

## The Relationships Between Coal Macromolecular Structure and Solvent Diffusion Mechanisms

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### Introduction

The diffusion of solvents through coal is the limiting step of many coal processes and measurement of the mechanism and kinetics of solvent diffusion has been the subject of numerous investigations<sup>1,2</sup>. It is generally accepted that solvent diffusion through coal is analogous to the diffusion of solvents through conventional glassy polymers and much of the formalism of the latter has been applied to coal<sup>3</sup>. The diffusion of solvents may vary between two extrema. If the diffusion is controlled by the concentration gradient between the center and the outside of the particle the diffusion mechanism is Fickian and, for diffusion into a sphere, the kinetics are expressed by the following expression<sup>4</sup>:

$$\frac{M(t)}{M_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2 t/a^2) \quad 1$$

where  $M(t)$  is the mass uptake at time  $t$ ,  $M_e$  is the equilibrium mass uptake,  $a$  is the particle radius and  $D$  is the diffusion coefficient. However, the mechanism of diffusion can deviate significantly from the Fickian mode when the diffusing solvent changes the viscoelastic properties of the glassy solvent. In the limit the diffusion of solvents is completely controlled by polymer relaxation and the solvent advances through the polymer with a well defined front such that ahead of the front the solvent concentration is zero and behind the front the solvent is at equilibrium concentration. Furthermore, ahead of the front the polymer is glassy and behind the front the solvent is rubbery. This kind of diffusion is referred to as "relaxation" or "Case II" diffusion and is characterized either by a polymer relaxation constant or the front velocity. Simple integration of the mass uptake at time  $t$  gives the following kinetic expression<sup>5</sup>:

$$\frac{M(t)}{M_e} = 1 - (1 - k_0 t / C_0 a)^3 \quad 2$$

where  $k_0$  is the relaxation constant and  $C_0$  is the equilibrium solvent concentration. The

front velocity is  $k_0/C_0$ .

Diffusion mechanisms for solvents through coals has been shown to vary between these limits<sup>2</sup>. However, the structural features of the coal macromolecular structure or the details of the macromolecular/solvent interactions which determine diffusion mechanisms remain undefined and are the subject of this paper.

The method used to monitor the amount of solvent that has diffused into the solvent is Dynamic Volumetric Swelling (DVS). Essentially, the amount of volumetric swelling is monitored as a function of time. Only solvent that has diffused into the "bulk" structure can cause coal to swell so that this technique is insensitive to occluded solvent. At any time  $T$ , the amount of solvent that has diffused into the bulk is proportional to the amount of volumetric swelling, so that:

$$\frac{M(t)}{M_e} = \frac{Q(t)}{Q_e} \quad 3$$

where  $Q(t)$  is the amount of volumetric swelling at time  $t$  and  $Q_e$  is the equilibrium swelling. Graphically, to distinguish between the extremal modes of diffusion it is conventional to plot the normalized mass (or swelling) uptake as a function of root normalized time,  $(t/t_e)^{1/2}$ . Figure 1 shows the normalized plots for the theoretical Fickian and Relaxation diffusion modes. It can be seen that under this regime the normalized Fickian curve increases monotonically whereas the Relaxation controlled mode has an inflexion at low  $(t/t_e)^{1/2}$ .

### Experimental

The apparatus was adapted from a design by Aida and Squires<sup>6</sup>. Essentially it consists of a glass cylinder 2 cm in diameter in which coal, supported by a quartz frit, interacts with the solvent. A light PTFE piston is placed on top of the coal and the increase in the height of the coal sample is monitored by a linear transducer connected to a microcomputer. The piston was of such a size as to allow a gap of about 1/4mm between the itself and the outer cylinder. The reaction chamber was surrounded by a constant temperature water bath, kept at 313K for these experiments. The coals were ground to between 60 and 30 Tyler mesh. With this particle size the diffusion of solvents through the coal bed was at least two orders of magnitude faster than diffusion into the particles. Coal was placed into the cylinder and the upper surface levelled. The initial height of the coal sample was measured and the piston and transducer placed on the coal. Solvent was introduced into the chamber to just below the frit and allowed to come to thermal equilibrium. Further solvent was added until the coal and piston were covered. The increase in sample height was monitored as a function of time. Since the approach to equilibrium swelling was asymptotic, the equilibrium time was chosen as the time to reach 99.5% of the equilibrium swelling value.

The coals were obtained from the coal bank of the Northern Carbon Research Laboratories and are described in Table 1. Two solvent sets were chosen, a set of

substituted pyridine molecules and a set of straight chain amines. The former were chosen because the steric properties of the molecules are similar but the basicity depends upon the substitution. In the latter, the molar volume increases with amine chain length whereas the basicity is relatively constant with amine chain length. The  $pK_b$  values and molar volumes of these solvent sets are given in Table 2.

