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REMOVAL OF AN IONIC SURFACTANT FROM WASTEWATER BY CARBON BLACKS ADSORPTION

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ABSTRACT

The adsorption of an ionic surfactant, sodium dodecyl sulfate (SDS), from aqueous solution onto six carbon blacks with different surface characteristics has been studied in various ranges of low concentrations. The process can be related to types of interactions that are always the same since the adsorption in these systems depends mainly on the porosity of the samples but not on the chemical composition of the surface. However, adsorption progresses follows two processes: the first one related to the adsorption of SDS into the narrowest pores with a suitable width, and the second one related to adsorption of SDS onto a more open surface.

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INTRODUCTION

Nowadays, the use of surfactants in many industrial processes has increased considerably.[1] A problem associated with this fact is the presence of surfactants in land water as contaminants; so there is great concern about suitable methods to remove them from wastewater.[2–4] One of the more extended techniques for this purpose is their adsorption onto solids with a large adsorptive capacity. This is the case of carbonaceous materials because of their high specific surface area and their well-developed porous structure.[5–10]

A proper understanding of the mechanism of surfactant adsorption is essential to improve the efficiency of the above-mentioned process in the field of environmental pollution control. There are many techniques to analyze the adsorption mechanism and the way the retained molecules are arranged in the adsorbed layer;[11] however, most of them require experimental procedures and instrumentation, which are not always available in laboratories. Thus, it is desirable to obtain as much information as possible about the adsorption system from the commonest source of data, such as adsorption isotherms. Adsorption isotherms combined with a theoretical adsorption model give valuable information concerning the solid capacity to retain the solute, and on the arrangement of adsorbed molecules on the surface.[12]

The purpose of this work is to study the adsorption from aqueous solutions of a well-known ionic surfactant, sodium dodecyl sulfate (SDS), onto six carbon blacks with different surface characteristics, in order to obtain information about the adsorbed layer and the mechanism of its formation in the range of dilute concentrations, well below the critical micelle concentration (cmc) of the surfactant, as can be found in wastewater.

MATERIALS AND EXPERIMENTAL SECTION

Materials

Six carbon blacks of different surface characteristics were used for the adsorption study. These carbon blacks, whose abbreviations are indicated within brackets, are Black Pearls 2000 (BP2000), Black Pearls 1300 (BP1300), Black Pearls 880 (BP880), Vulcan 6 (V6), Vulcan 3 (V3), and Sterling V (SV), which were kindly provided by Cabot (Cabot S.A., Spain). Some of the surface characteristics of these carbons had been evaluated in a previous work:[13] the nitrogen adsorption at 77K was used to calculate the BET specific surface area accessible to N_2 (S_{N_2}), the micropore volume (V_{mi}, pore width lesser than ~ 2 nm), and mesopore volume ($V_{me,a}$, pore width between ca. 2 and 50 nm); mercury porosimetry data were used to determine the mesopore volume ($V_{me,b}$)

and macropore volume (V_{ma}, pore width greater than ~50 nm). These results, as well as the percentage of macro, meso, and micropores (P_{ma}, $P_{me,a}$, $P_{me,b}$, P_{mi}) are listed in Table 1. The FT-IR spectra of the samples were also analyzed.[13] The FT-IR spectra showed that the chemical nature of the surface groups is similar in all the carbon blacks studied, although some differences in the relative concentration of surface groups were observed.

The surfactant employed was the anionic surfactant SDS, $CH_3(CH_2)_{11}SO_4^- Na^+$, (Merck with purity $> 99\%$). Its cmc in water at 20°C is 8.25×10^{-3} mol L^{-1}.[14] Water for solutions was distilled and deionized [Milli-Q Plus (Millipore Co., Bedford, MA, USA)].

