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Preparation and Characterization of Aminated Carbon from a Single-Step Reaction

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The paper describes a single-step procedure by which linear terminal diamines are directly anchored onto activated carbon in sizable amounts (∼5%). Evidence for the formation of real amide bonds is provided by using a range of spectroscopic and "in situ" electrochemical determinations (X-ray photoelectron spectroscopy, Brunauer−Emmett−Teller, Fourier transform infrared, Boehm titrations, and potentiometric acid−base titrations). Results on the reaction stoichiometry are also given, showing that diamines and surface carboxyls react in a close to 1:1 molar ratio. Terminal $-NH_2$ groups not engaged in amide bonds are free to react further and, in the present conditions, show well-defined proton adsorption behavior.

Introduction

Activated carbons have a relevant role in many applications concerning, for instance, consumer, industrial, and energy-oriented issues.[1−12] Carbons are effective sorbents for pollutant removal from surface and wastewaters and for reactant recycling in industrial processes.[13−16] An interplay of physical and chemical features is involved. Surface area, porosity, and pore size distribution cooperatively intervene together with a rich collection of surface functional groups[1,11,14,17] that may vary in kind and concentration depending on carbon origin, pretreatment, and modification purposely adopted to improve performance in one or another field of interest.[14,18−26] As a fact, carbon modification has become a main field of research on its own, with many techniques reported to increase the concentration of native groups[14,26−31] (mostly oxygen-based) or to substitute them by functionalities containing heteroatoms, like N and S.[14,18−22,32−35] Increased and more selective sorption behavior is expected and actually observed on such modified carbons.[14,23,28,36] A promising route to N-modified carbons is surface amide bond formation by means of bifunctional molecules containing a reactive amine group.[14,18−22,34,35] In

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a search of the literature this kind of modification is most often performed by a sequence of steps in which the first one is invariably aimed at activating the carbon surface, followed by an amination step.[14,18−22,34,35] In the following we report a one-step method allowing amine binding to be directly obtained, thus reducing costly purification of reaction intermediates. The starting point of view is to take advantage of carboxylic groups that normally exist at the carbon surface, reacting them in as straightforward a way as possible with linear terminal diamines, such as to anchor a single amine group to carbon while leaving the second one free to react further in other conditions.

Experimental Section

Reactants (1,3-diaminopropane (denoted as C3 in the following), 1,6-diaminohexane (C6), ethanol, diethylene glycol diethyl ether (diglyme), Fourier transform infrared (FT-IR) KBr; all Aldrich of analytical grade) were used as received. Activated carbon (Darco KB, Aldrich) was either used as received or purified by water washing as specified below. Milli-Q water was used throughout as well as high purity N_2 (5-Nine, Sapio).

Carbon Modification. In a typical run, untreated carbon (∼8 g) was suspended under stirring in diglyme (∼300 mL) and added with a large diamine excess (3.3×10^{-2} mol g^{-1} of carbon) with respect to the total amount of carbon acidic groups determined by the Boehm method (see below). The suspension was heated at $T = 140$ °C for ∼45 h. Reacted samples were filtered and redispersed several times in EtOH and finally in Milli-Q water until complete removal of organics, as monitored by UV analysis. Drying was performed in flowing N_2 for 24 h at $T = 90$ °C. Samples reacted with C3 and C6 are denoted D3 and D6, respectively.

To detect solvent and thermal treatment effects, a control sample was obtained in the same way, however without amine added (denoted as TH in the following). For internal reference a further sample (denoted as DB) was obtained suspending Darco KB in water under stirring for 1 week. Then it was extracted for a further week with water in a Soxhlet apparatus to remove soluble impurities and oven-dried in flowing N_2 at $T = 110$ and 120 °C in two separate 24 h steps to remove most physical water.

X-ray Photoelectron Spectroscopy (XPS). XPS measurements were performed with an M-Probe Instrument (SSI) equipped with a monochromatic Al Kα source (1486.6 eV) with a spot size of 200×750 μm and a pass energy of 25 eV, providing a resolution of 0.74 eV. The energy scale was calibrated with reference to the $4f_{7/2}$ level of a freshly evaporated gold sample (84.00 ± 0.1 eV) and to the $2p_{3/2}$ and 3s levels of copper (932.47 ± 0.1 and 122.39 ± 0.15 eV, respectively). An electron flood gun was used to compensate for the buildup of positive charge on insulating samples: a value of 5 eV was selected. For all samples, the C 1s peak level was taken as the internal reference at 284.6 eV. Accuracy of reported binding energies (BEs) is approximately ±0.2 eV. Quantitative data were carefully checked and reproduced several times. Uncertainty in spectral decomposition is estimated to be ±1%.

