

SORPTION MECHANISM OF VARIOUS ORGANIC VAPORS TO ARGONNE PREMIUM COAL SAMPLES

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ABSTRACT

Sorption of various organic vapors into Argonne Premium coals was systematically investigated to clarify coal-solvent interaction, sorption mechanism, and micropore and cross-linking structure of coals. Especially, the sorption at low vapor pressures was measured under temperature- and pressure-controlled gravimetric sorption system. Methanol was not only quickly sorbed into all ranks of coals used, but also easily desorbed under vacuum at 30 °C. While, pyridine was slowly sorbed into lignite and a significant pyridine was retained after desorption process. Methanol sorption isotherm for all ranks of coals could be explained by the dual-sorption model, i.e., a physical adsorption described by a Langmuir isotherm and a dissolution into bulk of coals described by Henry's law. For Illinois # 6 coal, in relative vapor pressures of 0.01-0.6, the sorption could be treated by the dual-sorption model, regardless of the kinds of organic vapors (methanol, benzene, pyridine, and cyclohexane). The adsorption mechanism by a BET equation did not fit the sorption data. At high relative vapor pressures, an equilibrium sorption could not be obtained, i.e., the sorbed amount was increasing with time, probably due to condensation of organic vapors in the pores and relaxation process of coal macromolecular structure.

INTRODUCTION

When a coal sorbs a solvent, several phenomena occur i.e., coal surface (functional groups)-solvent interaction, adsorption of solvent on the coal surface, coal cross-link-solvent interaction (specific interacting sites), diffusion of solvent into the bulk of coal (cross-link), extraction, swelling, and structural relaxation etc. Although the mechanism of solvent penetration into coal has no well been clarified, the study on the sorption of various organic substances including solvents is considered to be very useful for understanding coal chemistry such as the porosity structure and cross-linking structure of coals.

Hsieh and Duda have reported¹ that organic vapor sorption by coal particles can involve the several complex phenomena including the migration of mobile molecules in the coal and solvent-induced changes in coal structure, and that several analyses which have been used to investigate the structure of synthetic macromolecules were not directly applicable for coals. On the other hand, recently, Green and Selby² proposed that pyridine sorption isotherms can be modeled by a dual-mode sorption mechanism which have been widely used to explain the sorption isotherms of glassy polymers.³ This model is represented by two phenomena, i.e., a physical adsorption described by a Langmuir isotherm and a dissolution described by Henry's law. The linear portion of the pyridine isotherms represents dissolution of pyridine according to the Henry's law, i.e, sorption is linear with pressure. However, pyridine is sometimes troublesome for analysis of the sorption behavior, since pyridine strongly interacts with coals. Pyridine is considered to interact preferentially with the sites such as hydroxyl group in coals, attack the hydrogen-bonds, and disrupt all hydrogen-bonds. Pyridine also can cause the structural changes by diffusion into coal and it makes coals rubbery.^{4,5} Thus, the mechanism of solvent sorption can be dependent upon the chemical properties of solvents, and coal porosity and coal cross-links. The steric hindrance of the pore and the density of coal cross-links may be also an important factor on the vapor sorption.^{6,9}

In the present study, organic vapor sorption experiments were carried out by using Argonne Premium Coal Samples which are suitable for the sorption experiments since they have been stored under oxygen-free condition. The sorption mechanisms of various coal-vapor systems, coal porosity, and cross-linking structure of the coals will be discussed.

EXPERIMENTAL

Sample Preparation.

Argonne Premium Coal Samples were obtained in ampoules of 5 g of -150 μm . The coals were dried at 80 °C for 12 h under vacuum. As a organic solvent vapor, benzene, pyridine, cyclohexane, methanol were used without purification.

Sorption Experiments.

Sorption experiments was carried out in an acrylic box under temperature-control condition, using a quartz spring balance at 30 °C. The sorption was estimated by measuring the extension of a spring by a cathetometer with a telescope. Approximately 50 mg of the coal sample was placed in the quartz bucket, weighed, suspended from the quartz spring, vacuumed overnight at 30 °C. The deaeration treatment of organic solvent was carried out three times through freeze-thaw cycles three times to remove gases in the system. Two experiments were carried out. At a saturate vapor pressure, sorption change with time was measured. After 1 day, the desorption was measured under vacuum. In the other experiment, approximately 0.01 of relative vapor pressure of solvent was set and the sorption was measured until it attains an equilibrium. As the relative pressure was stepwise raised, the equilibrium sorption was measured.

RESULTS AND DISCUSSION

Sorption Behaviors.

For Pocahontas # 3, Illinois # 6, and Beulah Zap coals, the sorption was measured under at a saturate vapor pressure.

