POLAR AND DISPERSION INTERACTIONS AT CARBON SURFACES – FURTHER DEVELOPMENT OF THE XPS BASED MODEL

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Abstract

Enthalpy of immersion (ΔH_i) in water has been measured for a series of ozone oxidised non-porous carbon blacks and, as in our previous studies been found to correlate directly with the total surface oxygen level $[O]_T$ measured by X-ray photoelectron spectroscopy. An equation that allows calculation of either parameter from the other is given and shown to describe behaviour for a wide range of carbon black surfaces which contain ozone generated or native oxygen functional groups. Using this approach, the surface polarity and the relative hydrophilic character of such surfaces can be predicted. A molar enthalpy for the polar interaction between water and surface oxygen atoms of 17 kJ mol^{-1} is obtained by assuming a 1:1 co-ordination between water molecules and carbon surface oxygen atoms. The data lead to a predicted value of 37.5 mJm^{-2} for the immersion of oxygen free carbon black external surface into water. This equates to a value of 2.5 kJ mol^{-1} for the non-specific dispersion interaction between water and an oxygen free carbon black surface when a molecular area of 10.5×10^{-20} m^2 for water is assumed. The same carbon black when oxidised using nitric acid gives a different enthalpy of immersion to the ozone treated and native oxide materials, this is attributed to differing chemistry of the two surface types, this aspect is discussed. The nitric acid treated carbons do however give the same value as the ozonated and native oxide carbons (37.5 mJm^{-2}) for the immersion of an oxygen free carbon surface into water. A correlation between the point of zero charge (pH_{PZC}) of the carbons and ΔH_i or $[O]_T$ is also presented. The results from these measurements show extremely good agreement with data from other groups who have used TPD to assess surface oxygen concentration. This gives a firm basis for confident prediction of the thermodynamic properties of carbon surfaces from single measurement techniques.

1. Introduction

There is recurrent interest in the functional groups produced by the chemisorption of heteroatoms at carbon surfaces and the energies of interaction of these groups with molecules in adjacent fluid phases. These groups, which usually contain oxygen, but may also contain other heteroatoms such as nitrogen or sulphur, determine the behaviour of carbon surfaces used for selective adsorption or determine adhesion properties at composite interfaces. An understanding of the concentration and reactivity of surface groups is therefore essential for property control and optimisation in these applications.

There are many traditional methods for determining the surface oxygen concentration in carbon materials. Examples are: the active surface area concept [1], temperature programmed desorption methods [2], acid-base titration [3] and mathematical analysis of water adsorption isotherm data [4]. All of these give a measure of polar site concentration and reactivity. However, these methods generally require multiple measurements and take considerable periods of time. As a consequence, quick, simple and accurate methods for determining carbon surface reactivity allowing confident material selection are of interest. It is also desirable that new methods should take into account the existing depth of knowledge of carbon surface chemistry and thermodynamics.

The relationship between the surface polar site concentration of a wide range of porous and non-porous carbons and heat of immersion (ΔH_i) in water has been shown by Stoeckli and his co-workers [5] to be described by:

$$\Delta H_i = -25a_0 - 0.6(a_s - a_0) \qquad \ldots [1]$$

where a_0 is characteristic of the primary polar sites on the carbon surface, as defined by Dubinin-Serpinski [4] equation, and a_s is the limiting water adsorption value at saturation. Traditionally both these quantities are given in mmol.g^{-1}. This method allows prediction of carbon surface polarity using a single calorimetric measurement and also allows some predictions to be made about the relative hydrophilic character of carbon surfaces.

Our own initial work in this area has shown that both ΔH_i (water) and a_0 can be predicted from rapid measurement of the surface oxygen concentrations of non-porous carbon blacks using X-ray photoelectron spectroscopy (XPS) [6][7][8]. This work has shown a linear relationship between surface oxygen level and enthalpy of immersion in water. For each atomic % of chemisorbed oxygen per m^2 of carbon surface, -15×10^{-3} J of energy are generated upon immersion in water plus an additional -40×10^{-3} J m^{-2} due to the non-specific, dispersion, interaction between water molecules and the carbon surface. This gives the following expression:

$$-\Delta H_i(H_2O)\,(J\,g^{-1}) = [15 \times 10^{-3}\,([O]_T/m^{-2})^{-1}\,A] + [\,40 \times 10^{-3}\,A]\quad ……[2]$$

