

# On the characterization of acidic and basic surface sites on carbons by various techniques

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## Abstract

Active carbons of different origins have been oxidized with  $\text{H}_2\text{O}_2$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and their oxygen surface complexes have been characterized by TPD, classical titration following Boehm's method and by neutralization calorimetry. The net enthalpies of neutralization, determined by immersion calorimetry into NaOH and HCl 2 N lead to  $-41.1 \pm 1.8$  and  $-52.3 \pm 2.0$  kJ eq<sup>-1</sup> for the acidic and basic sites on the surface. Experiments with  $\text{NaHCO}_3$  lead to  $-39.7 \pm 1.7$  kJ eq<sup>-1</sup> for the carboxylic groups alone. These results suggest that the surface groups of active carbons can also be characterized by immersion calorimetry. Results are also given for the variation of the pH of the point of zero charge with the total oxygen content of the surface.

*Keywords:* A. Activated carbon; B. Oxidation; D. Functional groups

## 1. Introduction

The surface chemistry of carbon materials is basically determined by the acidic and basic character of their surface. The acidic behaviour is associated with oxygen surface complexes or oxygen functionalities such as carboxyls, lactones and phenols. On the other hand, functionalities like pyrones, chromenes, ethers and carbonyls are responsible for basic properties of the carbon surfaces [1–10]. However, and in spite of the fact that some functionalities are able to act as basic sites, the basic properties of the carbon surfaces are not well understood yet. For example, some authors [2,11–14] have identified basic properties associated with Lewis sites located at the  $\pi$  electron-rich regions within the basal planes of the graphitic microcrystals, away from the edges. Support for the existence of these basic sites is provided by the decrease in acidic adsorption observed for small increases in the oxygen content of the carbons [2] and, more recently, from calorimetric measurements [15]. This suggests that the basic character of carbon surfaces seems to

be associated essentially with the absence of oxygen-containing groups, which are predominantly of acidic nature [14].

It has been shown recently [16] that the oxygen surface complexes on activated carbons can be characterized by a combination of different techniques such as water adsorption analyzed by the Dubinin–Astakhov method, immersion calorimetry, titration of the oxygen functionalities by Boehm's method [1] and temperature-programmed desorption (TPD). In the present study, we try to get more insight into the nature of the acid and basic surface sites, by combining techniques such as titrations, the measurement of pH and oxygen content, with the enthalpies of immersion of the carbons into aqueous solutions of NaOH and HCl and into water. These enthalpies correspond respectively to the neutralization of the groups and to their enthalpy of hydration, all other conditions remaining the same. This approach has recently been described by Barton et al. [15], using a series of oxidized active carbons derived from active carbon BPL. We also applied the calorimetric technique to the case of  $\text{NaHCO}_3$  neutralization, where a good correlation has been found with direct titration of the carboxylic groups alone.

The present study, which also includes active carbons of

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different origins, therefore extends the work of the late S. Barton.

## 2. Experimental

### 2.1. Activated carbons

A variety of activated carbons (Table 1) has been used in this study. Samples H25 and AZ46 were prepared from olive stones, as described elsewhere with their characterization [16,17]. Sample BV46, also derived from olive stones, was prepared by carbonization in  $N_2$  at 1273 K for 1 h, followed by activation with steam at 1123 K for 7.5 h (46% burn-off). KF-1500 is an activated fibre, UO2 a commercial activated carbon derived from coal by steam activation [5] and CMS a carbon molecular sieve [18]. With the exception of KF-1500, which appears to have a high initial oxygen content and CMS-OX which was obtained from CMS with  $HNO_3$ , the carbons were oxidized with  $H_2O_2$  or  $(NH_4)_2S_2O_8$  for different periods of time. In the case of series AZ46, the last digit (0 to 24) refers to the oxidation time (hours) with  $(NH_4)_2S_2O_8$ . This procedure, described in detail elsewhere [19], allowed the introduction of various amounts of oxygen surface complexes.

