

SOLVENT SWELLING STUDIES OF SOMA LIGNITE (TURKEY)

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The volumetric swelling procedure was applied to Turkish Soma lignite using thirteen solvents to investigate the cross-linking in its macromolecular network. The theory of solvent swelling of cross-linked polymers developed by Flory and Rehner and extended by Kovac and Peppas was used to calculate number-average molecular mass per cross-link of organic structure (\bar{M}_c) in lignite samples. The results show that the volumetric solvent swelling of Soma lignite samples in non-polar and polar solvents roughly follows the regular solution theory.

Introduction

Coal is a sedimentary rock with a large three-dimensional cross-linked macromolecular network of polynuclear aromatic clusters connected by relatively strong bonds. The macromolecular structure of this complex mixture of organic material and inorganic components is characterized by its cross-link density. The lower the cross-link density, the more open the structure of coal. (The structure of a hypothetical coal molecule is given in Fig.1 [1]). Coal conversion processes involve changes in the macromolecular structure decomposing it. The coal organic part is insoluble in conventional organic solvents, and therefore solvent swelling, extensively used in the study of polymer structure, has been used to investigate macromolecular network properties of coal [2, 3].

The solvent swelling is the simplest method to characterize the macromolecular organic structure of coal and to gain insight into geochemical process of maturation. The rate of solvent diffusion into the macromolecule is related to the density of cross-links in its organic structure.

The theory of solvent swelling of cross-linked polymer was developed by Flory and Rehner. The starting point of this theory is that when brought into contact with a solvent, a cross-linked macromolecular system will absorb the solvent and swell.

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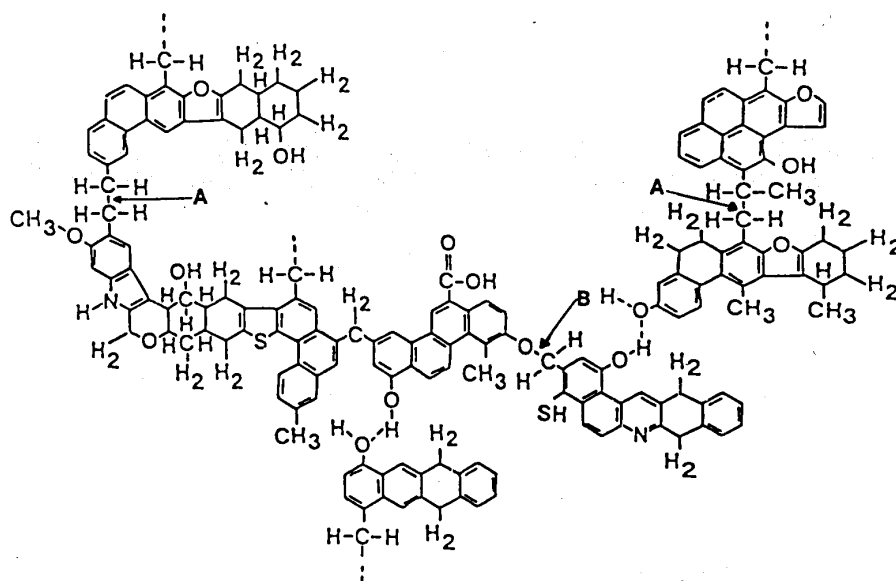


Fig. 1. Structure of a hypothetical coal molecule [1]: A – the bond between aliphatic carbons; B – the bond between oxygen and aliphatic carbon

At equilibrium free energy of the system must be minimum, and dissolution of the solvent in the macromolecule is balanced by elastic restoring force of the network. This force depends on the average length of the macromolecular chains between cross-links \bar{M}_c . The Flory treatment assumes that there is no specific interaction such as hydrogen bonding during the swelling process, or in other words, during polymer-solvent interaction the regular solution occurs [4, 5].

The Flory-Rehner equation is

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

where \bar{M}_c is the number-average molecular mass of the part between cross-links;

V_1 is the solvent molar volume;

v_2 is volumetric fraction of polymer at swelling equilibrium;

ρ is the polymer density.

