

# FUEL

the science and technology of Fuel and Energy

# Measurement of swelling of coals in organic liquids: a new approach

Jordan R. Nelson\*, Om P. Mahajan†, and Philip L. Walker, Jr.

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

(Received 30 April 1980)

The sorption of organic molecules on coals of various rank was studied using gravimetric and pycnometric techniques. The pycnometric technique was insensitive to sorption due to swelling. Hence, a comparison of sorption values obtained by these two techniques provides an accurate measure of solvent-induced swelling in porous samples. In this study the maximum degree of benzene and tetralin-induced swelling occurred in a coal of 75 wt% carbon content. Compressibility was also found to be at a maximum in this coal. These results suggest that at 75 wt% carbon content the size and/or flexibility of the chain segments between crosslinks in coal are at a maximum.

It is generally accepted that the insoluble residue remaining after exhaustive solvent extraction of coal is a crosslinked gel. This gel swells upon exposure to suitable solvents, but the presence of crosslinks<sup>1</sup> between the individual coal 'molecules' in the gel prevents solvation<sup>1-5</sup>. One method of investigating the macromolecular structure of crosslinked gel and the nature of the crosslinks is by sorption studies, that is, to measure the degree of solvent-induced swelling as a function of the solvent, temperature and relative vapour pressure.

Sorption studies of coals, however, present two special problems. Coals are highly porous solids; and, as such, sorption values will contain sizeable contributions from uptake due to physical adsorption and pore filling in addition to swelling. Furthermore, the high crosslink density of the gel in coal and/or stiffness of the hydroaromatic chain segments between crosslinks will severely limit swelling values.

In a non-porous polymeric solid, the increase in volume due to inhibition of the solvent can be measured either directly or calculated from the weight of solvent uptake<sup>6</sup>. However, coal is a highly porous solid. Failure to correct for solvent occluded, that is, amount adsorbed on the pore walls and condensed in the pores of the extensive pore network of coal can seriously inflate gravimetrically measured swelling values. To correct for the amount of occluded solvent, Dryden<sup>7</sup> estimated the pore volume of coal particles from helium and particle densities. Solvent sorption on filter-dried coal particles was also corrected for solvent occluded in the interparticle voids. However, the accessible pore volume of coal varies considerably with the nature of the solvent as well as with the coal, and it may be greater or less than that accessible to helium. The high degree of swelling induced by the class of solvents (amines) used by Dryden minimized the errors introduced from incorrectly estimating the amount of

occluded solvent. Other workers attempting to measure gravimetrically solvent-induced swelling of extracted coal samples ignored uptake due to occlusion of solvent<sup>3-5</sup>. Thus, depending on the porosity and pore size distribution of the extracted coal samples used, these workers overestimated the extent of solvent-induced swelling. This work, therefore, is directed towards distinguishing solvent uptake due to swelling from other sorption mechanisms and use of these swelling values to characterize the macromolecular structure of coals.

## EXPERIMENTAL AND RESULTS

### Description of samples

The identification, rank and analyses of the ten coals used in this study are given in Table I. The samples were supplied by the Coal Research Section of The Pennsylvania State University. Coal samples were ground, and except where noted in the solvent density studies, the 40 × 70 mesh fractions were used in adsorption studies.

SP-1 graphite, a spectroscopically pure natural graphite obtained from the Carbon Products Division of Union Carbide, was used as a calibrating standard for density measurements.

Graphon, a graphitized carbon black supplied by the Cabot Corporation, was selected as a non-porous standard for vapour phase adsorption studies because of its high surface area (78 m<sup>2</sup> g<sup>-1</sup>) and highly homogeneous surface consisting primarily of basal planes.

The precursor for microporous Saran carbon used in this study was Saran 853, supplied by the Dow Chemical Company. The sample was carbonized under argon at 900°C. The resultant char is highly microporous and gives Langmuir type adsorption isotherms with most organic adsorbates<sup>9,10</sup>.

Two macroporous crosslinked polystyrenes were provided courtesy of Ionac Chemical Company, Division of Sybron Corporation. The more highly crosslinked and macroporous of the two samples, P816, is a copolymer of styrene and divinylbenzene in a weight ratio of 84:16.

\* Present Address: RCA Laboratories, Princeton, New Jersey

† Present Address: Standard Oil of Indiana, Naperville, Illinois

Crosslinks can be any type of bond which joins together coal molecules and may include covalent and hydrogen bonds, entanglements, as well as the association of large aromatic regions of different coal 'molecules' to form graphite-like structures.