The oxygen content of the samples was obtained from the total amounts of CO and  $CO_2$  desorbed when heated up to 1273 K in an oven, at  $50\text{ K min}^{-1}$ . The amounts of desorbed gases, carried by a stream of helium, were monitored by a Thermocube mass spectrometer (Balzers, Liechtenstein), as reported earlier [16]. The total surface acidity and basicity of the samples were determined by titration with NaOH and HCl, following a standard procedure [16]. The carboxylic groups were titrated directly with  $NaHCO_3$  1 N.

The pH of the point of zero charge  $pH_{PZC}$ , i.e. the pH

above which the total surface of the carbon particles is negatively charged [13], was measured by the so-called pH drift method [20]. For this purpose,  $50\text{ cm}^3$  of a 0.01 M NaCl solution was placed in a jacketed titration vessel, thermostatted at 298 K, and  $N_2$  was bubbled through the solution to stabilise the pH by preventing the dissolution of  $CO_2$ . The pH was then adjusted to successive initial values between 2 and 12, by adding either HCl or NaOH and the activated carbon (0.15 g) was added to the solution. The final pH, reached after 48 h, was measured and plotted against the initial pH, as illustrated in Fig. 1. The pH at which the curve crosses the line  $pH(\text{final})=pH(\text{initial})$  is taken as the  $pH_{PZC}$  of the given carbon.

The enthalpies of immersion of the carbons into benzene and water,  $\Delta_i H(C_6H_6)$  and  $\Delta_i H(H_2O)$ , and the corresponding enthalpies of neutralization into NaOH and HCl 2 N,  $\Delta_i H(NaOH)$  and  $\Delta_i H(HCl)$ , were determined with a calorimeter of the Tian-Calvet type [5,16]. Five samples were also subjected to immersion into 1 N  $NaHCO_3$  solutions (Table 2), in order to examine the possibility of extending the calorimetric technique to specific sites (carboxylic groups in the present case). Prior to the experiments, the samples (0.1 to 0.2 g) were outgassed at  $10^{-2}$ – $10^{-3}$  Pa and at a temperature not higher than 383 K, in order to prevent thermal decomposition of the surface complexes. Every determination was repeated at least three times. The enthalpy of immersion into benzene,  $\Delta_i H(C_6H_6)$ , was used for quality control of the samples, since it only depends on the structural parameters of the solid.

## 3. Results and discussion

The results obtained with the different techniques are summarized in Tables 1 and 2. As pointed out earlier [16,18], for a given series of carbons, the enthalpy of

Table 1  
Acid and basic surface characteristics of the activated carbons

Sample	$-\Delta_i H(C_6H_6)$ ( $J\text{ g}^{-1}$ )	$-\Delta_i H(H_2O)$ ( $J\text{ g}^{-1}$ )	$-\Delta_i H(NaOH)$ ( $J\text{ g}^{-1}$ )	$-\Delta_i H(HCl)$ ( $J\text{ g}^{-1}$ )	[O] ( $\text{mmol g}^{-1}$ )	Total acidity (NaOH) ( $\text{meq g}^{-1}$ )	Total basicity (HCl) ( $\text{meq g}^{-1}$ )	$pH_{PZC}$
H25	109.7±2.6	29.7±2.7	35.0±2.1	60.7±4.6	0.53	0.24	0.56	9.9
H25-OX	105.0±1.0	55.4±1.3	72.5±1.2	80.6±3.2	2.11	0.57	0.37	6.7
BV46	131.4±2.2	28.0±1.6	33.5±1.1	63.2±2.2	0.32	0.22	0.62	10.1
BV46-OX	134.0±1.2	78.2±1.6	137.8±1.4	100.3±1.1	3.26	1.10	0.38	4.2
AZ46-0	110.0±2.9	45.7±2.0	52.0±2.7	77.3±2.7	0.81	0.11	0.72	10.9
AZ46-3	114.4±3.6	79.9±1.4	155.3±3.5	100.1±3.9	4.50	1.90	0.43	2.6
AZ46-24	113.2±2.2	95.0±1.1	202.5±2.0	108.0±1.3	7.00	2.72	0.21	2.2
KF-1500	146.0±7.0	76.0±3.1	98.3±2.7	118.1±4.2	1.59	0.42	0.81	7.4
UO2-OX	–	55.0±2.1	84.2±0.7	84.5±0.7	2.21	0.55	0.58	6.5
CMS	95.1 <sup>a</sup>	27.0 <sup>a</sup>	–	–	1.30	–	–	–
CMS-OX	92.0 <sup>a</sup>	82.0 <sup>a</sup>	–	–	6.34	–	–	–