When the distance between cross-links is not large and no longer follows Gaussian distribution, this equation does not hold. Another theory was developed by Kovac and Peppas for this case [2]. The principal changes they made were (1) removing the assumption of Gaussian distribution of chain length, and (2) introducing an additional parameter N , the number of rotatable segments between branch points.

Kovac equation is

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

In the present study, the swelling behavior of Soma lignites (SLIG) was investigated and the number-average molecular mass per cross-link of organic structure in coal was calculated using the theory of solvent swelling of cross-linked polymers developed by Flory and Rehner and extended by Kovac and Peppas.

Experimental

Coal Sample

The investigations were performed with lignite samples obtained from Soma-Manisa deposit in Turkey. The results of lignite analysis are as follows [6]: ultimate analysis, wt.% (db): C_{total} 60.4; $C_{organic}$ 58.7; $C_{inorganic}$ 1.7; H 5.6; N 0.9; S_{total} 1.2; proximate analysis, wt.% (as received): moisture 13.7; ash 14.6; volatile matter 37.3; fixed carbon 34.4. For swelling experiments, the samples were crushed and ground in a jaw mill until the desired particle size (<0.1 mm) and dried at 105 °C under N_2 atmosphere.

Solvent Swelling

All solvents used in swelling experiments were of high purity grade [7]:

Solvent	Solubility parameter, (cal/cm ³) ^{1/2}
Pentane (non-polar)	7.0
Cyclohexane (non-polar)	8.2
<i>o</i> -Xylene (non-polar)	8.8
Toluene (non-polar)	8.9
Tetrahydrofuran (H-bonding)	9.1
Benzene (non-polar)	9.2
Tetraline (non-polar)	9.5
Nitrobenzene (polar)	10.0
Pyridine (H-bonding)	10.7
Acetonitrile (polar)	11.9
Dimethyl sulfoxide (H-bonding)	12.0
Ethanol (H-bonding)	12.7
Nitromethane (polar)	12.7

The swelling behavior of SLIG was measured at ambient temperature using volumetric method [8, 9]. The samples (80–100 mg) were placed in a 6-mm o.d. tube and centrifuged for 3 min, thereafter the height of the sample (h_1) was measured. Excess organic solvent was added into the tube, the content of the tube was mixed, centrifuged for 3 min and the height of

the sample (h_2) was measured. The measurements were continued until no further volumetric change was observed over several days, indicating that the equilibrium had been reached. Sometimes the amount of extractable material was significant and in such cases it was necessary to add fresh solvent to the tubes by removing the contaminated solvent after centrifugation with a syringe, and then adding the fresh one. Measurements were repeated until equilibrium. The volumetric swelling ratios were calculated as

$$Q_v = \frac{h_2}{h_1} \quad (3)$$

And

$$Q_v = \frac{(v_c + v_s)}{v_c} \quad (4)$$

where v_s is the volume of solvent absorbed by a unit volume of coal v_c .

Reversibility of the swelling process has been also investigated by carrying out re-swelling experiments (Table 1). The tubes from the first swelling were subjected to solvent removal under nitrogen atmosphere and dried under vacuum. Before re-swelling measurement, the samples were again centrifuged for 5 min and the height of coal samples in tubes recorded.

Table 1. Reversible Swelling of SLIG in Dimethyl Sulfoxide, Tetrahydrofuran and Pyridine

Solvent	1st swelling	2nd swelling	3rd swelling
Tetrahydrofuran	1.8	1.8	1.7
Dimethyl sulfoxide	2.1	2.2	2.2
Pyridine	2.2	2.1	2.2

Results and Discussion

The volumetric swelling ratios of the coal samples were measured using thirteen different solvents, and the extent of cross-linking in the macromolecular network of SLIG was examined. All swelling experiments were performed with the samples of narrow size distribution.

According to the study of Otake *et al.* [10], the particle size has an effect on swelling behavior of coals due to artefacts associated with particle packing. This effect is attributable to particle size distribution rather than the actual size of the particles, and this was observed to lead to unreproducible results when samples of the broad particle-size range were examined.

