MACROMOLECULAR AND MOLECULAR MODEL OF COAL STRUCTURE*

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ABSTRACT

This paper presents a review of experimental data which point out that coal organic matter consists of a cross-linked macromolecular network and a complex mixture of relatively small molecules. The components of molecular phase are assumed to be clathrated in the macromolecular phase by means of electron-donor—acceptor interactions. Some parts of the molecular phase may be not extractable due to restricted orifice sizes of pores created by a macromolecular network. Determination of the content of a molecular phase in coals seems to be solved by the application of ^{1}H-NMR free-induction decay measurements. A comparison of calculated NMR line for Wiser's representative structure with Gaussian component of the experimental NMR line for some low rank coals indicates that the above structure is a good representation for building blocks of the macromolecular phase of some coals.

INTRODUCTION

One of the approaches which has often been used to illustrate the main chemical characteristics of coal, is the construction of chemical models of coal. Models help to summarize and evaluate the consistency of various experimental data. They could also play the same role in kinetic and mechanistic studies in coal chemistry just as knowledge of the structure of reactants plays such a role in other fields of organic chemistry.

New experimental data which have emerged during the last few years have prompted the author to construct a two-phase model of coal structure.

GENESIS OF A TWO-PHASE MODEL FOR COAL STRUCTURE

It has been known for a long time that all coals can be swollen in numerous organic solvents and that the swelling is always accompanied by solubilization of a part of coal substance. According to Larsen and Kovac

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[1] and Lucht and Peppas [2] swelling capability is evidence of the presence of cross-linkages which arrange coal material in a three-dimensional macromolecular network and prevent this part of coal from solubilization. Such a conclusion has been derived from polymer science — insoluble and swelling polymers are those which are cross-linked materials. Contrary to that situation, the soluble portion of coal (like soluble polymers) cannot be cross-linked matter.

It has also been known that the soluble part of coal contains relatively small molecules. This was pointed out by numerous analyses of various coal extracts [3]. Extraction of a low rank bituminous coal carried out at a temperature well below any thermal decomposition and application of field ionization mass spectrometry (FIMS) of the extracts revealed that the part which volatilized in the spectrometer (80—75 wt.%) consist of molecules from approximately 70 to 800 daltons [4]. These molecules constituted not less than 30 wt.% (daf) of the coal. Scarce data (but essentially the same as above) are available on molecular weight distribution of solubles of other coals and coal macerals [5, 6], since FIMS as well as field desorption mass spectrometry (FDMS), which are the only means that can provide reliable data, are rarely applied in analyses of coal solubles.

It has also been known that the yield of pyridine extracts from bituminous coals can be remarkably high. Yields increase from approximately 20 wt.% (daf) for low rank coals to approximately 38 wt.% (daf) for medium rank coals and then decrease rapidly [7]. The data indicate that, at least in some coals, a content of molecular phase may be high. Although the occurrence of a macromolecular cross-linked phase and relatively small molecules in coals is unquestionable, there is still a question as to the ratio of these two phases and how to determine this ratio in a given coal.

MACROMOLECULAR PHASE (MM PHASE)

MM phase in the model (see Fig. 1) is depicted by large shaded areas connected by cross-linkages (solid lines in Fig. 1). The segments of MM phase represent the projection (on one of the planes) of coal structure such as that published by Wiser [8]. It is not the author's intention to imply that Wiser's structural representation is a good representation of MM phase in all coals. There is the intention, however, to submit a first approximation of a structure of the MM phase as composed of aromatic units connected by aliphatic and alicyclic fragments and to emphasize that such a structure is far from being planar. This approximation transfers basic characteristics of all previous models of chemical constitution of a whole organic matter of coals [8—13] to MM phase of coals.

Jurkiewicz [14] carried out calculations of the theoretical NMR line for Wiser's structural model. He derived the second moment and spin—spin relaxation time T_2 thereafter which is a function of all proton—proton distances in a structure. The calculated value appeared to be strongly
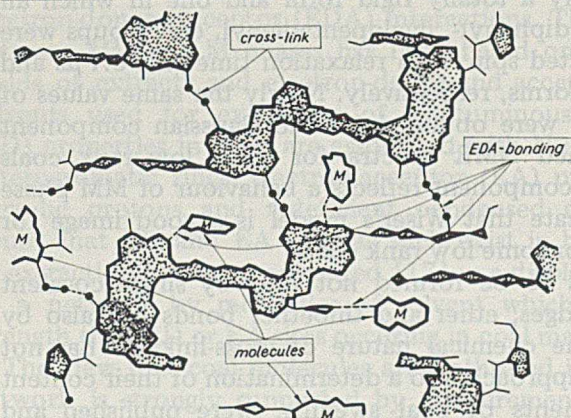
Fig. 1. The macromolecular and molecular model of low rank bituminous coal. Shaded areas — macromolecules. Unshaded areas with "M" inside — molecules. (—•—•—), cross-linkages between macromolecules; (————), electron-donor—acceptor interactions between molecules and macromolecular network.