Table 1 Analyses of coals

PSOC Coal No.	ASTM Rank	Proximate Analysis		Ultimate Analysis <sup>a</sup> (dmmf)					Pyritic Sulphur (wt %, dry)	Vitrinite (vol %, dmmf)
		Mineral Matter (wt %, dry)	VM (wt %, dmmf)	C	H	N	S <sub>Org.</sub>	O (By diff.)		
177	Anthracite	4.95	4.27	93.59	2.63	0.25	0.67	2.86	0.07	86.5
85	Anthracite	9.54	6.64	92.36	3.81	0.61	0.84	2.38	0.28	97.5
318 <sup>b</sup>	LV	6.52	19.30	89.51	4.70	1.71	1.73	2.35	—	86.2
254W	MV	6.91	27.02	88.04	5.26	1.72	0.74	4.24	0.32	72.4
268	HVA	5.52	33.93	86.50	5.42	2.15	1.53	4.41	0.02	70.5
223	HVB	4.56	41.42	81.92	5.71	1.72	0.66	10.00	0.60	71.0
212	HVC	3.05	39.74	79.33	5.38	1.46	0.73	13.10	0.11	72.6
248	Sbb-A	3.34	44.58	75.44	5.13	1.74	0.63	17.06	0.03	68.2
242	Sbb-B	6.72	46.04	74.45	5.43	1.68	0.46	17.98	0.11	76.9
246	Lignite	10.99	49.00	71.52	4.82	1.52	0.63	21.45	0.03	53.4

<sup>a</sup> Calculated by the modified Paar formula<sup>8</sup><sup>b</sup> Analysis for this coal are expressed on a daf basis

Table 2 Densities of materials

Samples	Density (g cm <sup>-3</sup> , dmmc)				
	Helium	Mercury <sup>a</sup>	Methanol	Benzene	Tetralin
PSOC-177	1.598	1.425	1.631	1.555	1.429
PSOC-85	1.449	1.382	1.508	1.398	1.394
PSOC-318	1.372	1.301	1.447	1.386	1.340
PSOC-254W	1.342	1.281	1.374	1.334	1.312
PSOC-268	1.320	1.293	1.386	1.321	1.300
PSOC-223	1.323	1.188	1.440	1.386	1.316
PSOC-212	1.344	1.234	1.486	1.393	1.295
PSOC-248	1.363	1.229	1.520	1.415	1.335
PSOC-242	1.381	1.279	1.558	1.395	1.352
PSOC-246	1.442	1.213	1.640	1.457	1.428
SP-1					
Graphite	2.256	1.724 (2.275) <sup>b</sup>	2.253	2.257	2.264
Graphon	1.872	0.689 (1.872) <sup>b</sup>	1.882	1.896	1.906
Saran	2.049	1.175	1.961	1.930	1.842
P818	1.075	0.849	1.078	1.101	—
P816	1.065	0.724	1.076	1.100	—

<sup>a</sup> Measured at 0.41 MPa<sup>b</sup> Measured at 68.9 MPa

while the P818 sample is a tripolymer of styrene, divinylbenzene and ethyleneglycol dimethylacrylate in a weight ratio 88:4:8. From these monomer ratios, the molecular weight between crosslinks was calculated to be 688 and 1243 g mol<sup>-1</sup> for P816 and P818, respectively.

Exploratory runs showed that in the case of the macroporous crosslinked polystyrene samples outgassing resulted in a weight loss of 0.3%, whether or not the samples were heated. Therefore, because of the possibility of plastic flow upon prolonged heating at higher temperature, the crosslinked polystyrene samples were outgassed at room temperature. All other samples were dried overnight at 110°C.

#### Solvents and gases used

Four solvents were used in this study. Benzene, methanol, and pyridine were 'Baker Analyzed' reagent grade. Fisher Scientific Company supplied the 'Purified' grade of 1,2,3,4-tetrahydronaphthalene (tetralin).

Research grade helium (99.9999% purity) used for helium density measurements was obtained from the Matheson Company in one litre flasks.

#### Helium density apparatus and procedures

The helium density ( $\rho_{He}$ ) apparatus was a modified version of that described by Howard and Hulett<sup>11</sup>. A detailed description of the apparatus and procedure has been given elsewhere<sup>12</sup>.

The precision of five helium density runs with a HVA coal (PSOC-268) was found to be  $1.320 \pm 0.002$  g cm<sup>-3</sup> (Table 2). The accuracy of helium density runs was checked with SP-1 graphite and its density was determined to be  $2.256 \pm 0.008$  g cm<sup>-3</sup> for eight runs. This value agrees very well with the true density of graphite of  $2.26$  g cm<sup>-3</sup><sup>13</sup>.

#### Procedure for mercury porosimetry

An AMINCO mercury porosimeter was used to determine apparent densities ( $\rho_{He}$ ) of coal, carbon samples and polystyrene by the displacement of mercury (Table 2). The precision in determining particle density at 0.41 MPa<sup>14</sup> for ten runs on a HVA coal (PSOC-268) was found to be  $1.271 \pm 0.003$  g cm<sup>-3</sup>.

