swell more rapidly than the extracted coal if the above prediction is correct.

The swelling data are shown in Figures 31 and 32 for the extracted and O-acetylated coals, respectively. Equilibrium is reached in roughly 200 min for the O-acetylated coal whereas it takes roughly 70 hrs for the extracted coal. Hence, even the partial hydrogen bond crosslink network of the extracted coal has an enormous effect on the rate of swelling. The rate of swelling of the unextracted coal is expected to be extraordinary slow, probably requiring several weeks to reach equilibrium.

The results presented in this section demonstrate that the kinetic behavior of these coals can be successfully analyzed in terms of the diffusional theories of polymers. Moreover, a substantial portion of the swelling process follows simple Fickian diffusion. Thus, the coals are well-behaved in spite of their complexity. The results also demonstrate that the rate of diffusion of solvents into coals can be significantly enhanced by a simple alteration of the coal structure. This is encouraging since the diffusion of reagents through solid coal may be the rate-limiting step in many reactions of coals.⁷⁰

F. Mixed Solvents and Coal

1. Alcohol/N,N-dimethylaniline Systems

Hombach used binary systems of alcohols and tertiary amines to estimate a solubility parameter range for coals of different rank.¹⁰³ The swelling ratio, $Q_{v,dry}$, was measured as a function of the composition of the solvent mixture. Equation 18 was used to calculate the

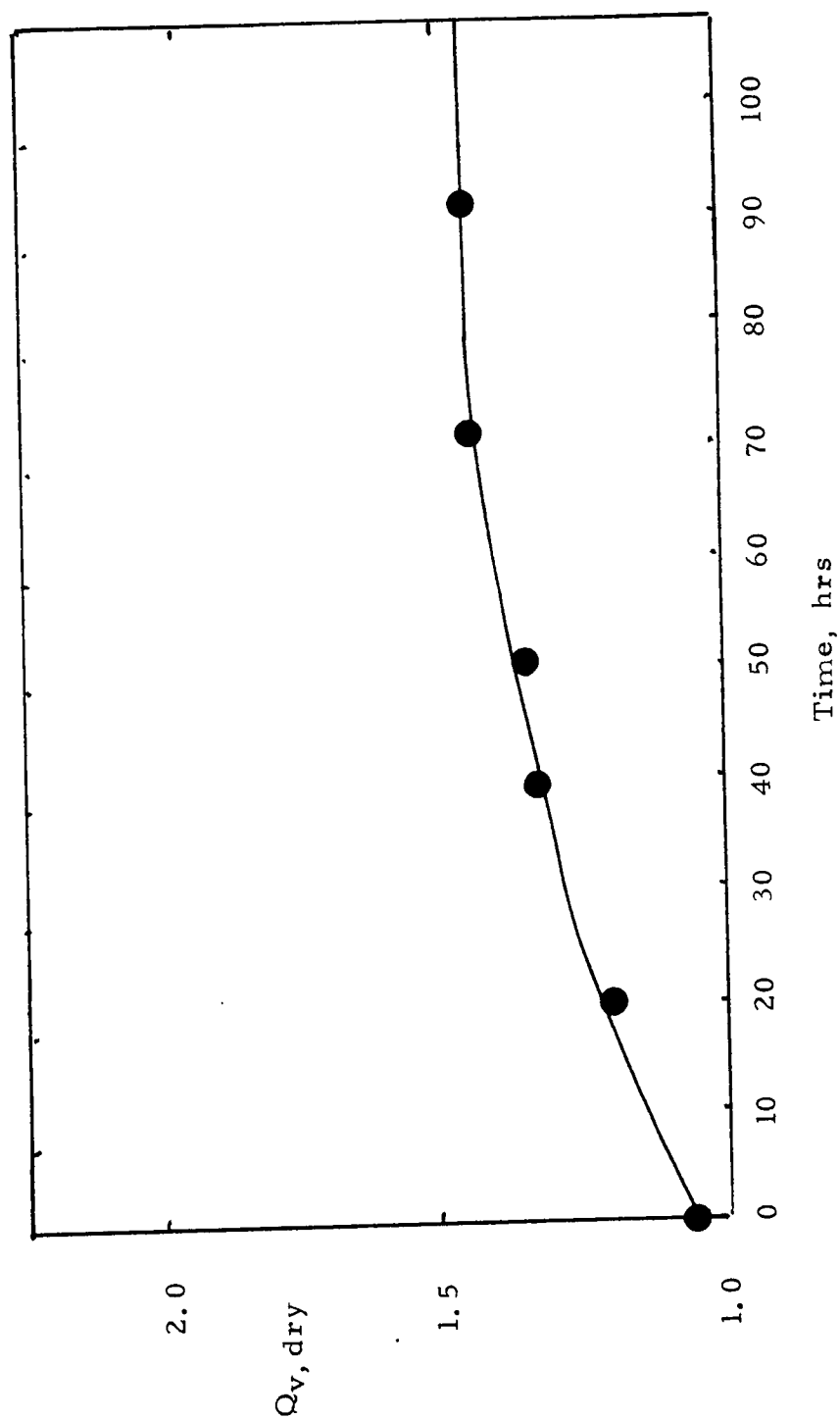


Figure 31. Plot of Time Versus $Q_{v,dry}$ for the Extracted Illinois No. 6(2) Coal and Tetralin.