dependent on many characteristics features of Wiser's model such as number and location of methylene and ether bridges, hydroaromatic rings and methyl groups. Spatial configuration of the whole structure is also an important factor. Distances between some protons in these fragments, or between these fragments are short, i.e., from 1.35 to 1.9×10^{-10} m and threfore the fragments give a large contribution to the calculated value for Wiser's entire structural model. In the calculations [14] two forms of the

TABLE 1

Calculated [14] spin—spin relaxation time T_2 of the Wiser's structure and experimental T_2 for some coals [15]

Wiser's structure	Relaxation time T_2 in microseconds 8.7—9.3			
	of Gaussian component[a]		of Lorentzian component[a]	
Coals, %C (daf)	in coal	in coal swollen in pyridine	in coal	in coal swollen in pyridine
64.0 %C	9.3 ± 2.0	12.2 ± 2.2	37.0 ± 2.0	265 ± 60
65.8 %C	8.8 ± 2.0	12.6 ± 2.0	33.0 ± 2.0	380 ± 80
67.6 %C	9.1 ± 2.0	10.5 ± 1.8	32.0 ± 2.0	360 ± 90
80.7 %C	11.9 ± 3.0	13.7 ± 2.3	36.0 ± 3.0	144 ± 25

[a] Gaussian and Lorentzian components of free-induction decay spectra reflect a behaviour of macromolecular and molecular parts of coals, respectively [15].

model were considered, namely a totally rigid form and one in which all fragments such as OH-, CH_3-, diphenyl-, cyclopentadienyl, etc. groups were allowed to rotate. The calculated spin–spin relaxation times are $8.7\,\mu s$ and $9.3\,\mu s$ for rigid and rotating forms, respectively. Nearly the same values of T_2, i.e. from $8.8\,\mu s$ to $12\,\mu s$ were obtained for the Gaussian component of the experimentally obtained NMR spectra for some low rank coals (Table 1). Since the Gaussian component reflects a behaviour of MM phase of coals [15], the data indicate that Wiser's model is a good image for building blocks of MM phase for some low rank coals.

Cross-linkages are supposed to be formed not only by single covalent bonds such as methylene bridges, ether and thioether bonds but also by larger fragments. Although the chemical nature of cross-linkages has not been fully confirmed, several approaches to a determination of their content in coals, based on measurements of coal swelling, were published and reviewed [2].

A three-dimensional macromolecular network would be expected to create a system of pores. In fact, pores in bituminous coals have a wide range of diameters and slit sizes and exhibit a trimodial distribution which comprises macropores (over 50 nm), mesopores (1.6–9 nm) and micropores of lower dimensions [16].

MOLECULAR PHASE (M PHASE)

Molecules are depicted in Figure 1 by means of small unshaded areas with an "M" inside. The term "molecular phase" is used when one is considering the whole noncross-linked part of coal which is composed of relatively small molecules compared to cross-linked macromolecules. It seems that the molecular phase in coals consists mainly of molecules which have molecular masses below 800 daltons. However, this upper limit has not yet been known. The term "molecular phase" in coals is not entirely adequate for the definition of "phase" given by Gibbs, since coal molecules do not create a state of matter which is uniform throughout in chemical composition and in physical state. The uniform characteristics of these "coal molecules" are manifested by a lack of swelling capability and by a capability to dissolve in some organic solvents.

The chemical nature of components of M phase shows remarkable diversity. Over 300 components which were identified by molecular formulae $C_nH_{2n-x}O_yN_z$ with the use of high resolution mass spectrometry in one of the bituminous coals, were reported [4]; the major types of components are aromatic hydrocarbons, phenol, pyridine and pyrrol homologs and benzologs. Low molecular-weight components which were identified with the use of GC or GCMS in numerous coals are listed in the review [3]. Owing to the application of GC, GCMS and HRMS, the chemical nature of molecules up to approximately 400 daltons has been quite well known. Conversely, very little is known about higher molecular weight components.

It is shown in Fig. 1 that molecules are attached to the network through electron-donor—acceptor (EDA) interactions. The concept of EDA bonding between MM and M phases has been based on correlation found between yields of extracts and electron-donor and acceptor properties of numerous solvents used for extraction of a bituminous coal [17]. Electron-donor (ED) properties in coals are associated with N and O atoms and π-excessive heteroaromatic rings; electron-acceptor (EA) properties with phenolic and pyrrolic protons and π-deficient condensed aromatic rings. There is no doubt that ED and EA sites as such exist in both phases. The mechanism of extraction has been envisaged [17] as a displacement of molecules bound to a network by molecules of solvent which exhibit higher ED or EA strength than ED or EA sites occuring in coal matter.

The view that coal molecules are clathrated in pores of a macromolecular network is strongly supported by measurements of inner surface areas of coals before and after solvent extraction [18]. Extraction by pyridine and some other solvents, which also have high electron donating abilities, has led to an increase of such area in coals [18].