Adsorption Isotherms

The adsorption isotherms were determined by measuring the solution concentration (C) after equilibration with the carbons was achieved. We weighed aliquots of 0.002–0.02 g of adsorbent in 20-mL stoppered tubes, and added 15 mL of a solution of known concentration (between 5.0×10^{-5} and 1.5×10^{-3} mol L^{-1}). Just prior to use, adsorbents were dried in an oven at 110°C for 24 hr and kept in a desiccator until samples attained room temperature. Tubes were placed in an end-over-end stirrer, at 11 rpm, in an air bath at 20.0 ± 0.1°C until adsorption equilibrium was attained. The time required to reach equilibrium was 48 hr, as determined in previous experiments. After centrifugation, with a centrifuge Selecta S-240 (Selecta S.A., Barcelona, Spain), the supernatant was separated and the equilibrium concentration was evaluated spectroscopically at 552 nm with a Spectronic 601 (Milton Roy, Rochester, NY, USA), after the formation of a 1:1 complex between the dodecyl sulfate anion (DS) and the cationic dye rosaniline hydrochloride.[15]

RESULTS AND DISCUSSION

The adsorption isotherms of SDS from aqueous solution onto the carbon blacks studied are plotted in Figs. 1–6, expressed as the amount of the surfactant adsorbed per gram of the adsorbent (X) vs. the equilibrium concentration (C). These isotherms were determined in all cases up to the same value of the equilibrium concentration, 1.0×10^{-3} mol L^{-1}, lower than its cmc. Two main different behaviors can be observed from these figures; BP1300 and BP880 have a very high slope at the lowest concentrations, and then approach a plateau value. On the other hand, samples BP2000, V3, and SV present a less sharp increase in X at the lowest C than the other samples, but this behavior extends to the whole range of C studied. Sample V6 has an intermediate behavior between both groups.

Table 1. Surface Characteristics of the Carbon Blacks, Taken from Ref. [13]

Sample	S_{N_2} ($m^2\,g^{-1}$)	V_{mi} ($cm^3\,g^{-1}$)	$V_{me,a}$ ($cm^3\,g^{-1}$)	$V_{me,b}$ ($cm^3\,g^{-1}$)	V_{ma} ($cm^3\,g^{-1}$)	P_{mi} (%)	$P_{me,a}$ (%)	$P_{me,b}$ (%)	P_{ma} (%)
BP2000	1443	0.271	0.90	0.89	3.75	40.01	59.99	19.17	80.83
BP1300	511	0.078	0.64	0.51	0.74	24.70	75.30	40.81	59.19
BP880	224	0.016	0.63	0.72	1.07	12.26	87.74	40.41	59.59
V6	114	0.004	0.22	0.75	1.26	17.42	82.58	37.16	62.84
V3	80	0.001	0.15	0.62	1.15	15.61	84.39	34.93	65.07
SV	37	0.001	0.05	0.04	1.52	21.74	78.26	2.45	97.55

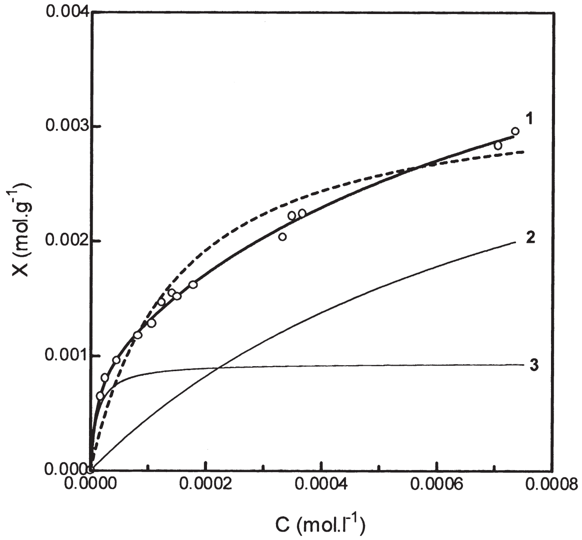

Figure 1. Fitting of the experimental data of adsorption of SDS on sample BP2000 by Langmuir equation (discontinuous curve), a rectangular hyperbola of four parameters (curve 1) and summed hyperbolae (curves 2 and 3).