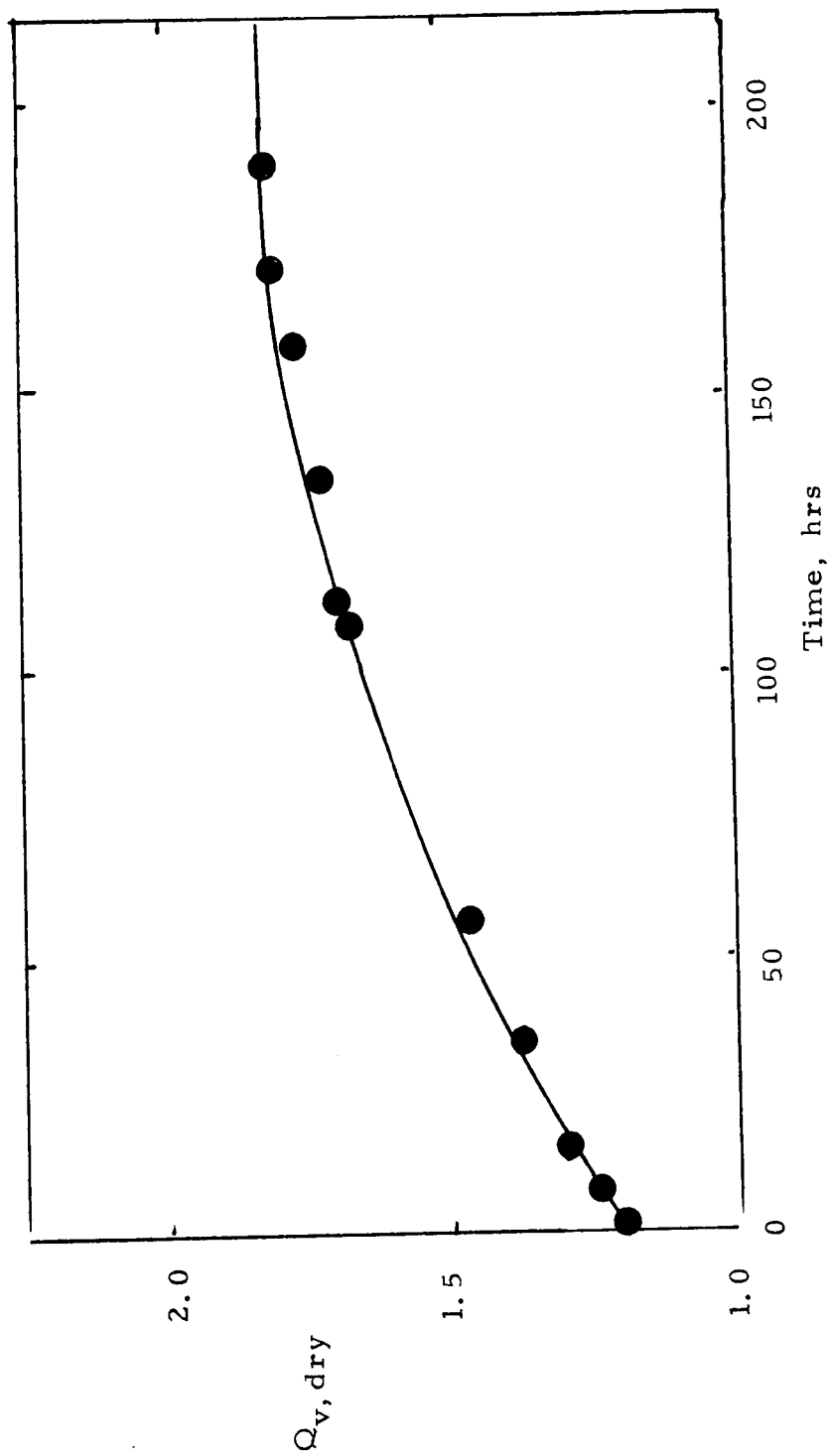


Figure 32. Plot of Time Versus $Q_{v,dry}$ for the O-acetylated Illinois No. 6(2) Coal and Tetralin.

solubility parameter of the mixture. The δ value of the mixture that provided maximum swelling was assigned to the coal. The mixture that provided maximum swelling also provided maximum extraction which was, however, not measured directly. The wavelength in the UV-visible spectrum that provided 1% transmission on this extractable portion was measured as an alternative to measuring the extractability. It is not clear what the relationship is between the wavelength and the extractability.

Any attempt to correlate the degree of swelling with the solubility parameter of the mixture assumes that the coal does not selectively absorb one solvent. With different solvent compositions inside and outside the coal, the definition of the correct solubility parameter is not immediately apparent. Since Hombach used solvents capable of hydrogen bonding with the coals (e.g. methanol), the assumption is worth testing.

An unextracted and a pyridine-extracted Bruceton coal were exposed to mixtures of methanol ($\delta = 14.5 \text{ (cal/cm}^3)^{1/2}$) and N,N-dimethylaniline ($\delta = 9.7 \text{ (cal/cm}^3)^{1/2}$), a mixture studied by Hombach. The swelling ratios were measured and the supernatants were then chromatographically analyzed to determine if selective absorption occurred. Figure 33 shows $Q_{v,dry}$ as a function of the solubility parameter of the mixture for both coals. The unextracted coal exhibits a maximum at an apparent solubility parameter of $11.3 \text{ (cal/cm}^3)^{1/2}$ and the shape of this curve is similar to those generated by Hombach.¹⁰³ More material appears to be extracted by the mixture that provided maximum swelling.

