

## DIFFUSION RATES OF ORGANIC SOLVENTS IN COALS: ACTIVATION ENERGIES

Yoshinobu Otake and Eric M. Suuberg  
Division of Engineering  
Brown University, Providence, RI, 02912

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### INTRODUCTION

Diffusional limitations are of concern in virtually all aspects of coal utilization. As a result, over the last few years there have been a number of studies of the factors that influence diffusion [1-24]. These studies, which have been mostly concerned with transport of solvents through coals, have generally indicated that diffusion in coals is similar in many respects to the diffusion of solvents through glassy polymers. The process of relaxation of coal structure by the solvents plays an important role in determining how fast the coal can take up additional solvent. The rates of solvent uptake are strongly influenced by factors such as the nature of the coal, the size of the coal particles [1], the strength of the solvent [15,17,18], the size and shape of the solvent molecules [7,8, 24], the temperature [5,6,17-19,23], the moisture content of the coal [19], and other features of its pretreatment [9,10,14,19,20,21]. The present paper presents results that shed further light on the role of temperature on the rates of diffusion. This is a key aspect of the process that requires further consideration, since most coal conversion processes are performed at elevated temperatures.

It is important to note at the outset that the diffusional processes that are of concern in this study involve movement of individual molecules of solvent through molecular scale openings in the coal. Thus we are not concerned with diffusion or flow in the macropores of coal, which would generally be much faster processes than those of interest here.

The main experimental method that is applied in this study is solvent swelling of coal. This method has been applied in earlier studies of diffusion in coals [7,8,15,17-21,23,24]. To be useful, this technique requires working with coal-solvent pairs that strongly interact, and that the coal measurably swell. This limited the study to solvents that are strong electron donors [25]. In our particular application of the technique, measurements of the extent of swelling were made manually, *vide infra*, which required at least a few minutes per measurement. This limited the study to systems that did not swell on a timescale faster than a few minutes. The timescale of experiments could be adjusted by variation of either temperature (lower temperatures slowed the process) or particle size (larger particles swelled more slowly). This limited the experimental matrix that could be conveniently studied, but a broad range of conditions was still available, as will be apparent below. It should be noted that the automated techniques for measuring swelling rates [7,8,15,23,24] were considered, but felt to pose certain problems with respect to heat transfer and maintenance of constant packing. The vapor sorption techniques require pre-extraction and corrections for pore filling [3,4,26,27], which made these unattractive for present purposes.

In this paper, discussion is limited to the effects of temperature on the swelling process. The temperature influences not only the kinetics of swelling, but also the nature of the swelling (whether Fickian or non-Fickian).

### EXPERIMENTAL

The data were obtained on the coals from the Argonne Premium Coal Sample Program [28]. Since the composition and properties of these coals have been carefully tabulated elsewhere, the information will not be repeated here. To assure uniformity among samples, all were dried for 3 hours at 373 K in vacua. As we have noted before, the effects of drying can be quite significant [19]. Studies of dried coals are nevertheless relevant, both because in practical applications coals are first dried, and because the fundamental phenomena of interest here are not changed in basic nature by the drying procedure (even if the kinetics are affected).

It was learned early in this study that particle size has a significant effect upon the results obtained. One major reason is that if a broad range of particle sizes is employed, packing of fine particles into the interstices between larger particles can cause significantly higher packing of the particles, and

lead to artifacts in the volumetric swelling measurements. Thus efforts were made to always work with relatively well-defined particle size fractions, even though the means of the size fractions varied widely from experiment to experiment, for the reasons noted above. When the results are given below, the size fractions will be indicated.

The swelling experiments were performed as described in an earlier paper [17]. The technique involved immersion of the prepared coal samples in pure, reagent grade solvents. The measurements were performed in constant diameter glass tubes of 3 mm inner diameter and about 5 cm in length. After a 30 to 100 mg sample was placed in the tube, it was centrifuged at 7500 rpm for 3 minutes in a 30 cm diameter horizontal rotor centrifuge, to permit accurate measurement of an initial dry packed height of coal. Solvent, prewarmed or precooled as necessary to the experimental temperature, was then added to the tube, and the contents were vigorously stirred with a thin rod. Such stirring is important to prevent the coal from rapidly swelling and forming a solid plug in the tube. The tube was then placed in a thermostatted water bath, for the desired time, and was agitated as noted during this immersion. The temperature of the water bath was controlled to about 0.1°K.

