

# THE CHEMICAL MEANING OF THE TERM $a_0$ IN THE DUBININ-SERPINSKI EQUATION

R H Bradley

School of Applied Sciences, The Robert Gordon University  
St. Andrew Street, Aberdeen AB25 1HG

## Introduction

The adsorption of polar vapours by carbon surfaces is characterised by relatively weak interactions (typically - 0.4 kJ mol<sup>-1</sup>) at specific adsorption sites. The equilibrium uptake at any given adsorption pressure is a function of the surface concentration of polar sites. It has been shown by a number of workers, that for water adsorption by pure carbons, the shape of the resulting equilibrium isotherm, is sensitive to the degree of carbon surface oxidation[1][2][3].

Analysis of equilibrium data for water vapour, using the Dubinin-Serpinski equation leads to an assessment of the primary adsorption sites, via the amount of water adsorbed on them, and is therefore a measure of the relative degree of surface polarity. A quantitative relationship between  $a_0$  i.e. surface polarity, and heat of immersion ( $\Delta H_i$ ) in water has already been established [4].

Whilst isotherm analysis gives a qualitative assessment of structural polarity for porous systems, it is limited in that it does not give any specific information about the chemical nature of the adsorption sites. More work is needed before the types of sites present at the external and internal surfaces of carbons are known. At low temperatures it is possible to envisage polar functionalities of the type associated with organic systems e.g. C-OH, C=O, COOH, CNH<sub>2</sub> etc. and, when these species are present at the external surfaces of carbons they should be detectable spectroscopically.

In this paper a general relationship between a X-ray photoelectron spectroscopically measured total surface oxygen concentration [ $O_T$ ], for non-porous carbon blacks, and  $\Delta H_i$  in water is demonstrated. The parameter [ $O_T$ ] can be factorised into individual chemical groups using XPS line shift data. The overall behaviour between polarity and energy is similar to that observed between  $a_0$  and  $\Delta H_i$  for poly[vinylidene chloride] based microporous carbons of varying polarity.

## Experimental

Carbon blacks from Cabot (as received and after surface oxidation in an ozone fluidised bed apparatus) have been characterised using X-ray photoelectron spectroscopy in order to obtain surface oxygen concentration and chemistry data.  $\Delta H_i$  for the blacks, which had [ $O_T$ ] values of 0.5 to 9 atomic %, have been measured using a Parr solution calorimeter. Microporous PVDC carbons, of differing pore wall polarities, were obtained by treating samples of an 850°C char in carbon dioxide to oxidative burn-offs of 30% and 65% by weight, or; by heat treating in argon at 1273, 1473 and 1674 K to desorb oxides. Equilibrium water isotherms were measured gravimetrically using calibrated silica springs and CI microbalances at a sample temperature of 293 K (+/-0.5 K).

## Results and Discussion

Figure 1 shows the linear relationship between polarity i.e. the oxygen content of the PVDC carbons compared to  $\Delta H_i$  in water.

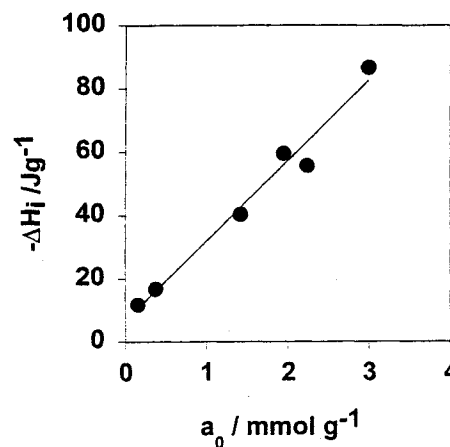


Figure 1. Relationship between  $a_0$  and  $\Delta H_i$  in water, for porous PVDC carbons (from Ref [3]).

A similar relationship is observed between surface oxygen concentration  $[O_T]$ , and  $\Delta H_i$  in water, for the range of non-porous carbon blacks studied, as shown in Figure 2.

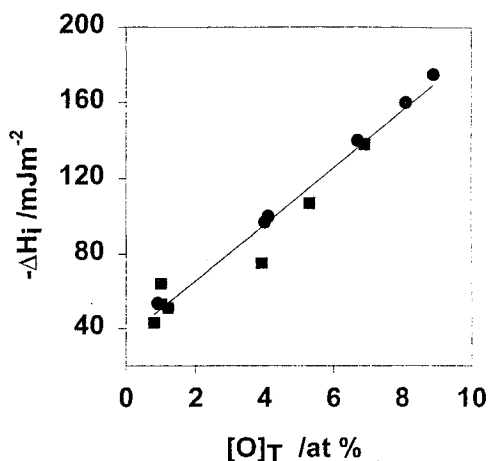


Figure 2. Relationship between  $[O_T]$ , and  $\Delta H_i$  in water for non-porous carbon blacks.

To a first order approximation, the relationship between polarity and energy is given by the following expression:

$$\Delta H_i/J \text{ g}^{-1} = -15 \times 10^{-3} ([O_T] \text{ atom}^{-1} \text{ m}^{-2})^{-1} A - 40(A)$$

where  $A$  is the specific external area of the carbon black in  $\text{m}^2\text{g}^{-1}$  derived using the BET or  $\alpha_s$  methods.

The XPS carbon 1s peak envelopes from the blacks all contain a major peak due to C-C bonding of the graphene structures. For the carbons with  $[O_T]$  values  $>4$  atomic %, a prominent peak at a shift of 4.4 eV from this main peak is evident which is consistent with the presence of carboxylic acid groups. This has been confirmed by FTIR and  $pH$  measurement. Thus, in these instances, a significant proportion of the oxygen which contributes to the surface polarity appears to be present as carboxylic acid groups (COOH).

## Conclusions

For non-porous carbon blacks, a quantitative relationship between  $\Delta H_i$  (water) and the spectroscopically measured surface oxygen concentration,  $[O_T]$  is demonstrated. This approach also gives chemical information about the polar surface sites which, for the

higher oxidised carbon blacks are largely COOH groups.

## References

1. Kiselev, A.V. and Kovalera, N.V. *Izvest. Akad. Nauk. SSSR. Khim. Nauk* 995 (trans) 1959.
2. Stoeckli, H.F. and Kraehenbuehl, F., *Carbon*, **19**, 353, 1981.
3. Bradley, R.H. and Rand, B., *Carbon*, **31**, 2, 1993.
4. Stoeckli, H.F., Kraehenbuehl, F. and Morel, D., *Carbon*, **21**, 589, 1983.
5. Bradley, R.H., Sutherland, I. and Sheng, E., *J. Chem. Soc Faraday Trans.*, **91**, 3201, 1995.