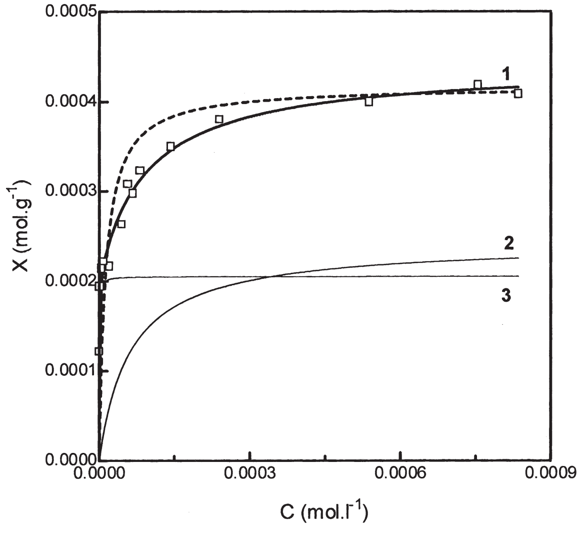

Figure 2. Fitting of the experimental data of adsorption of SDS on sample BP1300 by Langmuir equation (discontinuous curve), a rectangular hyperbola of four parameters (curve 1) and summed hyperbolae (curves 2 and 3).

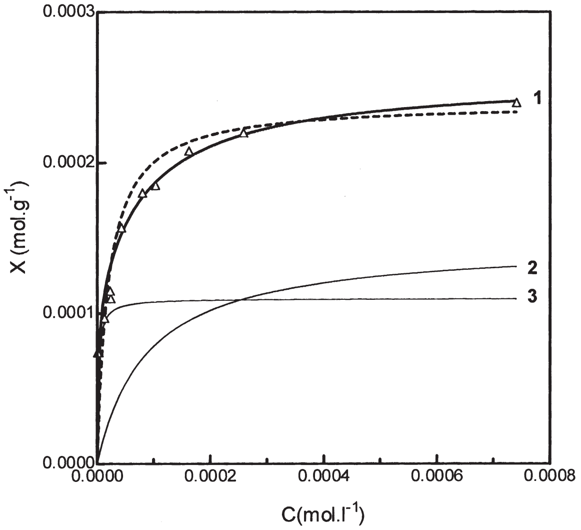

Figure 3. Fitting of the experimental data of adsorption of SDS on sample BP880 by Langmuir equation (discontinuous curve), a rectangular hyperbola of four parameters (curve 1) and summed hyperbolae (curves 2 and 3).

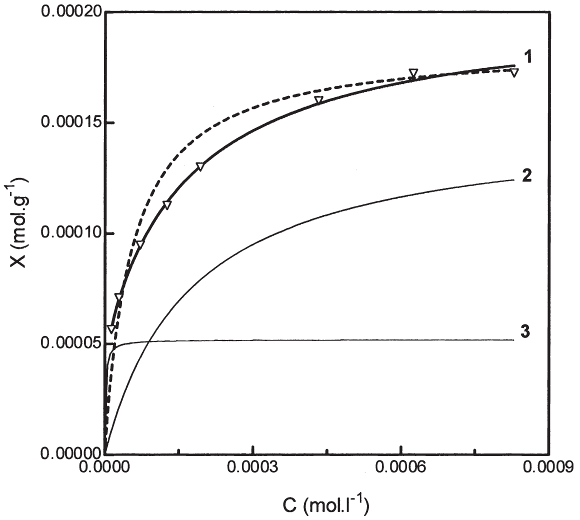

Figure 4. Fitting of the experimental data of adsorption of SDS on sample V6 by Langmuir equation (discontinuous curve), a rectangular hyperbola of four parameters (curve 1) and summed hyperbolae (curves 2 and 3).