<Pocahontas # 3 Coal> Figure 1 shows the result for Pocahontas # 3 coal using methanol, pyridine, benzene, and cyclohexane as an organic vapor. For all vapors, the quantity sorbed was small, due to developed aromatic ring systems in which a vapor is difficult to penetrate the coal. The rate of methanol sorption was the fastest of all and total sorption was also large after 1 day, although pyridine and benzene sorption contain even 1 day, suggesting that the sorption rate of pyridine and benzene was relatively slow. A similar tendency was obtained for Upper Freeport coal. We have reported^{10,11} that the swelling ratios of high-rank raw coals in solvents were small, compared to those of its extraction residues and extract fractions. These results suggests that the diffusion of a solvent in the coals might be retarded by structural factors in the coals, such as stacking among aromatic rings. We have also reported^{8,9} that the size exclusion effect of coal macromolecular structures is an important factor for penetration of aromatic compounds in the coals from a inverse liquid chromatography study. Even in liquid phase, pyridine could not extract all pyridine-extractables in the coals at room temperature, indicating that the penetration of pyridine into the coals was incomplete.¹² We have also found¹² that a carbon disulfide-N-methyl-2-pyrrolidinone mixed solvent gave high extraction rates as well as high extraction yields for some bituminous coals. The kinetics of solvent diffusion into the coals may greatly influence the extraction yield and the swelling ratio of the coals.

<Illinois # 6 Coal> Figure 2 shows the result for Illinois # 6 coal. Generally, the initial rate of sorption was high and the amount sorbed was large, compared to other coals, suggesting that Illinois # 6 coal has porosity and cross-linking structure which a solvent easily diffuses. The sorption of pyridine was the largest of the solvents used, while those of benzene and cyclohexane were small. Polar solvents such as pyridine and methanol was greatly sorbed by Illinois # 6 coal. These results suggest that adsorption on the surface and the diffusion easily occurs through interaction between polar solvents and the coal. Illinois # 6 c is known to contain more functional groups than higher rank coals such as Pocahontas # 3 and Upper Freeport coals.

<Beulah-Zap Coal> Figure 3 shows the result for Beulah-Zap coal. As expected, the sorption by benzene and cyclohexane was very small as well as for Illinois # 6 coal as indicated in Figure 2. Methanol gave a high initial rate of sorption and a high equilibrium sorption. Since Beulah-Zap coal has much more oxygen functional groups than the other coals used, polar solvents would preferentially diffuse through interaction between coal and solvent. Coal is considered¹³ to have two types of interacting sites, i.e., one is free interacting sites which have not interacted with other sites, and the other is interacting sites which interacted already with other sites of coal. The methanol sorption in Figure 3 suggests that methanol may diffuse the coal through disrupting noncovalent bonds such as hydrogen bonds, since it has a high polarity. While, it is noted that the pyridine sorption rate was unexpectedly slow compared to the case of methanol. Pyridine is known to disrupt almost of hydrogen bonds in coals, since pyridine forms a strong hydrogen bond with hydroxyl groups. However, the slow diffusion of pyridine suggests that the disruption is not so much fast as methanol. The difference of pyridine sorption between Illinois # 6 coal and Beulah-Zap coal may be attributed to a difference in the distribution of strength of hydrogen bonds in the both coals.

Dual-Mode Sorption Model.

Figure 4 (a)-(d) shows sorption isotherms for Illinois # 6. In the range of 0.1 - 0.7 of relative vapor pressure, sorption was linear with the pressure for all the cases. The

isotherms was examined to be interpreted by the dual-mode sorption model. The equilibrium isotherm of the model can be expressed by the following equation:

$$C = C_H + C_D = \{C_H \times b \times p / (1 + b + p)\} + k_D \times p \quad (1)$$

where C is the quantity of the sorption, and the first term represents physical adsorption followed by a Langmuir isotherm and the second term represents dissolution into the bulk of coals followed by Henry's law. C_H is the pore saturation constant, b is the pore affinity constant, p is the relative vapor pressure, and k_D is Henry's law dissolution constant. Figure 4 shows that the observed values are consistent with the calculated lines from the model, especially at low pressures, suggesting that the isotherm behaviors can be explained by the dual-mode sorption model. The calculated C_H and C_D lines are also shown in the Figure, respectively. For benzene, cyclohexane and methanol, in the low vapor pressure ranges the physical adsorption (C_H) predominates, while for pyridine there is a large contribution of dissolution even at low pressure ranges. The value of C_H was similar, 0.37, 0.32, and 0.33 (mmol / g-coal) for benzene, cyclohexane, and pyridine, respectively, although their total sorptions are considerably different, as shown in Figure 4.

Their adsorption area per molecule, i.e., van der Waals radius, is also similar. These facts indicate that the number of the solvent molecules adsorbed is independent of types of solvents. The Henry's law dissolution constant, k_D , was in the order of cyclohexane < benzene < methanol < pyridine, being consistent with the order of the extraction yield and the swelling ratio for Illinois # 6.

Figure 5 and 6 show the results of Pocahontas # 3 - methanol and Beulah-Zap - methanol systems, respectively. The data could be also analyzed by the dual-mode sorption model and the calculated lines are shown in Figure 5 and 6. It should be noted that for Pocahontas # 3 coal the physical adsorption was predominant for the sorption, indicating that the most of sorption is attributed to the adsorption on the surface. The result also corresponds a very low swelling ratio and extraction yield for Pocahontas # 3 coal in methanol. On the other hand, for Beulah-Zap lignite a significant amount of methanol diffused the coal, as shown in Figure 6. The dissolution constant, k_D , of methanol in Beulah-Zap coal was much higher, while the pore saturation constant, b , was much lower than those in Illinois # 6 coal, reflecting the affinity of methanol to the pore surface and cross-links of both coals.