The coal was then allowed to swell for the desired time, and then was removed from the bath and placed in an ice bath to slow the swelling to a negligible rate. Then the sample was again centrifuged as above, and the height of the column of coal remeasured. The ratio of the swollen height to the initial height is what is reported here as the volumetric swelling ratio. Several different samples were employed to determine the extent of swelling as a function of time, in cases in which the swelling was rapid. It was often necessary during the course of the swelling measurements to change the solvents, as they became visibly extract-laden. This was done by carefully decanting the extract-containing solvents, and replacing with fresh solvents. No attempt was made to pre-extract the coals prior to these measurements, since it was desired that the diffusion rates be studied in what was as close to the virgin coal state as possible, except that the coals were dried.

## RESULTS AND DISCUSSION

### *Effect of Temperature on the Extent of Swelling of Coals*

There are two potential effects of temperature on the swelling behavior of coals. Temperature may influence both the ultimate extent of swelling as well as the rate of swelling. Many workers have noted the insensitivity of ultimate swelling ratio on temperature [17, 23, 29]. In the present experiments, we have again confirmed that there is no significant effect of temperature on the extent of swelling, at least in the range from 10 to 60°C. This is understood in terms a near zero enthalpy of swelling near the equilibrium extent of swelling [25]. The near thermoneutrality of the swelling process is what dictates a temperature-independent final equilibrium, which may be easily seen as a consequence of the Gibbs-Helmholtz equation of classical thermodynamics.

It has also been argued that the weak dependence of the extent of equilibrium coal swelling on temperature could be a consequence of a rather special form of the equation describing the partial molar Gibbs free energy of elastic deformation [29]; in this case, the partial molar energy of coal elastic deformation must be temperature independent. The recognized need for inclusion of the combinatorial entropy of mixing raises questions about the validity of this theory, however, since this reintroduces the temperature dependence to the expression governing equilibrium.

It should be noted that there is one report of great sensitivity of the swelling ratio to temperature [1]. The experiments in question were conducted by allowing solvent uptake from a *vapor* phase, as opposed to the *liquid* phase, as in the other studies. In this case, there is always a significant (exothermic) enthalpy of solvent condensation, which dictates that condensation, and swelling, would be less extensive, the higher the temperature.

### *Solvent Swelling Kinetics*

The diffusion of solvents into coals, as governs their swelling, has been noted by virtually all workers to be highly non-Fickian in nature, in many cases. The behavior is often that observed in glassy polymers, and involves "Case II" diffusion, as defined by Alfrey et al. [30]. The Case II situation involves a solvent uptake process which is controlled by the relaxation of the macromolecular network structure, as opposed to diffusion itself. It is characterized by a sharp front separating the swollen and unswollen regions of the coal.

To the extent that solvent swelling is linearly related to mass uptake, it is possible to relate the two

quantities via:

$$M/M_{\infty} = (Q-1)/(Q_{\infty}-1) \quad (1)$$

where  $M$  refers to mass uptake of solvent by the coal,  $Q$  is the coal's volumetric swelling ratio, and the subscript  $\infty$  refers to the final equilibrium values. The error associated with the neglect of small amounts of empty voidage is generally negligible. Analysis of the nature of the diffusional process has been greatly aided by a simple empirical approach, which relates  $M/M_{\infty}$  to time [2]:

$$M/M_{\infty} = k t^n \quad (2)$$

where  $k$  is a constant related to the rate of swelling, and  $n$  is a number that crudely indicates the nature of the diffusion. For nearly spherical particles and for mass uptakes up to about 60% of the equilibrium value,  $n = 0.43$  for Fickian diffusion, and  $n = 0.85$  for Case II diffusion. Values above  $n = 0.85$  are possible, and are termed "super-Case II" [2].