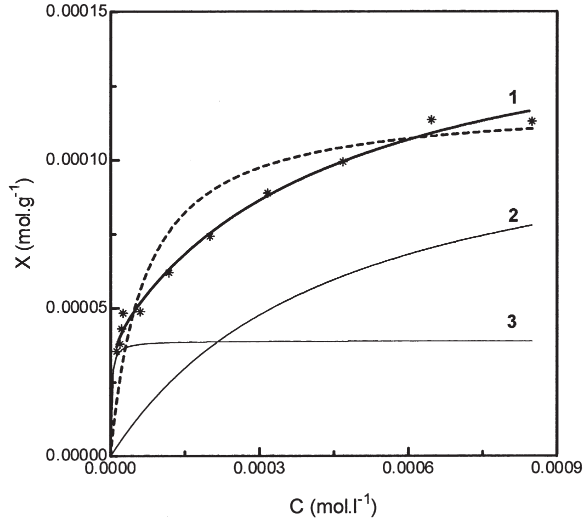

Figure 5. Fitting of the experimental data of adsorption of SDS on sample V3 by Langmuir equation (discontinuous curve), a rectangular hyperbola of four parameters (curve 1) and summed hyperbolae (curves 2 and 3).

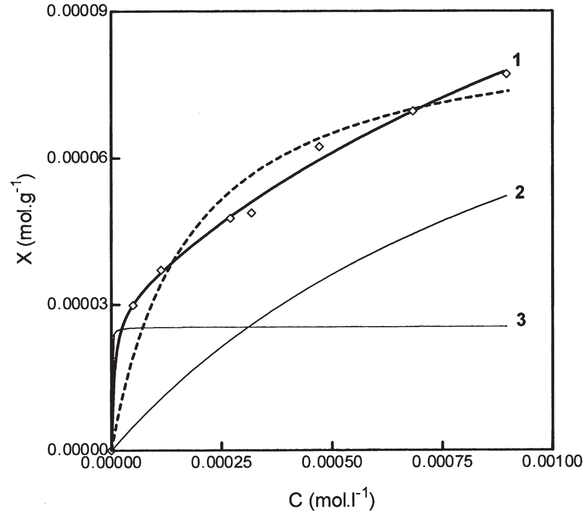

Figure 6. Fitting of the experimental data of adsorption of SDS on sample SV by Langmuir equation (discontinuous curve), a rectangular hyperbola of four parameters (curve 1) and summed hyperbolae (curves 2 and 3).

One of the most commonly used adsorption models is that proposed by Langmuir. However, its strict application is only valid if the adsorbent surface is assumed to consist of adsorption sites, if all adsorbed species interact only with a site and not with each other, and if adsorption is thus limited to a monolayer.[12] These restrictions limit the applicability of this model to a very low number of systems whose surface is energetically homogeneous, and consequently flat, and the adsorbates are retained without interactions among them. Despite these facts, the Langmuir model has proved to be a useful tool to study a great variety of systems.[9,10,12,16,17] Accordingly, we have fitted our experimental results to the Langmuir equation:

$$X = \frac{X_m C b}{1 + C b} \tag{1}$$

where X_m represents the monolayer capacity of the adsorbent, and b a parameter related to the adsorbate–adsorbent interaction free energy. However, the curves obtained from this adjustment, discontinuous line in Figs. 1–6, clearly do not match the experimental points. Thus the use of this equation must be discarded for the description of our adsorption systems.