There are a number of studies on kerogen swelling. The solvent swelling of a maturation series consisting of five Type I kerogens from the Uinta

basin has been studied by Larsen *et al.* [11]. The solubility parameters determined were within the range of 9.5–10 (cal/cm³)^{1/2}. The swelling of Göynük (kerogen Type I) and Beypazari (kerogen Type II) oil shales has been studied by Ballice. It was found that kerogen type had no remarkable effect on swelling behavior and solubility parameters of the oil shale samples studied [12]. The solvent swelling technique is effective for both coal and oil shale.

There are abundant data on coal swelling and on coal-solvent interactions [13–15]. The swelling of Illinois No. 6 coal was investigated by Larsen *et al.* [16]. They stated that swelling in non-polar solvents followed the regular solution theory, and the coal solubility parameters determined were about 9.5 (cal/cm³)^{1/2}.

The rates of solvent swelling of the Argonne Premium coal samples have been measured in various organic solvents at various temperature by Otake *et al.* [10]. They stated that the extent of swelling was independent of the temperature within the temperature range studied (10–60 °C). Therefore, over the past decade a number of studies have been made on the factors that influence diffusion in solid coals. The studies on diffusion of organic liquids have generally indicated that diffusion in coals is in many respects similar to the diffusion of solvents through glassy polymer [10].

The changes in the volumetric swelling ratios of coal samples are presented in Fig. 2.

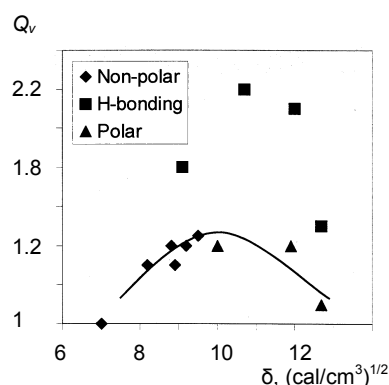


Fig. 2. Swelling ratio of SLIG sample as a function of swelling solvent solubility parameter

In the present study the organic part of SLIG was not isolated from its mineral matter. As the latter is not expected to swell, it occupies a certain volume. The effect of mineral matter on solvent swelling has been examined by many researchers. Kerogen has been both partially and completely isolated from Green River oil shale by Larsen *et al.* [2]. They stated that the inorganic part of kerogen did not have any large effect on swelling, and the presence of the mineral matter did not seem to hinder swelling [2]. The effect of demineralization on the macromolecular structure of coals was investigated also by Larsen *et al.* [17]. They reported that solvent swelling studies of lignites and of a subbituminous coal revealed no changes whether they were demineralized or not [17].

It is necessary to establish the reversibility of swelling measurements. If the swelling and re-swelling measurements do not give the same results, neither the initial nor the final state are at equilibrium. Some studies on kerogen swelling have been reported where swelling was not reversible [18]. According to the results given in Table 1, the SLIG samples after three swelling measurements swelled reversibly, and the height of dry bed of coal samples did not change due to re-swelling.

The regular solution theory predicts that there should be a maximum in the plot of swelling vs. solubility parameter, and that the maximum should occur at the solubility parameter of the polymer, in the present case the organic part of SLIG. If the combination of the polymer sample and solvent follows the regular solution theory, there will be a maximum in the solvent uptake, and thus will be a maximum in polymer swelling when the solubility parameter of solvent matches that of the polymer. As the solubility parameters of the polymer and different solvent diverge, swelling will be less.

The regular solution theory predicts a bell-shaped curve with no swelling for solvents quite unlike the polymer and a maximum when solubility parameters of solvent and polymer are nearly equal [2, 3]. It can be clearly seen in Fig. 2 that the system SLIG/non-polar solvent seems to follow the regular solution theory roughly. Drawing the curve by eye, the maximum falls between $9.5\text{--}10.5$ $(\text{cal}/\text{cm}^3)^{1/2}$. This is in accordance with the literature data [16].

There are also some troubling deviations from the regular solution behavior. Polar solvents behave similarly to non-polar solvents, whereas only hydrogen-bonding solvents, except for ethyl alcohol, show enhanced swelling. The solvent having the solubility parameter near that of hydrogen-bonding solvent gives less swelling than expected, and the reasons are not understood. We believe that this is due to the interaction between hydroxyl groups in the coal structure and hydrogen-bonding solvents.