Separation of the molecular phase from coals must rely upon solvent extraction carried out at temperatures which do not result in thermal decomposition of C—C bonds nor in release of "chemical combined" water, and carbon oxides or hydrogen. Therefore, a temperature below 180°C would be preferred. Yet, not all molecules can be extracted, presumably due to restricted orifice sizes in the pore systems of coals. Mudamburi [19] and Mudamburi and Given [20] separated hexane solubles from liquefaction products of a number of U.S. coals. By application of liquid and gas chromatography coupled with mass spectrometry they found homologous series of C_1—C_{15} or C_1—C_{20} monosubstituted alkyl naphthalenes, alkyl furans and alkyl phenols. On the other hand, neither pyridine nor benzene—ethanol extracts of the coals showed the presence of such homologous series. It is difficult to propose any structure of a macromolecular network capable of producing such a series of compounds by pyrolytic breakdown. Therefore, the authors concluded [20] that these molecules had been trapped in the network and were released during liquefaction.

Marzec and Czajkowska have studied the influence of pressure exerted on coal samples on pyridine extract yields — (unpublished data). Samples of coals and coal samples pressed with the use of a hydraulic press were extracted in Sohxlet extraction apparatus for 42 h; the pressed samples were ground again before extraction. The authors stated that pressure in 30—50 kg/cm² range exerted on low rank, 65—82 %C, coal samples led to a drop of extract yields compared to unpressed samples of the same coal. Drops of pyridine extractability as large as 6—9 wt.% were observed (examples are shown in Fig. 2). It is concluded therefore that coal extractability depends not only on a content of molecules which are present in a coal, but it may also depend on the pressure that coal experienced in a coal seam.
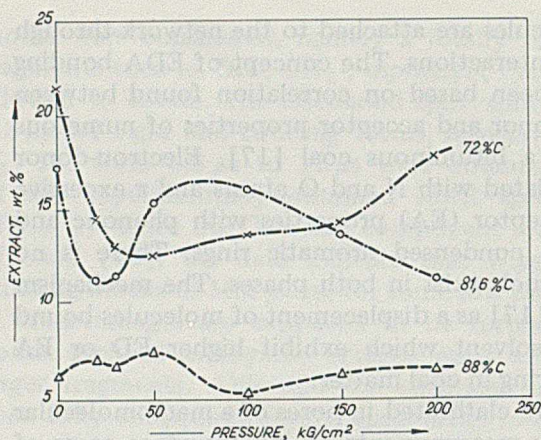
Fig. 2. Pyridine extract yield versus pressure exerted on coal sample. ×: 72 %C (daf) coal, ○: 81.6 %C (daf) coal, △: 88 %C (daf) coal.

Determination of the content of the two phases is a crucial point. A method of estimating the total content of molecular phase, no matter whether extractable or not extractable, has been described [15]. The method was derived from observations of molecular dynamics by means of NMR measurements of free-induction decay (FID) in coals which were soaked in deuterated pyridine. Pyridine is supposed to destroy all electron-donor—acceptor interactions between M and MM phases. The FID signal of swollen coal consists of two components, i.e., Gaussian and Lorentzian lines which can be seen after deconvolution. After this their separate amplitudes can be measured. The components correspond to macromolecular and molecular phases, respectively. The amplitudes of the Gaussian and Lorentzian lines correspond to a content of hydrogen atoms occurring in macromolecular and molecular phases. Measurements carried out for a number of low rank coals revealed that hydrogen occurring in the molecular phase was from 30 to 70 wt.% of the total hydrogen content [15].

Barton et al. [21] made a critical assessment of our method [15]. They agree that an exchange of coal hydrogen with pyridine deuterium atoms at room temperature appears to be insignificant, and does not interfere with the determination at all. They also stated that "solid echo" signals can be used as an alternative to the method based on FID signals. They expressed the view, however, that segmental mobility of the macromolecular network may contribute to a content of mobile (Lorentzian) protons which were ascribed by us to the molecular phase. Further arguments for, as well as against our method, are published as a debate [22].

CONCLUSIONS

Our proposed model envisages coals as systems composed of a three-

dimensional macromolecular network and relatively small molecules which are clathrated. Preliminary results for low rank coals, < 82 %C (daf), indicate that the molecular phase may represent 30—50% by weight of a whole coal organic matter and even more for some lignites. Detailed chemical structure of networks and a composition of the molecular phase in coals of various rank and origin, are still unknown.

The model presented in this paper has implications with reference to further studies of coal structure. It would be desirable to strip out the molecular phase from coals before starting any study intended to clarify the structure of the macromolecular phase. It is also desirable to apply two different sets of analytical techniques which are the best suited to solid, insoluble and non-volatile characteristics of the network and to the soluble and mostly volatile nature of the molecular phase.

It seems that the molecular phase and its behaviour on heating the coals which may include thermally activated diffusion of molecular components, can have rather important impacts on the kinetics and mechanism of carbonization, combustion and liquefaction processes.

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