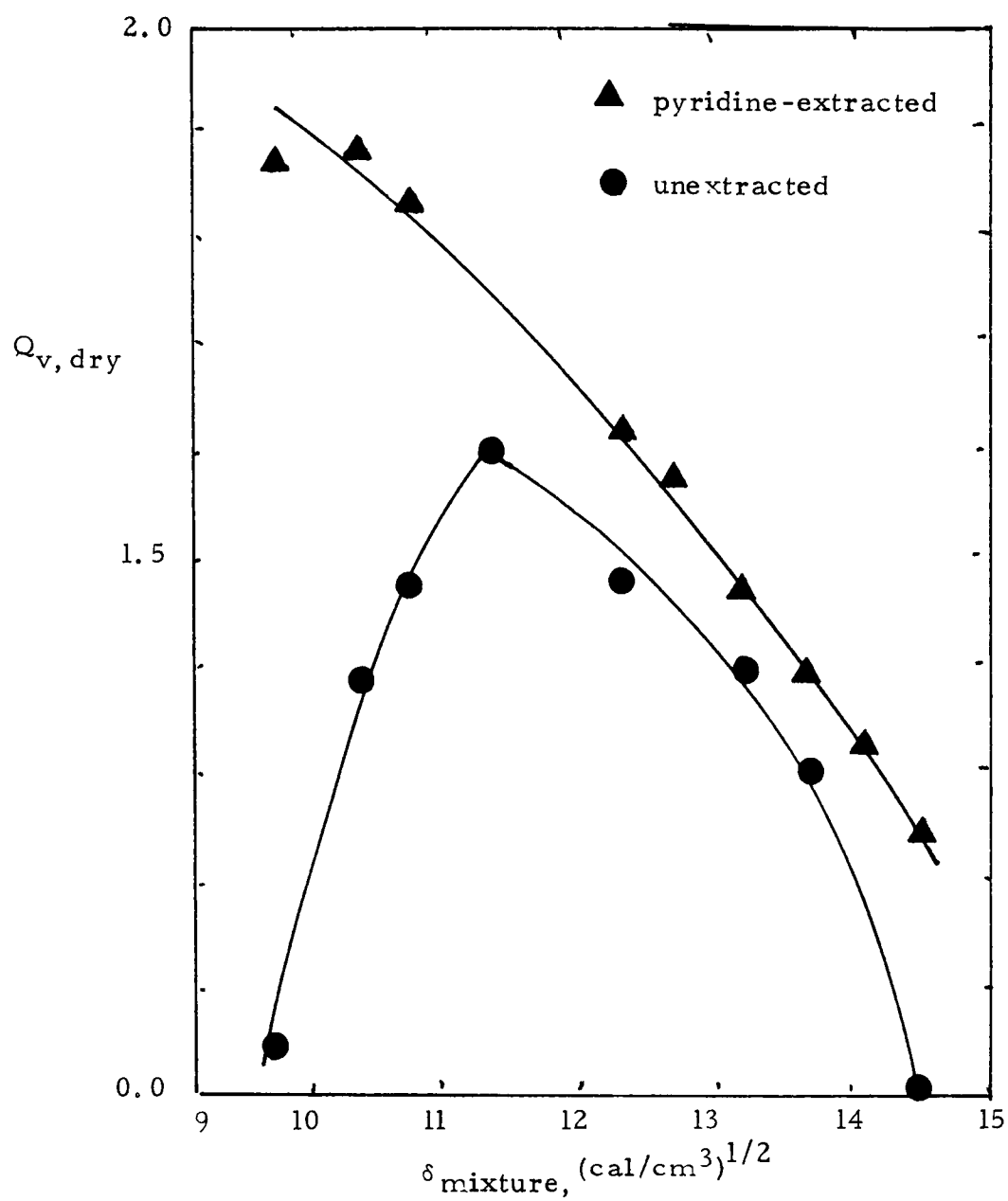


Figure 33. Plot of δ of Solvent Mixture Versus $Q_{v,dry}$ for the Methanol/*N,N*-dimethylaniline Mixtures and the Unextracted and Extracted Bruceton Coal.

The shape of the curve found using the extracted coal is noticeably different. Not only are the swelling ratios higher but the shapes of the curves are quite different with the swelling ratio of the extracted coal reaching a maximum in pure N,N-dimethylaniline. We will present the results of the g.c. analysis on the two systems and then offer some explanations as to why the two coals behave so differently.

An analysis of the composition of the supernatants using the unextracted Bruceton coal is presented in Table XXII. For almost every solvent mixture, the composition of the supernatant is different than that of the original mixture. Hence, the unextracted coal acts as a selective sorbent. The respective volumes of the solvents absorbed by the coal were calculated from Equations 26-29. The composition of the absorbed solvent mixture remains approximately constant regardless of the composition of the original mixture. The average solubility parameter of the absorbed mixture calculated from Equation 18 is $11.8 \text{ (cal/cm}^3)^{1/2}$.

It is clear from this analysis that the swelling ratio of the coal does not reflect the composition of the absorbed solvent mixture. The composition remains approximately constant yet the swelling ratio varies. There must be some other explanation other than the internal solvent composition for the observed swelling ratios. It is also clear that the δ values measured using this solvent mixture are unreliable.

The results of the analysis on the extracted coal reveal again that the coal acts as a selective sorbent (Table XXIII). However, the amount of methanol absorbed by the coal appears to remain constant regardless of the original solvent composition. This suggests that the

TABLE XXII

ABSORPTION DATA FOR THE N,N-DIMETHYLANILINE/METHANOL
MIXTURES AND UNEXTRACTED BRUCETON COAL^a

Percent MeOH in Mixture (vol)	Percent MeOH in Supernatant (vol)	Vol MeOH absorbed, ml ^b	Vol Amine absorbed, ml ^b	Percent MeOH Absorbed Mixture (vol)
10.0	6.5	0.11	0.18	38
20.0	16.8	0.14	0.22	39
30.0	28.5	0.17	0.29	37
50.0	51.5	0.15	0.22	41
70.0	74.8	0.10	0.21	32
80.0	84.0	0.09	0.14	39

^a 600 mg of dry coal and 1.50 ml of the solvent mixture.

^b Calculated from Equation 26-29 and converted to a volume per g of dmmf coal.

TABLE XXIII

ABSORPTION DATA FOR THE N,N-DIMETHYLANILINE/METHANOL MIXTURES
AND THE PYRIDINE-UNEXTRACTED BRUCETON COAL^a

Percent MeOH in Mixture (vol)	Percent MeOH in Supernatant (vol)	Vol MeOH absorbed, ml ^b	Vol Amine absorbed, ml ^b	Percent MeOH Absorbed Mixture (vol)
10.0	5.3	0.16	0.50	24
20.0	17.2	0.13	0.51	20
50.0	55.5	0.12	0.36	25
60.0	66.5	0.12	0.32	27
70.0	75.5	0.13	0.23	36
90.0	95.0	0.11	0.14	44

^a 600 mg of dry coal and 1.50 ml of the solvent mixture.

^b Calculated from Equations 26-29 and then converted to a volume per g of dmmf coal.

methanol is hydrogen bonding to specific sites in the extracted coal. The average volume absorbed corresponds to 3.6 mmoles of methanol per g of dmmf coal. This is somewhat greater than the number of hydroxyl groups estimated in the unextracted coal (1.8 mmol/g dmmf coal) (see Table XXVI). This is not surprising since the methanol is capable of hydrogen bonding to a variety of structures in the coal (e.g. ether groups).

