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which should be used for any reference to this work

Specific and non-specific interactions on non-porous carbon black surfaces

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Abstract

The interactions which occur between methanol, ethanol or propanol and the surfaces of non-porous carbon blacks with increasing levels of oxygen chemistry have been studied using adsorption isotherm analysis and immersion calorimetry. Surface oxygen has been controlled by ozone treatment and characterised using X-ray photoelectron spectroscopy, which gives a direct and quantitative measure of surface composition from first-principles, and has not yet been extensively employed in detailed carbon adsorption studies. Nitrogen adsorption at 77 K and heat of immersion $-h_i$ (mJ m^{-2}) data for toluene, show that the physical structure of the carbon blacks is not modified by ozone treatment. A systematic shift to higher adsorption values, due to increasing specific hydrogen bonding interactions between the alcohol –OH groups and surface oxygen, is observed in all of the alcohol isotherms as the total oxygen content of the carbon surfaces ($[O]_T$/at.%) increases. This effect is most significant for methanol confirming that the mechanism of adsorption is dominated by hydrogen bonding and therefore dependant on the surface concentration of oxygen sites. It is also observed for ethanol and propanol but is less marked due to the increasing non-specific, dispersion, interactions of the alkyl chain with the non-polar carbon surface. This description is in agreement with the data obtained for the specific enthalpies of immersion $-h_i$ (mJ m^{-2}) into the alcohols and into water or toluene which allow a semi-quantitative assessment off the relative polar and dispersion contributions to the overall interactions as functions of both carbon surface oxygen composition and the molecular structure of the alcohols. An overall correlation is observed between adsorption behaviour, $[O]_T$/at.%, the resulting $-h_i$ values and the characteristic energy E (kJ mol^{-1}) of the DRK equation. It is also observed that the values of the affinity coefficient β_{DRK} increase directly as a function of $[O]_T$ indicating that this latter parameter may provide a basis for predicting the adsorption isotherms of certain polar vapours on non-porous carbon surfaces. The effects of carbon surface chemistry on the character of adsorption isotherms, which change from Type III for the base N330 (and for a graphitized carbon black N234G) to Type II for the oxidised N330 materials, is discussed and the resulting effects on the surface area parameters S_{DRK} and S_{BET} (m^2 g^{-1}) are considered.

1. Introduction and theoretical

The interaction between carbon surfaces with most organic molecules is dominated by dispersion forces and is therefore non-specific. In contrast, limited but relatively strong specific interactions may take place through hydrogen bonding between polar, or polarizable, molecules and specific sites on the carbon surface. The latter are usually oxygen-containing surface groups located mainly on the edges of the graphene layer-planes of the carbon structure. This is the case for water and to some extent for alcohols, as discussed by a number of workers [1–9]. In the case of non-porous carbons, direct evidence of this is provided by the change in the specific enthalpy of immersion $-h_i$(water) (mJ m^{-2}), which increases linearly with the surface oxygen content from the lower limit of approximately 35 mJ m^{-2} which defines the non-specific (dispersion) interaction of an oxygen free carbon. The same type of

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behaviour does of course occur for the interactions of polar molecules with porous carbons but, in this instance, the precise relationship is much more difficult to quantify since complications arise due to: the positions of the polar sites, which may be located within the complex pore structure of the carbon, making them less readily available to direct interrogation, for example, by spectroscopic means; and kinetic effects, which may arise due to the slow diffusion of water in hydrophobic regions of microporosity.

An important issue in this field is the correlation between the surface chemistry of carbon, the precise structure of the adsorptive and the character of the resulting adsorption isotherm. When firmly established this will allow predictions of adsorption behaviour on the basis of simple structural and chemical parameters. As shown by Stoeckli [5,7] this can be achieved for microporous carbons within the framework of Dubinin's theory of adsorption and its extension to immersion calorimetry, where the latter provides complementary information on the specific interactions. In this respect coherent descriptions have been offered for the water isotherm and the isotherms of methanol and ethanol using the classical Dubinin–Radushkevich approach in which the so called affinity coefficient (β), which is normally calculated using the ratio of physical parameters, for example the molar volume (M_V) of the adsorbate, (i) i.e. (M_{Vi}) to that of a suitable reference (M_{Vref}) such that $\beta(i) = M_{Vi}/M_{Vref}$, is shown to vary with the level of the specific interactions and hence the surface chemistry of the carbon.

For non-porous surfaces and in particular graphitized carbons, adsorption can be described by an alternative to the classical Dubinin–Radushkevich equation [10,11], namely the Dubinin–Radushkevich–Kaganer (DRK) equation [12] in which the equilibrium adsorption volume W ($cm^3\ g^{-1}$) and the micropore volume W_0 ($cm^3\ g^{-1}$) of the former expression are replaced with the terms N_a and N_{am} and the term E_{DRK} equates to the characteristic energy of the first monolayer rather than micropore filling. In its modern formulation and for relatively low pressures, i.e. in the sub-monolayer region, the equation takes the form

$$N_a = N_{am}(\mathrm{DRK}) \exp[-(A/E_{DRK})^2] \quad (1)$$

where N_a is the amount adsorbed at temperature T and pressure P and N_{am} is the monolayer capacity. The quantity $A = \mathrm{RTln}(P_0/P)$ is the adsorption potential $-\Delta G$, also used in the classical DR equation for the theory of volume filling of micropores (TVFM) [10,11], P is the equilibrium pressure, P_0 the saturated vapour pressure at T.

