

Empirical Evaluation of Coal Affinity for Various Chemicals

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INTRODUCTION

Coal is a complicated natural product which has several functional groups in its cross-linked macromolecular structure. Because of this fact the diffusion mechanism of the penetrant molecule into the matrix of a solid coal is not so simple. It is quite important to know the affinity between the penetrant molecule and the macromolecular structure of coal for the coal scientists who are challenging to develop efficient chemical transformations of coal such as liquifaction, gasification and etc.. Nevertheless the reliable methodology to determine the affinity has not yet been developed. One of the most practical approach to this goal will be to use the solvent swelling behaviours of coal. Because as it is mostly true that better solvent makes coal better swelling, the equilibrium swelling value(Q-value) of the penetrant may reasonably reflect its affinity to the coal. However, there are some problems in this idea. One of the most critical problems will be how to determine the Q-value of solvents(chemicals) which used to be a solid(crystal) under the measuring condition. Furthermore the steric bulkiness of the penetrant molecule also will provide an aserious error on the net Q-values(1).

Some years ago, we revealed the steric requirement of coal toward the penetrant molecule is significantly relaxed in binary solvent system which is composed with normal solvent such as methanol or DMF and sterically hindered molecule(i.e., triethylamine or HMPA)(2). The mechanism of the relaxation of the steric requirement of coal is considered as follows; the preferential petration of the normal solvent into solid coal makes the coal-solvent gel. Then, the significant expansion of the cross-linked network of coal is induced and thus it makes the bulky molecule easy to penetrate. These findings hinted us to use this swelling system for evaluating the affinity of various chemicals toward coal.

This paper presents the results of the studies on the new methodology to evaluate the coal affinity of various chemicals.

EXPERIMENTAL

The swelling measurements were carried out as described into previous paper(3). Coal, Illinois No.6 coal, used in these studies was from the Ames Laboratory Coal Library. Prior to use, the coal was ground, sized, dried at 110°C overnight under vacuum, and stored under a nitrogen atmosphere. The solvents were distilled by ordinary procedures before use.

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RESULTS AND DISCUSSION

Swelling of Illinois No. 6 Coal in Various Solvent

Coal swells in the various solvent with the different manners. Figure 1 shows the relation between the equilibrium swelling value of the solvent which were determined by our instrument and its electron donor number(DN). This type of data treatment had been reported by Marzec et al.(4), and they recognized some correlation between them. However as far as the data shown in this Figure, it seems to be quite difficult to find out such correlation. As we discussed before(1), one of the problems in this figure is that the Q-values measured always involve their steric factor, that is, the sterically hindered solvents are restricted the penetration into the macromolecular structure of coal by the steric requirement, probably due to the cross-linking density. If in this Figure we can pick up only the solvents which are not sterically bulky and also have relatively high dielectric constant(>20), the correlation becomes very clear and almost linear as shown in Figure 2. It is quite interesting that the dielectric constant of the penetrant also seems to be one of the key parameters controlling the coal affinity. This fact may suggest that there are the significant contribution to the macromolecular cross-linking structure of coal from relatively weak bonding interactions such as van der Waals, hydrogen bonding, charge transfer bonding and π - π bonding.

Introduction of Coal Affinity Parameter

Although these data shown above suggest the possibility to use the equilibrium swelling value(Q-value) as a convenient scale for evaluating the affinity to the coal, there seems to be at least two big problems, that is, the first of all is how to determine the Q-value of solid chemicals(crystal) by means of the solvent swelling measurement, and the second of all is how to eliminate the steric factor from the observed Q-value.

Table 1 summarizes the swelling behaviours of Illinois No.6 coal in the steric isomers of butylamine. It is obvious that there is a significant steric requirement on their swelling which is reflected not only on the swelling rate(V-value), but also on the Q-value. Thus, the Q-value measured in the neat solvent always involves the contribution from the steric factor. Namely, in order to use the Q-value as a tool for evaluating the coal affinity, we have to find out the methodology to extract the net Q-value from the observed one.