### Results and Discussion

Figure 2 shows the swelling curves for Gedling coal as a function of time. As would be expected, the time to equilibrium swelling (as defined above) increases as a function of amine chain length or molar volume. The amount of swelling also increases with amine molar volume, as observed by Green and West<sup>7</sup>. However, Figure 3 shows that when the swelling is normalized and plotted against root normalized time the curves have the same trajectory. Therefore all of the amines have the same swelling mechanism, regardless of molar volume.

Figure 4 shows the normalized DVS data for the substituted pyridine set. The diffusion changes from an anomalous mode for the pyridine and 2-methylpyridine to Fickian for the 2-fluoropyridine.

The principal mechanism of swelling for bases such as the amine and substituted pyridine sets appears to involve the disruption of inter chain hydrogen bonds<sup>8,9</sup>. Coal hydrogen bonds have a range of bond energy<sup>9</sup>. One result of this is that weaker bases, such as the 2-fluoropyridine, are able to disrupt only the weakest hydrogen bonds, stronger hydrogen bonds act as *de facto* crosslinks. As solvent basicity increases in the substituted pyridine set the solvents are able to disrupt increasing numbers of hydrogen bonds. Eventually a point is reached at which all of the hydrogen bonds are disrupted. This is manifested as a plateau in swelling/basicity curves<sup>9</sup>.

One explanation of the progressive change from anomalous diffusion to Fickian diffusion could be that as the bases disrupt hydrogen bonds so the viscoelastic properties of the coals change from glassy to increasingly rubbery in the presence of the solvents. However, Figure 4 shows that pyridine and 2-methylpyridine have the same diffusion mechanism, even though their basicities are significantly different. This can be rationalized by noting that pyridine and 2-methylpyridine swell Gedling coal to the same extent<sup>9</sup> and, by hypothesis, disrupt the same number of hydrogen bonds.

Further corroborative evidence for the above theory comes from the diffusion mechanisms of the straight chain amine set. The amine chain length has little effect on molecular basicity and the observed increase in swelling with chain length has been attributed to the presence of increasingly larger molecules within the coal structure<sup>7</sup>. Green and West<sup>7</sup> have presented evidence to suggest that the molar amount of amine is absorbed per unit weight of coal is independent of amine size. This is consistent with the idea of

solvent basicity determining the number of hydrogen bonds disrupted.

From the above a consistent picture can be made of the factors which determine diffusion mechanisms for basic solvents. In its usual state Gedling coal is glassy at room temperature. When hydrogen bonds are disrupted by basic solvents the effective crosslink density decreases. There is an associated change of the coal viscoelastic properties as the coal becomes more rubbery. The degree to which coal becomes rubbery is a function of the density of hydrogen bonds disrupted. No assumptions are made about the mechanism by which basic solvents disrupt hydrogen bonds. However, the disruption of hydrogen bonds in itself may not be sufficient to change coal viscoelastic properties. Lucht *et al.*<sup>10</sup> have shown that  $T_g$  is reduced only to a limiting value of about 410K following sorption of pyridine vapor. There is a certain amount of evidence from work by Brenner<sup>11</sup> to suggest that solvent which makes coal rubbery is weakly associated in the coal structure. This may imply some sort of a solvent plasticization effect. These observations are not inconsistent with the picture presented above because during the uptake of liquids, for the Anomalous and Relaxation controlled diffusion, the concentration of solvent behind the solvent front must be sufficiently large to cause the rubbery behavior. In summary, the above picture only seeks to stress that an essential part of the glass to rubber conversion is the disruption of hydrogen bonds. Recent, unpublished, work suggests that solvents which would be expected to have a plasticization effect similar to pyridine (such as chlorobenzene) in themselves do not change coal viscoelastic properties.

With the preceding in mind, an attempt can now be made to interpret the diffusion properties of a rank range of coals. The diffusion mechanisms are presented in Figure 5 with pyridine as the diffusing solvent. The lignite displays a Fickian diffusion and the diffusional mode becomes increasingly Relaxation controlled as rank increases. The diffusional mode for Cortonwood is well outside of the theoretical Relaxation controlled limit. Now, if the change in viscoelastic properties were simply a function of the density of hydrogen bonds disrupted then relaxation controlled behavior would be expected for coals with high oxygen contents. In fact the opposite is true. This can be rationalized by assuming that the change in viscoelastic property is, *ceteris paribus*, a function of the ratio of crosslink density before and after solvent diffusion *i.e.*  $(M_c/M_c + M_h)$ . Where  $M_c$  is the covalent crosslink density and  $M_h$  is the hydrogen bond crosslink density. If this is indeed the case then the ratio of hydrogen bond to covalent (and other non-scissile) crosslinks increases as a function of coal rank in the range 50-87% carbon content. supportive evidence for this hypothesis comes from a body of data, derived from a variety of coal chemical and physical properties, which suggests that the crosslink density of coal reaches a minimum at about 87% carbon content<sup>3,8</sup>.