Total open pore volume ( $V_T$ ) accessible to helium was calculated from the relation:

Table 3 Apparent pore volumes (dmmf) accessible to different fluids

Sample	$V_M$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_T$ ( $\text{cm}^3 \text{g}^{-1}$ )		$V_S$ ( $\text{cm}^3 \text{g}^{-1}$ )	
		Helium	Methanol	Benzene	Tetralin
PSOC-177	0.003	0.080	0.094	0.062	0.002
PSOC-85	0.005	0.038	0.067	0.009	0.007
PSOC-318	0.017	0.049	0.090	0.058	0.031
POSC-254W	0.013	0.039	0.056	0.033	0.019
PSOC-268	0.011	0.017	0.055	0.017	0.004
PSOC-223	0.014	0.090	0.154	0.126	0.086
PSOC-212	0.010	0.069	0.142	0.096	0.040
PSOC-248	0.015	0.083	0.161	0.111	0.067
PSOC-242	0.017	0.062	0.150	0.070	0.045
PSOC-246	0.086	0.147	0.242	0.155	0.139
Saran	0.008	0.362	0.341	0.333	0.308
P818	0.237	0.248	0.250	0.270	—
P816	0.425	0.442	0.452	0.472	—

$$V_T = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}} \quad (1)$$

With the precision of measuring the particle and helium densities (dmmf) of PSOC-268 coal, the uncertainty in calculating its  $V_T$  from the equation (1) was found to be  $\pm 0.004 \text{ cm}^3 \text{g}^{-1}$ . Total accessible pore volume for all sorbates ( $V_S$ ) calculated in an identical manner are given in Table 3.

Following determination of particle density, a pore size distribution in the coal samples was measured by slowly increasing the applied pressure from 0.41 to 20.68 MPa. Over the range of applied pressures corresponding to macroporosity in PSOC-268, the precision of five runs exceeded  $0.001 \text{ cm}^3 \text{g}^{-1}$ . Above a certain applied pressure, the level of mercury in the penetrometer was found to fall essentially as a rectilinear function of the applied pressure. This observed rectilinear decrease in mercury level was due to compression of the coal sample, with small contributions from compression of the mercury and the container<sup>15,16</sup>. From such a measurement, compressibility of the coals used in this study could be determined<sup>17</sup>.

#### Sorption of organics

The sorption of organic vapours onto carbonaceous solids of 0.5 g weight was measured using a McBain balance apparatus. The apparatus is described in complete detail elsewhere<sup>17</sup>. The apparatus could be used for adsorption studies between 25°C and  $\approx 90^\circ\text{C}$ . Weight changes of less than 0.1 mg during adsorption were measured gravimetrically using helical quartz spring balances. Because of long equilibrium times of 2–7 weeks at 25°C, four samples using four separate quartz spring balances were studied simultaneously. A relative vapour pressure (r.v.p.) of 0.95 was set in the sample tubes by varying the temperature of a temperature-controlled bath, the coldest point in the system.

#### Apparent densities of coals in liquids

Apparent densities of coals at  $25 \pm 0.2^\circ\text{C}$  were determined using benzene, tetralin and methanol as the displacing fluids (Table 2). Because of the deleterious effect of air contained in the micropore structure of coals on the kinetics of adsorption<sup>17</sup>, an apparatus was constructed which enabled the addition of the displacing fluid to the pycnometer under vacuum. The density apparatus was a modified version of that used by Toda<sup>18</sup> and Toda and Toyoda<sup>19</sup>.

Measurements of apparent density of non-porous carbons (SP-1 graphite and Graphon) in different liquids gave a reproducibility of better than  $\pm 0.003 \text{ g cm}^{-3}$ . This reproducibility is slightly better than that ( $\pm 0.005 \text{ g cm}^{-3}$ ) reported by Toda<sup>18</sup>. The greater precision obtained in this study is presumably due to the larger sample size (8 to 12 g) used.

#### Solvent-induced swelling

Gravimetric sorption measures the extent of uptake by weight. However, the solvent density method measures only the volume occupied by a unit weight of sample. Thus, the solvent density method would be insensitive to any solvent penetration (by weight) of the sample if it were accompanied by an equal volume expansion or swelling of the sample. Comparison, therefore, of the total uptake obtained gravimetrically to that obtained from solvent densities provides a measure of solvent-induced swelling.

Measurement of solvent-induced swelling, as described above, assumes that the bulk density of the solvent is similar to that of the solvent when imbibed. Two highly crosslinked macroporous polystyrene samples (P818 and P816) were selected to ascertain the validity of the above assumption. The close agreement between helium and methanol densities (Table 2) is expected since methanol is a poor solvent for polystyrene. The total open pore volumes accessible to benzene (an excellent swelling agent for polystyrene) are about 9% higher than those accessible to methanol and helium (Table 3) due to filling of voids within the samples by benzene. In spite of varying degrees of swelling (85 and 39% measured at 25°C for P818 and P816, respectively) benzene densities of both the polystyrene samples are identical (Table 2). This is only possible if the imbibed benzene has a density equal to that in the bulk state<sup>20</sup>. Near equality of bulk and imbibed solvent densities is also strongly indicated by early weight and optical swelling studies of both polymers<sup>6</sup> and coals<sup>7</sup>.