With respect to the BET approach [13], for many non-porous surfaces Eq. (1) suffers from the shortcoming that N_{am}(DRK) and the corresponding surface area S_{DRK} ($m^2\ g^{-1}$) are frequently different from N_{am}(BET) and S_{BET} obtained from the same isotherm, but at higher relative pressures ($0.05 < P/P_0 < 0.30$–0.35). As discussed by Hugi-Cleary et al. [14], this is likely to be because the exponent 2 corresponds to a distribution of the adsorption energy (surface heterogeneity) which does not reflect reality for a given solid. Therefore it was suggested that the classical DRK Eq. (1) might be more usefully replaced by a flexible expression with a variable exponent n and by accepting that N_{am}(BET) corresponds to the real surface area of a non-porous solid but it should be noted that, as discussed by Stoeckli and Centeno [15], this is not necessarily the case for porous solids. It then follows, that a reasonable working equation is

$$N_a = N_{am}(\mathrm{BET}) \exp[-(A/E_{DRK})^n] \quad (2)$$

In the case of graphitized carbon blacks, a value of $n \sim 1.8$, which is not too far from the classical DR value $n = 2$ has been found to be appropriate. Under these conditions and as a first and good approximation, one may use as a working expression

$$N_a = N_{am}(\mathrm{BET}) \exp[-(A/E_{DRK})^2] \quad (3)$$

As shown earlier [16] for the adsorption of non-specific vapours such as C_6H_6, N_2, CCl_4, CH_2Cl_2 and CO_2 onto microporous carbon blacks XC-72 and XC-72-16, one obtains relatively good linear logarithmic plots for the low pressure, monolayer, data with the corresponding characteristic values of E_{DRK}. It also appears, from data obtained at different temperatures, that the principle of temperature-invariance of E_{DRK}, required by Dubinin's theory, is fulfilled. On the other hand, it appears that the affinity coefficient (β) of a vapour (i) derived for a non-porous carbon surface using the DRK method i.e. β_{DRK}(i) and given by the following expression:

$$\beta_{DRK}(\mathrm{i}) = E_{DRK}(\mathrm{i})/E_{DRK}(C_6H_6) \quad (4)$$

where E_{DRK}(i) is the characteristic energy derived from the slope of the DRK plot for the vapour (i) and $E_{DRK}(C_6H_6)$ is the energy for the reference vapour which is usually chosen as benzene; is close to, but not necessarily exactly equal to, the value found by Wood for the volume filling of micropores [17]. This means that keeping benzene as the reference requires the actual determination of its isotherm, as well as the isotherms of other vapours (nitrogen, alcohols, etc.). Hence, if one chooses nitrogen adsorbed at 77 K as the reference instead of benzene, which may be convenient since it is frequently used for adsorption characterisation studies and therefore reference isotherms are often readily available, then $E_{0DRK} = E_{DRK}(C_6H_6)$ is not necessarily given by the simple expression $\{0.33E_{0DRK}(N_2)\}$ i.e. by assuming that $\beta_{nitrogen} = 0.33$.

From the above, it is tempting to correlate β_{DRK} for alcohols, or indeed other polar adsorptives, adsorbed on non-porous carbons with the amount of surface oxygen $[O]_T$ measured indirectly by TPD or directly by using X-ray photoelectron spectroscopy (XPS). By so doing, it may become possible to predict the adsorption isotherm for a specific system on the basis of Eqs. (1)–(3) with the help of the parameters N_{am}(BET), E_{0DRK} and the function $\beta_{DRK}(\mathrm{alcohol}) = f([O]_T)$.

In this paper we describe the adsorption of the alcohols methanol, ethanol and propanol 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 XPS. We show that this approach allows a systematic study of the effects of surface oxygen chemistry 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 or in water 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 classical BET and the Dubinin–Radushkevich–Kaganer equations, as applied to adsorption on non-porous carbon surfaces, and the degree of fit assessed. Of particular interest in this work are the resultant values of the affinity coefficients (β_{DRK}) for the alcohols on the different surfaces which have, as mentioned above, previously been observed to change with surface polarity but for which no quantitative relationship with directly measured surface oxygen currently exists. Water has been used as a probe for immersion calorimetry in this work, but the more complex relationships between water vapour adsorption and the effects of changing carbon black surface oxygen levels have also been investigated. The findings of this study will be reported shortly in a separate publication.

2. Experimental

The 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 $m^2 g^{-1}$ and has been used in several previous adsorption studies where areas of 80.0 $m^2 g^{-1}$ (± 8 $m^2 g^{-1}$) have been reported from nitrogen adsorption isotherm analysis using both BET and α_s methods [18,19]. The material used in this study has an intrinsic surface oxygen level of 1.7 at.% measured by X-ray photoelectron spectroscopy (XPS). Ozonation of this material in a fluidised bed system of the type described in previous publications [19] for duration times of 5, 10, 30 and 60 min leads to surface oxygen levels of 7.3, 8.1, 10.3 and 11.2 at.%. Adsorption of the alcohols onto a graphitized (2973 K) carbon black, Cabot N234G, has also been investigated. This material has a BET surface area of 92 $m^2 g^{-1}$ (± 4 $m^2 g^{-1}$), a surface oxygen level of 0.5 at.% (XPS) and an enthalpy of immersion in water of $-h_i(H_2O) = 28.0$ mJ m^{-2}. This material was used as the reference for the construction of the α_s plots. Vapour adsorption and immersion calorimetry work was carried out using analar grade liquids: methanol (Acros Organics), ethanol, propan-2-ol and Toluene (Fisher Scientific). Toluene was chosen as a non-polar probe with which to carry out immersion in preference to benzene which is a known carcinogen.

XPS measurements have been made using a Kratos HSi 5-channel monochromated instrument at a residual vacuum of 10^{-8} Torr with Al $k\alpha$ 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 (absolute error of $\pm < 10\%$).

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, $-h_i$ (mJ m^{-2}) have been calculated using $S_{BET}(N_2)$ values. Adsorption isotherms for methanol, ethanol and propanol at 303 K 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 [20]). 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 nm^2 and a P_0 value of 987 mbar. For the alcohols, molecular areas of (0.180 nm^2) methanol (0.229 nm^2) ethanol and (0.274 nm^2) propanol have been calculated using the method described by Gregg and Sing [21] and respective saturated vapour pressure (P_0) values of 218, 105, 78 mbar derived using the Antoine equation [22]. Isotherm data were fitted to the classical BET equation or to the DRK Eq. (1) the later using a value of $n = 2$.

