

## HEATS OF IMMERSION OF BITUMINOUS COALS IN LIQUIDS

J. P. Wightman, J. O. Glanville, J. B. Hollenhead, K. M. Phillips and K. N. Tisa

Chemistry Department, Virginia Tech, Blacksburg, VA 24061

### INTRODUCTION

The interaction of liquids with solid surfaces may be studied by a variety of experimental methods including both thermodynamic and spectroscopic ones. Immersional calorimetry as a thermodynamic tool has proven particularly useful in probing this interaction. A dated but nonetheless excellent review of immersional calorimetry has been given by Zettlemoyer (1). Although coal has a complex pore structure (2), a number of researchers have reported the heats of immersion of a variety of coals in a number of different liquids [3-13]. Indeed, Callanan has summarized [14] the case for additional studies of heats of immersion in a report describing measurement needs for coal. The objective of the present work was to assess the effects of wetting liquid chain length and coal surface oxidation on the heat of immersion of bituminous coals in both n-alkanes and n-alcohols and in water.

### EXPERIMENTAL

Two bituminous coals were used in this study, Virginia-C and Pocahontas No. 3 obtained respectively from Buchanan County, Virginia and McDowell County, West Virginia. The coals were crushed and sieved to -325 mesh (<44 microns). The ash content of Virginia-C and Pocahontas No. 3 coals was 5.22 and 5.0%, respectively; the moisture content was 0.15 and 1.04%, resp. The ultimate analysis of the two coals is listed in Table I. The surface area of the Virginia-C and the Pocahontas No. 3 coal was 1.9 and 2.0 m<sup>2</sup>/g, respectively, as determined by low temperature gas adsorption. Some Pocahontas No. 3 coal was extracted with methanol in a Soxhlet apparatus for 24 hours.

Table I. Ultimate Analysis of Coals

Element	Weight Percent (MF basis)	
	Virginia-C	Pocahontas No. 3
Carbon	87.0	84.8
Oxygen (by difference)	6.9	8.9
Hydrogen	4.25	4.6
Nitrogen	0.97	0.97
Sulfur	0.64	0.61
Chlorine	0.20	0.08

Heats of immersion were determined in a Setaram Calvet MS 70 microcalorimeter using a previously reported procedure [11]. A known weight of coal (20-50 mg) outgassed at <10<sup>-4</sup> torr for 2 hours at room temperature in a custom pyrex bulb was immersed in 5 ml of the wetting liquid. The precision of a typical heat of immersion was about 10%. A heat of empty bulb breaking correction was determined and applied.

Oxidation of the coal samples was achieved by heating the coal for varying time periods (10 - 1440 minutes) in a thermostatted forced air oven over a range of temperatures (110 - 320°C).

The XPS ( $\alpha$ -ray photoelectron spectroscopy) spectra of the powdered coal samples were obtained using either a Kratos XSAM-800 electron spectrometer or a Perkin Elmer PHI 5300 electron spectrometer. Both spectrometers use a magnesium x-ray source (1254 eV) and a hemispherical analyzer. Coal powder was mounted on the sample probe with doublestick tape. The atomic fraction of each element was determined from the corrected area of the elemental photopeak.

## RESULTS AND DISCUSSION

The heats of immersion of Virginia-C coal determined in a series of n-alcohols are listed in Table II. A decrease in the heat of immersion is noted as the carbon number of the alcohol increases. This decrease in the heat of immersion for coal is in contrast to the increase in the heat of immersion observed for graphitized carbon black [15]. This marked difference in behavior is due to differences in the structure of coal and carbon black. Larsen, et al. [16] have suggested that coal be treated as a cross-linked macromolecule. The swelling of coal by methanol is well known and this swelling phenomenon is typical of cross-linked polymers. Thus, the decreasing heat of immersion for coal undoubtedly reflects the inability of the larger alcohols to penetrate coal. Microcalorimetric measurements afford yet another measure of this diminished penetration by wetting liquids of increasing bulkiness. The time required for complete liberation of the heat of immersion can be followed conveniently in the microcalorimeter and is termed the immersion time. This time of immersion is short for methanol and n-dodecanol but is a maximum for n-butanol. The heats and times of immersion are consistent with a rapid and complete penetration of coal by methanol and a still rapid, but complete exclusion, of n-dodecanol by coal. Immersion in n-butanol gives intermediate heat and time results. The effect of outgassing temperature on heat of immersion is only modest. For example, the heat of immersion in methanol of Virginia-C coal outgassed at room temperature and at 120°C was 24 and 28 J/g, respectively.