in which $[O]_T$ is the XPS measured surface oxygen concentration expressed in atomic % (1 atom % is equivalent to 5×10^{17} atoms m^{-2} of carbon) and A is the *specific external surface area* of the carbon from nitrogen BET or α_s methods. The heat of immersion for unoxidised carbon surface is 40×10^{-3} J m^{-2} as previously reported [7]. We have also pointed out that the XPS method can be used to identify other polar groups besides oxygen and in this case the total polarity of the surface $[P]_T$ will be given by the sum of all polar surface species that are identified by XPS:

$$[P]_T = [O]_T + [N]_T …etc \quad ……[3]$$

where the precise concentrations of each heteroatom (e.g. N_T for nitrogen as shown) is above the lower detection limit of the technique (approximately 0.05 atom % but precisely dependent upon the photoionisation cross-section of the heteroatom). The data obtained in all of our studies indicates that for the ozone-oxidised carbon blacks the measured oxygen is on, or very near, to the carbon surface and available for hydrogen bonding with polar probes. The effective range for hydrogen bonding being accepted as <2 nm. Carbons or other materials with intrinsic bulk or deeper subsurface oxygen may not necessarily follow the behaviour predicted here.

In more recent work several groups have used temperature programmed desorption [9] or titration methods [10] to characterise the surface oxygen levels and polarity of carbons and have correlated the resulting data with ΔH_i. From the results of these studies it is evident that precise quantitative measures of surface polarity can be achieved by a number of methods and that the resulting characteristic parameters have real physical and chemical meanings giving a quantitative description of carbon surface behaviour. In particular a direct relationship between a_0 (mmol g^{-1}) surface oxygen level $[O]_T$ (atom % or mmol g^{-1} measured by XPS, TPD or titration methods) and $\Delta Hi_{(water)}$ is emerging. Further, for certain applications, single measurement methods of surface characterisation such as XPS or ΔH_i hold some attraction in terms of efficiency over methods which require multi-point data acquisition.

In this paper we reappraise our initial results in this area and present additional data for non-porous carbon blacks oxidised using an ultraviolet ozone fluidised bed system. The new data support our initial findings regarding the quantitative relationship between spectroscopically measured oxygen for non-porous carbon blacks and ΔH_i in water. We also consider data for the same carbon black but after oxidation using nitric acid which do not follow this behaviour. The point of zero surface charge (pH_{PZC}) method is used as an additional means of characterising the ozone surface oxidised carbons and again the resulting data are integrated into a general model relating carbon surface chemistry and adsorption/immersion energy.

2. Experimental

Immersion calorimetry has been carried out using a Setaram C80 calorimeter. Carbon samples were sealed into glass ampoules, thermally equilibrated in the calorimeter chamber containing water for a minimum of 16 hours and then broken. The energy released is then converted directly to the enthalpy of immersion.

XPS measurements of surface oxygen levels have been obtained using a Kratos Axis instrument with monochromated Al $K\alpha$ radiation of energy 1486.6 eV and a 5 channel counting system. Spectra were recorded at 1.33×10^{-6} Pa. Surface oxygen levels (atomic

%) have been calculated from the areas of the carbon 1s and oxygen 1s peaks from narrow scan spectra (275-300 eV and 525-545 eV respectively) measured at a pass energy of 20 eV after subtraction of a Shirley background. Correction of peak areas using atomic sensitivity factors, which compensate for photoionisation cross section, angular asymmetry of photoemission, and the attenuation length of the photoelectrons has been made. All spectra have been charge referenced to the carbon (C-H) 1s peak at 284.6 eV. The errors on each measurement are +/- 10% determined by the analysis of standards. Greater details of the applications of XPS to carbon surface have been discussed elsewhere [11].

Carbon black N330 from Cabot which has an external surface area of 78 m^2g^{-1} has been used in all of the present work. This has been oxidised in one of two ways. Using an ozone fluidised bed system, whereby a controlled flow of O_2/O_3 is passed through the carbon black bed (containing 4g of carbon) for variable times (see later) at ambient temperature in order to achieve differing oxidation levels. Alternatively samples were oxidised by refluxing 5g of carbon black in 7, 14, 17.5 and 35 % nitric acid solution made up from 16 mol.l^{-1} (70%) concentrated solution nitric acid for 1 hour. Samples were then water washed until the *pH* of the effluent water was the same as the influent (5.3). Samples were then dried overnight at 293 K. The ozone method has previously been shown to have no effect on the carbon surface area [6].