FT-IR Spectroscopy. FT-IR spectroscopy was used to determine the vibrational frequencies of surface functional groups. The 2500−3600 cm^{-1} and 1300−1800 cm^{-1} regions were particularly investigated, using diffuse reflectance infrared fourier transform spectroscopy (DRIFT) and reflectance FT-IR microspectrometry. DRIFT spectra were collected over the whole wavelength range (450−4000 cm^{-1}) by means of a Spectrum One FT-IR spectrophotometer (Perkin-Elmer, MA), equipped with a DRIFT accessory. Reflectance FT-IR microspectroscopy spectra were acquired by a Multiscope FT-IR microscope (Perkin-Elmer, MA) over the wavelength range 600−4000 cm^{-1}. In the DRIFT approach, FT-IR grade KBr was ground for 5 min and dried overnight at 120 °C. KBr was then thoroughly mixed with carbon in an agate mortar for 1 min at 0.2% (w/w) concentration. Spectra were recorded selecting a scan number of 64 and a 4 cm^{-1} resolution. The background of pure KBr was separately recorded using the same conditions and automatically subtracted from sample spectra.

In reflectance microspectroscopy, spectra were directly collected on a flat carbon layer obtained by gently pressing the powder onto a mirror finished aluminum support. A minimum of 20 sampling areas were explored at a scan number of 64 with 4 cm^{-1} resolution. Background from the sample holder was automatically subtracted.

Specific Surface Area. Surface area and porosity were determined by low temperature ($T = -196$ °C) N_2 adsorption using a SA3100 Coulter apparatus. Before measurement, samples were outgassed at $T = 80$ °C for 3 h. Surface area and porosity were calculated from nitrogen isotherms using the instrumental software (Version 2.12).

Boehm Titrations. Boehm titrations were carried out according to standard procedures.[37] Independent carbon samples (0.2 g) were placed in 25 mL of NaOH, Na_2CO_3, $NaHCO_3$, and HCl (all 0.05 N). Vials were sealed and equilibrated for 24 h by bottom-up rotation and filtered. To determine the amount of acid groups, aliquots (5 mL) from the basic solutions were added to excess 0.05 N HCl and back-titrated with NaOH. Similarly, basic groups were determined by direct NaOH titration of solutions from HCl equilibration. Titrations were performed in triplicate under flowing N_2 to exclude CO_2 contamination from the used reactants and the atmosphere. Results were calculated assuming that NaOH reacts with all acidic carbon groups (phenols, lactones, carboxyls), that Na_2CO_3 reacts with lactonic and carboxylic groups, to the exclusion of phenols, and finally, that $NaHCO_3$ only reacts with carboxyls.

Potentiometric Titrations. Quasi-equilibrium acid−base titrations were performed under CO_2-free N_2 at 25 °C in KCl as the supporting electrolyte. Carbon (0.25 g) was suspended in KCl (40 mL) at the lowest used concentration (1×10^{-3} M), stirred, and N_2 purged for 0.5 h. Separate glass and reference electrodes (Metrohm) were used, the latter one connected to the test solution by a salt bridge at the used electrolyte concentration. Titration was started by adding 0.1 M HCl or KOH in 10 μL aliquots (Metrohm, Dosimat 665) in a three-cycle back and forth method to assess reproducibility. Thereafter, the electrolyte concentration was increased adding the necessary amount of solid KCl. Further titrations were performed at 1×10^{-2} and 1×10^{-1} M KCl. To achieve quasi-equilibrium a homemade PC-controlled system was used comprising an Amel 338 pHmeter, a MOXA multiplexer board, and control software. A pH stability-over-time criterion was adopted, imposing ΔpH/min < 0.005 for pH acceptance and further titrant addition. A titration time of ∼16−24 h was necessary for each complete titration set. To minimize hysteresis between forward and backward titrations, trial tests were performed to determine a suitable pH titration range. Proton adsorbed amounts were calculated as the difference between added and analytically measured (quasi-equilibrium) H^+ concentration. Corrections were applied for KCl activity coefficients[38] and acid−base water behavior.[39]