In Figure 1, tetralin, benzene and methanol uptake by PSOC-248, a Sbb-A coal, was measured (1) gravimetrically; and (2) from solvent density values over a 24 h period. As described previously, the difference between these two uptake values at equilibrium for a given coal is a measure of the solvent-induced swelling. Note that the rate of uptake of occluded solvent is much more rapid than the rate of solvent imbibition, which produces swelling.

The percent of solvent-induced swelling (S) for the coals and polymers (given in Table 4) was calculated from the equation:

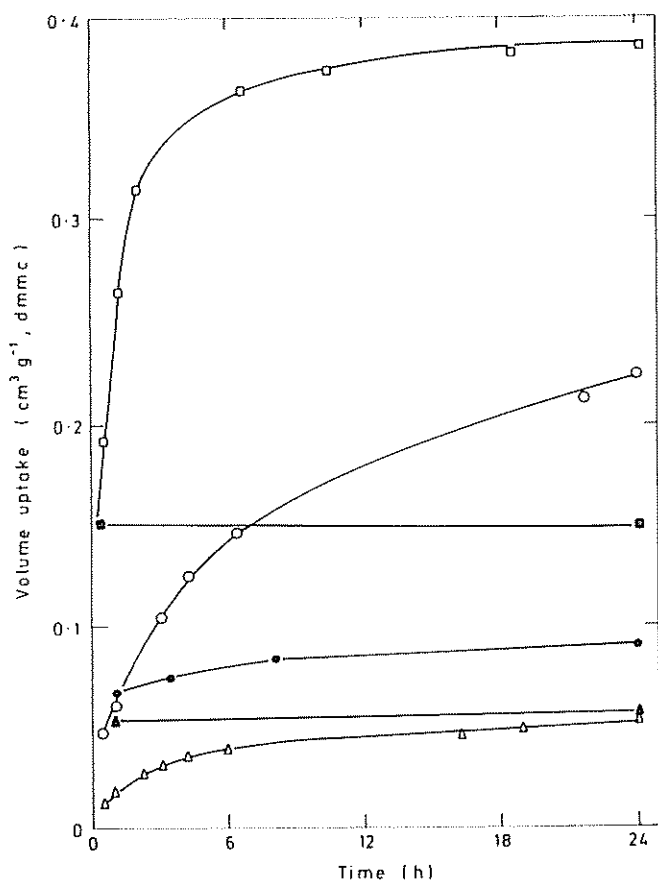


Figure 1 Volume uptake of organics on a HVA coal (PSOC-248) as measured by gravimetric adsorption and pycnometric methods. Gravimetric: □, Methanol; ○, benzene; △, tetralin. Pycnometry: ■, methanol; ●, benzene; ▲, tetralin

$$S = 100 \cdot \rho_2 [(W_1/\rho_1) - V_s + V_M] \quad (2)$$

where:  $W_1$ , solvent uptake measured gravimetrically,  $\text{g g}^{-1}$  (dmmf) at r.v.p. of 0.95 (see Table 5);  $\rho_1$ , bulk density of the solvent,  $\text{g cm}^{-3}$ , that is 0.874, 0.787 and 0.966 for benzene, methanol, and tetralin at 25°C;  $\rho_2$ , density of the sample in the solvent,  $\text{g cm}^{-3}$  (dmmf);  $V_s$ , porosity accessible to the solvent,  $\text{cm}^3 \text{g}^{-1}$  (dmmf);  $V_M$ , macropore volume of the coal sample (see Table 3), that is, volume contained in pores larger than 50 nm,  $\text{cm}^3 \text{g}^{-1}$  (dmmf). It is estimated from the Kelvin equation that pores with diameters greater than  $\approx 35$  nm will not be filled by capillary condensation at a r.v.p. of 0.95. Thus, pore volume of the coal accessible to adsorbate ( $V_s$ ) under immersion conditions is corrected by the macropore volume ( $V_M$ ) to approximate uptake at a r.v.p. of 0.95.

The exact size of the largest pore filled by capillary condensation is unimportant since a lack of significant porosity ( $< 0.001 \text{ cm}^3 \text{g}^{-1}$ ) in mesopores larger than 10 nm was noted for all samples<sup>17</sup>. For example, benzene pore filling of Saran carbon at 0.95 r.v.p. from  $V_s$  and  $V_M$  values is  $0.325 \text{ cm}^3 \text{g}^{-1}$ , in excellent agreement with the gravimetric value of  $0.327 \text{ cm}^3 \text{g}^{-1}$ . The importance of these corrections for pore filling is reflected in that even when significant imbibition of solvent occurred in coal the percentage of total uptake attributed to swelling ( $T_s$ ) was invariably between only 40 and 70% (Table 4).