If methanol is hydrogen bonding to specific sites in the extracted coal, then other alcohol/N,N-dimethylaniline/coal systems should behave similarly. We therefore analyzed some other systems, the alcohols being ethanol, 2-propanol, and t-butanol. The results are presented in Table XXIV. The mode of analysis was slightly different than that of the methanol/amine systems in that a known amount of an internal standard methylcyclohexane was added to the coal/solvent mixture immediately prior to analysis. Methylcyclohexane is a poor swelling solvent and therefore is not expected to significantly perturb the system. The volume of the solvent component absorbed was calculated from Equations 23 and 24.

The results show that the number of mmoles of ethanol, 2-propanol, and t-butanol absorbed per g of dmmf coal remains fairly constant for the mixtures of any given alcohol. The average amount (moles) of ethanol and 2-propanol absorbed is also the same as the amount of methanol absorbed. This seems to confirm that the alcohols are binding to specific sites in the coal. The fewer moles of t-butanol absorbed suggests that this larger alcohol is sterically hindered and therefore has fewer sites available to it for binding.

TABLE XXIV

ABSORPTION DATA FOR THE N,N-DIMETHYLANILINE/ALCOHOL MIXTURES
AND THE PYRIDINE-UNEXTRACTED BRUCETON COAL^a

Percent Alcohol in Mixture (vol)	mmol of Solvent Absorbed per g of dmmf coal ^b					
	Ethanol	Amine	2-Propanol	Amine	t-butanol	Amine
80.0	3.6	1.0	2.5	0.95	1.7	1.1
60.0	3.8	1.6	3.9	1.8	1.8	2.0
40.0	3.2	1.9	3.9	2.3	2.0	2.2
20.0	3.4	2.6	3.3	3.5	1.6	2.8
	---		---		---	
Average:	3.5		3.4		1.8	

^a 600 mg of dry coal and 2.00 ml of the solvent mixture.

^b Calculated from Equations 23 and 24 and then converted to a dmmf basis.

Finally, the swelling ratios calculated for the ethanol/amine system using the absorption data (Equation 25) are in good agreement with the measured swelling ratios (Table XXV). This confirms that the addition of the methylcyclohexane does not significantly perturb the system.

It is clear from Figure 29 that the behavior of the unextracted and extracted coals is substantially different in the methanol/N,N-dimethylaniline mixtures. We offer two explanations that may account for the different behaviors. First, the chemical potential of the solvent components in the presence of the unextracted coal probably changes as result of material that is dissolved from the coal. No dissolved material was observed in the supernatants of the extracted coal. Certainly, this is playing some role but it is probably small. Another explanation is based on the observation that the effective crosslink density of the extracted coal is substantially different than that of the unextracted coal.

We previously demonstrated that the hydrogen crosslink system of the Bruceton coal was partially disrupted by extraction of the coal with pyridine. Apparently, N,N-dimethylaniline does not possess an ability to disrupt the system since the degree of swelling of the unextracted coal in this solvent is very low. Since it cannot break hydrogen bonds, the unextracted coal cannot swell to contain it and the absorption remains low. However, the amine has a significant affinity for the coal because it swells the extracted coal substantially. In this coal, the hydrogen bonds were already disrupted by the pyridine and, with these bonds broken, the coal can expand to contain the solvent. This explanation is reasonable if the hydrogen bonding

TABLE XXV

COMPARISON OF MEASURED AND CALCULATED SWELLING RATIOS FOR THE
ETHANOL/N,N-DIMETHYLANILINE MIXTURES AND
THE PYRIDINE-EXTRACTED COALS

Percent Alcohol in Mixture (vol)	$Q_{v,dry}^a$	Q_{calc}^b
80.0	1.41	1.45
60.0	1.57	1.55
40.0	1.62	1.56
20.0	1.68	1.69

^a Measured without the internal standard present.

^b Calculated from Equation 25.

ability of the solvent is considered; its enthalpy for the interaction with p-fluorophenol, ΔH_f^0 , is only about 4 cal/mol.^{44,45} In comparison, ΔH_f^0 for pyridine is better than 7 kcal/mol.

Methanol, in contrast to N,N-dimethylaniline, is expected to disrupt the hydrogen bond crosslinks of the unextracted coal. Addition of a small amount of methanol to the amine/coal system should decrease the hydrogen bond crosslink density of the coal, allowing the coal to absorb the amine. Any potentially, extractable material that is physically trapped in the coal matrix can escape since the matrix is expanded. Likewise, any material complexed by hydrogen bonds to the insoluble matrix will be "broken off" since the methanol can compete with the binding site. This is a reasonable explanation for the observed increase in the amount of extractable material that accompanies the increase in swelling of the extracted coal.

The analysis demonstrates that the observed swelling behavior of the extracted Bruceton coal in methanol/N,N-dimethylaniline mixtures is probably a consequence of the disruption of the hydrogen bond crosslinks by the methanol and not of the solubility parameter of the mixtures. For this reason there are serious doubts concerning Hombach's estimation of the solubility parameters of coals.

Hombach also claims that the reason a mixture of xylene and pentanol gives a higher extraction yield than either of the pure solvents is because the solubility parameter of the mixture is more suitable for coal solubility than those of the pure solvents.¹⁰³ The mixture is more suitable for coal solubility but this probably should not be attributed to its composite solubility parameter. Pentanol is

not an effective extraction solvent because it has a low affinity for the hydrocarbon portion of the coal. We demonstrated in Section V.B. that the nonpolar solubility parameter is an important factor to consider in determining the effectiveness of a solvent. The nonpolar solubility parameter of pentanol is probably close to that of pentane ($\delta = 7.0 \text{ (cal/cm}^3)^{1/2}$), predicted to be a poor solvent for coals (see Figures 12 and 13). Xylene is aromatic and has a nonpolar solubility parameter better suited for coals ($\delta = 8.8 \text{ (cal/cm}^3)^{1/2}$). But xylene cannot disrupt the hydrogen bond network and therefore the degree of swelling is low. Addition of pentanol provides the necessary hydrogen bonding capability that xylene lacks. So pentanol forms some hydrogen bonds with the coal, allowing the structure to open up and release some of the soluble molecules that were hydrogen bonded to the coal. The aromatic xylene then solubilizes the soluble molecules and molecule-pentanol complexes. This same argument can be made for benzene and ethanol, an effective azeotropic extraction mixture used commonly by coal chemists.

