

## The Application of Microdilatomety to Solvent Swelling of Coals

George D. Cody, Alan Davis, Semih Eser, and Patrick G. Hatcher

Energy and Fuels Research Center and the Fuel Science Program  
The Pennsylvania State University, University Park, PA 16802

### Introduction

Since Sanada and Honda's initial application of polymer solution theory to solvent swelling to coals (1), many researchers have used solvent swelling as a useful means of obtaining at least qualitative information on the nature of coal's macromolecular network. Solvent swelling analysis exploits the thermodynamic relationship between solvent-coal mixing and elasticity of coal's macromolecular network. As was shown by Flory and Rehner (2), at equilibrium a polymer immersed in an excess of solvent will contain a specific volume of solvent, the total amount of solvent constitutes a thermodynamic balance between the reduction of the free energy due to mixing and the increase in elastic free energy of the network resulting from dilation.

To date, a variety of analytical techniques have been used to measure the equilibrium volume of solvent in coal. No one technique is free of difficulties. Moreover, the specifics of a given research problem may dictate which technique is chosen. In this paper a new means of measuring equilibrium swelled volumes is introduced and compared to values obtained using a more traditional method.

Sanada and Honda's measurements employed a temperature controlled gravimetric device. The equilibrium volume of a solvent (they used pyridine) was determined from the weight gain of approximately 0.1 g of coal measured from the extension of a quartz spring. They report a high degree of precision such that + or - 0.8 mg weight change is detectable. Since their study many other researchers have employed gravimetric methods to determine the equilibrium swelled volume of solvents in coal. Obvious advantages to the gravimetric technique are 1) the high degree of sensitivity and 2) solvent swelling measurements, at solvent activities less than 1.0 can be readily obtained. A disadvantage of this technique is that significant condensation of solvent can occur within coal's pore structure. This potential error is dealt with by correcting the gravimetric data assuming that capillary condensation has occurred in pores. Thus prior to swelling the extent of porosity in coals must be known. One problem with this correction, however, is that it has been shown that upon swelling of coal in pyridine significant changes in coal's pore structure take place (3), therefore, a correction based on "dry" pore volume may not be sufficient.

Liotta et. al (4) published a simple technique for measuring the equilibrium volume of solvent in coal by simply measuring the volume expansion of the coal. Green et al.(5) confirmed the accuracy of this technique by comparing results so obtained to those gathered using gravimetric techniques. The advantages of the volumetric technique is that it is rapid, exhibits good

reproducibility, and requires no special equipment. A potential error is that interparticle volume contributes to the total volume of the sample. This potential source for error is typically addressed by using very fine mesh coal particles and assuming that the change in interparticle void volume upon swelling is exactly proportional to the increase in coal's volume upon swelling. The volumetric method enjoys much use by many coal researchers today because of its convenience and high degree of reproducibility.

In addition to these methods there are a variety of other techniques which although fundamentally related to one or the other of the above techniques use significantly different means by which a measurement is obtained. Aida and Squires (6), for example measured the volume expansion of particulate coal using an apparatus similar in concept to a vapor pressure osmometer. They reported that their apparatus gave results which compared well to established techniques and afforded a greater facility in measuring the kinetics of swelling. Cody et. al. (7) used solvent swelling of coal thin sections using the preparation method designed by Brenner (8) and recorded the equilibrium solvent uptake via changes in linear dimension measured parallel and perpendicular to the bedding plane. This method also yielded values comparable to bulk values and was especially well suited for studying effects of residual network strain and subsequent strain relaxation upon the swelling behavior of un-extracted coals.

This paper will focus on the application of a high sensitivity microdilatometer for the purpose of measuring linear expansion of coal slabs following immersion in a solvent.

#### Experimental:

The microdilatometer employed in this study was originally used to study the expansion of particulate coals under gasification conditions (9). Figure 1 is a schematic diagram of the dilatometer. The microdilatometer measures the change in position of a linear variable differential transformer (LVDT) core composed of soft iron. The LVDT is attached directly to a glass probe which rests on top of the sample. The position of the LVDT between two electric coils within the dilatometer is sensitively detected using the principles of mutual inductance. At its most sensitive setting extremely small vibrations in the lab are readily detectable by the dilatometer. Thus, the practical lower limit in measurement without resorting to a vibration dampening table is on the order of 1  $\mu\text{m}$ . As will be discussed shortly, in the current experiments expansions of coal due to solvent swelling are on the order of hundreds of microns using millimeter scale samples.