The point of zero charge (PZC) [12] for each surface has been determined by shaking samples of carbon black of 0.1, 0.5, 1.0 and 5.0 wt% for 24 hours in 10 cm^3 of individual solutions of either sodium nitrate, nitric acid or sodium hydroxide which had respective *pH* levels of 3, 6 and 11. The equilibrium *pH* was then measured.

3. Results and Discussion

In this, as in previous studies, we have used the ozone fluidised bed system to produce carbon black surfaces of increasing oxygen concentration. The oxygen chemisorption profile obtained in this present study is shown in Figure 1 and Table 1 contains the relevant physico-chemical data for the carbon blacks. Figure 2 contains data for ozone oxidised carbons from our earlier study [7] plus the new data obtained in the present work. The data agree well with the findings from our previous

studies and are generally consistent with equation [2]. The intercept of the plot yields a value of 35 mJm^{-2} for the immersion of a carbon black surface which contains no chemisorbed oxygen which is therefore characteristic of the non-specific interaction of that surface. Other groups [10,13,14] have also reported similar values for this measurement.

A number of workers have proposed the existence of non-heteroatomic Lewis base sites which are characterised by regions of π electron density on the carbon basal planes [10,15,16]. These sites are additional to, but may not be independent of, chemisorbed heteroatoms sites which occur at carbon surfaces. Oxidation of the carbon surface is reported to diminish electron density and lowers the basicity of the carbon surface [15]. Using this approach, the total number of polar sites on a carbon surface might be made up of heteroatomic sites with acidic (COOH) or basic (OH, NH_2) character plus electronic Lewis sites. The Lewis basic sites, which have previously been denoted C_π [16], can undergo redox reactions and can therefore be titrated.

Heteroatomic sites are detectable by XPS or by titration methods. In the present work we differentiate only between polar interactions, which occur at oxygen or other heteroatom sites and which are detected and quantifiable by XPS, and non-polar interactions which occur across the mean carbon surface depending on local electron polarisability, i.e. Dispersion forces, as described by London [17]. The latter are also known to decrease in intensity as a function of increasing carbon surface oxidation [6,18].

Assuming that one m^2 of carbon surface contains approximately $5x10^{19}$ atoms (i.e. $6.023x10^{23}/12x10^3m^2$ where 10^3m^2 is the approximate surface area of 1g of carbon). One atomic percent is therefore $5x10^{17}$ which produces an enthalpy of immersion in water of 15 mJm^{-2}. Assuming the simplest 1:1 co-ordination between water molecules and surface oxygen atoms, the specific enthalpy of interaction of water with polar surface groups is 17.0 kJ mol^{-1}. This condition requires that all surface oxygen atoms become co-ordinated with water molecules which is not unrealistic in an immersion experiment. However, the number of water molecules that can attach to each surface oxygen site may not be fixed. Other workers have used a 2 waters:1 surface oxygen co-ordination model which would mean that the molar energy becomes 8.5 kJ

mol[-1] in the present work. Both values are realistic in terms of specific polar interactions and are consistent with previously reported values [10,19]. Using the same approach, the non-specific dispersion interaction between water and the non-polar carbon surface is 2.3 kJ.mol^{-1} which is as expected for this type of interaction [10] and derived assuming a molecular area of 10.5×10^{-20} m^2 for water [20]. The data give a correlation coefficient of 0.91 and lead to the following expression which allows calculation of the polar and non-polar interaction of water with the carbon black surface:

$$-\Delta H_i\ (H_2O)/mJm^{-2} = [14[O]_T + 35] \qquad ......[4]$$

This expression describes the immersion behaviour in water for a number of non-porous carbon black surfaces containing native oxide levels <3.8 atom % and carbon black N330 ozone oxidised up to 8.8 atom % (a correlation coefficient of 0.96 is obtained for the ozone oxidised materials alone).

Figure 2 also contains data for the immersion of a series of carbon blacks, which have been oxidised using nitric acid. These data do not align with the native oxide and ozone oxidised surfaces and their ΔH_i values are generally lower. Regression analysis of these points gives a correlation coefficient of 0.97 and a slope which changes the multiplier in equation [2] to 4×10^{-3}. The intercept however gives a characteristic energy for immersion of the pure carbon surface of 40 mJm^{-2}, which is the same as that obtained from the other family of data points.

