

# CORRELATION OF WATER ADSORPTION ISOTHERMS WITH OXYGEN GROUPS ON CARBON BLACK SURFACES

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## Abstract

The adsorption of polar molecules, such as water and alcohols, on carbon surfaces is strongly dependant on specific, hydrogen bonding, interactions which occur with polar sites, usually oxygen functional groups, on carbon surfaces. In this paper we correlate the surface oxygen levels of non-porous carbon blacks, controlled using ozone oxidation and quantified by x-ray photoelectron spectroscopy, with the precise shape of vapour adsorption isotherms and with enthalpies of immersion ( $-h_i$  /mJm<sup>-2</sup>) for water. Resulting Type III adsorption isotherms are displaced to higher adsorption values as the carbon total surface oxygen level [O]<sub>T</sub> (atomic %), measured by XPS, increases. The data are analysed using the Dubinin-Serpinsky equation and the resulting parameter,  $a_0$ , which describes the surface concentration of primary polar adsorption sites, shown to correlate with [O]<sub>T</sub> which also influences both the degree of fit to the equation and the limiting experimental water adsorption value  $a_s$ .

## Keywords:

Water adsorption, non-porous carbon black, surface chemistry, specific interaction, Dubinin-Serpinsky, x-ray photoelectron spectroscopy, immersion calorimetry

## Introduction and Theoretical

In contrast to the non-specific, dispersion force dominated interactions which occur for most organic species, the interaction of polar molecules at carbon surfaces takes place by relatively strong hydrogen bonding at specific sites. These are usually oxygen-containing surface groups located mainly on the edges of the graphene layer-planes of the carbon structure and their surface concentration governs the overall interaction which occurs between carbon surfaces and molecules such as water and alcohols and therefore the qualitative and quantitative characteristics of resulting isotherms (Bradley and Rand, 1987; Bradley and Rand, 1991; Bradley and Rand, 1995; Rodriguez-Reinoso et al., 1997; Lopez-Ramon et al., 1999; Stoeckli and Lavanchy, 2000; Lopez-Ramon and al., 2000; Carrott and al., 2001; Tarasevich and Aksenenko, 2003).

The first formal description of water adsorption on carbon surfaces, based on this mechanistic approach, i.e. where surface polar groups act as primary adsorption centres to which water molecules hydrogen bond forming secondary centres which, at higher relative pressures, nucleate clusters, was presented by Dubinin et al. (1955); their equation, after slight modification (Dubinin and Serpinsky, 1981; Barton et al., 1991) takes the form

$$a = c(a_0 + a)(1-ka)P/P_0 \quad (1)$$

where  $a$  is the equilibrium water adsorption value,  $a_0$  is the surface concentration of primary hydrophilic sites,  $c$  is the ratio of the rate constants for the adsorption and desorption processes (i.e.  $k_{ads}/k_{des}$ ) and  $P$  and  $P_0$  are respectively the equilibrium and saturation water pressures at the adsorption temperature.  $k$  represents the loss of secondary sites due to the cluster formation and its value therefore affects the limiting adsorption capacity,  $a_s$ , which is the value of  $a$  at  $P/P_0 = 1$ .

Using equation (1), and its many derivations and extensions, for example as reviewed by Furmaniak et al. (2005), it is common practice to characterise the surface polarity of carbons from water adsorption data, for example, via  $a_0$  and  $a_s$ . Implicit in these approaches is that the carbon surface possesses some defining property in

terms of hydrophobic or hydrophilic character. However, these terms are mostly used in a relative manner which makes an absolute definition of carbon surface polarity difficult to achieve. Consequently, the precise relationships between the physical structure of carbon surfaces, their absolute concentration of functional groups and the resulting characteristics of equilibrium water isotherms is still not firmly established.