Two important modifications to the dilatometer have enabled its use in precisely measuring solvent swelling. First, the dilatometer probe is modified as follows. In place of the solid pyrex probe, a hollow probe with vents at the probe tip has been manufactured. Higher up on the probe lies an access port for a syringe for the purpose of injecting solvent. Second, the entire probe/LVDT assembly weighs approximately 20 g. Using a counter balance it is possible to reduce the effective weight of the probe/LVDT assembly to approximately 100 mg. This weight is just

enough to exceed frictional forces within the system. The error that this force adds to the final expansion value is evaluated as follows. The elastic modulus of coal will be the least at the most swollen state. For solvent swollen coal the elastic modulus (on compression) was measured by Doug Brenner and is in the range of 500 psi (10). The typical compressive stress on the samples in this study are in the range of  $5 \times 10^{-2}$  psi. Using a standard equation for strain for uniaxial compression of a polymeric material (equation 1)(11) we calculate a deviation of the true expanded dimension to be less than one tenth of 1 percent.

$$P = E/3(\lambda - \lambda^{-2}) \quad (1)$$

In equation 1,  $P$  = pressure,  $E$  = the elastic modulus, and  $\lambda$  is the compression ratio.

The second important aspect of this experiment involves preparation of the samples. Table 1 lists the samples and other pertinent information. Three of the coal samples are vitrains from large coal blocks, the other two are coalified logs. For the purpose of comparing the volume expansion values measured using the microdilatometer with values obtained using a bulk volumetric analysis pyridine extracted (exhaustively) samples were required.

The following sample preparation protocol was applied for solvent swelling using a microdilatometer. Vitrain bands were selected from large particle samples of each coal (in the case of the coalified woods all of the matter is vitrain). Small slabs were cut from each sample using a fixed SiC disc grinding wheel. The initial size of the sample is typically on the order of  $1 \times 1 \times 1.5$  mm. To avoid forming microcracks during extraction each slab was first equilibrated with pyridine vapor, typically 1 -2 days of equilibration. Following this the samples were immersed in a large excess of pyridine liquid (approximately 10 ml) and gently heated at a temperature of about 40 °C. After no less than 4 days of immersion, the samples were de-swelled by sequential series of dilutions with chlorobenzene, each dilution was 9:1 chlorobenzene to solution by volume. Finally the samples were placed "wet" in a desiccator with a tray of chlorobenzene and allowed to come into equilibrium with chlorobenzene vapor. The "dry" samples were then transferred to a vacuum oven and dried for approximately 1 day. This protocol generally resulted in samples free of microcracks.

Prior to swelling each sample was carefully inspected under the microscope for the presence of microcracks. Only Pittsburgh No. 8 presented major difficulties. Regardless of the amount of time allowed for each step of the preparation protocol, samples of Pittsburgh No. 8 exhibited significant microcracks parallel to the bedding plane. Thus, for this sample a second stage of preparation following extraction was required. Using a binocular microscope, microtweezers, and a razor knife it was possible to carve out apparently microcrack-free regions of the original slabs of this coal.

Sample preparation and solvent swelling protocol applied for bulk volumetric solvent swelling analysis is identical to that described by Liotta et al. (4). Approximately 1.0 g of finely ground, extracted coal is charged into a calibrated centrifuge

tube. An excess of solvent is added and the sample is vigorously shaken to ensure free volumn expansion. After 24 hr the equilibrium swelled volume of the sample was measured from the increase in height of the coal-pyridine interface.

The actual solvent swelling analysis using the microdilatometer is straightforward. The prepared sample is placed in the sample cavity and the dialotometer head is placed on top of of the sample. From the point that solvent is charged into the probe via a syringe, linear expansion data is continuously recorded. When no further expansion takes place this maximum value is taken to equal the cube root of the coal's equilibrium swelled volume.