Table 1 gives the results for the Argonne Premium Coal Samples, swollen by pyridine. All results were obtained on particles of 150-212  $\mu\text{m}$  size range, unless noted otherwise. The results show the measured values of the parameter  $n$ , as a function of temperature. Generally speaking, the values of  $n$  are reasonably constant with temperature, though in two cases, they showed a significant decrease with temperature above 40°C. The values indicate a range of behaviors ranging from clearly Fickian (Illinois No.6) to clearly Case II (or even super-Case II, in Pittsburgh No.8). This range of behaviors is precisely the same as has been recently reported for a suite of British coals [23]. It should be noted that we provide no values for two Premium Sample Coals (Pocahontas and Upper Freeport), because as has been noted earlier, these coals swell to a negligible degree until thermally relaxed at much higher temperatures [21].

Given the values of  $n$  from Table 1, it is possible to evaluate activation energies for the swelling process, from:

$$E = -nR \left[ d(\ln 1/t_f)/d(1/T) \right] \quad (3)$$

where  $E$  is the activation energy,  $R$  is the gas constant and  $t_f$  refers to the time at a fixed extent of swelling. This definition of activation energy is based upon the rate law (2), and is slightly different from that which we used earlier [17,18]. The values from (3) are more directly comparable with other values recently published [23]. The results for the Argonne Coals are again shown in Table 1. The values range from about 20 to 50 kJ/mol. It may be noted that the coals with the higher rates of swelling (indicated by the time to achieve 50% swelling,  $t_{50}$ ), generally exhibit lower activation energies for swelling. It is logical to associate a lower energy barrier to swelling with a higher rate. In fact, swelling in the coal with the lowest activation energy, Illinois No. 6, apparently was limited by ordinary Fickian diffusion, though with a reasonably high activation energy of 20 kJ/mol.

Earlier, we reported that low rank coals generally exhibit higher activation energies for swelling than do higher rank coals [18]. The opposite conclusion was more recently presented by another group [23], but they examined a somewhat narrower range of rank. Here, we again see a low rank coal show a high activation energy, but now there is no clear trend with rank. The conclusion is that there is no definite trend of activation energy with rank. The actual rates of swelling were also earlier reported to show no correlation with rank [18, 23]. Again, this is seen to be the case here as well.

There is a strong dependence of activation energy on the nature of the solvent. The results obtained using various solvents to swell the Pittsburgh No. 8 sample are shown in Table 2. It has been earlier concluded that the degree of coal swelling is strongly correlated with the electron donor strength of the swelling solvent [25], or equivalently, the basicity of the solvent [23]. It was also earlier reported that the basicity is an important factor only during initial swelling, prior to initial relaxation of the coal structure [23]. In the case of raw coals it was suggested that the stronger the base, the faster the initial swelling. The results of Table 2 show that there is little correlation of activation energy for swelling of raw coals with basicity alone. Butyl- and hexyl-amines are stronger bases than is pyridine, which is stronger than THF. Recently, this issue was addressed in another similar study with alkyl amines, in which it was shown that activation energy increases with the size of the amine [24], as is seen also in Table 2. The conclusion that both size and electron donor strength need to be considered in predicting activation energies is supported by the present results. The present results, however, suggest that the shape of the molecule has an enormous influence, as the much weaker electron donor THF exhibits an activation energy intermediate between the much larger and stronger bases butylamine and hexylamine. It should be recalled that despite this, THF swells the coal less and much more slowly than either of the two

bases.

We have earlier shown that this Pittsburgh No. 8 coal can be thermally relaxed by heating to 350°C at 8°C/min [20,21]. We explored the swelling kinetics of samples treated in this manner. The results are also shown in Table 2. These results show that the activation energies for swelling are only slightly decreased by the thermal relaxation and that in pyridine, the ultimate degree of swelling is unaffected, but that the rate is slightly increased. In THF, both the ultimate extent and rate of swelling are significantly increased. These pre-pyrolytic effects are a result of relaxation of the structure. The relaxation does not, however, change the activation energy. This appears to suggest that the activation energies for swelling are determined by a relaxation which is distinct from that which is thermally induced, and from its magnitude, might be speculated to be associated with breaking single hydrogen bonding interactions. Hydrogen bonding interactions have long been known to be a key in determining swelling behavior [e.g.,31]. The range of activation energies observed is in the ranges typically reported for hydrogen bonding in coals [e.g., 32,33].