In a previous paper, we successfully analyzed the adsorption behavior of a nonionic surfactant from aqueous solutions onto carbon blacks by the application of a scheme of a double Langmuir.[18] According to that proposal, the experimental results were fitted to an equation, which is a double rectangular hyperbola of four parameters (the numerical treatment was performed with the aid of the “GradPad Prism” software package), i.e., two summed hyperbolae, or two Langmuirian equations, because the mathematical structure of the Langmuir equation is a simple rectangular hyperbola of two parameters. The curve resulting from that adjustment, labeled as 1 in Figs. 1–6 was plotted together with each of the summed hyperbolae curves labeled as 2 and 3; so curve 1 is the sum of curve 2 plus curve 3. From these figures, it can be seen that curve 1 matches the experimental data very accurately and that the shape of the adding curves 2 and 3 is different. Curve 3 shows a pronounced slope at the lowest C and then it reaches a well-defined plateau. On the other hand, curve 2 is increasing over the whole range, although the change of slope with C depends on the samples, being higher for the carbons BP1300 and BP880 than for the other samples. So, the behavior of curve 1 is controlled by curve 3 at the lowest concentrations. At the highest C the influence of curves 2 and 3 is similar on 1, although in all cases curve 2 remains above curve 3 in the whole range of C studied. This behavior suggests the analysis of SDS adsorption as a two-step process, each of them described by a Langmuir equation. On the basis of this assumption, from the parameters found from both hyperbolae identified with those corresponding to the Langmuir equation, we evaluated the monolayer capacity, X_m, and the parameter b for each of the assumed adsorption processes (Table 2, with a sub-index representing the curve from which they were obtained).

The X_{m3} values found are between $9.40 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$ for BP2000 and $0.25 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$ for SV, decreasing in the same order as S_{N_2} does (Table 1), as well as X_{m2}, whose values are between 42.50 and $1.18 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$ for BP2000 and SV, respectively. For all the carbon blacks, X_{m2} is greater than X_{m3}, although they are closer for BP1300 and BP880 than for the other carbons.

From the parameters X_{m3} and X_{m2} and the accessible surface area of the carbon blacks to the adsorbate, S, it is possible to evaluate an occupied area per adsorbed SDS molecule for each of the two processes, A_{m3} and A_{m2}, respectively, according to:

$$A_m = \frac{S}{X_m N_A} \tag{2}$$

where N_A is the Avogadro's number. If the surface area accessible to the adsorbate is taken to be S_{N_2} (Table 1), the values of the area per molecule obtained from Eq. (2) are those listed in Table 3, A_{m3} being higher than A_{m2}, especially for samples BP2000 and SV. However, the surface area accessible to N_2 molecules is known to give an overestimation of the surface area accessible to other molecules of size greater than N_2,[19] and the presence of porosity on the samples should force the adsorbed molecules to arrange on the surface in different ways depending on the zone of the surface where they are retained. In these systems, therefore, the values of A_{m3} and A_{m2} must be considered only as an average value from the arrangement of SDS on these adsorbents.[19]

It is possible to compare the areas per molecule found from this analysis to the area of the SDS molecule evaluated from its dimensions. The SDS molecule is formed by an apolar hydrocarban chain (*n*-dodecane) grafted by an oxygen atom at the polar head ($\text{—O—SO}_3\text{Na}$). Janczuk and co-workers,[20] assumed that for DS ions the apolar chain dimension corresponds to the dimension of the dodecyl group. Therefore, the area of the DS^- chain, $S_{CH} = (0.11 + 11 \times$

Table 2. Parameters Found from Curves 3 and 2

Sample	X_{m3} ($10^{-4}\,\mathrm{mol\,g^{-1}}$)	b_3 ($10^5\,\mathrm{L\,mol^{-1}}$)	X_{m2} ($10^{-4}\,\mathrm{mol\,g^{-1}}$)	b_2 ($10^3\,\mathrm{L\,mol^{-1}}$)
BP2000	9.40	0.88	42.50	1.21
BP1300	2.05	32.84	2.35	10.52
BP880	1.10	4.64	1.52	11.49
V6	0.52	6.35	1.50	5.73
V3	0.39	5.38	1.19	2.23
SV	0.25	26.73	1.18	0.88