Finally, Liotta has demonstrated that the methylation of the hydroxyl groups in an Illinois No. 6 coal dramatically increases its benzene solubility from 0.7 to 14.7% (by wt).¹¹² Here the hydrogen bond interactions have been removed. Not only can physically trapped material be extracted more easily but small molecules previously hydrogen bonded to the coal can be extracted as well.

2. Chlorobenzene/Pyridine System

The existence of the hydrogen bond virtual crosslinks in coal leads directly to several predictions of coal behavior. One of these

predictions is that the addition of a good hydrogen bond acceptor to a coal swollen with a good nonpolar solvent should increase the degree of swelling because it will break hydrogen bonds, allowing more of the nonpolar solvent to be absorbed. To test this prediction, a pyridine-extracted Illinois No. 6(2) coal was exposed to several solutions of pyridine in chlorobenzene. Chlorobenzene is a reasonably good solvent for the coal and the addition of a small amount of pyridine should enhance its ability to swell the coal.

Four hundred mg of the extracted coal were exposed to 2.00 ml of the solvent mixture and the equilibrium swelling ratios were then measured. The supernatants were then analyzed and the solvent composition of the absorbed mixture was calculated from Equations 26-29. The results are shown in Figure 34 in which the swelling ratio, $Q_{v,dry}$, is plotted against the mmoles of pyridine absorbed per g of dmmf coal. The absorption of only 0.35 mmol of pyridine (0.028 ml) increases $Q_{v,dry}$ from 1.58 to 1.91. This corresponds to an increase in volume of 0.25 ml, approximately ten times of the volume of pyridine absorbed. Clearly, the coal is absorbing more chlorobenzene as a result of the disruption of the hydrogen bond crosslinks by the pyridine.

The amount of chlorobenzene absorbed is plotted against the amount of pyridine absorbed in Figure 35. This figure reveals that the coal absorbs roughly half as much more chlorobenzene as a result of the addition of the pyridine. Interestingly, the amount of chlorobenzene absorbed then remains constant until the amount of pyridine absorbed by the coal exceeds about 4 mmoles per g of dmmf coal.

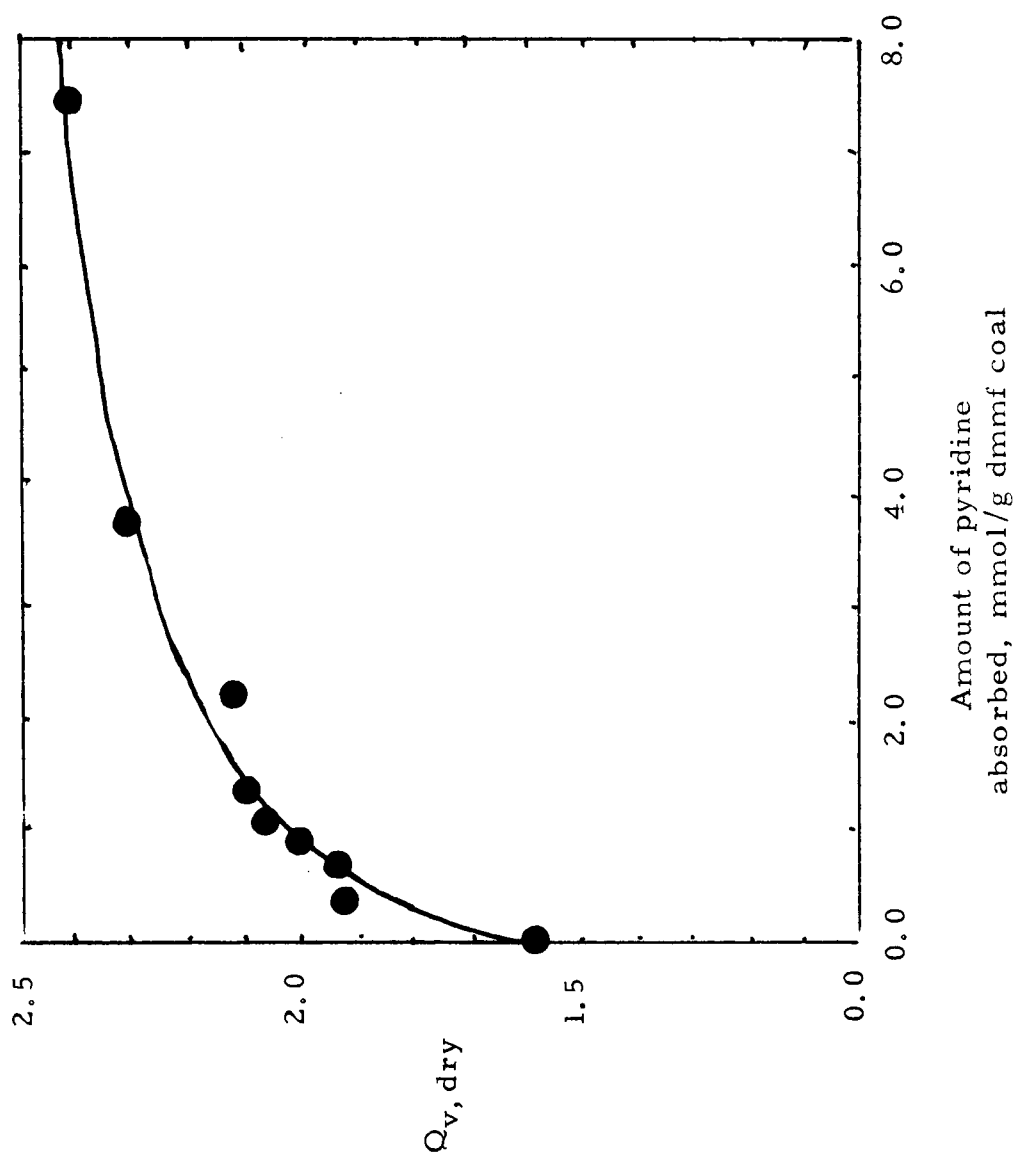


Figure 34. Plot of Amount of Pyridine-Absorbed Versus $Q_{v, \text{dry}}$ for the Extracted Illinois No. 6(2) Coal Using Chlorobenzene/Pyridine Mixtures.