In this paper we describe the adsorption of water vapour on a series of non-porous carbon black surfaces which have the same physical characteristics but increasing levels of oxygen controlled by ozone oxidation and quantified by x-ray photoelectron spectroscopy (XPS). We include data for the adsorption of methanol for comparison and discuss the effects of directly measured surface oxygen levels on the dominant mechanisms of adsorption and on the resulting vapour adsorption isotherms. The observed behaviour is also reflected in calorimetric data for immersion of the carbons in the corresponding liquid phases of the adsorptives which gives an indication of the relative specific and non-specific interactions for each system. The isotherm data are analysed within the framework of the Dubinin equations, in particular, the relationship between the applicability of the Dubinin-Serpinsky equation to the water data, the resulting equation parameters and the correlation with the real surface oxygen level measured by XPS, ( $[O]_T$ /atomic %), is investigated.

## Experimental

A non-porous carbon black N330 (Cabot Co.) has been used as the base material for treatment in order to produce a small range of materials with increasing and controlled surface oxygen levels. N330 has a Cabot quoted surface area of  $77 \text{ m}^2\text{g}^{-1}$  and has been used in several previous adsorption studies where areas of  $80.0 \text{ m}^2\text{g}^{-1}$  ( $\pm 8 \text{ m}^2\text{g}^{-1}$ ) have been reported from nitrogen adsorption isotherm analysis using both BET and  $\alpha_s$  methods (Bradley et al., 1995; Bradley et al., 2002). The material used in this study has an intrinsic surface oxygen level of 1.7 atomic % measured by x-ray photoelectron spectroscopy (XPS). Ozonation of this material in a fluidised bed system of the type described in previous publications (Bradley et al., 2002) for duration times of 5, 10, 30 and 60 minutes leads to surface oxygen levels of 7.3, 8.1, 10.3 and 11.2 atomic %. Adsorption onto a graphitized (2973 K) carbon black, Cabot N234G, has also been investigated. This material which represents a near-limiting, hydrophobic, surface in terms of water adsorption, has a BET surface area ( $S_{\text{BET}}$ ) of  $92 \text{ m}^2\text{g}^{-1}$  ( $\pm 4 \text{ m}^2\text{g}^{-1}$ ), a surface oxygen level of 0.5 atomic % (XPS) and an enthalpy of immersion in water,  $-h_i(\text{H}_2\text{O})$ , of  $28.0 \text{ mJm}^{-2}$ . This material was also used as the reference for the construction of nitrogen  $\alpha_s$  plots. A preliminary study using N234 has also been carried out, this has a  $S_{\text{BET}}$  of  $108 \text{ m}^2\text{g}^{-1}$  a surface oxygen level of 1.5 atomic % and a  $-h_i(\text{H}_2\text{O}) = 68.6 \text{ mJm}^{-2}$ . Vapour adsorption and immersion calorimetry work was carried out using analar grade methanol (Acros Organics) and Toluene (Fisher Scientific).

XPS measurements of carbon surface oxygen levels have been made using a Kratos HSi 5-channel monochromated instrument at a residual vacuum of  $10^{-7}$  Torr with  $AlK\alpha$  radiation of energy 1486.6 eV and with the analyser in FAT mode and carbon samples presented in shallow sample dishes. Surface compositions have been calculated from the areas of elemental peaks, after subtraction of a linear background, using Kratos relative sensitivity factors i.e. 0.25 for C1s and 0.66 for O1s photoelectron peak areas.

Immersion calorimetry has been carried out in a Setaram/Calvet C60 Instrument on samples that had been sealed in glass ampoules after being out gassed to  $10^{-2}$  Torr at room temperature. Enthalpy values,  $-h_i$  ( $\text{mJm}^{-2}$ ) have been calculated using  $S_{\text{BET}}(\text{N}_2)$  values. Adsorption isotherms for water and methanol have been measured using a Hiden/IGA gravimetric system after out gassing to constant weight at 353 K (which was chosen in order to minimise thermal rearrangement and decomposition of surface oxygen groups i.e. significantly below the first thermal desorption peak usually observed in TPD data at 450 K (De La Puente et al., 1997)). Equilibrium adsorption for each point of  $P/P_0$  was defined from kinetic data such that no effective weight changes occurred. Isotherms for nitrogen at 77 K were measured using a Micromeritics ASAP2010 Volumetric apparatus, after out gassing as above, assuming a molecular area of  $0.162 \text{ nm}^2$  and a  $P_0$  value of 987 mbar. Saturated vapour pressures of 218 mbar (methanol) and 42 mbar (water) were derived using the Antoine equation (Ohe, 1976). Nitrogen surface areas have been calculated using the BET and DRK equations and the non-polar interactivity of the surfaces has been probed using immersion in toluene.