Table 3. Surface Area Per Molecule from Curves 3 and 2, Maximum Experimental Value of X from Curve 2 and Its Area Per Molecule

Sample	A_{m3} (nm^2 molecule^{-1})	A_{m2} (nm^2 molecule^{-1})	$X_{2,máx}$ (10^{-4} mol g^{-1})	$A_{2,máx}$ (nm^2 molecule^{-1})
BP2000	2.6	0.6	20.00	1.2
BP1300	4.1	3.6	2.35	3.7
BP880	3.4	2.5	1.35	2.8
V6	3.6	1.3	1.25	1.5
V3	3.4	1.1	0.80	1.7
SV	2.5	0.5	0.50	1.2

$0.127 + 0.127/2) \times 0.26 = 0.4083\,\text{nm}^2$, where 0.26 nm is the width of the chain,[21] 0.11 nm is the distance of the C—H bond, and 0.127 nm is the C—C (tetradhedral angle) bond. In the case of the head of DS$^-$, $S_H \cong 0.36\,\text{nm}^2$.[22] Thus, the contactable SDS surface area equals 0.7683 nm^2. This value is lesser than that of A_{m3} and A_{m2}, except A_{m2} for the samples BP2000 and SV whose values are only slightly higher than the area of the hydrocarbon chain of SDS. This suggests, taking into account the nonaccessibility of the whole S_{N_2} surface area to the SDS molecules, that the A_{m2} values of BP2000 and SV would only be compatible with the interactions between adsorbed molecules. However, it is worth noting that lateral interactions at the adsorbed layer take place at equilibrium concentrations close to the cmc of the surfactant and this should be experimentally displayed by a sharp increase in the isotherm,[16,23] which is not our case. In addition, from an inspection of Figs. 1–6 and Table 2, it can be observed that the calculated values of X_{m2} are much higher than the maximum value of X read from curve 2 in our experimental range, $X_{2,max}$ (Table 3), this difference being more important the lower curve 2 slope is. So it cannot be asserted that the mechanism needed for the formation of such a monolayer associated with the X_{m2} value was acting in the range of the concentrations studied; therefore, $X_{2,max}$ values give a more accurate picture than X_{m2} of the maximum occupation according to the process that can be related to curve 2, in the experimental range for our systems. In consequence, from $X_{2,max}$ and Eq. (2), we calculated the area per molecule at the maximum experimental coverage, $A_{2,max}$ (Table 3)—all of which are greater than the contactable surface area of SDS and, obviously, A_{m2}.

According to these results, the processes represented by curves 2 and 3 cannot be related to two different adsorption mechanisms: a direct interaction between the carbon black surface and adsorbate molecules, and the adsorbate–adsorbate interaction at the adsorbent–solution interface. But they are probably related to the same adsorption mechanism, adsorbate–adsorbent interactions, distinguished by the characteristics of the part of the surface where adsorption occurs.

The adsorption data can also give information on the thermodynamics of the process. The adsorption free energy corresponding to each of the assumed adsorption processes, ΔG_{ads3} and ΔG_{ads2} were evaluated from the parameters b_2 and b_3, respectively, according to Refs.[10,24]

$$\Delta G_{ads} = -RT\ln(b\omega) \tag{3}$$

where ω is the molar concentration of water ($55.55\,\mathrm{mol\,L^{-1}}$ at 20°C), listed in Table 4, as well as their values per molecule, Δg_{ads3} and Δg_{ads2}. The Δg_{ads3} values are between -7.7 and $-6.9 \times 10^{-20}\,\mathrm{J\,molecule^{-1}}$ for BP1300 and BP880, respectively. For each sample, Δg_{ads2} is lower in absolute value than Δg_{ads3}, indicating that the strength of the SDS interaction with the adsorbent is lower as the concentration increases.