The polar energy difference between the two surfaces could be explained by the differences in functional groups produced by each treatment. We have observed previously, and it is well known, that nitric acid treatment of carbon blacks [6.] and carbon fibres [11] produces high levels of carboxylic acid groups (COOH). We have attempted to probe the chemistries of the two surface types using XPS but so far the resulting carbon 1s and oxygen 1s spectra have been too similar to yield conclusive evidence. Groszek has recently suggested that the energies of interaction of acidic groups on active carbon (BPL) surfaces are lower than those of basic groups [21]. This may explain the difference in the immersion energy behaviour of the two types of surfaces however, the nature of this difference is not presently known. Previous studies of ozone oxidation of carbon blacks have indicated that the predominant groups formed are also

carboxylic acid [8] and therefore the surface chemistry differences between the two types of materials might not be expected to differ greatly. It is also possible that the lower immersion energy is due to nitrogen containing species, residual on the carbon surface at very low levels even after extreme washing. Two of the acid oxidised samples (7.3 and 8.4 atom % oxygen) also show trace levels (<1 atom %) of nitrogen. If inorganic, these species may undergo endothermic hydration when immersed in water hence decreasing the overall exotherm. It is known that the removal of such species by water washing is very difficult which does cast some doubt on the use of nitric acid oxidised carbons for detailed and controlled surface chemical studies. Nitric acid treatment is also known to change carbon topography by removing fine structure and leaving a smoother surface. Thus some loss of surface area may also contribute to the lower ΔH_i values observed.

Measurement of the pH_{PZC} values for the carbons has been carried out according to the method described by Noh and Schwarz [12] which simply requires titration of samples of the carbon using solutions of different pH (here we have used pH 3, 6 and 11). This leads to a plot of the type shown in Figure 3 with the pH_{PZC} being given by the point of convergence of the plot i.e. where all surface groups have been reacted. The pH_{PZC} value obtained is sensitive to the acid-base character, and therefore the surface oxidation chemistry, of the carbon. The data resulting from the ozone oxidised carbon blacks are shown plotted against $[O]_T$ (total surface oxygen/atom %) in Figure 4. They show good correlation with the data of a number of other groups [15][19][22], which are also given on the plot. The greatest sensitivity to surface oxidation is at low oxygen levels i.e.$[O]_T$<3-4. The direct proportionality between carbon surface oxygen level measured by TPD and expressed in mmol.g^{-1}and $[O]_T$ from XPS is also supported by these data (1 atom % = 1 mmol.g^{-1}, both equating to 10^{17} oxygen atoms per m^2 of carbon surface). Hence, the oxygen levels appear to be measurable by either method. Figure 5 shows the correlation between pH_{PZC} and ΔH_i which results from these measurements at the higher levels of oxidation.

4. Conclusions

We present additional data for ozone oxidised carbon blacks which support our initial findings that ΔH_i can be predicted from a single XPS measurement of surface oxygen or

vice-versa using a simple equation. Assuming a 1:1 co-ordination between surface oxygen atoms and the wetting water molecules an enthalpy of polar interaction of 17 kJ mol^{-1} for water is obtained. A value of 35-40 mJm^{-2} is derived for the immersion of an oxygen free surface and is therefore characteristic of the non-specific dispersion interaction of water with the carbon surface which proceeds with an interaction energy of 2.3 kJ mol^{-1}.of water. It is tentatively suggested that the PZC method provides an additional means of determining the approximate oxygen and heat response for the materials studied.

Acknowledgements

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Table 1: Chemical characteristics of carbon blacks

Carbon	$[O]_T$ atom%	$\Delta H_i(H_2O)$ Jg^{-1}	$\Delta H_i(H_2O)$ mJm^{-2}	pH_{PZC}	Symbol
[b]N110	0.6	-6.4	-45.9	a	♦
[b]N336	0.6	-3.6	-46.6	a	♦
[b]N550	0.9	-2.7	-69.5	a	♦
[b]N726	1.1	-1.7	-53.3	a	♦
[b]K354	3.8	-8.3	-76.3	a	♦
[a]N330	1.3	-0.7	-9.1	8.37	●
[c]N330/O$_3$	0.9	-4.4	-55.8	a	■
[c]N330/O$_3$	4.1	-7.6	-96.0	a	■
[c]N330/O$_3$	4.3	-7.9	-100.0	a	■
[c]N330/O$_3$	6.7	-11.2	-142.0	a	■
[c]N330/O$_3$	8.2	-13	-165.0	a	■
[c]N330/O$_3$	8.8	-14.1	-178.0	a	■
N330/O$_3$	6.4	10.2	130.5	2.38	●
N330/O$_3$	6.3	-10.1	-129.9	2.31	●
N330/O$_3$	7.5	-11.0	-140.8	2.15	●
N330/O$_3$	5.3	-7.6	-97.9	2.53	●
N330/O$_3$	6.9	-9.6	-123.3	2.25	●
N330/O$_3$	7.7	-10.8	-137.9	a	●
N330/O$_3$	4.8	a	a	2.68	●
N330/HNO$_3$	3.4	-4.4	-56.9	a	▲
N330/HNO$_3$	8.4	-5.6	-71.2	a	▲
N330/HNO$_3$	7.3	-5.1	-65.6	a	▲
N330/HNO$_3$	10.7	-6.3	-80.1	a	▲