There is no easy explanation in this framework for the behavior of Cortonwood coal. The swelling appeared to be a two-stage process with a quasi-equilibrium followed by a very slow approach to swelling equilibrium. A detailed picture of the factors influencing

coal diffusion mechanism requires more work. The role of solvent plasticization is unexplored.

### Conclusions

The mechanism of diffusion of a solvent through a coal is, in part, determined by the degree to which the diffusing solvent changes the coal viscoelastic properties. One factor which influences this is the density of hydrogen bonds disrupted by the solvent in ratio to the non-scissile coal crosslinks. Solvent steric properties influence the kinetics, but not the mechanism of diffusion.

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Table 1

Coal	%C	%H	%O*	%N	%Mineral
ND Lignite	50.0	4.3	45.7	-	-
Gedling	81.6	5.2	9.4	1.7	2.8
Cresswell	84.5	5.5	5.9	1.9	3.0
Cortonwood	87.2	5.6	3.9	1.7	2.7

\* by difference

**Table 2**

Solvent	pK <sub>b</sub>	Molar Volume (cm <sup>3</sup> /mol)
Propylamine	3.3	82.2
Butylamine	3.2	98.8
Propylamine	3.4	115.9
Hexylamine	3.4	132.1
2-methylpyridine	8.0	98.8
Pyridine	8.6	80.9
2-chloropyridine	13.5	94.6
2-fluoropyridine	14.4	86.1

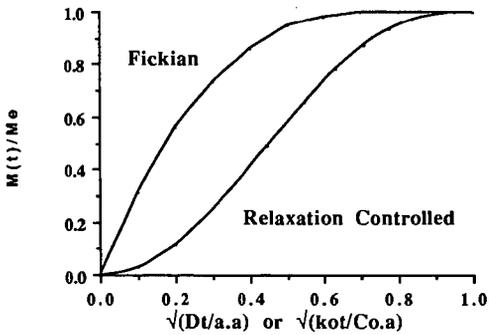


Figure 1. The normalized, theoretical, modes for Fickian and Relaxation-controlled diffusion into a sphere.

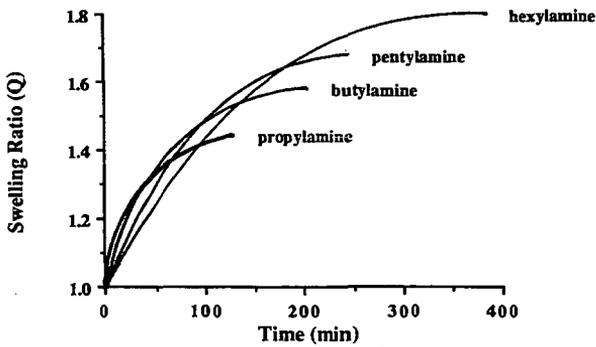


Figure 2. The dynamic volumetric swelling for straight chain amines in Gedling

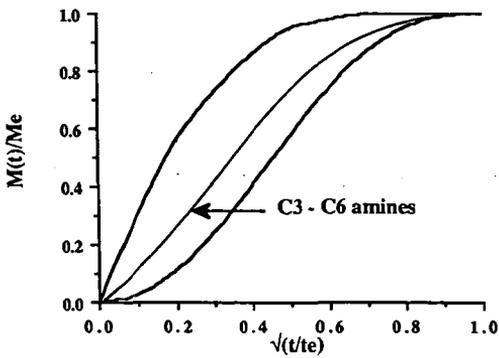


Figure 3. The diffusion mechanism for straight chain amines into Gedling coal at 313K as deduced from dynamic volumetric swelling.

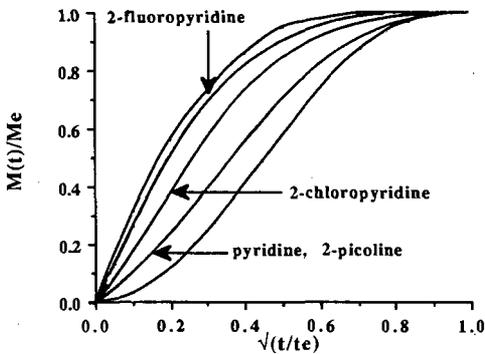


Figure 4. The diffusion mechanisms for substituted pyridines into Gedling coal at 313K, as deduced from dynamic volumetric swelling.

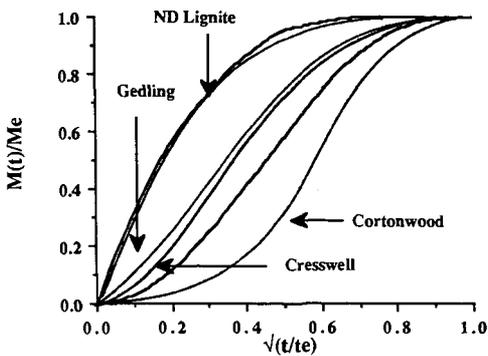


Figure 5. The diffusion mechanisms for pyridine into a range of coals at 313K, as deduced from dynamic volumetric swelling.