<sup>a</sup>From Ref. [18].

Table 2  
Neutralization of different active carbons by  $\text{NaHCO}_3$

Sample		AZ46-0	AZ46-1	AZ46-4	AZ46-10	BV46-OX
$-\Delta_i H(\text{NaHCO}_3)_{\text{net}}$	$\text{J g}^{-1}$	$14.4 \pm 2.0$	$18.6 \pm 1.5$	$39.3 \pm 1.8$	$47.7 \pm 2.0$	$20.9 \pm 1.9$
Titration	$\text{meq g}^{-1}$	0.23	0.48	0.95	1.28	0.48

immersion into benzene is not modified by the oxygen content of the material, which confirms the observation that mild oxidation does not modify the structural properties of the original carbon. This has also been confirmed by Barton [15,21].

Figure 1 shows four typical curves obtained with the pH-drift technique, which lead to the  $\text{pH}_{\text{PZC}}$  values of the corresponding samples. As illustrated by Fig. 2, which includes further data taken from the literature [16,22], the  $\text{pH}_{\text{PZC}}$  decreases rapidly as the oxygen content increases from 0 to 3  $\text{mmol g}^{-1}$ . Beyond this content,  $\text{pH}_{\text{PZC}}$  stabilizes around 2.5–3. This behaviour appears to be common to all carbons and it reflects the increase in surface acidity.

In agreement with the recent data of Barton et al. [15] for a series of oxidized BPL carbons, our calorimetric experiments show a good correlation between the net enthalpy of neutralization into NaOH or HCl 2 N (Fig. 3 and Fig. 4) and the number of milliequivalents of acid or base obtained from direct titration. The net enthalpy of neutralization is the difference between the enthalpy of neutralization and the enthalpy of immersion into water, i.e.

$$\Delta_i H(\text{NaOH})_{\text{net}} = \Delta_i H(\text{NaOH}) - \Delta_i H(\text{H}_2\text{O}) \quad (1)$$

and

$$\Delta_i H(\text{HCl})_{\text{net}} = \Delta_i H(\text{HCl}) - \Delta_i H(\text{H}_2\text{O}) \quad (2)$$

As seen in Table 1,  $\Delta_i H(\text{H}_2\text{O})$  is relatively important and varies from carbon to carbon. It corresponds to the interaction of water with the carbon and the surface groups [16] independently of the neutralization reaction. This can be verified by measuring the enthalpy of neutralization after wetting the samples by exposing them to saturated water vapour for at least 18–24 h. As illustrated by samples AZ46-3 to AZ46-24 (Fig. 3), under these conditions the enthalpy of neutralization by NaOH is equal to  $\Delta_i H(\text{NaOH})$ . This technique, also used by Barton [15,21], takes more time, but it reduces the overall experimental uncertainty by requiring only one immersion experiment.