Figure 3 demonstrate the swelling behaviour of Illinois No.6 coal in the binary mixture of the butylamine and methanol. In the case of n-butylamine-methanol system, the observed Q-values have a nice linear relationship versus the concentration. Meanwhile in the mixed system of more sterically bulkier isomers such as sec- and tert-amine a kind of the synergistic effect were observed. It is particularly interesting that the values obtained by the extrapolation(dotted line on the Figure) from the Q-value at the lower concentration region seems to reasonably reflect their own values. We had revealed this phenomena as the relaxation of the steric requirement by the coa-gel formation(2). Now, we may be able to define for the extrapolated values obtained on the Figure to be their potential Q-value(Q_{pot}) which used to be hidden by the steric factor.

If these speculation are correct, we can use this swelling system as a general procedure for evaluating the coal affinity. Namely, as far as the chemicals are soluble in the solvent (reference solvent), gas, liquid even solid or crystal, the potential Q-value(Q_{pot}) must be empirically determined by this method. Furthermore, very fortunately, because of the binary solvent system the steric factor in the observed Q-value can be minimized.

Based on these considerations, we propose a new empirical parameter to evaluate the affinity to the macromolecular structure of coal, as the Coal Affinity Parameter(κ_Q) which is calculated following equation.

$$\kappa_Q = Q_{pot} / Q_{DMF}$$

In this study we have adopted N,N'-dimethylformamide(DMF) as the reference solvent. The reason is that it has a powerful ability to solve many kinds of chemicals even inorganic compounds and it is also easy to purified.

Table 2 summarizes the typical example of Coal Affinity Parameter(κ_Q -value) determined for various chemicals. In these data it is particularly interesting that the β -naphthol(mp 122-123°C), nitrobenzene and maleic anhydride(mp 54-56°C) have higher κ_Q -values than pyridine. These compounds have long been assumed to have reasonably good affinity to coal, but their relative abilities were never compared.

Figure 5 shows the relation between Coal Affinity Parameter(κ_Q -value) and the electron donor number(DN). Surprisingly, a good correlation was observed towards wide range of organic compounds. particularly, a solid(crystal) compound such as ethylenecarbonate(mp.35°C) and a sterically hindered compound such as hexamethylphosphoramide(HMPA) in which coal used to give very small degree of swelling, probably because of the steric hindrance. As previously discussed there seems to be reasonable relationship between coal affinity and electron donor number(DN), and now we can see a similar relation between the Coal Affinity Parameter(κ_Q -value) and DN. Although this methodology proposed may not be a perfect one to evaluate the affinity to coal, but as far as the results shown in this Figure and Table 2, we are very much encouraged to use the κ_Q -value for the study on the chemical transformations of coal.

It will be also interesting to examine the dependency of κ_Q -value on the coal rank or the nature of the reference solvent, which are now underway in our laboratory.

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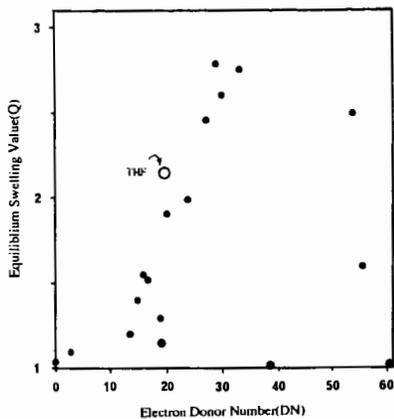


Figure 1 Correlation between Q-value and Electron Donor Number(DN)
(Illinois No. 6 Coal: 60-100mesh; at 20°C)

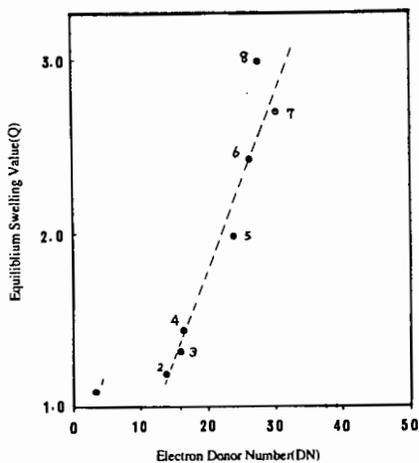


Figure 2 Correlation between Q-value and Electron Donor Number(DN)
(Illinois No. 3 Coal: 60-100mesh; at 20°C)
SOLVENT: 1 nitroethane, 2 acetonitrile, 3 n-butylamine, 4 acetone,
5 trimethylphosphane, 6 DMF, 7 DMSO, 8 N-methylpyrrolidone