3. Results and discussion

Fig. 1a shows isotherms for the adsorption of nitrogen a 77 K by the five carbon blacks and Fig. 1b contains corresponding analyses obtained using the α_s method [23,24]. As can be seen from Table 1 whilst the oxygen levels range from 1.7 to 11.2 at.% there is minimal change in the physical structure of the CBs as reflected by S_{BET} or $S\alpha_s$ ($m^2 g^{-1}$). Since the observed values of $-h_i$(Tol) do not change significantly across this series it is concluded that neither nitrogen or toluene is sensitive the oxygen chemistry changes induced in the carbon black surfaces by the ozone treatment. The absolute values of $-h_i$(Tol) observed are similar to those measured previously for benzene [15] and for *n*Heptane [18]. Previous calculations of surface free energy values from nitrogen spreading pressures [18,25] for non-porous carbons of differing surface oxygen levels have also shown that nitrogen adsorption is not sensitive to changes in surface chemistry. In those instances the absolute free energy values where 100–110 mJ m^{-2} and therefore similar to the $-h_i$(Tol) values shown. Hence we propose that nitrogen may conveniently be used a the reference vapour in place of benzene, for example in evaluating β_{DRK}(alcohol) using Eq. (4).

As shown in Fig. 2a the experimentally determined $-h_i(H_2O)$ values increase in direct proportion to the surface oxygen levels of the CBs which is a marked contrast to the $-h_i$(Tol) figures. The water values are close to those previously reported for a wide range of carbon blacks of various types and levels of oxidation measured by XPS [19] and are also consistent with studies by other authors based on pH_{pzc} and temperature programmed desorption of oxygen complexes [5,26,27].

Regression analysis of Fig. 2a, for water and toluene, leads to the following which is consistent with previously reported relationships [3,19,28,29]:

$$-h_i(H_2O)_{expt}\ (\text{mJ m}^{-2}) = 37.6 + 11.61\ [O]_T \quad (5)$$

$$-h_i(C_7H_8)_{expt}\ (\text{mJ m}^{-2}) = 106.4 + 1.41\ [O]_T \quad (6)$$

Adsorption isotherms for methanol, ethanol and propanol, given in Fig. 3, are Type III for the untreated N330 and

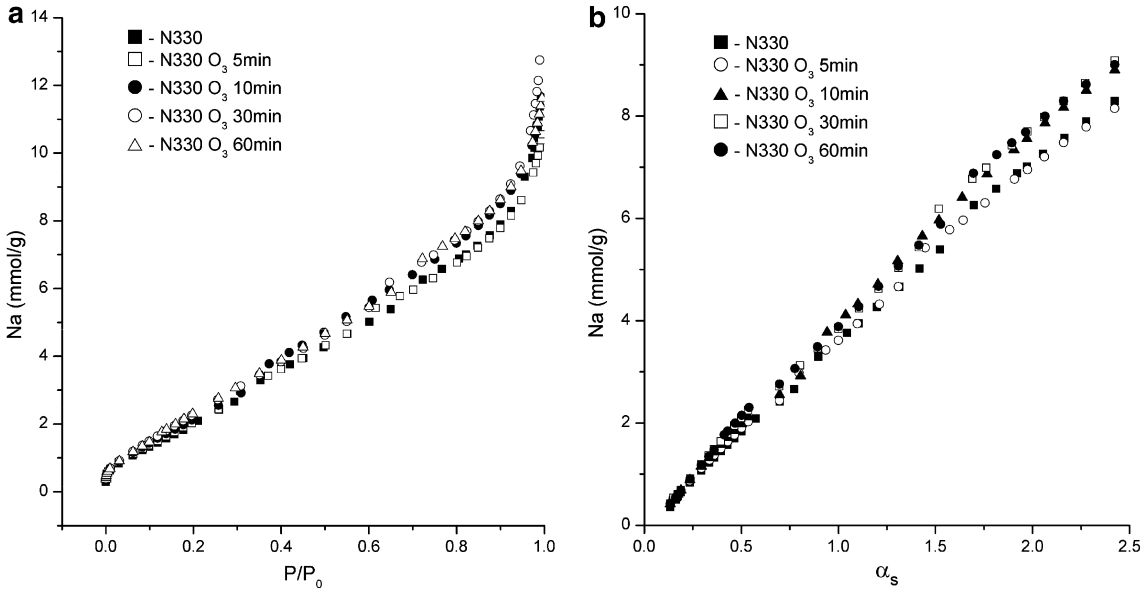

Fig. 1. (a) Nitrogen adsorption isotherms at 77 K for carbon blacks and (b) corresponding α_s plots.

Table 1
Characteristics of carbon blacks

Carbon	S_{BET} (N_2) ($m^2\ g^{-1}$)	$S\alpha_s$ (N_2) ($m^2\ g^{-1}$)	S_{DRK} (N_2) ($m^2\ g^{-1}$)	$[O]_T$ (at.%)	E_{DRK} (N_2) (kJ mol^{-1})	$-h_i$(Tol) (mJ m^{-2})	$-h_i(H_2O)$ (mJ m^{-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

Nitrogen surface areas from BET (S_{BET}), α_s ($S\alpha_s$) and DRK (S_{DRK}) methods, total surface oxygen level from XPS $[O]_T$/at.% and enthalpy of immersion for toluene $-h_i$(Tol) and water $-h_i(H_2O)$.

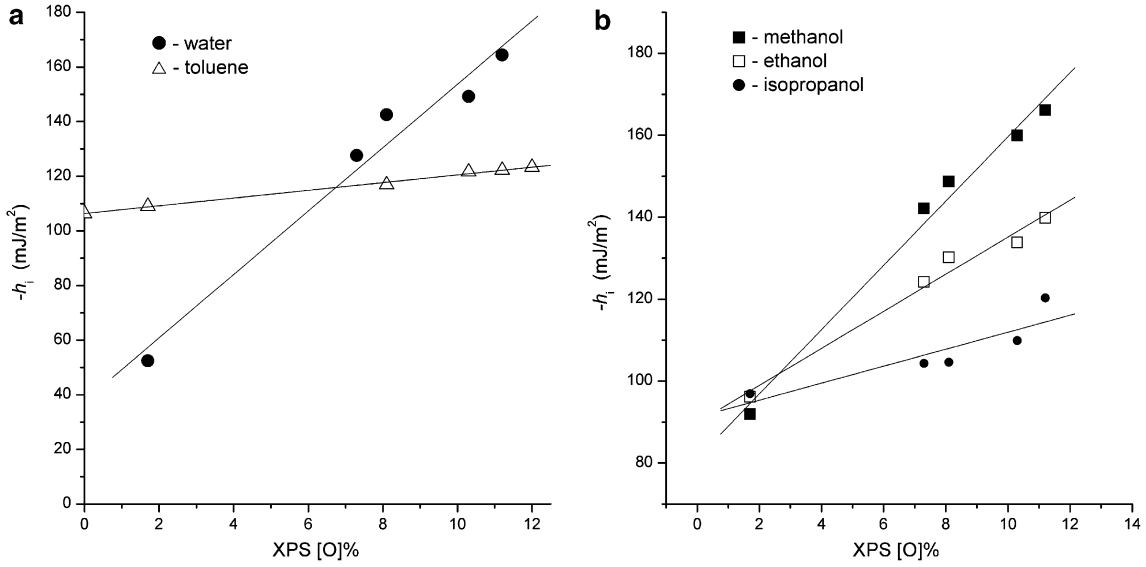

Fig. 2. (a) $-h_i$ values as a function of surface oxygen levels for water and toluene and (b) for methanol, ethanol and isopropanol.