The present study suggests net enthalpies of neutralization of  $-41.1 \pm 1.8 \text{ kJ eq}^{-1}$  for acidic sites and  $-52.3 \pm 2.0 \text{ kJ eq}^{-1}$  for basic sites, against  $-42$  and  $-38 \text{ kJ eq}^{-1}$ , as obtained by Barton for the BPL series [15]. The enthalpy of neutralization of basic sites was also calculated, following Barton's method [15], from the enthalpy of neutralization and the number of basic surface sites when the oxygen content was extrapolated to zero.

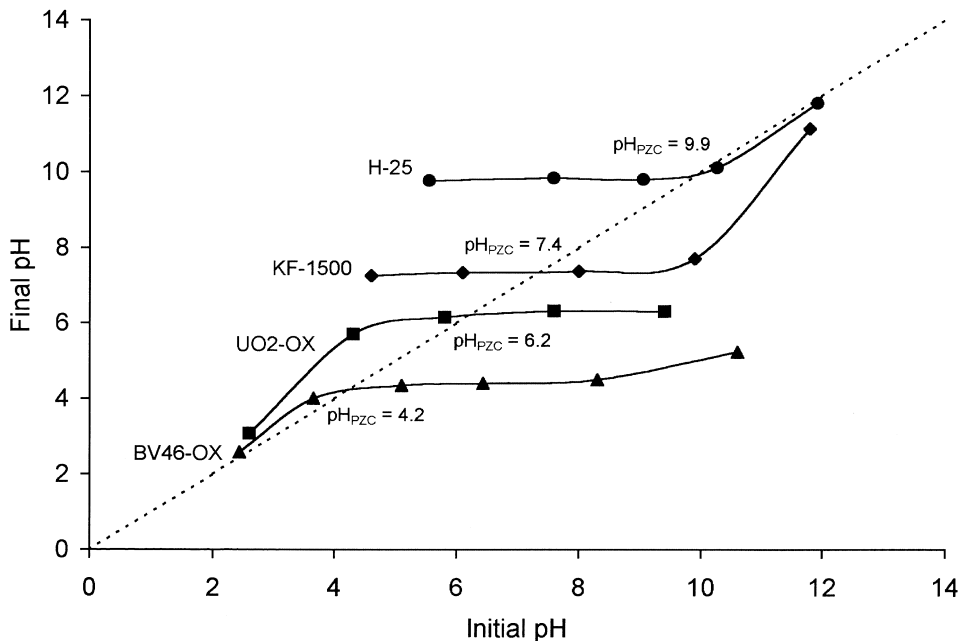


Fig. 1. pH drift method to obtain the  $\text{pH}_{\text{PZC}}$ .