In Figure 2,  $S$  values calculated for tetralin, benzene and methanol are plotted against the respective carbon content of the coal sample. From error analysis of the individual experimental determinations necessary to obtain per cent solvent-induced swelling, it was estimated that these values are accurate to within 1%. Methanol-induced swelling is markedly different from that of tetralin

Table 4 Solvent-induced swelling of coals and polymer samples at r.v.p. of 0.95 at 25°C

Sample	Methanol			Benzene			Tetralin		
	$S$ (%)	$T_s$ (%)	$S_p$ (%)	$S$ (%)	$T_s$ (%)	$S_p$ (%)	$S$ (%)	$T_s$ (%)	$S_p$ (%)
PSOC-318	2.0	9.9	1.8	1.3	13.9	1.2	—	—	—
PSOC-254W	3.3	31.5	3.1	1.6	36.0	1.5	—	—	—
PSOC-268	6.1	47.0	5.7	3.3	78.1	3.2	—	—	—
PSOC-223	18.3	51.3	15.7	15.0	47.2	12.9	3.6	24.6	3.2
PSOC-212	28.7	62.4	23.8	19.8	61.6	17.5	5.8	59.5	5.5
PSOC-248	34.1	63.7	27.5	24.4	64.7	21.1	9.1	55.9	8.4
PSOC-242	42.3	68.3	34.5	11.9	59.7	10.9	1.0	15.8	0.9
PSOC-246	50.1	64.2	36.4	9.0	42.3	7.4	—	—	—
P818	—	—	—	84.9	98.6	65.5	—	—	—
P816	—	—	—	38.9	95.4	25.6	—	—	—

Table 5 Gravimetric sorption values

PSOC Coal No.	Uptake ( $\text{mg g}^{-1}$ , dmmc) at r.v.p. of 0.95				
	Tetralin (25°C) (equil)	Benzene (25°C) (equil)	Methanol (25°C) (equil)	Methanol (50°C) (24 h)	Pyridine (50°C) (24 h)
318	—	41.6	63.7	63.7	27.1
254w	—	27.3	49.4	46.9	16.5
268	—	23.9	65.3	58.9	112.5
223	92.2	185.4	225.9	211.5	598.3
212	71.6	195.7	275.8	258.6	611.9
248	113.8	235.1	316.6	302.1	684.3
242	32.1	115.0	329.8	313.0	678.5
246	—	104.5	342.6	328.1	493.8

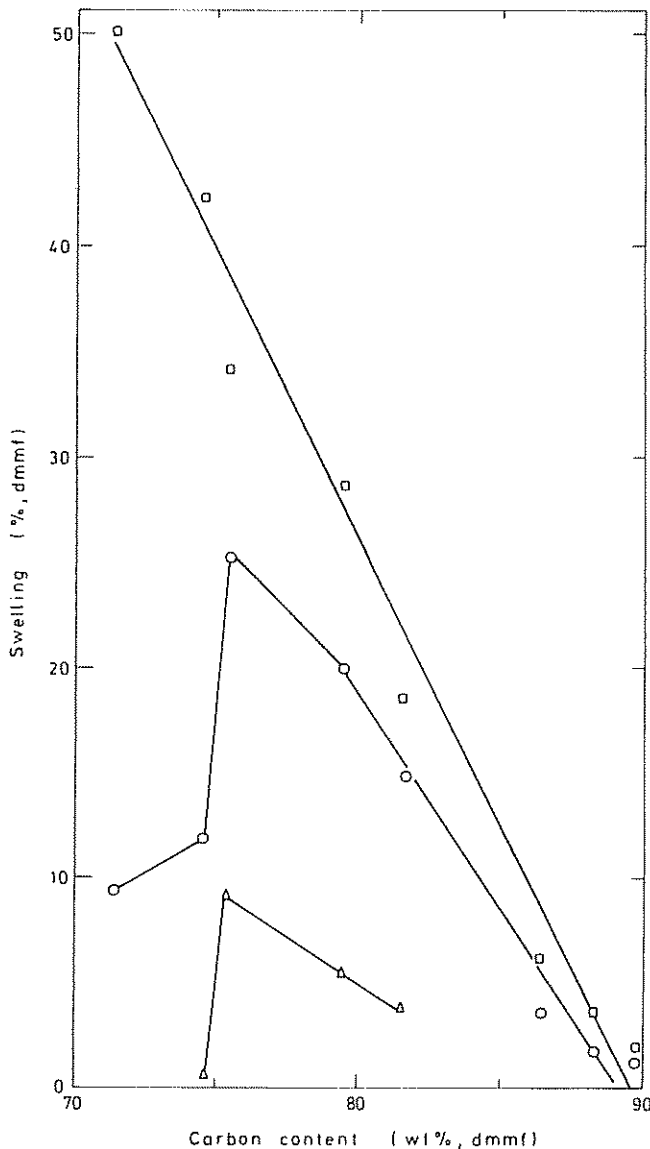


Figure 2 Solvent-induced swelling in coals of varying carbon contents at 25°C. □, methanol; ○, benzene; △, tetralin

or benzene.  $S$  values for methanol decrease rectilinearly with increasing carbon content of the coal. For eight coals (lignite to LV) the correlation coefficient for a rectilinear plot between  $S$  and the rank parameters (carbon content or oxygen content) was calculated to be 0.99. The point of zero swelling was calculated by least squares to be 89.2 wt % carbon content, a value in agreement with the 89 wt % carbon content estimated by Sanada and Honda<sup>3,4</sup> for zero swelling on Japanese coals using pyridine as the solvent. It is noteworthy that whereas the minimum in the present study as well as in the study of Sanada and Honda is located at about the same carbon content, the maxima in the two cases are widely different. In the present study, maxima in  $S$  for benzene and tetralin occur at a carbon content of about 75 wt % whereas in the study of Sanada and Honda and others it occurs at about 84–86 wt % carbon content. Although methanol was found to be a strong swelling agent for coal, it extracted less than 1 wt % material from the coals at 25°C.