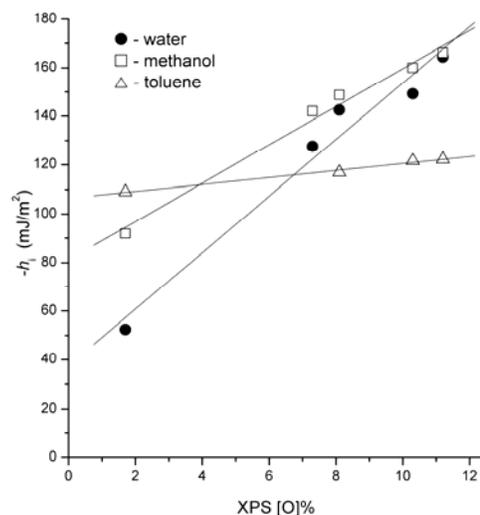
## Results

Data for the adsorption of nitrogen at 77 K by the five carbon blacks analysed using the BET, DRK and Sing's  $\alpha_s$  methods show that whilst the oxygen levels range from 1.7 to 11.2 atomic % there is minimal change in the physical structure of the carbons (Table 1). This is supported by the enthalpy of immersion data for toluene,  $-h_i(\text{Tol})$ , which is non-polar and therefore insensitive to surface chemical changes but might be expected to reveal significant area modifications or the development of surface porosity.

Figure 1, which gives enthalpy of immersion data for water, methanol and toluene as a function of carbon surface oxygen level, shows clearly the dependence of the water and methanol interactions on the carbon polarity in relation toluene. Water, being the most polar probe, exhibits a greater slope than the methanol. At low surface oxygen levels the methanol has the higher values due to the combined effect of the hydrogen bonding with the dispersion interaction of the methyl group. At higher surface oxygen levels the plots for each liquid converge indicating that specific interactions become dominant. It is also possible that, as previously observed for *n*-heptane (Bradley et al., 1995), a decrease in the dispersion interactivity of the carbon surface may also arise as the number of oxygen functionalities increases. This may have two causes: a reduction in the total notional area available for dispersion interactivity coupled with a loss, due to the formation of covalent bonds with oxygen atoms, of electrons which would otherwise be free to participate in dispersion interactions.

**Table 1.** Characteristics of carbon blacks

Carbon	$S_{\text{BET}}(\text{N}_2)$ ( $\text{m}^2 \text{g}^{-1}$ )	$S\alpha_s(\text{N}_2)$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_{\text{DRK}}(\text{N}_2)$ ( $\text{m}^2 \text{g}^{-1}$ )	$[\text{O}]_{\text{XPS}}$ (atom %)	$E_{\text{DRK}}(\text{N}_2)$ ( $\text{kJ Mol}^{-1}$ )	$-h_i(\text{Tol})$ ( $\text{mJm}^{-2}$ )	$-h_i(\text{H}_2\text{O})$ ( $\text{mJm}^{-2}$ )
N330	81.3	82.0	93.6	1.7	4.0	109.0	52.4
N330-5	83.9	82.6	86.8	7.3	4.6	/	127.6
N330-10	86.2	89.1	88.1	8.1	4.6	116.9	142.5
N330-30	89.0	90.0	88.7	10.3	4.6	121.6	149.2
N330-60	88.0	90.2	86.8	11.2	4.7	122.2	164.4