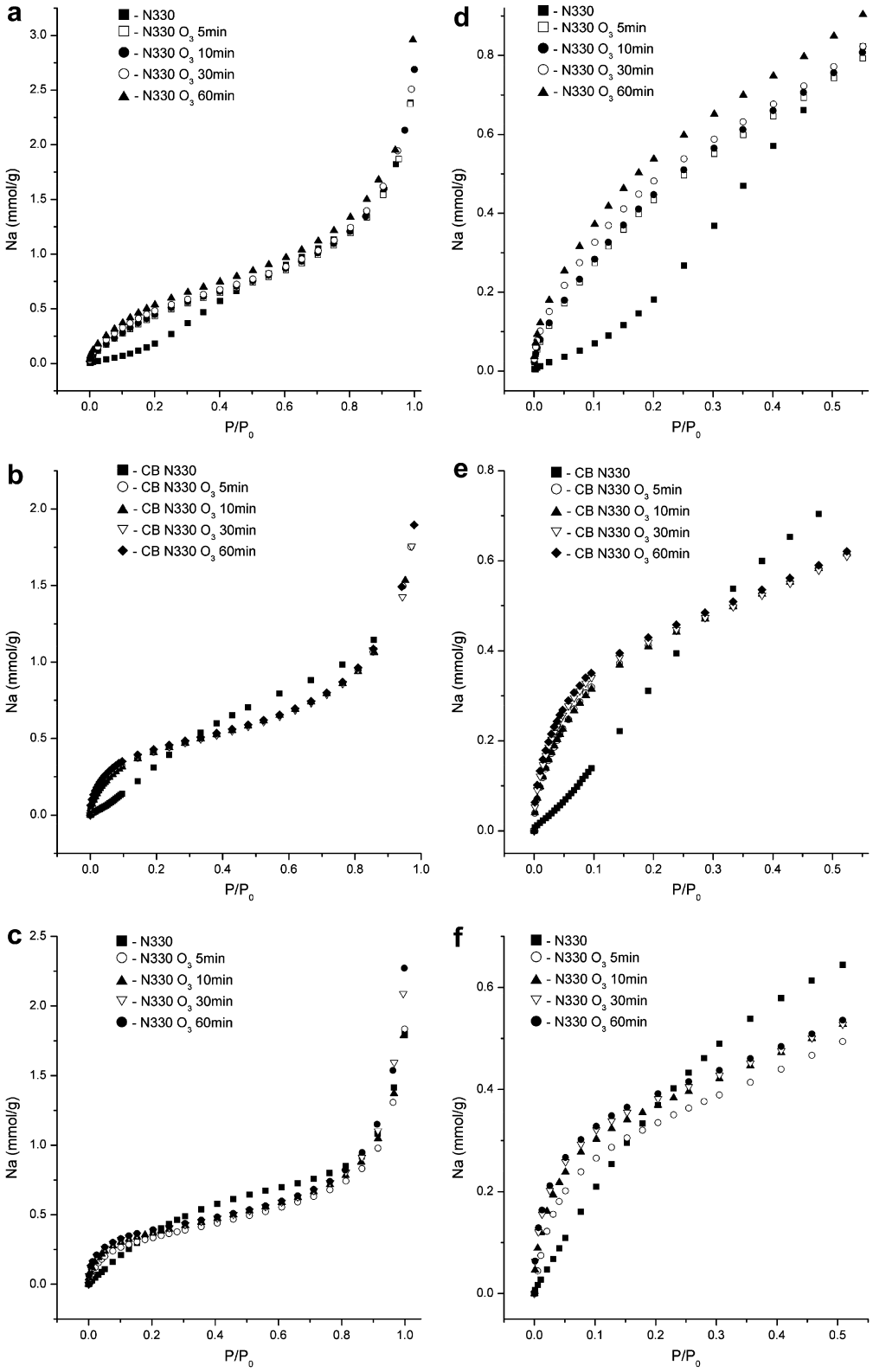

Fig. 3. (a, b and c) Adsorption isotherms for methanol, ethanol and isopropanol including (d, e and f) expanded low pressure domains ($P/P_0 < 0.5$) showing displacement due to increasing specific interactions in sub-monolayer region and isotherm convergence near monolayer capacity.

Type II for the oxidised materials. Fig. 3a–c shows clearly that the Type II isotherms are displaced sequentially to higher adsorption values as the CB surface oxygen levels increase. From Fig. 3(d,e,f), which show the low pressure ($P/P_0 < 0.6$) data expanded for clarity, it is seen that displacement occurs for all three adsorptives as a function

of CB oxidation but is most marked for methanol where the relative contribution of the polar –OH group is most prominent compared to the dispersion interaction of the alkyl chain. The P/P_0 values at which the displaced isotherms converge with the isotherm of the base N330 are 0.5 and 0.3 for methanol and ethanol which correspond to areas of 77 and 69 $m^2\,g^{-1}$ (for propanol the situation is a little more complex since the convergence of individual curves takes place over a range of P/P_0 values which equate to areas of 66–70 $m^2\,g^{-1}$) but overall, the values confirm that the displacements are confined within the monolayer capacity for each adsorptive and therefore relates directly to specific interactions with carbon surface groups.