Swelling can also be expressed on the basis of percentage increase in particle volume as a result of solvent imbibition, that is  $S_p$ . For this calculation,  $\rho_{H_2}$  is sub-

stituted for  $\rho_2$  in equation (2). Table 4 presents values for  $S_p$ . The relation between  $S_p$  and carbon content in the coals is qualitatively similar to that shown in Figure 2.

#### Effect of swelling on uptake of organics

Helium is the smallest adsorbate. Therefore, solvent penetration of coal to a greater degree than that which occurs with helium must be due to special interactions (e.g., swelling) between solvent molecules and the organic structures present in the coal (Table 3). A measure of these special interactions is the difference between the solvent and the helium penetration of the pore network of the coal particle, that is,  $(V_s - V_T)$ . Indeed it was found that swelling values ( $S$ ) obtained for methanol for five coals (ranging in rank from lignite to HVB) which show significant swelling have a rectilinear correlation coefficient of 1.00 with  $(V_s - V_T)$ . If, however, the data for all the eight coals investigated are plotted (Figure 3), the correlation coefficient decreases to 0.95. It is noteworthy that for each of the four coals (Sbb-B to HVB) that exhibit swelling in methanol, benzene and tetralin, rectilinear correlation coefficients of 0.98 or better were found between  $(V_s - V_T)$  and the corresponding  $S$  values (Figure 3).

#### DISCUSSION

The extent of methanol-induced swelling was found to increase rectilinearly with the oxygen content of the coal. This suggests that as the oxygen content of coal 'molecules' increases, the affinity of coal 'molecules' for methanol increases. As a result, the density of the coal in a solvent will increase due to increased penetration of the solvent into the swollen organic structures of coal. Thus, any micropores formed by cage-like structures in coal 'molecules'<sup>21</sup> would become more accessible to solvent as the extent of solvent-induced swelling of coal 'molecules' increases. Filling of these micropores would result in increased densities of the coals in solvent. Relations between the extent of solvent-induced swelling and densities of coals in solvents were found (Figure 3). Helium, with a kinetic diameter of 0.26 nm, can readily penetrate the open pore structure of coal. Hence, densities of coals in solvents which are greater than the corresponding helium densities indicate solvent-enhanced penetration of the organic structures present in coal. The difference between the pore volume accessible to the solvent and helium ( $V_s - V_T$ ) is a measure of solvent penetration of that part of

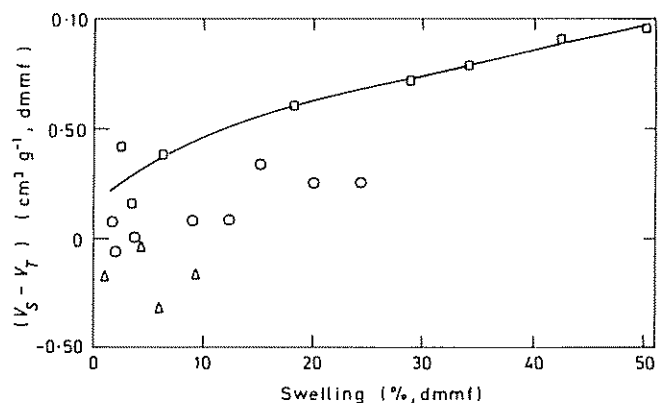


Figure 3 Penetration of the pore network of coals by various solvents as a function of swelling. Helium is used as a reference. □, Methanol; ○, benzene; △, tetralin