Table II. Heats of Immersion of Coals in n-Alcohols and n-Alkanes

Liquid	Carbon No.	Heat of Immersion (J/g)	
		Virginia-C	Pocahontas No. 3
Methanol	1	24.	
n-Propanol	3	19.	
n-Butanol	4	15.	
n-Hexanol	6	4.6	
n-Dodecanol	12	4.6	
n-Octane	8		6.9
n-Nonane	9		5.5
n-Decane	10		5.1
n-Undecane	11		4.3
n-Dodecane	12		5.3
N-Tridecane	13		4.1
N-Tetradecane	14		3.7
N-Pentadecane	15		3.7
N-Hexadecane	16		3.7
n-Heptadecane	17		3.7
n-Octadecane	18		3.7
n-Nonadecane	19		3.2

The heats of immersion in water of Virginia-C coal heated for 24 hours at different temperatures are shown in Table III. There is nearly a fifty-fold increase in the heat of immersion for coal heated at 320°C compared to unheated coal. The change in the heat of immersion is modest until the coal is heated above 150°C. The surface composition of unheated coal and of coal heated to different temperatures can be determined by XPS analysis. The oxygen/carbon atomic ratios calculated from the XPS spectra of the unheated and heated coals are listed in Table III. The O/C ratio increases as the temperature to which the coal is heated increases. Indeed, the heat of immersion and XPS results are complementary, and the agreement reflects increasing numbers of surface polar (oxygen-containing) groups.

Table III. Heats of Immersion in Water and XPS Results for the Oxidation of Virginia-C Coal

<u>Oxidation Temperature (°C)</u>	<u>Heat of Immersion (J/g)</u>	<u>Surface [O/C] Ratio</u>
	2.5	0.053
110	3.0	0.065
150	4.5	0.087
175	9.0	0.11
210	23.5	0.16
225	34.0	0.18
250	59.0	0.22
300	75.0	0.27
320	99.0	0.28

The heats of immersion of Pocahontas No. 3 coal determined for a series of n-alkanes are listed in Table II. An initial decrease in the heat of immersion is noted as the carbon number of the alkane increases. Again, the exclusion of the longer alkane molecules by coal is demonstrated. The heats of immersion in water of Pocahontas No. 3 coal heated at 320°C for different times are shown in Table IV. An initial rapid increase in the heat of immersion with oxidation time is followed by a slower increase in the heat of immersion. For example, there is about a ten-fold increase in the heat of immersion for coal heated for only 2.5 hours compared to a two-fold increase over the next 20 hours. The oxygen/carbon ratios calculated from XPS spectra of the heated coals are listed in Table IV. The O/C ratio increases as the time of heating of the coal increases. Again, the heat of immersion and XPS results are quite complementary. Prior extraction of Pocahontas No. 3 coal by methanol has no significant effect on either the heat of immersion or the oxygen/carbon ratio.

#### SUMMARY

Differences in the heats of immersion of bituminous coals in a homologous series of n-alcohols and n-alkanes relate directly to the ability of these liquids to penetrate the coals. Heats of immersion of oxidized coals in water can be used to follow the extent of oxidation. Changes in the surface oxygen composition of oxidized coals determined by XPS parallel changes in the heats of immersion in water.

Table IV. Heats of Immersion in Water and XPS Results on the Oxidation of Pocahontas No. 3 Coal

Oxidation Time (min)	Heat of Immersion (J/g)	Surface [O/C] Ratio
0.0	3.6 *	0.071 *
0.0	3.8	0.086 *
10	28.	0.30
20	30.	0.33
30	41.	0.33
60	45.5	0.38
120	51.	0.38
180	52.	
300	69.	
360	75. *	0.46 *
600	75.5	
720	80. *	0.37 *
1080	84. •	0.43 *
1080	83.	
1440	88.	0.46
1440		0.43 *

\* - value for methanol extracted coal

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