**Figure 1.**  $-h_i$  values as a function of surface oxygen levels for water, toluene and methanol.

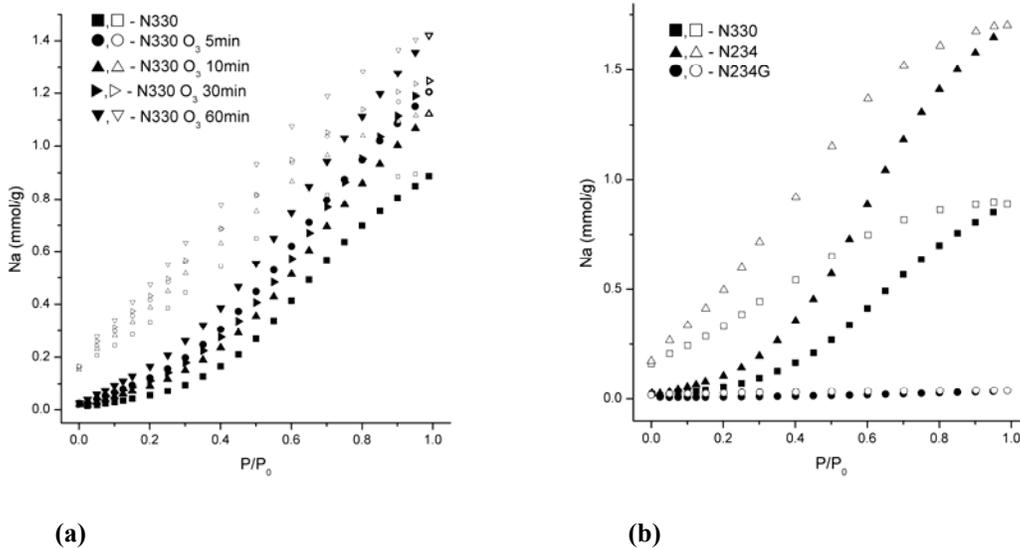
Regression analysis of the data lead to equations 1 to 3 below, the polar and dispersion components of which show clearly the shift from the polar dominated interaction for water compared to the importance of the dispersion component for toluene.

$$-h_i (\text{H}_2\text{O})_{\text{expt}} (\text{mJm}^{-2}) = 38 + 11.6 [\text{O}] \quad (1)$$

$$-h_i (\text{CH}_3\text{OH})_{\text{expt}} (\text{mJm}^{-2}) = 81.2 + 7.85 [\text{O}] \quad (2)$$

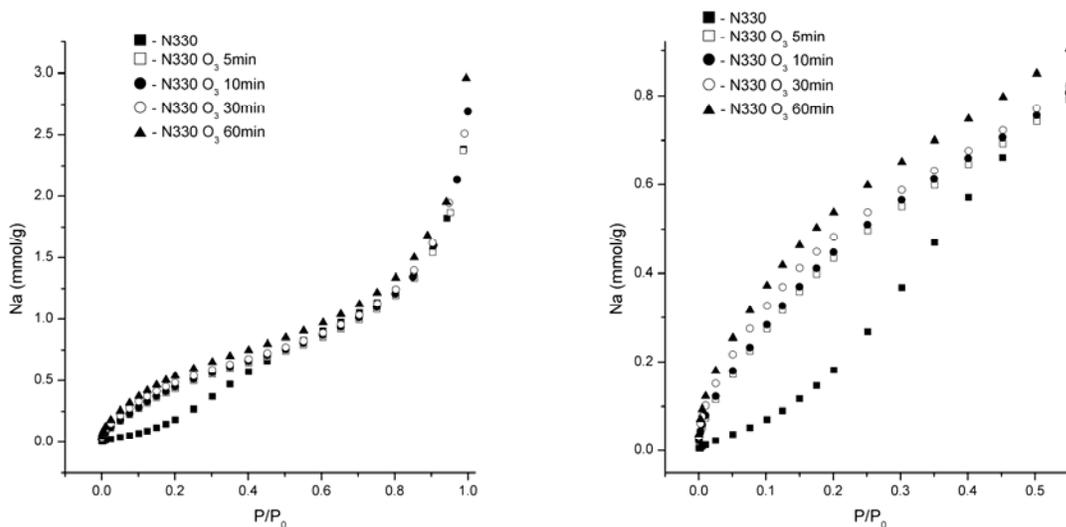
$$-h_i (\text{C}_7\text{H}_8)_{\text{expt}} (\text{mJm}^{-2}) = 106.4 + 1.41 [\text{O}] \quad (3)$$