Results and Discussion

Before reporting results we want to mention some experimental tests that were carried out to get an understand-

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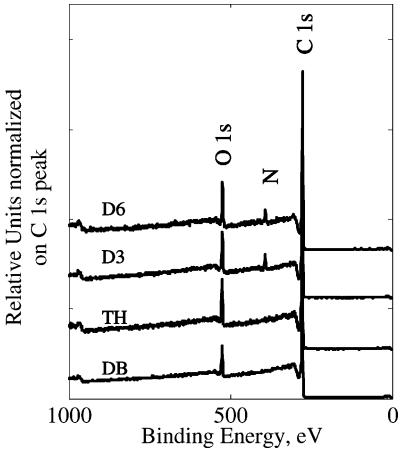

Figure 1. XPS survey spectra.

Table 1. Atomic C, O, and N Percent Sample Compositions

	sample description	C %	O %	N %
DB	washed carbon	93.1	6.9	
TH	carbon thermally treated	89.9	10.1	
D3	carbon thermally treated with 1,3-diaminopropane	86.2	9.0	4.8
D6	carbon thermally treated with 1,6-diaminohexane	85.0	9.6	5.4

ing of the amine−carbon reaction and to improve binding efficiency. Darco KB was chosen as the test carbon because of the high carboxyl content revealed by Boehm titrations. A large diamine excess and fast amine−carbon mixing were used to minimize reaction of amine with carboxyls in adjoining positions and at the surface of different carbon particles. To the same end, 1,3- and 1,6-diamines were adopted for steric reasons. In a first attempt Darco KB was reacted at $T = 150$ °C in an autoclave with C3 dissolved in water (2 M). Despite the large amine excess a rather low elemental N percent was determined by XPS (∼2.7%). This result was considered unsatisfactory and attributed to water in the used medium intervening to shift the reaction equilibrium backward. Tests were, therefore, addressed to single out a solvent with high water affinity such as to shift the reaction forward. Candidates were found in the ethylene glycol family. After a few tests these compounds were abandoned in favor of the corresponding diethers where end alcoholic functions are protected by ether groups thus making the solvent less reactive with respect to the carbon surface. Diglyme was adopted because of the suitably high boiling point ($T = 180-190$ °C), allowing ambient pressure conditions to be used.

XPS survey analyses (Figure 1) show that nitrogen is present in amine-treated samples (D3, D6) at a concentration that, from elemental percentage results in Table 1, ranges to ∼5% regardless of the used amine. This value favorably compares, and even surpasses, previous results from multistep procedures.[19,34,35] Moreover, by comparison with the above results in water-based media, this result supports that water-producing equilibria are involved in the overall amine-to-carbon binding.

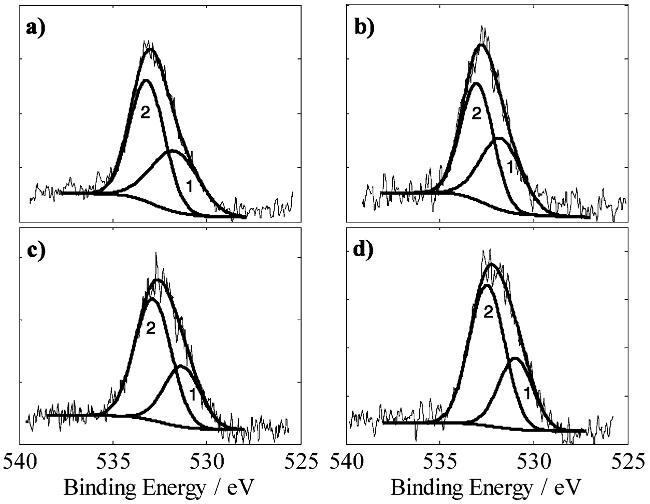

Figure 2. High-resolution O 1s spectra: (a) DB; (b) TH; (c) D3; and (d) D6. 1 and 2 are defined in the text.