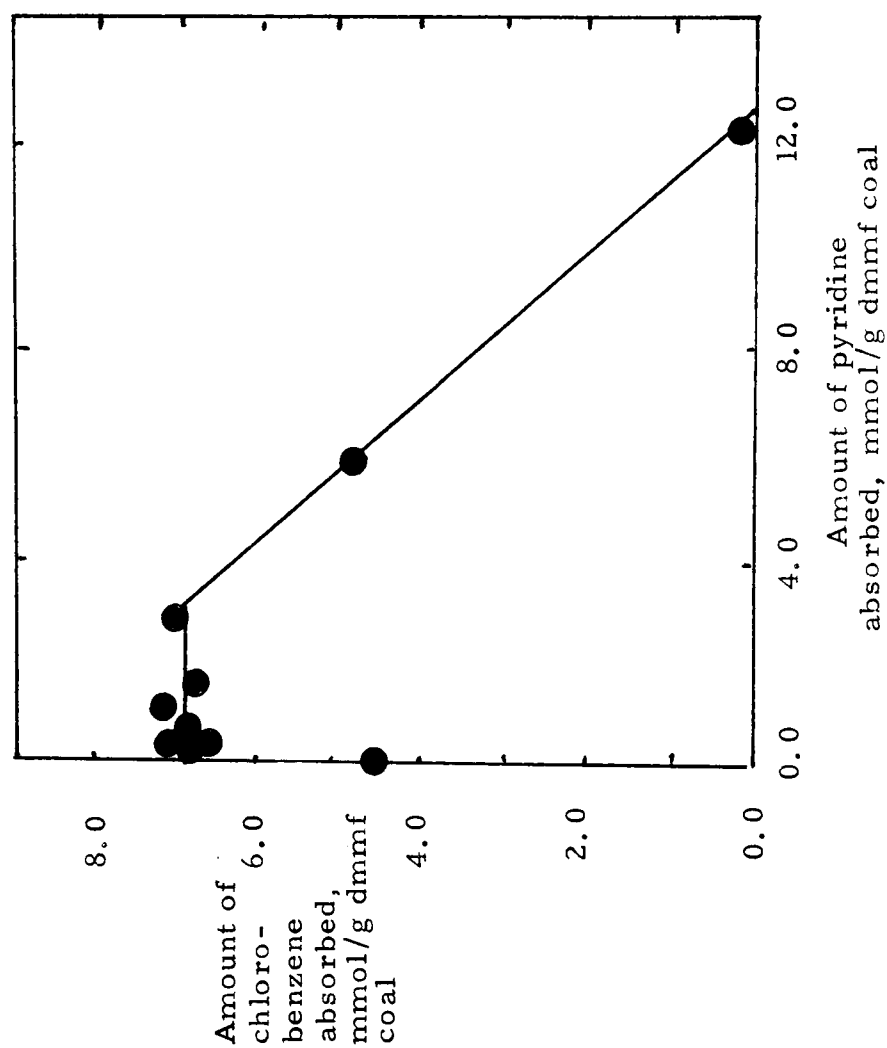


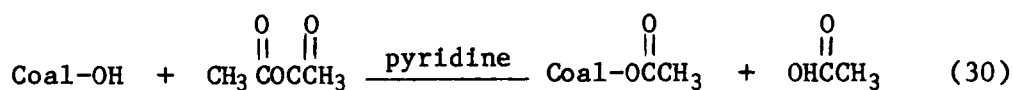
Figure 35. Plot of Amount of Pyridine Absorbed Versus Amount of Chlorobenzene Absorbed for the Extracted Illinois No. 6 Coal.

It is reasonable to assume that the pyridine initially absorbed hydrogen bonds to hydroxyl groups in the coal. Once these sites are filled, the pyridine would begin to replace chlorobenzene in the coal as the external concentration of pyridine increases. If this assumption is correct, the break in the absorption curve should correspond to the number of pyridine molecules that hydrogen bond to the coal. Although more points are obviously desirable, the "endpoint" corresponds to 3.9 mmol of pyridine/g of dmmf coal, which is very close to the 3.3 mmol of OH groups/g of dmmf coal known to be present in the unextracted coal.¹²² Thus, it appears that one pyridine molecule hydrogen bonds to each hydroxyl groups in the coal.

This correct prediction is encouraging. It lends additional support to the claim made in this work that hydrogen bonds play an important structural role in coals. It is not clear whether this "titration" method can supply any quantitative information about the population of the hydrogen bond crosslinks in the coal. Clearly this technique should be explored further. Unextracted coals should probably be used in future studies since it is clear that the number of hydrogen bond crosslinks is reduced by the extraction with pyridine.

G. Acetylation of Hydroxyl Groups

The Bruceton and Illinois No. 6(2) coal were O-acetylated by the method of Blom which consists of reflexing the coals in pyridine in the presence of acetic anhydride.¹¹⁰



Since pyridine is the solvent in the reaction, these coals were both O-acetylated and pyridine-extracted prior to swelling.

Important to these studies is a good estimate of the number hydroxyl groups in the coals. These quantities are listed in Table XXVI. For the Illinois No. 6(2) coal, two quantities are listed. One is the result of titrating the acetic acid liberated from hydrolysis of the O-acetylated coal. Equation 31 was used to calculate this quantity. Liotta's estimate of the hydroxyl content of this coal is also listed, which was determined by O-methylation of the coal using tetrabutyl ammonium hydroxide followed by alkylation with methyl iodide.¹²³ Since only one titration of the hydrolyzed product was made here, Liotta's estimate is considered to be more reliable.

For the Bruceton coal, no direct determination of the hydroxyl content was made. However, Given et al. have determined the hydroxyl content of another coal from the same seam (Pittsburgh) using Blom's method.¹²³ This quantity is therefore listed.