Adsorption isotherms for water on N330 and the N330 oxidised carbon blacks are all Type III but show significant displacement to higher adsorption uptakes at each  $P/P_0$  value as the surface oxygen level (atomic %) increases as shown in Figure 3(a). Water data for the N234G carbon, which has 0.5 atomic % oxygen is given in Figure 3(b) as an example of a limiting, hydrophobic, surface in terms of water uptake with the N330 (unoxidised) water data included for comparison. Data are also shown for the carbon black N234 which has only a slightly higher surface area ( $S_{\text{BET}} = 108 \text{ m}^2\text{g}^{-1}$ ) than N330 and a similar  $[\text{O}]_{\text{T}}$  value (1.5 atomic % oxygen) but an  $a_s$  value of 1.71 compared to 0.90 for N330. This confirms that the water adsorption process is also influenced by carbon type and structure as well as the total concentration of oxygen centres. This structural aspect might be expected to directly influence the distribution of primary sites on the carbon surface, and thereby their coordination with adsorbing water molecules, and also the entropic contribution to the adsorption process.



**Figure 2.** Water adsorption isotherms at 303 K for (a) N330 and N330 oxidised carbon blacks and (b) N330, N234 and N234G (graphitized) and carbon blacks.

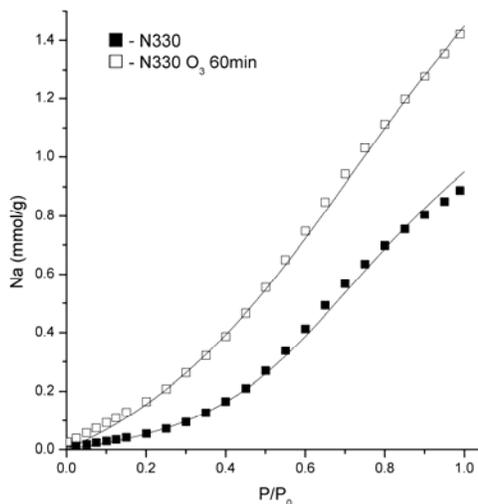
Isotherms for methanol on the unoxidised N330 are Type III but Type II isotherms are observed for the oxidised materials as shown in Figure 3. The change being explained by the additional polar interactions as discussed for Figure 1. Overall, the data confirm the strong specific hydrogen bonding dependence of both adsorptives on the concentration of primary polar sites as reflected by the measured surface oxygen levels. For methanol, the additional interaction changes the isotherm type.



**Figure 3.** Adsorption isotherms for (a) methanol and (b) expanded low pressure domains ( $P/P_0 < 0.5$ ).

The mechanism of adsorption for small polar molecules such as water and methanol has been previously been discussed by a number of workers (Barton et al., 1973; Dubinin and Serpinsky, 1981; Bradley and Rand, 1993; Barton and Evans, 1997). At low pressures, and surface coverage, hydrogen bonding occurs at polar surface groups