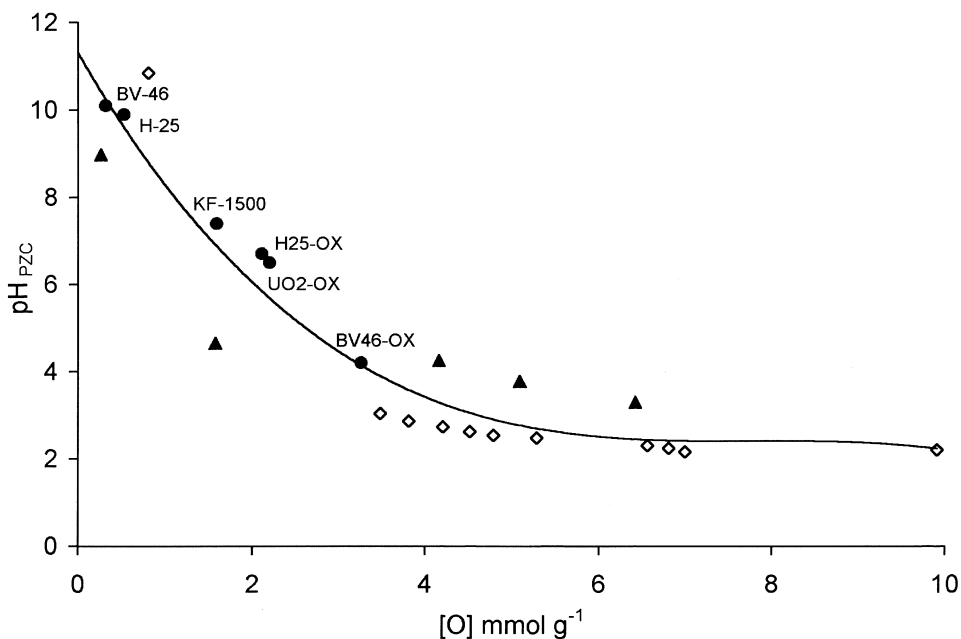


Fig. 2. Relationship between the  $\text{pH}_{\text{PZC}}$  and oxygen content of activated carbons with different origin. ●, Samples from the present study; ◇, samples from Ref. [16]; ▲, samples from Ref. [22].

The values obtained were  $-36.2 \text{ J g}^{-1}$  and  $0.69 \text{ meq g}^{-1}$ , respectively, which yielded a value of  $-52.4 \text{ kJ eq}^{-1}$  for the enthalpy of neutralization of basic sites. This value

coincides with that obtained from the slope of Fig. 4. At this stage, no explanation can be offered for the difference observed between our result and the value reported by

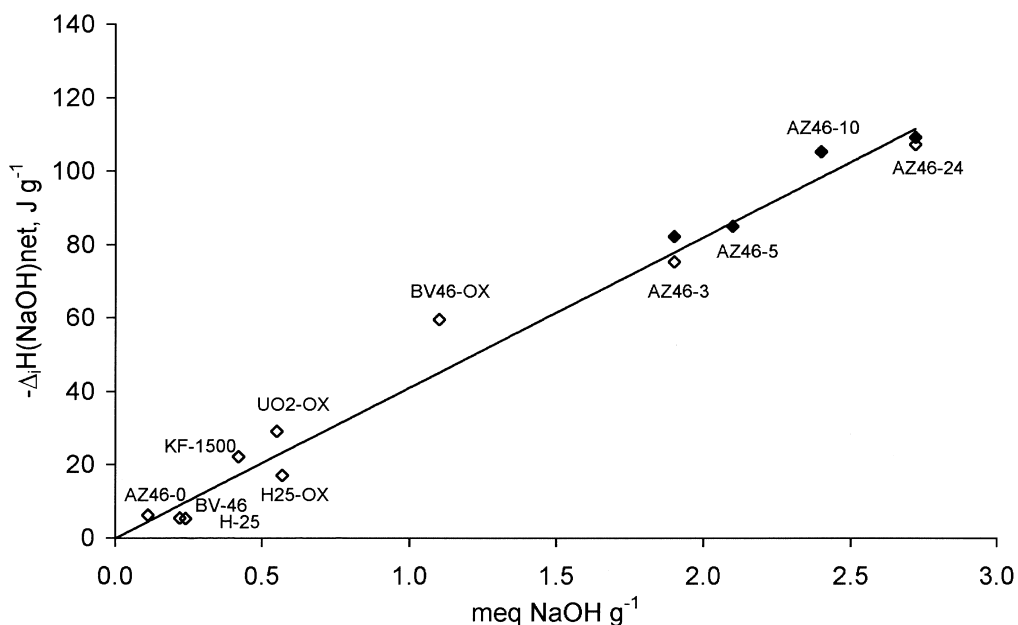


Fig. 3. Correlation between the net enthalpy of neutralization by NaOH 2 N and the number of acidic sites obtained from NaOH titration. The data points (◇) correspond to samples wetted by exposure to saturated water vapour for 22 h.