a) not measured for these samples

b) previously reported in Reference [6]
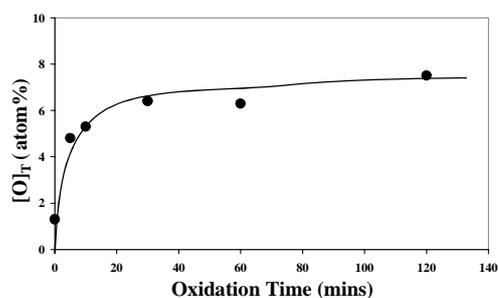
c) previously reported in Reference [7]

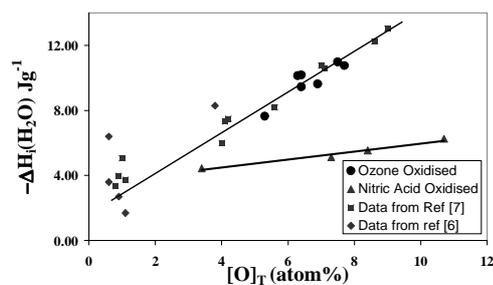Figure 1: Carbon black surface oxygen level $[O]_T$ (atom % by XPS) as a function of ozone oxidation time.

Figure 2: Correlation between ΔH_i (H_2O) and total surface oxygen $[O]_T$ measured by XPS for ozone and nitric acid oxidised carbon blacks and native oxide materials from Ref. [6].
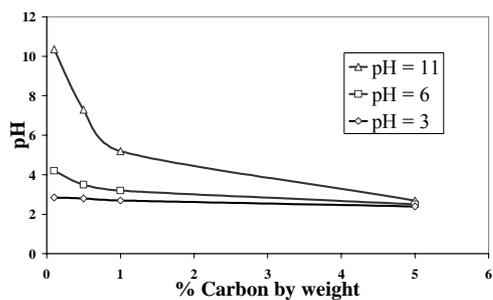
Figure 3: *pH* against wt% carbon black showing pH_{pzc} of 2.53 for N330 with $[O]_T$ of 5.3 atom %.
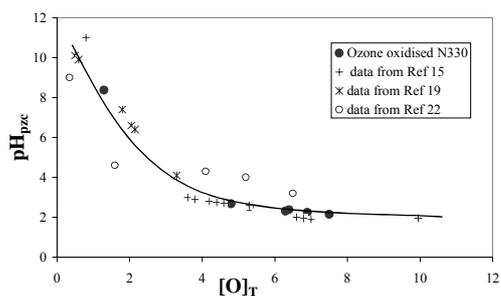

Figure 4: Correlation between pH_{pzc} and $[O]_T$ for ozone oxidised N330 carbon black expressed in atom % from XPS and active carbons expressed in mmol g^{-1} by TPD and titration from Refs. [15,19,22] (1 atom % = 1 mmol g^{-1} = 10^{17} atoms per m^2 of carbon surface).
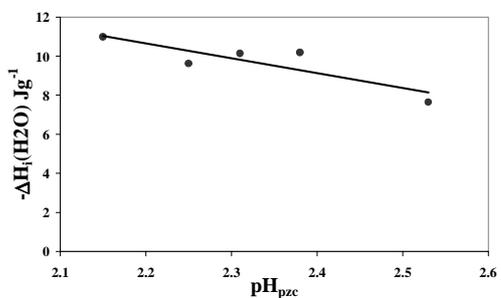

Figure 5: ΔH_i (H_2O) as a function of pH_{pzc} for ozone oxidised carbon black N330.