We also obtained FTIR spectra of the O-acetylated coals to determine if the hydroxyl groups had quantitatively reacted. A spectrum of the Illinois No. 6(2) coal is shown in Figure 36. The hydroxyl OH stretch absorbance is a broad band stretching from 3600 to 2000 cm^{-1} . The broadness of the band is attributed to hydrogen bonding. A spectrum of the O-acetylated coal is shown in Figure 37. Note the OH stretch absorbance disappears, confirming that all hydroxyl groups were reacted. Furthermore, absorbances appear at 1760 and 1200 cm^{-1} , which are attributed to the C=O and C-O stretch absorptions of the ester.

TABLE XXVI

HYDROXYL CONTENTS OF BRUCETON AND ILLINOIS NO. 6(2) COALS

Coal	Hydroxyl Contents,	mmol per g dmmf coal
Illinois No. 6(2)	4.0 ^a	3.3 ^b
Bruceton	1.8 ^a	---

^a Measured without the internal standard present.

^b Calculated from Equation 25.

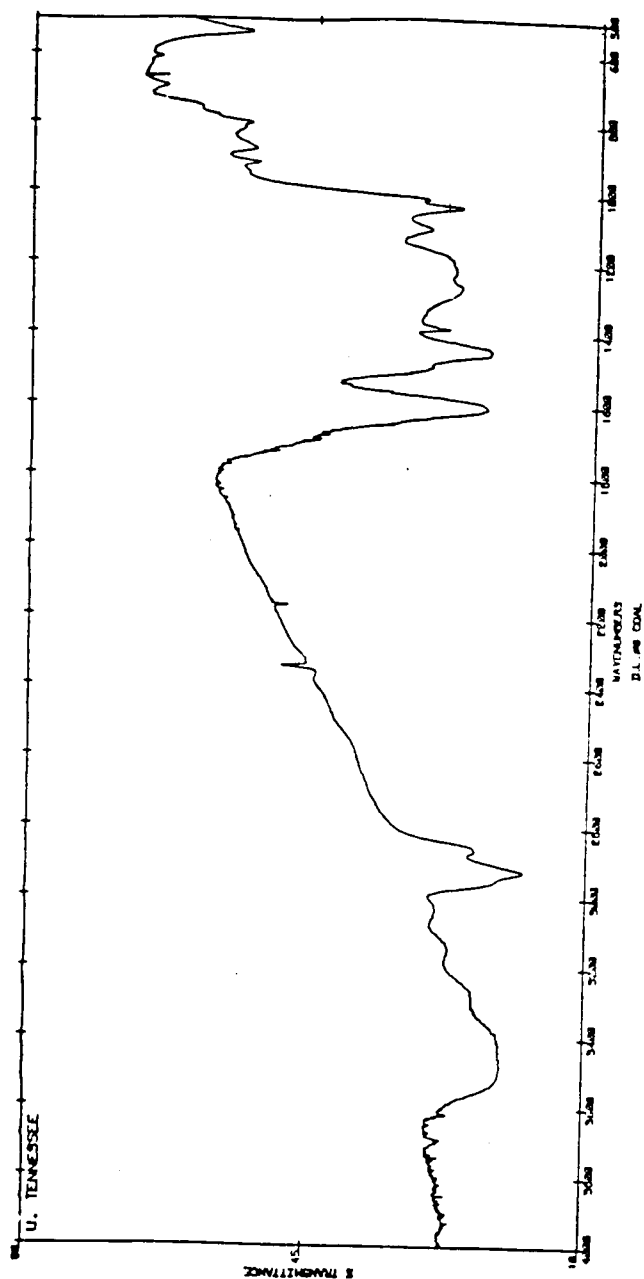


Figure 36. FTIR Spectrum of the Dry, Unextracted Illinois No. 6(2) Coal.

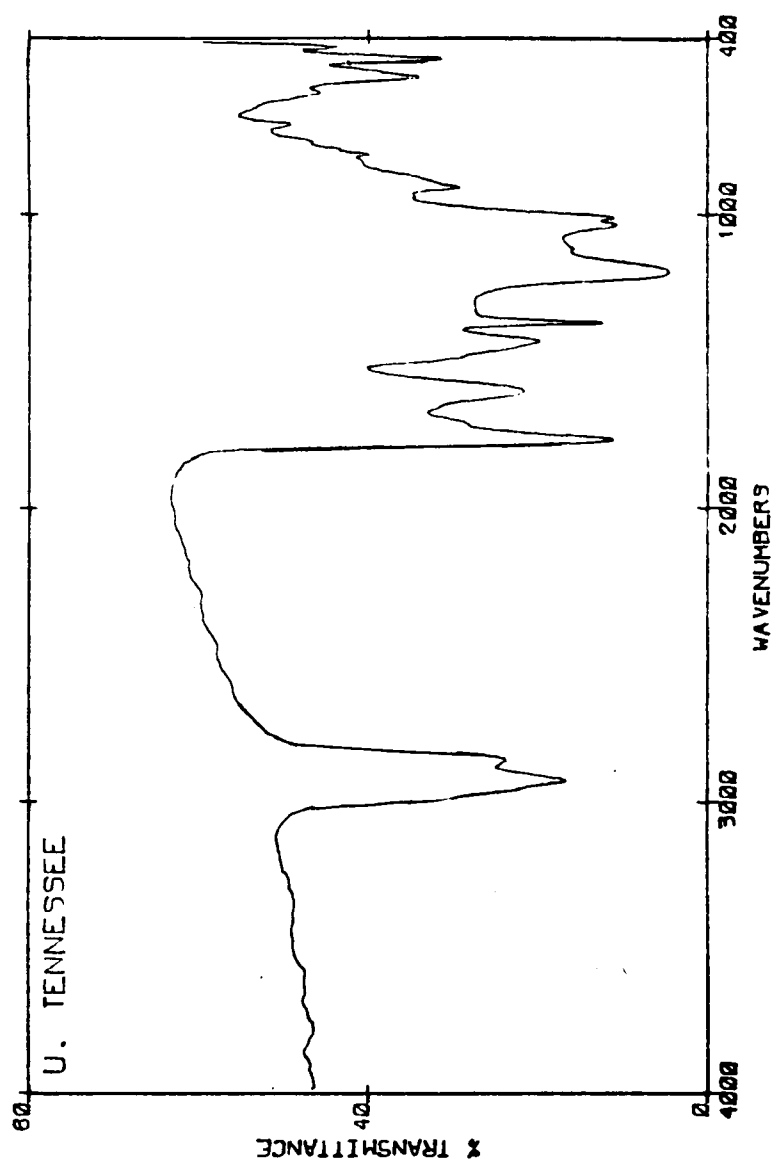


Figure 37. FTIR Spectrum of the Dry, O-acetylated Illinois No. 6(2) Coal.