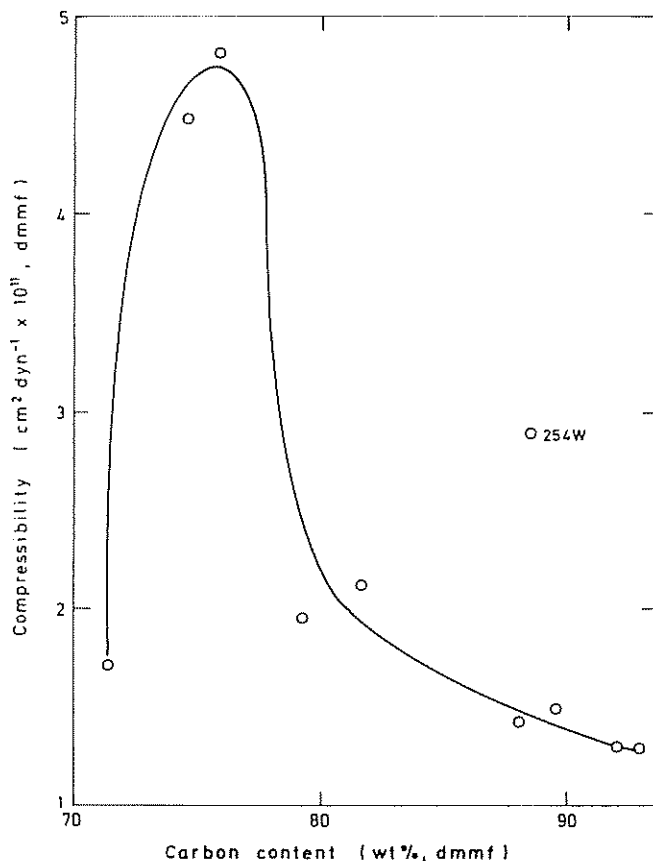


Figure 4 Compressibility of coals as a function of carbon content

the fine pore structure of coal which is not accessible to helium. It was found that methanol penetration of the fine pore structure of coal increases rectilinearly with corresponding solvent-induced swelling of the coal (Figure 3). The scatter of data is most pronounced at low swelling values and may reflect diffusion limitations to swelling as parts of the organic structures of coal become impervious to solvent molecules.

The extent of solvent-induced swelling in coal is directly related to three factors: (1) affinity of the chain segments for the solvent; (2) the average size of the chain segments between crosslink points ( $M_c$ ); and (3) flexibility of the chain segments. The low swelling values observed for coals can be attributed to restriction of solvent imbibition by one or more of the above factors. Methanol-induced swelling of coals decreases rectilinearly with decreasing oxygen content of the coal. This suggests that with methanol imbibition in coal, a major limiting factor is the affinity of the coal 'molecules' for methanol. This is reasonable when one considers the Hildebrand solubility parameters ( $\delta_H$ ) of  $14.5 \text{ cal}^{1/2} \text{ mol}^{1/2} \text{ cm}^{-3/2}$  for methanol<sup>5</sup> and  $\delta_H$  values of  $\approx 10$  to  $15 \text{ cal}^{1/2} \text{ mol}^{1/2} \text{ cm}^{-3/2}$  for coals varying in rank from HVA to lignite<sup>4,5,22</sup>. The greater the similarity between the solubility characteristics of coal 'molecules' and the solvent the higher the interaction between the two species<sup>23</sup>. Maximum solvent-induced swelling is observed when the solubility characteristics (as approximated by  $\delta_H$  values) of the solvent and coal 'molecules' are equal. As the  $\delta_H$  value of methanol is close to the  $\delta_H$  values estimated for lignites, these should exhibit maximum possible swelling in methanol. Higher-rank coals with lower  $\delta_H$  values would exhibit progressively lower swelling values.

However, Kirov *et al.*<sup>5</sup> found that  $M_c$  values of solvent-extracted coal residues decreased with increasing carbon content between 75.9 and 88.2 wt % of the raw coal sample. In addition, it is well-established that the average degree of aromaticity of the organic phase in coal increases; and hence, the flexibility of the coal 'molecules' decreases with increased carbon content. Thus, while it appears that methanol-induced swelling of coal is limited by the affinity of the coal 'molecules' for methanol the effects of crosslink density and chain flexibility cannot be overlooked.

Benzene and tetralin-induced swelling of coals is markedly different from that of methanol (Figure 2). Benzene and tetralin exhibit the highest degree of swelling in a coal sample of  $\approx 75$  wt % carbon content (PSOC-248, a Sbb-A coal). As  $\delta_H$  values for benzene and tetralin, 9.2 and  $9.5 \text{ cal}^{1/2} \text{ mol}^{1/2} \text{ cm}^{-3/2}$ , respectively<sup>5,22</sup>, are less than those for coals with carbon contents less than 88 wt %, the observed maximum in swelling cannot be attributed to maximum affinity of benzene and tetralin for coal 'molecules' of PSOC-248 coal. Noting the improvement in the match of solubility parameters as carbon content increases, these results suggest that the highest  $M_c$  and/or chain flexibility values occur in coals of less than  $\approx 75$  wt % carbon content. Physical properties of polymers such as compressibility are dependent on both the flexibility of the chain segments and  $M_c$  values<sup>23</sup>. It is noteworthy that with the coals we have studied, a similar correlation is observed; that is, benzene and tetralin-induced swelling as well as corresponding compressibility values exhibit maxima at about 75 wt % carbon content (Figures 2 and 4). The compressibility data for PSOC-254W, a washed MV coal, is higher than expected for its carbon content of 88 wt %. The reason for this is not understood at this time.