Atomic compositions in Table 1 self-consistently and independently concern each investigated sample. However, a comparison among them shows that sample heating, both in the absence and in the presence of amines, causes the carbon and oxygen contents to vary decreasing and increasing, respectively, with respect to the untreated sample. Given the lack of oxidizing power of diglyme and amines, this extra oxygen has an uncertain origin. It is, nevertheless, interesting that O is at a maximum on TH and decreases somewhat on both amine reacted samples. Though admittedly at the limit of the experimental resolution, this trend suggests that this extra oxygen gives rise to surface groups that behave similar to the native ones, reacting further with excess amine.

A more detailed picture is obtained from high-resolution spectra.

O 1s signals (Figure 2) contain contributions from two maxima at BEs corresponding to C=O (peak 1, BE = 530.4−531.4 eV)[27,40−45] and C−OH and C−O−C bonds (peak 2, BE = 532.4−533.1).[27,40−45] It is relevant that no signal is present at higher BEs, thus excluding weakly bound oxygen forms, like physical and chemical water or adsorbed molecular oxygen. Therefore, total oxygen, the above extra oxygen included, is chemically bonded to the surface.

C 1s spectra (Figure 3) are composed of many individual components that in order of decreasing magnitude represent (1) graphitic and aliphatic carbon (peak 1 at BE = 284.5−285.1 eV);[27,40−43,45,46] (2) single bond C−O and C−N groups (i.e., ether, alcohol, phenol, and amine; peak 2, BE = 286.3−287.0 eV);[27,34,40−43,45,46] (3) carbonyls and quinones (peak 3, BE = 287.5−288.1 eV);[27,40−43,45,46] and (4) carboxyl and ester groups (peak 4, BE = 289.3−290.0);[27,40−43,45,46] of concern is also the shake-up satellite (5) due to $\pi-\pi^*$ transition in aromatic rings (peak 5, BE = 291.2−292.1 eV).[47]

High-resolution nitrogen (N 1s) spectra (Figure 4) show a single component peak (BE = 399.5−400.5 eV)[34,48,49]

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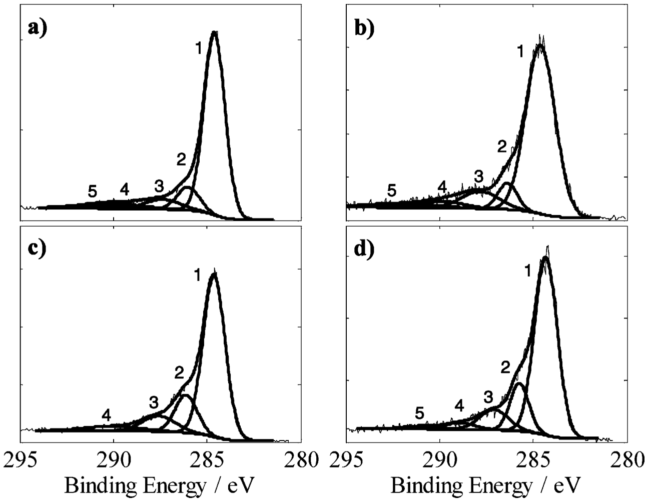

Figure 3. High-resolution C 1s spectra: (a) DB; (b) TH; (c) D3; and (d) D6. 1−5 are defined in the text.

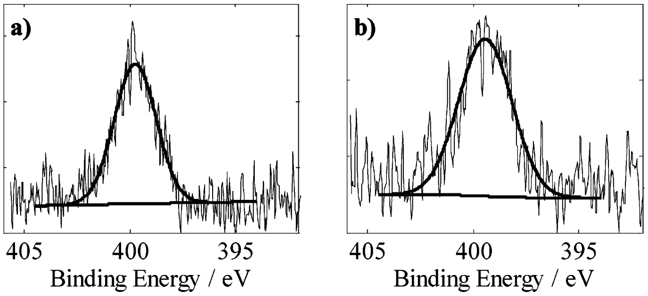

Figure 4. High-resolution N 1s spectra: (a) D3 and (b) D6.