Table 2 shows the increases in $-h_i$(alcohol) which result from the increases in carbon black surface oxygen. The greater effect is observed for methanol whose smaller molecular size allows a higher proportion of –OH interactions per unit area of surface and, as shown in Fig. 2b, the slopes of the plots decrease as the alcohol series is ascended. From regression analysis of the experimental data we obtain the expressions

$$-h_i(CH_3OH)_{expt}\ (mJ\,m^{-2}) = 81.2 + 7.85\ [O]_T \quad (7)$$

$$-h_i(C_2H_5OH)_{expt}\ (mJ\,m^{-2}) = 89.9 + 4.53\ [O]_T \quad (8)$$

$$-h_i(C_3H_7OH)_{expt}\ (mJ\,m^{-2}) = 91.2 + 2.07\ [O]_T \quad (9)$$

The limiting values between 80 mJ m^{-2} and 92 mJ m^{-2} correspond ideally to the non-specific, dispersion, interaction between the alcohols and a non-oxidised carbon surface. The difference can easily be ascribed to the higher proportion of oxygen per unit surface area in the case of CH_3OH and the fact that carbon shows less affinity for oxygen than for organic groups. As the alkyl chain length increases this value tends toward that of 100–110 mJ m^{-2} obtained for pure hydrocarbons such as benzene, toluene and hexane as mentioned above and the contribution from specific interactions with oxygen groups decreases. Comparison of the relative terms in the expressions given in Eqs. (5)–(9) shows clearly the systematic change from hydrogen bonded dominated interactions for water through to non-specific, dispersion dominated, for toluene. Consistent with the enthalpic data and the displacement of the adsorption isotherms, the BET C values increase with surface polarity (within the ranges 9–16 for methanol and 31–56 for ethanol and 41–99 for propanol).

Plotting the isotherm data for nitrogen and the alcohols in the form of Eq. (1) leads to the plots given in Fig. 4 where (a) confirms that the nitrogen data coincide across all of the pressure range studied except for a very small deviation observed for the three lowest pressure points measured on the base material (see later) and consequently the resulting S_{DRK}(nitrogen) and E_{DRK} values change little across the series of carbons as shown in Table 1 . The alcohols, Fig. 4b–d) all superimpose in the high pressure, low adsorption potential, regions but reflect clearly the effects of the surface chemistry i.e. the differing levels of specific interactions, in the low pressure (high potential) sub-monolayer domains which lead to the S_{DRK} values given in Table 2. The increase in uptakes due to surface oxidation, seen in Fig. 3 as positive displacement of the initial regions of the isotherms, and observed as a decrease of slope in the low pressure regions of the DRK plots, results in values of E_{DRK}(alcohols) which increase with carbon surface polarity as shown in Table 2. We note that the overall linearity of the plots is variable and the E_{DRK} values are given only for comparative purposes and do not relate directly to those derived using the classical form of the equation for micropore filling. For methanol on the base N330 material the non-linearity of the data is consistent with the relatively weak non-specific interaction of the alkyl group coupled with the low level of surface oxygen and hence specific interactions with the polar –OH group of the methanol as described by Carrott [8]. Hence, the isotherm is effectively type III in character but with a slight positive inflexion in the P/P_0 region 0.4–0.5 as the adsorbate–adsorbate hydrogen bonding becomes significant. Generally, the low pressure linearity of the DRK plots improves as the carbon surface oxygen is increased and the initial region of the isotherm (Fig. 3a and d) becomes concave to the pressure axies i.e. changes to type II. The degree of linearity and low pressure fit improves for ethanol and propanol reflecting the tightening of the isotherm knee.

Turning to the surface areas S_{BET} and S_{DRK} (Table 2) we see that, as previously observed [8] for both methods the alcohol values are lower than those derived using the nitrogen data. For methanol, S_{BET} is always higher than S_{DRK} but the latter increases markedly as a function of surface oxygen i.e. as the number of specific adsorption sites increases. For ethanol and propanol the values for S_{BET} are lower than those for S_{DRK} but the differences are less

Table 2
Surface area (BET and DRK), characteristic energy E_{DRK} and enthalpy parameters from alcohol data

Carbon	Methanol				Ethanol				Propanol			
	S_{BET} ($m^2\,g^{-1}$)	S_{DRK} ($m^2\,g^{-1}$)	E_{DRK} (kJ mol^{-1})	$-h_i$ (mJ m^{-2})	S_{BET} ($m^2\,g^{-1}$)	S_{DRK} ($m^2\,g^{-1}$)	E_{DRK} (kJ mol^{-1})	$-h_i$ (mJ m^{-2})	S_{BET} ($m^2\,g^{-1}$)	S_{DRK} ($m^2\,g^{-1}$)	E_{DRK} (kJ mol^{-1})	$-h_i$ (mJ m^{-2})
N330	–	–	8.4	91.9	–	–	7.4	96.1	–	–	7.4	96.9
N330-5	52.9	24.9	11.0	142.1	49.9	69.7	8.6	124.2	47.9	67.7	8.8	104.3
N330-10	54.0	26.1	11.1	148.7	51.0	67.8	8.8	130.2	51.4	66.4	10.5	104.6
N330-30	52.0	30.6	11.6	159.9	49.8	69.0	9.4	133.8	51.9	67.9	11.3	109.9
N330-60	57.4	36.0	11.7	166.1	50.6	69.9	9.7	139.8	53.1	69.2	11.5	120.3