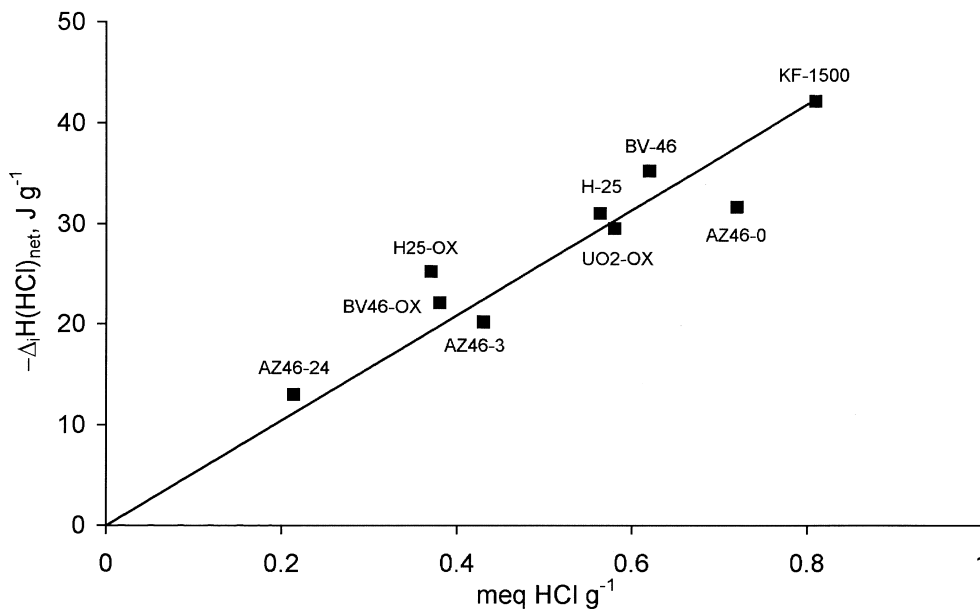


Fig. 4. Correlation between the net enthalpies of neutralization by HCl 2 N and the number of milliequivalents obtained from HCl titration.

Barton for the basic sites. This point will be investigated further, but it should be pointed out that in the present case a variety of carbons have been used and there is little doubt about the higher value for the neutralization of basic sites by HCl. It is also important to note that the enthalpies of neutralization of acidic and basic surface sites are not

necessarily equal, because the titration processes are not the same: acid groups release H<sup>+</sup> ions which are titrated with NaOH and lead to water, whereas the basic groups are mainly associated with π electron-rich regions which accept H<sup>+</sup> ions from HCl (see below).