Table 2. Relative Peak Areas (RPA%) of C 1s Peaks Corresponding to Figure 3

	BE (eV)	description	DB	TH	D3	D6
1	284.5−285.1	graphitic and aliphatic carbon	70.5	70.9	63.4	60.0
2	286.3−287.0	single bond C—O and C—N groups	17.6	17.0	26.4	27.4
3	287.5−288.1	carbonyls and quinones	5.1	5.1	5.2	5.4
4	289.3−290.0	carboxyl and ester groups	3.7	3.1	5.0	6.3
5	291.2−292.1	$\pi-\pi^*$ transition in aromatic rings	3.1	3.9	−	0.9

Table 3. Specific Surface Area

sample	DB	TH	D3	D6
specific surface area (m^2 g^{-1})	1671	1559	1085	571

related to aminic and amidic nitrogen, thus showing that amine-to-carbon binding has taken place.

Amine−carbon interactions are evidenced by C 1s spectra (Table 2). In the first entry line of the table, untreated (DB) and thermally treated (TH) samples have similar graphitic and aliphatic relative peak area components (RPA%) that comparably decrease by ∼7−10% on both amine treated samples, somewhat more definitely for the amine with longer (D6) rather than shorter chain length (D3). By comparison, the second line shows that RPA%s of DB and TH are again comparable and, probably not coincidentally, increase by approximately the same amount as above (∼10%) after amine treatment. At the relevant BE, C—O and C—N contributions from phenols, alcohols, and amines are indicated so that some distinction is needed before peak assignment. Most relevant is the fact that, from Boehm titration results in the next section, the surface groups classified as phenols undergo a large increase, actually more than doubling after thermal treatment in diglyme (see Table 3). No similar effect is present in the second line data where, as stated above, DB and TH have comparable RPA% values. This lack of correspondence is unexplained and might be due to ever continuing discrepancies between “dry” and “wet” determinations. From this behavior we feel justified in assuming that phenol signals do not also contribute to the RPA% increase observed in passing from TH to amine-treated samples. Then, and also disregarding as chemically unprobable any formation of new surface ether groups, the RPA% increase in the second line can be mainly attributed to C—N bonds belonging to free and reacted amino groups. It can be observed that directly evidencing amidic carbon would require an increase in D3 and D6 RPA%s in the third line,[50] which is again not observed. However, in the case of amide bond formation at the carbon surface it could expected that a decrease in conjugation occurs between formerly −COOH groups and any relevant COOH-bearing aromatic ring in the substrate, with effects possibly propagating at a distance over the graphitic system of the carbon surface. This is in accordance with RPA%s of the $\pi-\pi^*$ transition (see the fifth line in the table). On DB and TH these values are initially comparable. After amine treatment they decrease to fractional and zero values. Though weak, these signals are direct evidence for amide bond formation in the used conditions. It can be stressed that “this signal is only detected on predominantly graphitic/aromatic surfaces”.[47]

FT-IR spectra are usually collected in the transmission mode using KBr pellets. When examining sensitive materials, like, for example, carbon, DRIFT is generally preferred because perturbing effects from sample preparation are reduced to a minimum. In a further improvement and to a better spectral quality, FT-IR microspectroscopy can be used. After extensive comparison between these latter methods, microspectrometry was preferred because of its least interfering sample preparation, also considering the ease by which replicate results are obtained on independent sample areas. The main panel of Figure 5 shows a sample comparison in the whole spectral range investigated (600−4000 cm^{-1}). Several modifications are apparent in passing from untreated (DB) to thermally treated (TH) and amine-treated (D3, D6) samples. More detailed results are observed in separate spectral regions concerning symmetric and asymmetric C—H stretching (2700−3000 cm^{-1}, box a), C═O stretching (1490−1780 cm^{-1}, box b) and C—H bending (1350−1490 cm^{-1}, box c). In box a, the relative intensities of C—H stretching vibration bands are seen to increase just moderately from DB to TH, more definitely on D3 and the more so on D6. This evidence can only be attributed to CH$_2$ groups introduced at the surface by the used method, their number increasing with the amine chain length. Box b shows a broad absorption band system due to C═O stretching from carbonylic moieties. When considered altogether, DB and TH