### CONCLUSIONS

The swelling kinetics of several raw coals have been examined in various solvents at various temperatures. These data have been examined in terms of apparent activation energies. Both size and shape of the solvent molecules appears to play a role in determining the values, as does the electron donor strength of the solvent. The overall rates of diffusion were naturally lower, the bigger the solvent. There was generally an enormous variability in diffusional/swelling rates, which did not correlate well with coal rank. In cases in which the swelling was relaxation-controlled, the activation energies for diffusion were of the same order of magnitude as hydrogen bonding interactions.

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**Table 1- Summary of Swelling Results on Argonne Premium Coal Samples in Pyridine**

Coal	$Q_{\infty}$	$T(^{\circ}\text{C})$	$t_{50}(\text{min.})$	$n$	$k \cdot 10^3$	$E(\text{kJ/mol})$
Beulah-Zap Lignite	2.33	25.8	230.0	0.67	12.7	51.1
		45.8	35.5	0.70	40.2	
		59.5	11.3	0.72	87.8	
Wyodak Subbit.*	2.42	11.9	47.0	0.65	41.5	36.8
		24.2	12.8	0.77	72.8	
		42.1	5.1	0.47	231.4	
Illinois No. 6 hvb*	2.23	11.9	4.5	0.53	206.9	20.1
		24.0	1.7	0.43	378.6	
		44.7	0.7	0.50	588.0	
Blind Canyon hvb*	2.22	11.9	92.0	0.76	16.2	44.9
		24.3	30.0	0.70	47.1	
		42.1	7.3	0.67	129.4	
Lewiston - Stockton hvb	1.94	20.0	41.0	0.67	40.2	37.3
		40.7	9.4	0.77	92.6	
		50.9	5.3	0.70	151.1	
Pitts. No. 8 hvb	2.14	11.7	90.0	1.04	5.0	51.9
		24.1	30.5	0.81	30.1	
		41.0	8.5	0.68	113.4	

\* Particle size: 212-300  $\mu\text{m}$ .

**Table 2. Swelling of Pittsburgh No. 8 Coal in Various Solvents**

Solvent	$Q_{\infty}$	$T(^{\circ}\text{C})$	$t_{50}(\text{min.})$	$n$	$k \cdot 10^3$	$E(\text{kJ/mol})$
Pyridine (80.9)*	2.14	11.7	90.0	1.04	5.0	51.9
		24.1	30.5	0.81	30.1	
		41.0	8.5	0.68	113.4	
Butylamine (98.8)*	1.93	25.3	16.2	0.82	36.6	22.2
		35.5	10.5	0.90	43.1	
		46.7	8.1	0.85	58.8	
Hexylamine (132.1)*	2.28	25.3	117.0	1.09	2.6	55.0
		35.5	62.0	1.31	2.3	
		46.7	35.2	1.23	6.4	
THF (81.0)*	1.41	24.2	143.0	0.92	5.6	39.3
		34.9	80.0	0.94	8.7	
Pyridine (Heat Treated) <sup>o</sup>	2.18	15.5	35.0	0.79	32.2	48.3
		24.1	15.4	0.94	39.0	
THF (Heat Treated) <sup>o</sup>	1.76	19.1	16.2	0.67	96.1	38.5
		24.2	8.9	0.86	81.1	
		34.9	4.6	ND	ND	
		40.0	3.0	ND	ND	

\* Molar volume of solvent, in cc/mol

<sup>o</sup> Samples heat treated at 8 $^{\circ}\text{C}/\text{min}$  to 350 $^{\circ}\text{C}$ , then quenched