Table 1 Solvent Swelling of Illinois No. 6 Coal^a in
Butylamines at 20.0 ± 0.5 °C

| amine | V_{ret}^b | Q^c | η_{20}^d cP | CSA ^e |
|-----------------|-------------|-------------------|------------------|------------------|
| n-butylamine | 1.0 | 2.56 | 1.54 | 32.7 |
| isobutylamine | 11.9 | 2.57 | | 32.8 |
| sec-butylamine | 5.4 | 2.41 | 1.37 | 33.2 |
| tert-butylamine | 599 | 1.96 ^e | 1.48 | 34.1 |

^a100-200 US mesh. ^b $V_{ret} = V_{n-Bu} / V_{isomer}$; $V_{n-Bu} = 3.7 \times 10^{-1}$ min⁻¹. ^cMeasured after 10 days' swelling. ^dDetermined by means of Ubbelohde viscometer at 20.00 ± 0.02 °C. ^eSwelling is still continuing.

^e Cross-sectional Area(Å²)

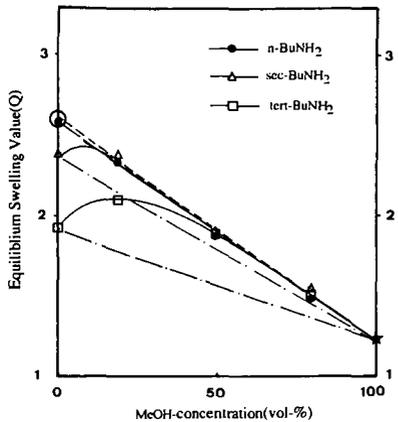


Figure 3 Coal Swelling in Binary mixture (Illinois No. 6 Coal; 60-100mesh; at 20°C)

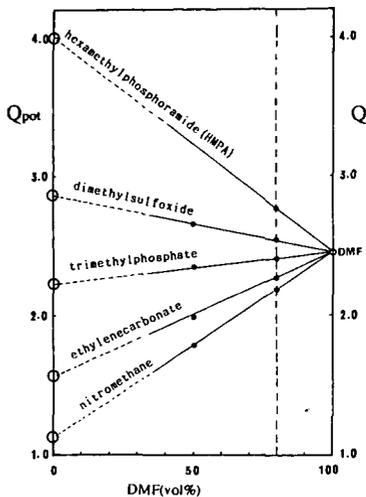


Figure 4 Determination of Potential Q-value (Q_{pot}) (Illinois No. 6 Coal; 60-100mesh; at 20°C)

Table 2 κ_Q -values of various Chemicals (Illinois No. 6 Coal; 60-100mesh; at 20°C)

| Chemicals | $^{\circ}\kappa_Q$ |
|-----------------------|--------------------|
| nitromethane | 0.43 |
| acetonitrile | 0.41 |
| n-butyronitrile | 0.52 |
| ethylenecarbonate | 0.61 |
| acetone | 0.68 |
| trimethylphosphate | 0.88 |
| DMF | 1.00 |
| pyridine | 1.08 |
| DMSO | 1.14 |
| N-methylpyrrolidinone | 1.21 |
| HMPA | 1.62 |
| nitrobenzene | 1.13 |
| b-naphthol | 1.22 |
| maleic anhydride | 1.30 |
| benzoic acid | 0.80 |

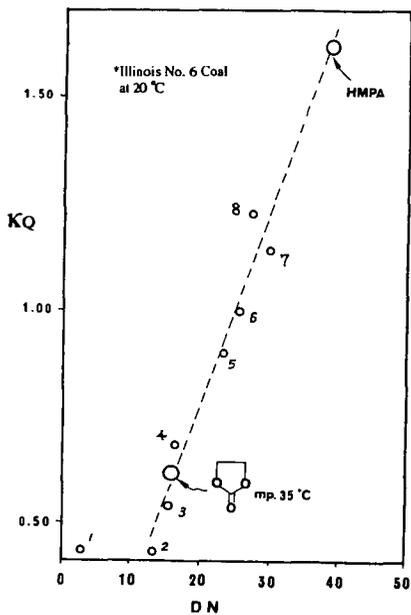


Figure 5 Correlation between K_Q -value and Electron Donor Number(DN)
(Illinois No. 6 Coal; 60-100mesh; at 20°C)

SOLVENT : 1 nitromethane, 2 acetonitrile, 3 n-butyl nitrile, 4 acetone,
5 trimethylphosphate, 6 DMF, 7 DMSO, 8 N-methylpyrrolidone