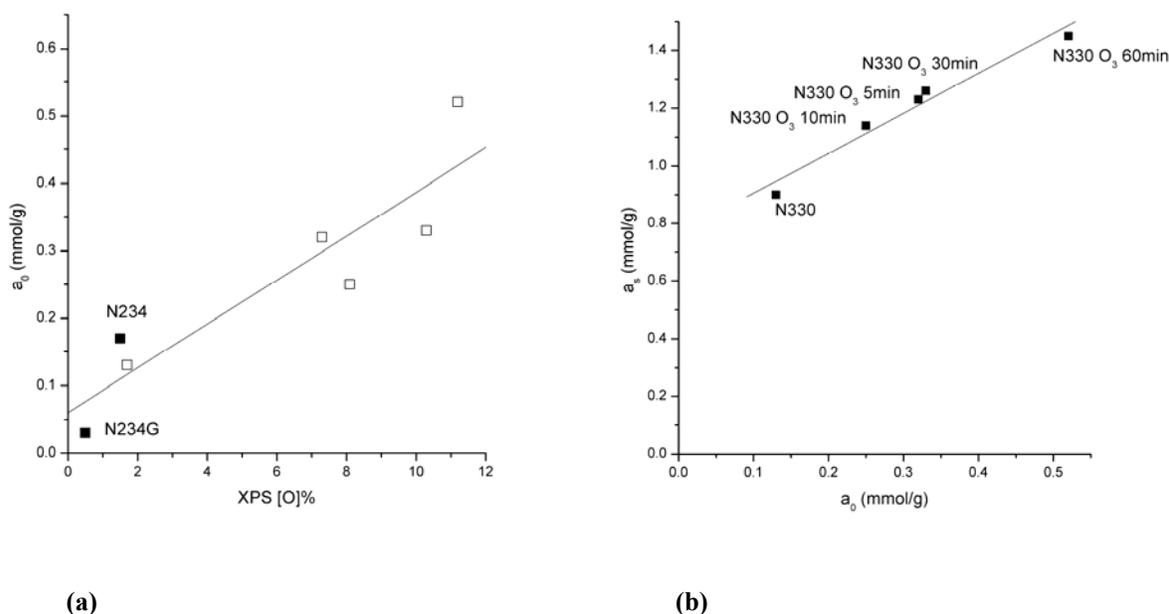
which can be considered as primary adsorption sites. At higher pressures and as surface coverage increases, the molecules adsorbed at primary sites act as secondary sites. The overall process is therefore characterised by the formation of adsorbed “clusters” at chemisorbed oxygen, or other polar sites, followed by the formation of an extended network structure in which the adsorbed polar molecules are constrained. The absolute structure and density of the clusters and the network in relation to liquid water are not currently known. In this situation, and as typified by our data, the isotherm is described by the expression  $\{N \text{ (mmol.g}^{-1})\} = f(P, [O]_{\text{tot}})_T$  where the additional term to the normal isotherm expression  $\{[O]_{\text{tot}}\}$  describes the concentration of polar oxygen groups, for example, as measured here by XPS.



**Figure 4.** Fits of experimental data points to equation (1) solid lines for N330 base material (1.7 atomic % oxygen) and N330 60 min. (11.2 atomic % oxygen).

Water isotherm data have been fitted to the modified DS equation (examples are given in Figure 4 for the least and most oxidised surfaces). This gives a satisfactory description of the adsorption on the N330 material across most of the pressure range but with a slight over estimation of uptake at values of  $P/P_0 > 0.9$ . The later, as discussed for example by Dubinin and Serpinsky (1981) and Barton et al. (1991) being most probably due to the lack of availability of, or access to, the secondary sites at high surface coverage. For the 11.2 atom % oxygen surface a slight underestimation of uptake is observed in the low pressure region of the fit ( $P/P_0 < 1.6$ ) where presumably the primary nucleation process is positively influenced by the high concentration of surface sites.

The resulting values of  $a_0$  are found to increase with  $[O]_T$  as shown in Figure 5 which also contains data for the limiting water uptake,  $a_s$ , as a function of  $a_0$  which clearly demonstrates the dependence of the overall packing density of the adsorbed water on the surface concentration of oxygen atoms (i.e. primary sites).



**Figure 5.** (a) Relationship between  $[O]_T$ , the carbon black surface oxygen level in atomic %, and the primary adsorption site parameter,  $a_0$ , of the DS2 equation (correlation coefficient = 0.92) and (b) the effect of  $a_0$  on the measured limiting water adsorption parameter  $a_s$ .

## Conclusions

XPS has been used to make direct measurements of the surface oxygen levels ( $[O]_T$ /atomic %) of a series of carbon blacks treated using ozone oxidation. Water isotherms are shifted to higher adsorption uptakes as  $[O]_T$  increases. The Dubinin-Serpinsky equation gives a reasonable description of the water isotherm data across much of the pressure range. An overestimation of uptake is observed on the least oxidised N330 carbon (1.7 atomic % oxygen) whereas for N330 carbons of higher oxygen levels (approximately > 10 atomic %) the equation underestimates the adsorption when compared to the experimental uptakes.  $[O]_T$  correlated directly with  $a_0$  of the equation and is also shown to have a direct influence on  $a_s$ .