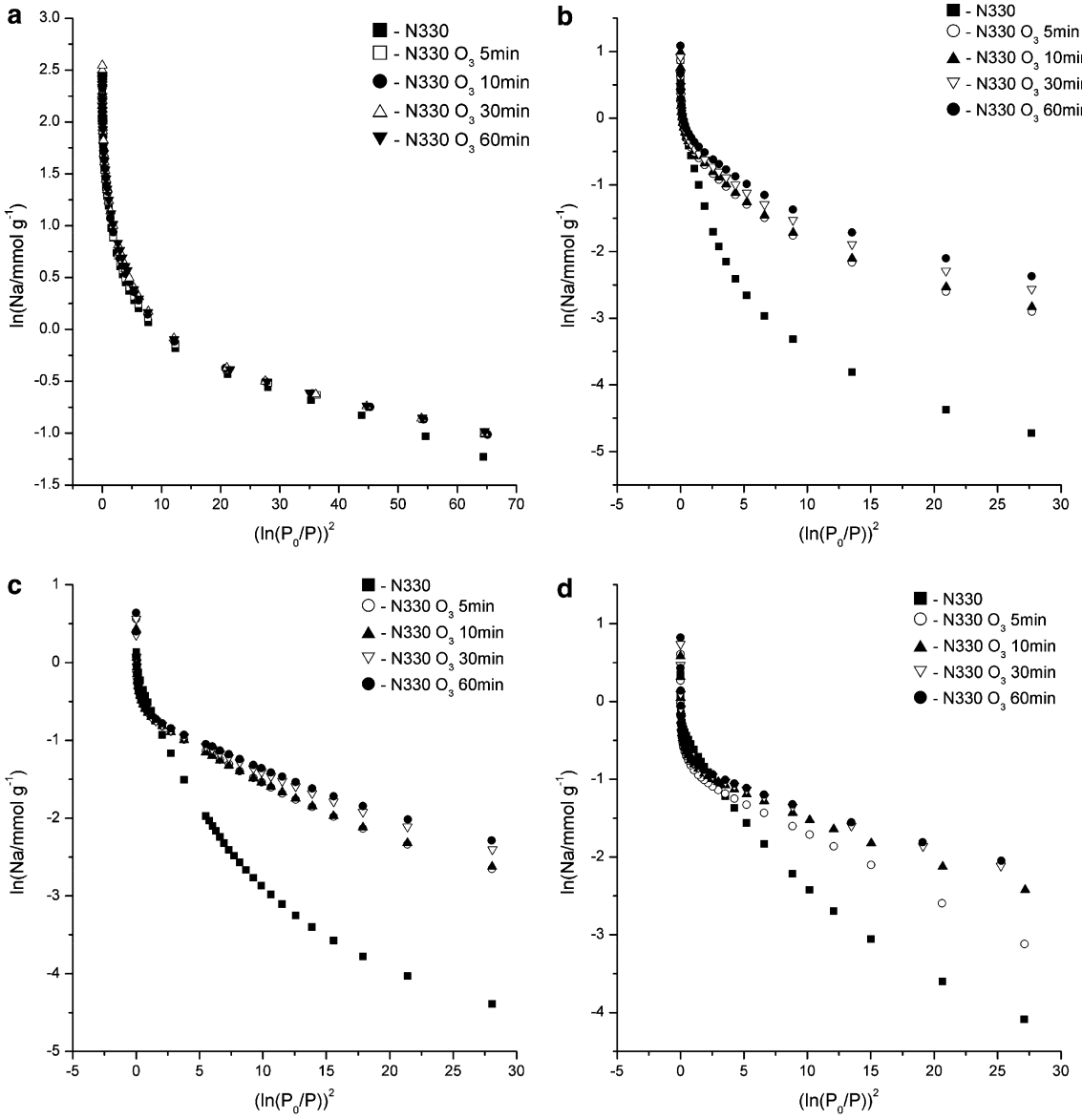

Fig. 4. DRK plots for the adsorption of (a) nitrogen at 77 K and (b) methanol (c) ethanol and (d) isopropanol at 303 K. *Note*: marked differences in the low pressure ($\ln(P_0/P)^2 > 5$) adsorption of the alcohols due to specific interactions with carbon surface groups.

and the S_{DRK} values are, within error, constant for each adsorptive and are not influenced by the surface chemistry changes of the carbon showing the influence of non-specific interactions of the alkyl chains on the adsorption process.

The work of Carrott [8] indicates that the adsorption of methanol onto carbon blacks at low pressures is significantly influenced by hydrogen bonds which form with polar groups on the carbon surface and that when the levels of surface oxygen are low the adsorption of methanol is limited. Our results confirm this in that firstly the methanol adsorption we observe on untreated N330, which has 1.7 at.% oxygen, yields an isotherm which is effectively Type III in character whilst the adsorption of methanol onto the N234G graphitized carbon black, which has 0.5 at.% oxygen but is of course structurally distinct from the N330, adsorbs even less methanol at low pressures and hence behaves in a similar way to the Sterling FT graphitized black reported in [8]. Secondly, our results show clearly that as the surface oxygen concentrations of the carbon black increase then the methanol isotherms are displaced to higher adsorption values such that their initial, submonolayer, regions become concave toward to pressure axis, they become type II in character and are differentiated according to the oxygen level of the carbon surface. It is of note from Table 2 that the values obtained for S_{BET} for methanol are significantly lower than the true surface area of the N330(80 $m^2\ g^{-1}$) for all of the oxygen levels studied whilst those values derived for S_{DRK} are lower still but actually increase with the surface oxygen level. Whilst neither equation provides a coherent description of the methanol data it is intriguing that the DRK method, which places emphasis on the extreme low pressure data,

produces areas which reflect the increase in uptake as a function of carbon surface polarity.

Carrott has argued [8] that the mechanism of methanol adsorption on carbon blacks is similar to that which has been discussed by a number of workers, for example [30–33] for water in that at low pressures, and surface coverage, hydrogen bonding occurs between methanol and polar surface groups which can be considered as primary