Thus, measurements of isotherms using various organic vapors are a useful method to elucidate interaction between coal and solvent, coal surface, chemical properties, and cross-linking structure (the distribution of the molecular weight between cross-links) of coals. Further works is continued by changing the experimental parameters such as temperature, types of organic vapors, coal samples (extract and extraction residue).

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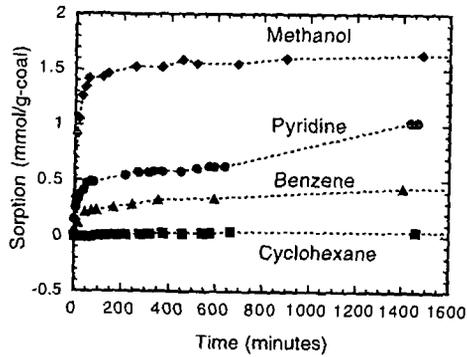


Figure 1 Sorption Behaviors Various Solvent Vapors by Pocahontas #3 Coal at 30 °C

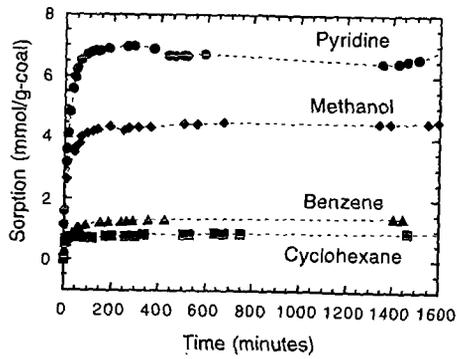


Figure 2 Sorption Behaviors Various Solvent Vapors by Illinois #6 Coal at 30 °C

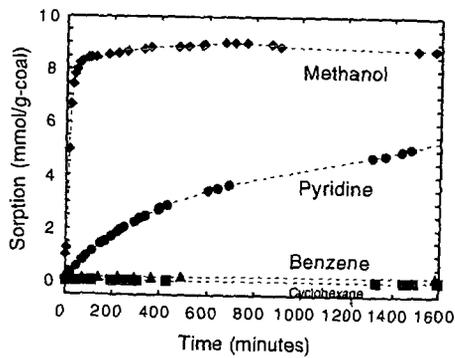


Figure 3 Sorption Behaviors Various Solvent Vapors by Beulah-Zap Coal at 30 °C

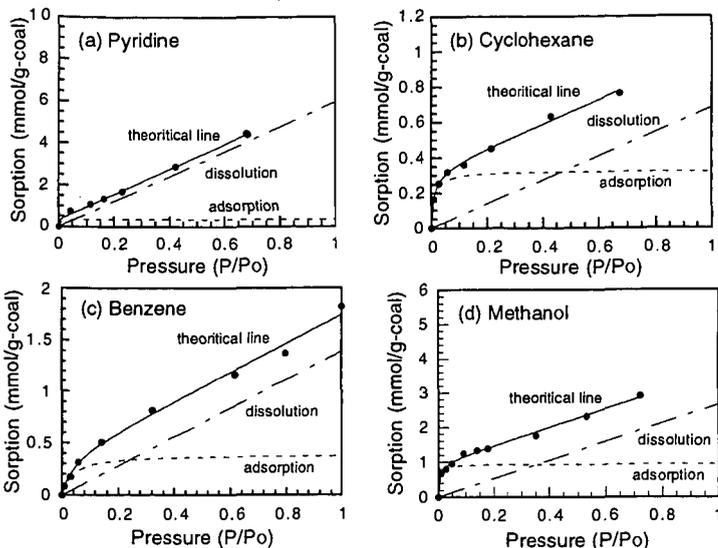


Figure 4 Pyridine Sorption Isotherm of Illinois #6 Coal at 30 °C and the theoretical lines.

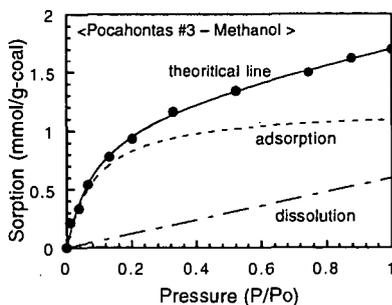


Figure 5 Methanol Sorption Isotherm of Pocahontas #3 Coal at 30 °C and the theoretical lines.

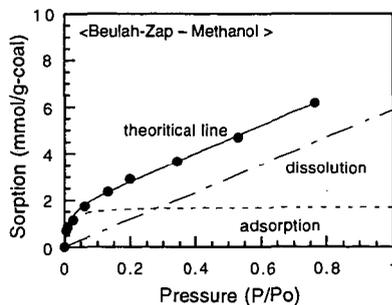


Figure 6 Methanol Sorption Isotherm of Beulah-Zap Coal at 30 °C and the theoretical lines.