In order to explore the possibilities offered by the

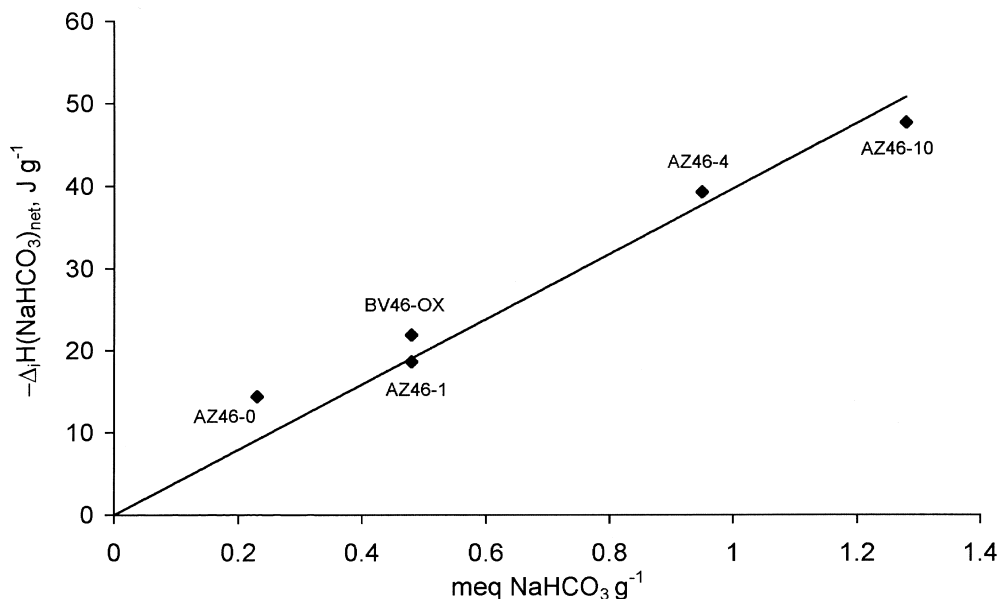


Fig. 5. Correlation between the net enthalpy of neutralization by NaHCO<sub>3</sub> 1 N and the number of milliequivalents obtained by direct titration.

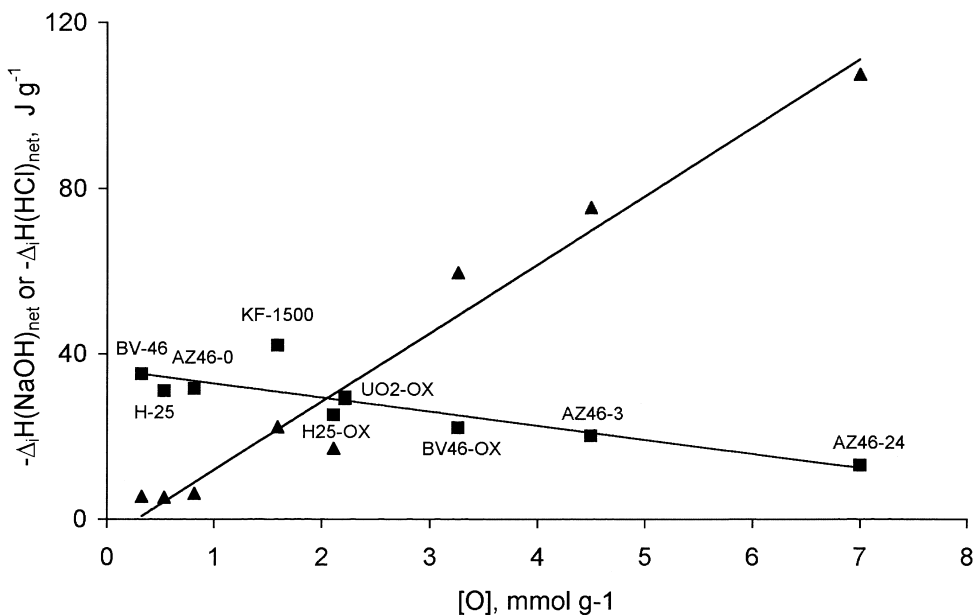


Fig. 6. Variation of the net enthalpies of neutralization  $\Delta H(\text{NaOH})_{\text{net}}$ , ▲, and  $\Delta H(\text{HCl})_{\text{net}}$ , ■, with the total amount of oxygen on the surface.

calorimetric approach (selectivity of the sites), experiments were also carried out with aqueous solutions of  $\text{NaHCO}_3$ , which neutralizes exclusively carboxylic groups. As illustrated by Fig. 5, one obtains a good correlation between the net enthalpy of neutralization  $\Delta_f H(\text{NaHCO}_3)_{\text{net}}$  using a 1 N solution, and the number of milliequivalents derived

from classical titration with  $\text{NaHCO}_3$  (Table 2). The value of  $-39.7 \pm 1.7 \text{ kJ eq}^{-1}$  is close to the result obtained with NaOH for the bulk of the acidic groups. As before, preliminary wetting of the solid will increase the accuracy of the calorimetric approach. These experiments show that it is possible to distinguish also by the calorimetric