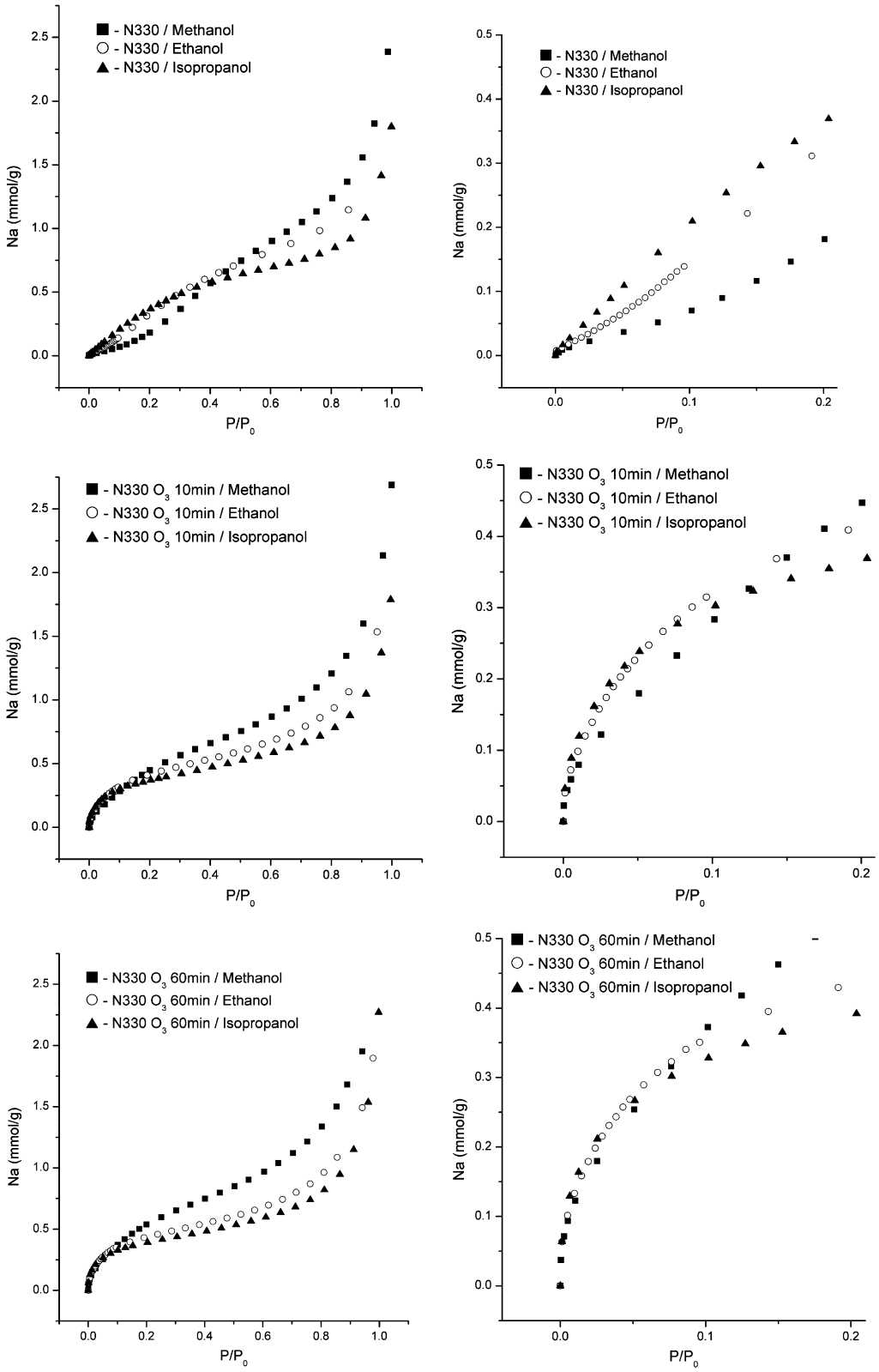

Fig. 5. Alcohol isotherms plotted on N330, N330 (10 min) 8.1 at.% oxygen and N330 (60 min) 11.2 at.% oxygen showing effects of adsorbate chemistry.

adsorption sites. At higher pressures and as surface coverage increases, the methanol adsorbed at primary sites acts 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 although the absolute structure and density of the clusters and the network in relation to liquid methanol are, as is also the case for water, not currently known. In this situation, and as typified by our data, the isotherm is described by the expression $\{\text{Na (mmol g}^{-1}) = f(P,[\text{O}]_{\text{tot}})_{\text{T}}\}$ where the additional term to the normal isotherm expression $\{[\text{O}]_{\text{tot}}\}$ describes the concentration of polar oxygen groups, for example, as measured here by XPS. Since specific interactions occur at fixed sites whilst the non-specific dispersion forces occur over the geometric mean of the surface, resulting in a mobile adsorbed layer, the entropic contribution to the adsorption process is likely to be significantly more important in the former situation where the adsorbed layer has greater 'structure'. For the ethanol and propanol, although the hydrogen bonding effect becomes less dominant as the emphasis changes from specific to non-specific interaction with increasing alkyl chain length, its effects are still clearly evident in the isotherm data. In these two instances the values obtained for S_{BET} are still low compared to the nitrogen values but the S_{DRK} values are significantly increased (to between 66.4 and 69.9 $\text{m}^2\,\text{g}^{-1}$) in relation to the methanol figures.

Figs. 3 and 4 show the effects of the *adsorbent* on the alcohol isotherms i.e. that increasing the surface oxygen levels of the carbons leads to systematic increases in the hydrogen bonding interactions and marked differences in sub-monolayer regions of the isotherms for the individual alcohols. In terms of the *adsorbate* effects, when the data for the three alcohols on each carbon are plotted the isotherms are differentiated only for the base N330 material (1.7 at.% oxygen) as shown in Fig. 5a. Here, the initial, sub-monolayer, region of the methanol curve is convex to the pressure axis i.e. it behaves rather like water, which is indicative of a relatively weak overall interaction whilst the propanol isotherm is concave to the pressure axis indicating a stronger interaction. The ethanol appears to be intermediate in behaviour in this case. The limiting behaviour for an oxygen free surface is provided (Fig. 6) by adsorbing the alcohols onto a graphitized carbon black (N234G) which shows clearly that low pressure data for all three alcohols follow the pressure axis indicating that specific interactions play a significant role in the initial stages of adsorption for these adsorbates.

On each of the other carbons i.e. where the oxygen levels are higher (example are given in Fig. 5b and c for 8.1 and 11.2 at.% oxygen containing surfaces) the isotherms for the three alcohols coincide in the submonolayer regions and have positive curvature to the pressure axis showing that the *adsorbate* chemistry has a less significant influence on the isotherm character for adsorbents with appreciable surface oxygen levels. The isotherms are still differentiated in the multilayer regions as a result of differing adsorbate–absorbate interactions which are strongest for methanol. Examples of this behaviour are given for the three alcohols on the N330 base material (1.7 at.% oxygen) and the 11.2% material in Fig. 5.