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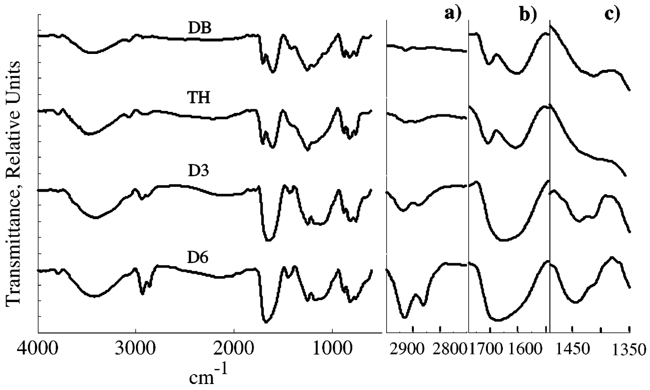

Figure 5. FT-IR microspectroscopy spectra of the DB, TH, D3, and D6 samples. C—H stretching, C═O stretching, and C—H bending spectral regions are shown in boxes a−c, respectively.

spectra can be assimilated to a single response, as it is also the case for D3 and D6 even though the response is very different from the previous one. Then, we see that a sharp transition occurs between the two responses, only attributable to amine anchoring. Complementary evidence is obtained in box c related to the absorbance increase of aliphatic C—H bending.

Unfortunately, no direct evidence could be observed for aminic hydrogen. The most diagnostic signal from N—H stretching is expected at 3200−3400 cm^{-1}, and in the present spectra it is actually lost within the broad O—H stretching bands in the main panel. Nevertheless, it is observed that this band shifts to lower frequencies as a result of amine treatment. However, from a spectroscopic point of view, results suggest that amine anchoring has successfully taken place. On more general grounds they also show the ease and sensitivity by which carbon can be investigated by FT-IR microspectroscopy. To our knowledge the technique is seldom used for this purpose.

From Brunauer−Emmett−Teller (BET) determinations, surface areas (Table 3) anyway decrease with respect to the untreated carbon (DB) by amounts that depend on modification conditions. A moderate percentage decrease (∼7%) occurs for the TH sample reacted in the absence of amines. The decrease becomes greater on D3 (∼35%) and actually dramatic on D6 (∼66%). The effects were not investigated in detail so that we may resume the explanation of a similar behavior observed[18] by using 1,2-diaminoethane and 1,6-diaminohexane which are just one CH_2 group shorter than the present C3 and actually the same C6 diamine, respectively, used in this work. In a further meaningful aspect of that paper, a family of carbons with variable pore sizes was used thus permitting surface area effects due to alkyl chain length at a given carbon pore size to be detected. As a result, it was proposed that surface area variations are attributable to filling accessible pore volumes by diamines with different aliphatic chain bulkiness. This is in accordance with Table 3 results, even though a single carbon with given, constant pore size is used.

The next sections are devoted to the acid−base carbon behavior and modifications thereof induced by amine treatment.

Table 4. Results of Boehm Titrations

	carboxyls (μequiv m^{-2})	lactones (μequiv m^{-2})	phenols (μequiv m^{-2})	total acids (μequiv m^{-2})	total bases (μequiv m^{-2})	total groups (μequiv m^{-2})
DB	0.087	0.182	0.114	0.383	0.182	0.565
TH	0.185	0.076	0.302	0.563	0.187	0.750

Boehm titrations were only performed on non-aminated carbons. Given the relevant dissociation constants, free amine and carboxyl groups undergo protonation and deprotonation, respectively, at overlapping pH, thus making difficult or impossible for any direct separation between them.[35,51−53] Similar behavior expectedly also occurs on corresponding carbon-bonded groups.[35] Boehm results are given in Table 4 after normalization with respect to specific surface areas from BET determinations (Table 3). Carboxyls, phenols, and lactones are present on the untreated carbon (DB). In the Boehm method these groups are overall classified as acidic. They sum up to a greater total than that of the basic functions. The carbon surface is, therefore, amphoteric with dominating acidic character, as from producer specifications. After heating in diglyme, carbon (TH) becomes more acidic with, on one hand, nearly unchanged basic groups and, on the other, extra carboxyls and phenols generated at the expense of a fraction of previously present lactones. This suggests that lactone rings may thermally open to yield carboxyls and phenols in a 1:1:1 ratio. However, a lack of stoichiometric mass balance appears in Table 4 with respect to this hypothesis. By taking differences between the relevant data, a greater amount of carboxyls (0.098 μequiv m^{-2}) and phenols (0.188 μequiv m^{-2}) is generated than that of lactones lost (0.106 μeq m^{-2}), thus showing that other reactions intervene to increase the overall carbon acidity and the total amount of oxygen groups that was already mentioned when discussing XPS survey analyses.