### Results and Discussion

The size of samples in this study varied from 1.3 to 1.9 mm in the direction parallel to the dilatometer probe. Expansions due to solvent swelling are, therefore, on the order of a 100 to 400  $\mu\text{m}$ . Table 2 gives the comparative results. It is clear that in all cases the linear expansion ratios obtained using microsamples of coal in the microdilatometer are comparable to the cube root of the bulk swelling ratio obtained using the bulk volumetric method. Thus for solvent swelling analysis of small amounts of sample the dilatometer is a reliable tool.

Implications derived from the comparison between the two sets of data are 1) the assumption implicit in volumetric swelling that the increase in the interparticle volume with swelling is proportional to an increase in swelled particle volume is reasonable, 2) the assumption that for vitrinite rich coals the bulk swelling behavior is dominated by the swelling behavior of vitrinite is also supported by this comparison.

The microdilatometer can accurately and precisely measure the dilation of coal during solvent swelling. For cases where only a very small amount of sample is available for analysis this instrument is invaluable. For example, solvent swelling analysis of phytoclasts (organic particles) liberated from organic rich rocks is now readily possible.

### References

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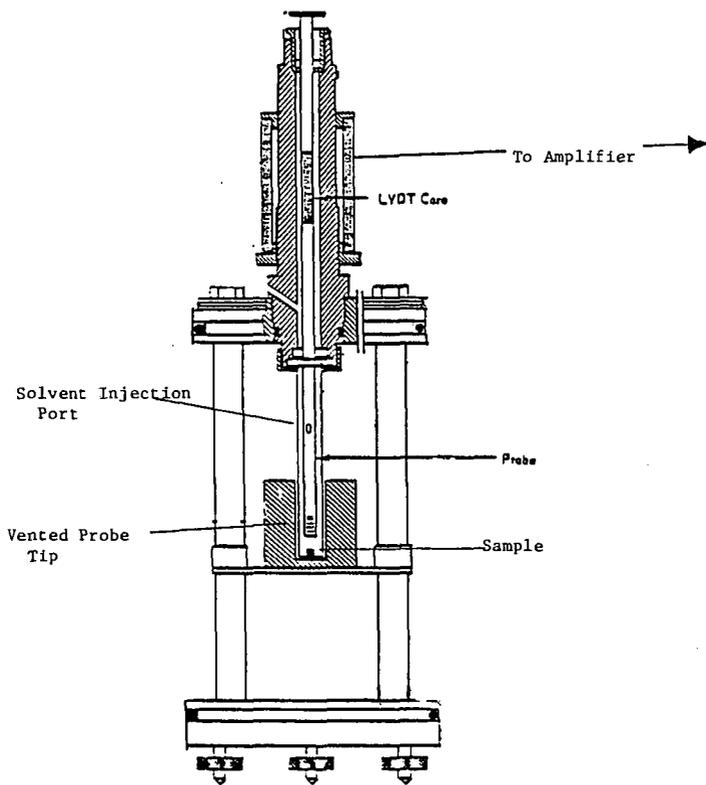


Figure 1: Schematic of microdilatometer modified after Khan, 1985

Table 1 - Coal Samples Studied

<u>SAMPLE</u>	<u>% C</u>	<u>% H</u>	<u>% O</u>	<u>% N</u>	<u>% S</u>	<u>RANK</u>
Smith Seam	70.8	5.0	22.8	0.9	0.5	subbit C
Illinois No. 6	81.9	5.5	9.4	1.4	2.2	Hvb C
Pittsburgh No.8	84.8	5.7	7.4	1.4	0.8	Hvb A
Wyodack/Anderson*	-	-	-	-	-	subbit
Ferron*	78.0	5.3	14.0	1.0	1.7	subbit

\* = coalified log

Table 2 - Comparison of Solvent Swelling Results

<u>SAMPLE</u>	<u>Q<sub>r</sub>/Q<sub>i</sub></u>	<u>L<sub>r</sub>/L<sub>i</sub>(calc)*</u>	<u>L<sub>r</sub>/L<sub>i</sub>**</u>
Smith Seam	1.26	1.08	1.10
Illinois No.6	2.30	1.32	1.29
Pittsburgh No.8	2.30	1.32	1.29
Wyodack/Anderson	1.67	1.19	1.22
Ferron	1.67	1.19	1.19

\*linear expansion ratio, the cube root of the bulk swelling ratio Q<sub>r</sub>/Q<sub>i</sub>.

\*\*linear expansion ratio, measured with microdilatometer