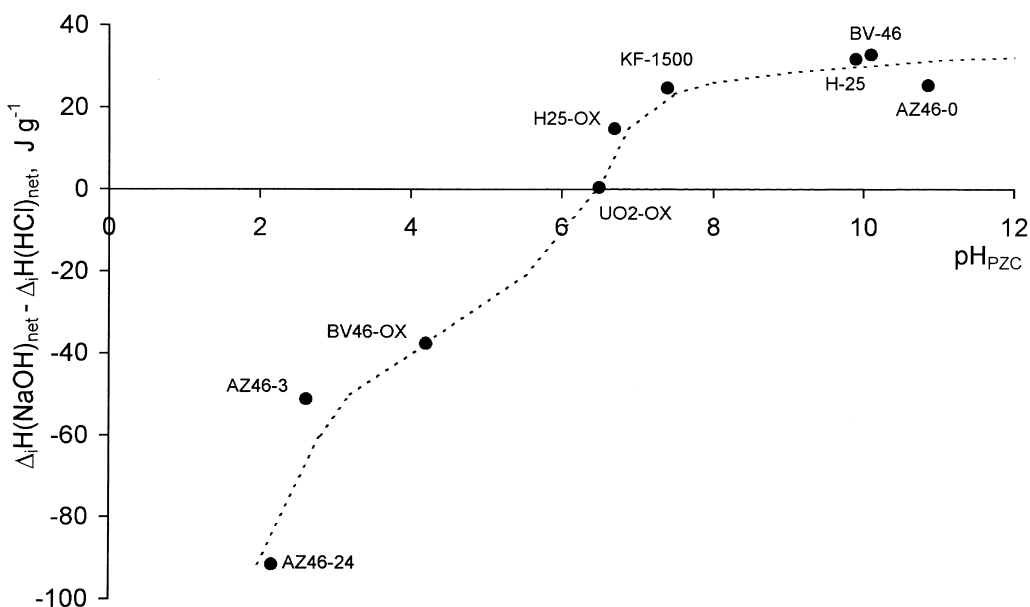


Fig. 7. Variation of the differences in enthalpies of neutralization of acid and basic sites with the  $\text{pH}_{\text{PZC}}$  of the activated carbons.

technique the carboxylic sites from the other acidic sites, which also include lactones and phenolic groups.

Figure 6 shows the variations of the net enthalpies of neutralization by NaOH (total acidic sites) and by HCl (total basic sites), as functions of the oxygen content of the different active carbons used in this study. As observed by Barton [15],  $\Delta_i H(\text{NaOH})_{\text{net}}$  increases with the oxygen content [O] of the surface, whereas  $\Delta_i H(\text{HCl})_{\text{net}}$  decreases.

The present results, obtained with activated carbons of different origins, suggest that the surface basic sites of the activated carbons are essentially of the Lewis type, associated with  $\pi$  electron-rich regions found on the basal planes of the graphitic microcrystals. This can be justified by the fact that an increase in the oxygen content of the carbon diminishes the electronic density of the basal planes and consequently reduces the basicity of the carbon surface. In other words, the oxygen surface complexes are predominantly of acidic character. However, for low oxygen contents (approximately below  $2 \text{ mmol g}^{-1}$ ), when the enthalpy of neutralization of basic sites is higher than that for acidic sites, the coexistence of basic oxygen groups, with chromene-, pyrone- and quinone-type structures [6–10], would be possible.

Finally, a plot of the differences between the net enthalpies of neutralization of the different carbons vs. the  $\text{pH}_{\text{PZC}}$  (Fig. 7) suggests that the two enthalpies are equal when the  $\text{pH}_{\text{PZC}}$  is just below 7. This could be in agreement with the somewhat higher enthalpy of neutralization observed for the basic surface sites.

The present study extends the work of Barton and shows that, in principle, immersion calorimetry can be used for the characterization of acidic and basic surface groups on active carbons of different origins and having been subjected to various chemical treatments (it is implicit, that the carbons contain no impurities which may react with the neutralizing agents). As suggested by further experiments with  $\text{NaHCO}_3$ , it also appears that specific groups such as carboxylic functions can be characterized by this technique. Work is currently in progress and further results will be published in due course.

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