Quasi-equilibrium titrations of carbon suspensions are reported in Figure 6a−c. Adsorbed proton (H^+-OH^-) charge values are normalized with respect to BET surface areas. With increasing pH, the charge/pH relation of the untreated carbon in 1×10^{-3} M KCl (DB, Figure 6a) is at first convex and then concave to the abscissa axis, with a well-defined, almost horizontal inflection point between the two. With increasing KCl concentration, charge/pH relations become steeper and near linear and intersect with each other at pH = 4.5, in close correspondence of the inflection point. This feature is characteristic of amphoteric surface behavior as best exemplified by insoluble oxides.[54] The intersection point is unaffected by electrolyte concentration so that even though there is a lack of comparison with other electrolytes, K^+ and Cl^- appear to interact with the carbon surface nonspecifically, mainly through electrostatic forces. Therefore, the intersection point is identified with that pH where the absolute charge of the unmodified surface is zero (pH = pH_{pzc} and (H^+-

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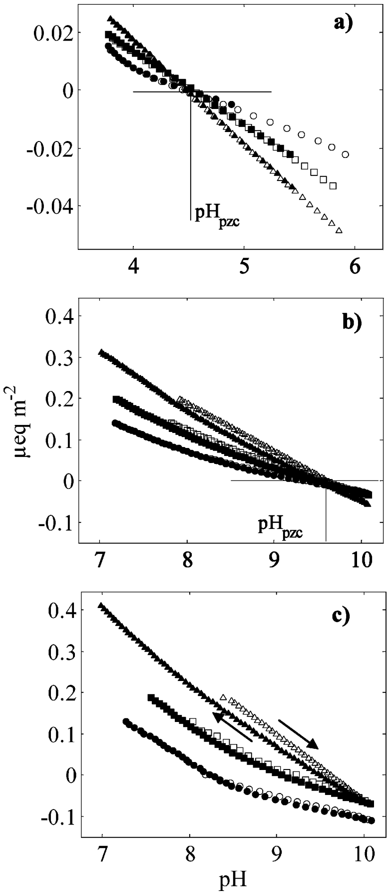

Figure 6. Potentiometric titration curves of (a) DB; (b) D3; and (c) D6: (○, ●) 1 × 10^{-3} M; (□, ■) 1 × 10^{-2} M; and (△, ▲) 1 × 10^{-1} M KCl (T = 25 °C). Full symbols, acid-going runs; open symbols, basic-going runs. See also the arrows in Figure 6c.

OH^-) = 0).[55,56] This parameter is specific of the surface and surface state under examination in no general relation, other than occasional, with the spontaneous pH experimentally recorded prior to titrant addition, which is often used interchangeably for the same purpose. For instance, in the present case the spontaneous pH is 4.9 as compared to pH_{pzc} = 4.5. In accordance with the above definition, the absolute zero in the charge axis scale of Figure 6a is fixed at pH = 4.5.

Carboxyls are indicated as the relevant surface groups. In Boehm determinations, after equilibrating in the weakest used alkali ($NaHCO_3$), DB suspensions are normally at pH ∼ 8.6. Carboxyls are measured so that these groups are only relevant to proton sorption−desorption processes taking place in the more acidic pH range of Figure 6a, any other group determined in Boehm titrations being in this case electrically neutral and charge ineffective. In a general way, depending on pH, SOH_2^+ and SO^- can be envisaged as the charge-determining carbon surface groups. For pH = pH_{pzc} these groups balance with each other to a zero net (H^+-OH^-) charge. Under these aspects it is relevant that even moderately extending the upper titration limit to higher pH destroys the excellent back and forth titration reproducibility in the figure, causing hysteresis loops, likely due to incipient, irreversible H^+/OH^- interactions with lactones that, in the acidity scale of Boehm determinations, are next to carboxyls.