## References

- Barton, S. S., Evans, M.J.B, Harrison B. H. Surface studies on carbon: Water adsorption on polyvinylidene chloride carbon. *J. Colloid Interface Sci.* 1973; 45: 542-548.
- Barton, S. S. Evans, M. J.B. MacDonald, J. A. F. The adsorption of water vapor by porous carbon. *Carbon* 1991; 29: 1099-1105.
- Barton, S.S, Evans, M.J.B. Adsorption of Water vapour on Nonporous Carbon. *Langmuir* 1997; 10: 4250-4252.
- Bradley, R.H., Rand, B. Adsorption of Alcohols and Water Vapour onto Active Carbons, Proc. Of 18th Biennial Conf. on Carbon. Worcester Mass. Amer. Carbon Soc., 1987; 94-95.
- Bradley, R.H., Rand, B. A Comparison between the Adsorption Behaviour of Nitrogen, Alcohols and Water Vapour toward Active Carbons. *Carbon* 1991; 29: 1165-1172.
- Bradley, R. H., Rand, B. The adsorption of vapours by activated and heat-treated microporous carbons. Part 2. Assessment of surface polarity using water adsorption. *Carbon* 1993; 31(2): 269-272.

- Bradley, R.H., Rand, B. On the Physical Adsorption of Vapours by Microporous Carbons. *J. Colloid Interface Sci.* 1995; 169: 168-176.
- Bradley, R.H., Sutherland, I., Sheng, E. Relationship Between Carbon Black Surface Chemistry and Energy. *J. Chem. Soc. Faraday Trans.* 1995; 91: 3201-3207.
- Bradley, R.H., Daley, R., Le Goff, F. Polar and dispersion interactions at carbon surfaces: further development of the XPS-based model. *Carbon* 2002; 40: 1173-1179.
- Carrott, P., Ribeiro Carrott, M., Cansado, I. Reference data for the adsorption of methanol on carbon materials. *Carbon* 2001; 39: 193-200.
- De La Puente, G., Pis, J.J. *et al.* Thermal stability of oxygenated functions in activated carbons. *Journal of Analytical and Applied Pyrolysis* 1997; 43: 125-138.
- Dubin, M. M., Zaverina, E.D., Serpinsky, V.V. The sorption of water vapour by active carbon. *J. Chem. Soc.* 1955 (part. 2): 1760-1766.
- Dubin, M.M., Serpinsky, V.V. Water vapour adsorption on microporous activated carbons. *Doklady AN SSSR* 1981; 285: 1151-1157.
- Dubin, M. M., Serpinsky, V.V. Letter to the Editor. Isotherm equation for water vapor adsorption by microporous carbonaceous adsorbents. *Carbon* 1981 19(5): 402-403.
- Furmaniak, S. Gauden, P. A. Terzyk, A. P. Wesolowski, R. P. Rychlicki, G. Improving fundamental ideas of Dubin, Serpinsky and Barton – Further insights into theoretical descriptions of water adsorption on carbons. *Annales – Universitatis Mariae Curie – SKŁODOWSKA LUBIN POLONIA* 2005; LX.11, Section AA.
- Lopez-Ramon, M.V., Stoeckli, H.F., Moreno-Castilla, C., Carrasco-Marin, F. On the characterization of acidic and basic surface sites on carbons, by various techniques. *Carbon* 1999; 37: 1215-1221.
- Lopez-Ramon, M.V., Stoeckli, H.F., Moreno-Castilla, C., Carrasco-Marin, F. Specific and Nonspecific Interactions Between Methanol and Ethanol and Active Carbons. *Langmuir* 2000; 16: 5967-5972.
- Ohe, S. in *Computer Aided Data Book of Vapor Pressure; Data Book*. Publishing Co.: Tokyo, Japan: 1976.
- Rodriguez-Reinoso, F., Molina-Sabio, M., Gonzalez, M.T. Effects of Oxygen Surface Groups on the Immersion Enthalpy of Activated Carbons in Liquids of Different Polarity. *Langmuir* 1997; 13: 2354-2358.
- Stoeckli, F., Lavanchy, A. The adsorption of water by active carbons, in relation to their chemical and structural properties. *Carbon* 2000; 38: 475-494.
- Tarasevich, E.V., Aksenenko, E.V. Interactions of Water, Methanol and Benzene Molecules with Hydrophilic Centres on Partially Oxidised Model Graphite Surfaces. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 2003; 215: 285-291.