H. Cyclohexane Densities

The densities of the pyridine-extracted coals in cyclohexane at 30°C (+ 0.02°C) were measured in order that the weight of swollen coal to unswollen coal (W_{dry}) obtained in the gravimetric swelling measurements could be converted to a volumetric basis. The results are presented in Table XXVII for three coals. The densities of the coals on a dmmf basis were calculated from the following equation.

$$\rho_{c,\text{dmmf}} = (100-x)/100/(\rho_{c,\text{dry}} - x/2.7) \quad (52)$$

where x is the weight percent of mineral matter in the dry coal. The weight percent of mineral matter (MM) of the coals were calculated from the Parr formula.

$$\text{MM} = 1.08\text{Ash} + 0.55\text{S} \quad (53)$$

where S is the percent sulfur. Given points out the inadequacies of this equation to estimate the percent mineral matter.¹²⁴ One objection is that this formula treats all sulfur as pyritic sulfur. Some coals contain a substantial amount of organic sulfur. The Given-Parr formula is therefore preferred.

$$\text{MM} = 1.13 \text{ Ash} + 0.4S_p + 0.5 \text{ Cl} \quad (54)$$

where S_p is the weight percent of pyritic sulfur and Cl is the weight percent of chlorine. Unfortunately, neither of these quantities were known for the extracted coals. Therefore, the Parr formula was used to approximate the percent mineral matter.

TABLE XXVII
APPARENT DENSITIES OF PYRIDINE-EXTRACTED COALS
MEASURED IN CYCLOHEXANE^a

Coal	$\rho_{c,dry}$ (g/ml)	$\rho_{c,dmmf}$ (g/ml) ^b
Bruceton	1.344	1.309
	1.351	1.313
Illinois No. 6(1)	1.358	1.304
Illinois No. 6(2)	1.398	1.286

^a Measured at 30°C.

^b Calculated from Equation 53.

CHAPTER VI

SUMMARY AND SUGGESTIONS FOR FURTHER WORK

This dissertation represents an investigation of the macromolecular structure of bituminous coals. More accurately, it represents an investigation of the physical chemistry of coal-solvent interactions. Although only two coals were examined in detail, we feel confident that the conclusions below will apply to bituminous coals in general. They are:

(1) Bituminous coals have an extensive internal hydrogen bond network. The hydrogen bonds contribute significantly to the structural integrity of the coals, serving as crosslinks between the macromolecular chains.

(2) The interaction of polar and nonpolar solvents with bituminous coals can be treated quantitatively. The best solvents will possess a high affinity for the hydrocarbon portion of the coal as measured by its nonpolar solubility parameter, and an ability to disrupt the hydrogen bond crosslinks. The enthalpies for the interaction of p-fluorophenol with the solvents are good quantitative indicators for assessing this ability.

(3) Regular solution theory and solvent swelling techniques can be used to estimate the relative crosslink densities of bituminous coals. By treating χ as an adjustable parameter, self-consistent results were obtained on two coals. The results indicate that there are several times as many hydrogen bond crosslinks as covalent crosslinks. The number of hydrogen bond crosslinks predicted from the

treatment is roughly equal to the estimated number of hydroxyl groups in the coal.

(4) The diffusion theories of polymers can be used to interpret the kinetics of swelling of coals. A substantial portion of the swelling process for two polar solvents and the extracted Bruceton coal follows Fickian diffusion. Thus, the behavior of the coal is typical of a rubbery polymer. The rate and extent of diffusion of solvents into the coal can be enhanced by removal of the hydrogen bond crosslinks.

(5) Coals can act as selective solvents. The use of mixed solvents to determine the solubility parameters of coals is therefore very risky, particularly if solvents capable of forming 1:1 complexes with acid or basic sites in the coal are employed.

While it is clear that considerable insight into coal structure and coal-solvent interactions has been gained, much more work remains. We suggest some areas that deserve consideration.

1. The Nature of the Elastic Restoring Force in Coals

An underlying assumption in the application of the Flory-Rehner or Kovac equation to coals is that the elastic restoring force is primarily entropic in nature. This assumption remains untested for coals and therefore deserves consideration. Experiments designed to probe this question would be very worthwhile.

2. χ Parameters

We estimated χ parameters for several coal-solvent pairs using regular solution theory. This technique should be applicable to other

bituminous coals, but there remain serious question about its application to lower rank coals, particularly lignites. Lignites are much more polar (often 20 wt% oxygen) and, as repeatedly emphasized in this paper, regular solution theory applies only to nonpolar systems. Indeed, bituminous coals are not strictly nonpolar systems in themselves and one can only assume that this does not significantly affect the results of the treatment. Low rank coals may not be amenable to a regular solution theory treatment.

We can only assume that the χ parameters estimated for the coal-solvent pairs represent reasonable values at this time. However, other independent methods for measuring χ on coal-solvent systems need to be developed so that direct comparisons can be made.

Finally, one of the problems in defining χ lies not in the measurement but in the nature of coal itself. Coals are terribly heterogeneous materials and comprise a variety of organic structure. Clearly, any χ value estimated for a particular coal-solvent system must be regarded as an average value. In spite of this complication, the coals examined in this study were surprisingly well-behaved and follow the predictions of regular solution theory.

3. Crosslink Density

The relationship between covalent crosslink density and coal reactivity needs to be investigated. Also, what is the relationship between corsslink density and coal rank? Is there a minimum in crosslink density at 86% carbon? Investigations of this nature must take into account the existence of the hydrogen bond crosslinks.

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