From Figs. 3 and 4 it follows that the β_{DRK} values will be sensitive to the surface chemistry of the carbon, and will therefore differ from those derived assuming a single liquid density for the adsorbed phase, which is indeed confirmed by the experimental data as shown in Fig. 7 which shows the direct relationship between β_{DRK}(alcohols) values obtained for methanol, ethanol and propanol using

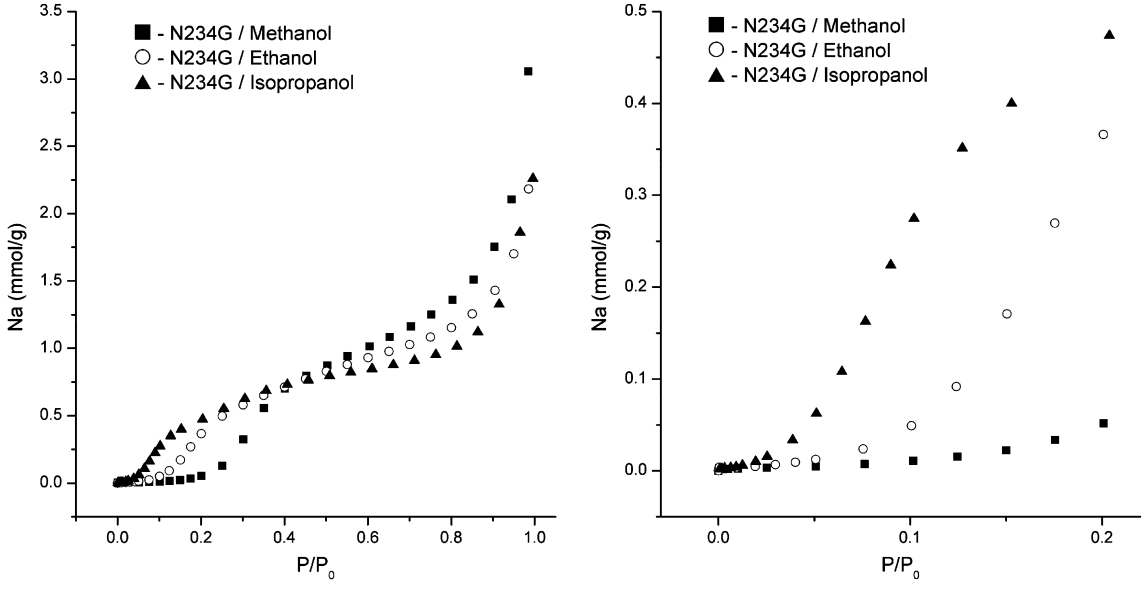

Fig. 6. Alcohols adsorbed on graphitized carbon black N234G showing type III/V character of initial regions of isotherms.

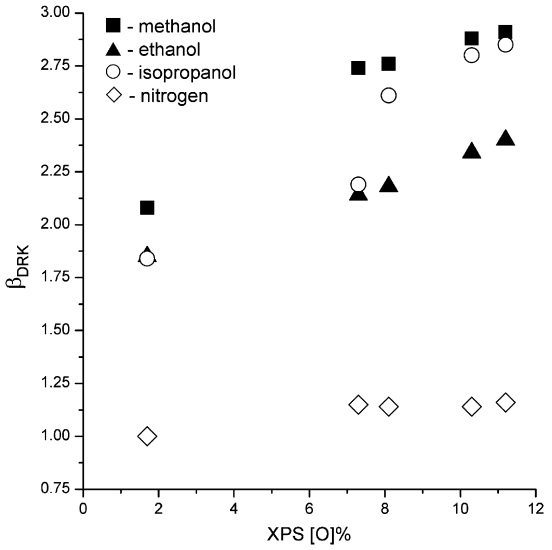

Fig. 7. Values of β_{DRK}(alcohols) (with N_2 as reference) as a function of total surface oxygen $[O]_T$/at.%.

nitrogen as the non-polar reference adsorptive i.e. by substituting $E_{DRK}(N_2)$ into Eq. (4) in place of $E_{DRK}(C_6H_6)$, and $[O]_T$ from XPS measurements. We note in this respect a very slight decrease in slope of the nitrogen DRK plots for the oxidised carbons relative to the base material which leads to a β value of 0.38 rather than 0.33 for the nitrogen reference as predicted in Section 1.

Since β_{DRK} appears to be available from one-off direct XPS measurements of carbon surface compositions, it seems reasonable to assume that this approach may, in the future, prove helpful in the fields of both isotherm prediction and in refining computer modelling methods.

4. Conclusions

The interactions of methanol, ethanol and propanol with the surfaces of a series of N330 carbon blacks, which have increasing total oxygen levels ($[O]_T$/at.%) measured directly by XPS, have been studied using vapour adsorption and immersion calorimetry.

Strong correlations between $[O]_T$ and the structure of the adsorbate molecules is observed which allows interpretation of the mechanisms of interaction with the carbon. In particular, the low pressure adsorption of the alcohols is highly sensitive to $[O]_T$ and the isotherms for these vapours are significantly displaced to higher adsorption values as this parameter increases.

The data indicate transitional behaviour within the limits defined by water, the interactions of which are known to dominated by hydrogen bonding at polar surface sites (oxygen groups), and toluene, which has a (much weaker) dispersion interaction with the non-polar carbon surface. A shift from hydrogen bonding dominated interactions to a more significant dispersion force contribution to the interactivity is observed as the alcohol series is ascended.

Isotherms of Type III character are observed for the un-oxidised N330 (1.7 at.% oxygen) but Type II curves result for the oxidised materials confirming that the low pressure, low coverage, domains of the isotherms are still dominated by specific interactions which increase as a function of $[O]_T$.

A semi-quantitative analysis of the relative influence of the specific to non-specific interactions is possible from the heat of immersion data which show both the relative sensitivity of each alcohol to $[O]_T$ and also the shift from specific to non-specific interaction as the alkyl chain length of the alcohols increases.

These specific (sub-monolayer) interactions are reflected in the C constant derived by application of the BET equation to the alcohol adsorption data although some difficulty was encountered in fitting the data especially that for the un-oxidised N330 carbon black which gives Type III isotherms. Non-linearity was also observed in the low pressure, high A (kJ mol^{-1}) domains of the DRK plots for these systems but better fits were obtained for the alcohols on the oxidised surfaces which gave Type II isotherms.

E_{DRK} (kJ mol^{-1}) and β_{DRK}(alcohols) are shown to be sensitive to the level of specific interaction and consequently a dependence on $[O]_T$ is observed Correlations between these equation parameters and measurable physico-chemical variables, such as $[O]_T$, is highly attractive for both isotherm prediction and for the refinement of adsorption models. XPS is shown to provide direct, quantitative, first principle information about carbon surfaces which correlates with their interactions with fluid phases and consequently it has potential for increasing our detailed understanding of the specific processes which occur at such surfaces.

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