Titrations of D3 and D6 in comparable conditions are shown in Figure 6b,c. To directly show amine treatment effects no pH range optimization was performed, thus possibly contributing to the readily observed residual hysteresis between back and forth titration runs (see especially D6 in Figure 6c). On the better defined results of D3 (Figure 6b), titrations sharply intersect at pH = 9.6. As in the above and leaving unprejudiced any interaction with electrolyte ions, this pH is identified as pH_{pzc} at absolute zero surface charge. More complex behavior occurs for D6 (Figure 6c) where titrations in 1 × 10^{-2} and 1 × 10^{-1} M KCl definitely intersect at pH = 10, however, being shifted upward in no clear relation with that in 1 × 10^{-3} M electrolyte. For these reasons the sample pH_{pzc} is left undefined and experimental charge values are used.

As a main feature, both samples show an impressive charge increase with respect to the untreated carbon. Moreover, the charge is only positive (D3), or nearly so (D6), and becomes more positive with decreasing pH and increasing electrolyte concentration. These features outline a proton adsorbing (basic) rather than amphoteric behavior, as it is the case for the untreated sample. By reference to protonation constants of the free used amines, pK_{b1} ∼ 10. 6−10.8[52,57,58] and 10.9[52] are found for C3 and C6, respectively. Even more significant is the comparison with N-alkylbenzamides ($PhCONH(CH_2)_nNH_2$, n = 2−4) where protonation of unreacted terminal $-NH_2$ groups is characterized by pK_b values that increase with increasing chain length, that is, pK_b = 9.12 (n = 2), pK_b = 9.92 (n = 3), and pK_b = 10.34 (n = 4).[59] The close correspondence of pK_b = 9.92 with the experimental pH_{pzc} of D3 (pH_{pzc} = 9.6) can be considered to show that protonation involves comparable chemical states of $-NH_2$ groups in the model benzamide and in functional groups at the carbon surface. On these grounds, pH_{pzc} of D3 becomes well-defined, primary evidence that amide bonds are formed between amines and surface carboxyls. However, with the above-mentioned uncertainties concerning D6, this point of view is also supported by the difference in the experimental crossover points of D3 and D6.

Potentiometric and Boehm data can be examined further to obtain insights into amine binding stoichiometry. To this end, graphical tangents and slopes of titrations at the maximum electrolyte concentration are used as simplified criteria, these being independent of differences in the zero charge reference and uncertainties from the lowest used electrolyte concentration. Titrations of DB, D3, and D6 in 0.1 M KCl are close to straight lines, with characteristic numerical slopes of 0.036, 0.12, and 0.14 μequiv m^{-2} pH^{-1} (titrations denoted by open simbols (△) in Figure 6a−c are used). The charge increase from untreated (DB) to amine

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treated samples (D3, D6) is represented by the ratio between these figures, namely, 0.30 for DB/D3 and 0.26 for DB/D6.

This numerical similarity is somewhat surprising and suggests that the reacting carbon surface more or less reproducibly obtains the given chemical state during amine treatment, regardless of the aliphatic diamine chain length. Though unknown, this carbon state may be assimilated to that of sample TH, only subjected to thermal heating without added amines. Then, an independent estimate of the above charge ratios is obtained assuming that titrable $-NH_2$ groups correspond in number to the total of carboxyls and lactones from the Boehm results, these groups reacting with $-NH_2$ either directly or after base-catalyzed opening of the lactone ring. From TH data (Table 4) carboxyls and lactones amount to $0.185 + 0.076 = 0.261$ μequiv m^{-2}. This is to be compared with 0.087 μequiv m^{-2} carboxyls of the untreated carbon. Then, the ratio $0.087/0.261 = 0.33$ is calculated and favorably compares with the above DB/D3 and DB/D6 ratios separately obtained from potentiometric titration data.

From this comparison amide bond formation occurs involving both pre-existing and thermally generated carboxyls and lactones in a ∼1:1 molar ratio with amines.

To this same conclusion, non-secondary importance is attributed to the reaction yield increase, from ∼2.7 to ∼5%, that was observed by using a nonaqueous solvent instead of water as the reaction medium.

As an overall comment, the reported results offer a range of independent instrumental results that complement one another in showing that amines present at the carbon surface are actually amide-bonded to carboxyls. In this, potentiometric titrations are seen as the most relevant.

To assess the general validity and feasibility of this analysis it would be interesting to extend this kind of instrumental interplay and internal cross-checking to other carbons.

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