There are many data on the interaction between oil shale kerogen and organic liquids [2, 3]. The swelling of Type I (Green River and Rundle) and Type III (Pittsburgh No. 8 coal) kerogens has been investigated by Larsen *et al.* [16]. They observed that the less polar O/C Type I kerogen followed the regular solution theory, and more polar higher O/C Type-I kerogens came close to it, but the data for polar and non-polar liquids were more scattered. It has been interpreted as a specific interaction with hydrogen-bonding solvent [3].

FT-IR analysis of the SLIG samples was made to get information about the coal structure in order to explain this specific interaction between coal samples and hydrogen-bonding solvent *via* possible hydroxyl groups in the coal structure. However, the spectra did not indicate the presence of polar groups in coal.

According to the literature data, great deviations in the case of H-bonding solvents (such as pyridine, tetrahydrofuran, and dimethyl sulfoxide) were

due to their special interaction with organic structure rather than to mineral effect [3, 10]. The great swelling ratio in the case of H-bonding solvents is due to specific interaction of solvent with the organic structure by forming hydrogen bond at a specific site in the polymer, resulting in a deviation from the regular solution theory. Stronger specific interactions lead to greater solvent uptake resulting in enhanced swelling. The hydrogen bond between different polymer chains in coal organic part may persist in non-polar solvents and serve as cross-link. A good H-bonding solvent may disturb the polymer–polymer hydrogen–hydrogen bond replacing it by polymer–solvent bond(s). In this case, a cross-link has been destroyed. The more lightly cross-linked a polymer is, the more it will swell, and especially when the polymer mentioned is the coal organic structure.

Except for pyridine and tetrahydrofuran, quantitative approximations can be done on the number-average molecular mass between the cross-links for non-polar and polar solvents. The calculation results can be compared within the data for H-bonding solvents and other ones. The number-average molecular mass between cross-links (\bar{M}_c) was unreasonably low in the solvent–coal systems with the solubility parameter difference exceeding two [$(\delta_{coal} - \delta_{solvent}) > 2$]. For that reason, the systems having the coal-solvent solubility parameter difference less than two [$(\delta_{coal} - \delta_{solvent}) < 2$] were used to obtain more realistic values.

Both the Flory–Rehner, and Kovac equations were used to calculate the number-average molecular mass between cross-links (Table 3).

Table 2. Number-Average Molecular Mass per Cross-Link (\bar{M}_c) for SLIG

Solvent	\bar{M}_c			
	Flory–Rehner equation	Kovac equation		
		$N = 1$	$N = 2$	$N = 3$
Cyclohexane (non-polar)	115	430	319	282
<i>o</i> -Xylene (non-polar)	446	1673	1208	1053
Toluene (non-polar)	219	828	603	528
Tetrahydrofuran (H-bonding)	546	2048	1437	1233
Benzene (non-polar)	214	805	581	507
Tetraline (non-polar)	358	1342	965	839
Nitrobenzene (polar)	213	800	578	503
Pyridine (H-bonding)	937	3583	2457	2081
Acetonitrile (polar)	198	746	538	469
Average	361	1361	965	833

The density and solubility parameters of SLIG were assumed to be 1.4 g/cm^3 and $10.0 \text{ (cal/cm}^3)^{1/2}$, respectively. The Flory–Rehner equation gave $\bar{M}_c = 361$, and Kovac equation resulted in $\bar{M}_c = 1361$ (for $N = 1$). The number of rotatable segments between branch points, N , was varied from

1 to 3. The number-average molecular mass between cross-links \bar{M}_c calculated using Flory–Rehner equation is lower than the value calculated using Kovac equation. It can be assumed that the distance between the cross-links follows Gaussian distribution because the chain length between cross-links \bar{M}_c calculated from Flory–Rehner equation is large enough to make this assumption.

Conclusions

Solvent swelling behavior of Soma lignite has been investigated. Experimental results show that the system SLIG–hydrogen-bonding solvent deviates from the regular solution behavior, but SLIG with non-polar and polar solvents roughly follows the regular solution theory. The interaction between Soma lignite and hydrogen-bonding solvent is not describable by any existing definite model, and the process seems to be dominated by specific effects one ought to study thoroughly. Only then the structure of Soma lignite and possible interactions at swelling could be understood.

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