In the present study, higher-rank coals with carbon contents above 88 wt % exhibit negligible amounts of solvent-induced swelling (Figure 2). In these coals sorption values show a strong molecular sieving effect. For example, at  $50^\circ\text{C}$ , 24 h sorption values for methanol are 2–3 times greater than the corresponding pyridine values (Table 5) because of the smaller overall dimensions of the methanol molecule. However, pyridine is a better swelling agent than methanol for lower-rank coals with carbon contents less than 88 wt %<sup>21</sup>. The data in Table 5 show that pyridine sorption values, which rise sharply to a plateau beginning at  $\approx 85$  wt % carbon content are 2–3 times those of methanol for the coals ranging in rank from HVA to Sbb-B.

The sorption pattern described previously for pyridine in raw coal samples is in good agreement with that measured on pyridine-extracted coals by Sanada and Honda<sup>3,4</sup>. It is reasonable that both the raw and pyridine-extracted coal samples exhibit similar sorption properties, as the organic fraction extracted from coal is generally believed to be similar in chemical composition to the insoluble residue. This agreement in pyridine sorption data is also noteworthy since this shows that the maximum at 75 wt % carbon content observed in benzene-induced swelling of raw coals is not an artefact of abnormal coal sample(s). It is noted that in the benzene sorption study of Sanada and Honda the maximum occurs at  $\approx 85$  wt % carbon content. However, these workers used pyridine-extracted coals in their study. The significance of this use of pyridine-extracted coals is not obvious. The different workers used pyridine-extracted

coals to study pyridine-induced swelling in coal structures. Pyridine dissolves a considerable fraction of coal; thus, the solubility would vitiate any rational study of reversible swelling induced by pyridine. In contrast to pyridine, benzene and methanol dissolve little or no coal. Probably, pyridine extraction of coals changes sufficiently the physical structure of the residue to affect in turn the subsequent benzene-induced swelling. It can be speculated that these changes include disruption of weak crosslinks, for example, hydrogen bonds between organic structures in coal 'molecules'. Once the weak crosslinks are broken, benzene sorption in coals above 75 wt % carbon content increases and the point of maximum benzene-induced swelling changes from 75 to 85 wt% carbon content because the affinity of benzene for coal increases with rank in this range as discussed earlier.

#### ACKNOWLEDGEMENTS

The authors are indebted to Professors P. Given, I. Harrison and F. Vastola for many helpful discussions. Professor W. Spackman supplied the coals used in this study. The financial support of this work by the US Department of Energy on Contract No. EX-76-C-01-2494 is gratefully acknowledged.

#### REFERENCES

- 1 Keller, D. V., Jr. and Smith, C. D. *Fuel* 1976, **55**, 273
- 2 van Krevelen, D. W. *Fuel* 1976, **44**, 229
- 3 Sanada, Y. and Honda, H. *Fuel* 1966, **45**, 295
- 4 Sanada, Y. and Honda, H. *Fuel* 1966, **45**, 451
- 5 Kirov, N. Y., O'Shea, J. M. and Sergeant, G. D. *Fuel* 1967, **46**, 415
- 6 Doty, P. and Zable, H. S. *J. Polymer Sci.* 1946, **1**, 415
- 7 Dryden, I. G. C. *Fuel* 1951, **30**, 145
- 8 Given, P. H., Cronauer, D. C., Spackman, W., Lovell, H. L., Davis, A. and Biswas, B. *Fuel* 1975, **54**, 40
- 9 Dacey, J. R. and Thomas, D. G. *Trans. Faraday Soc.* 1954, **50**, 740
- 10 Ainscough, A. N., Dollimore, D. and Heal, G. R. *Carbon* 1973, **11**, 189
- 11 Howard, H. C. and Hulett, G. A. *J. Phys. Chem.* 1924, **28**, 1082
- 12 Mahajan, O. P. and Walker, P. L., Jr. 'Analytical Methods for Coal and Coal Products' (Ed. C. Karr, Jr.), Academic Press, New York, 1978, **1**, 125
- 13 Kotlensky, W. V. and Walker, P. L., Jr. 'Fourth Carbon Conference', Pergamon Press Ltd., London, 1959, 423
- 14 Gan, H., Nandi, S. P. and Walker, P. L., Jr. *Fuel* 1972, **51**, 272
- 15 Zwietering, P. and van Krevelen, D. W. *Fuel* 1954, **33**, 331
- 16 Toda, Y. and Toyoda, S. *Fuel* 1972, **51**, 199
- 17 Nelson, J. R. *Ph.D. Thesis*, The Pennsylvania State University, 1979
- 18 Toda, Y. *Fuel* 1972, **51**, 108
- 19 Toda, Y. and Toyoda, S. *Carbon* 1973, **11**, 68
- 20 Holly, E. D. *J. Polymer Sci.* 1964, **A2**, 5267
- 21 van Krevelen, D. W. 'Coal', Elsevier Publishing Co., New York, 1961, 139
- 22 Mitchell, D. L. and Speight, J. G. *Fuel* 1973, **52**, 149
- 23 Flory, P. J. 'Principles of Polymer Chemistry', Cornell Univ. Press, Ithaca 1953