At the earliest stages of the adsorption process, it is expected that SDS retention takes place preferentially on the positions of the surface where there is an enhancement of the adsorption potential. These stages can be related to the presence of chemically active surface groups or with the microporosity of the sample. When the adsorption is carried out in pores with at least one of their dimensions similar to the molecular size of the adsorbate, an enhancement of the adsorption enthalpy depending on the pore shape is found due to simultaneous interaction of the adsorbed molecule with the pore walls.[25]

Gas adsorption results indicate that the samples V6, V3, and SV are carbons with an almost negligible microporous volume (see Table 1). As a consequence, it can be stated that adsorption at low coverage on these samples takes place on the most energetic sites of the surface, but not related preferentially with microporosity. On the other hand, for the samples BP2000, BP1300, and BP880, which have well-developed porosity, including mainly micropores, the beginning of adsorption can occur on the most energetic sites of

Table 4. Free Energy of Adsorption from Curves 3 and 2

Sample	ΔG_{ads3} ($\mathrm{kJ\,mol^{-1}}$)	ΔG_{ads2} ($\mathrm{kJ\,mol^{-1}}$)	Δg_{ads3} ($10^{-20}\,\mathrm{J\,molecule^{-1}}$)	Δg_{ads2} ($10^{-20}\,\mathrm{J\,molecule^{-1}}$)
BP2000	−43.5	−27.1	−7.2	−4.5
BP1300	−46.5	−32.3	−7.7	−5.4
BP880	−41.5	−32.5	−6.9	−5.4
V6	−42.3	−30.8	−7.0	−5.1
V3	−41.9	−28.5	−7.0	−4.7
SV	−45.8	−26.3	−7.6	−4.4

the surface that are similar to those of the nonmicroporous samples from a chemical point of view,[13] and on the micropores. However, the similarity found between the Δg_{ads3} values in both groups of samples suggests that the SDS adsorption mechanism at low concentration is similar for all samples, despite their differences in microporosity.

Measurements of zeta potential of these systems,[26] performed under the same conditions as with the isotherms, gave a decrease in zeta potential with the equilibrium concentration identical to that given by the amount adsorbed in the adsorption isotherms. Consequently, it can be asserted that the DS ions are retained in the Stern layer of the double layer with their ionic head towards the solution phase. This fact suggests that the adsorption process described by curve 3 is related to adsorption on areas of the surface wide enough to allow the contribution of the ions to the double layer of the particle.

An approximation to the porosity range where this process takes place is indicated by the A_{m3} values and the percentages of micro, meso, and macropores of the carbon blacks (Table 1). The inspection of the mesopore–macropore relation found from mercury porosimetry indicates a good correlation with the values of A_{m3}, that is, the highest value of A_{m3} corresponds to the sample BP1300 that has the lowest macropore percentage and similarly, the more macroporous samples, BP2000 and SV, present the lowest A_{m3} values. However, this correlation is not complete. Carbon BP880, with a macropore percentage similar to BP1300, gives an area per molecule lower than for BP1300 and close to the areas per molecule obtained for slightly more macroporous samples (V6 and V3). Moreover, it is not wholly acceptable to assume that the most energetic positions would be the surface of the macropores.

A noteworthy difference between carbons BP1300 and BP8880 is their micropore–mesopore relation obtained from nitrogen adsorption (Table 1). This shows that sample BP1300 is less mesoporous than BP880, and indicates that once the adsorbate is able to accede to more internal positions of the surface, a facility indicated by P_{ma}, retention is avoided in large fractions of the BP1300 surface area related to the narrowest pores. However, adsorption must be on pores wide enough to allow the enhancement of the adsorption potential by the wall interactions, and this must be a more important fraction for BP1300 than BP880, as shown by the Δg_{ads3} value. Carbons V6 and V3 have P_{ma} and $P_{me,b}$ similar to those found for BP880 and consequently also their A_{m3} values. It must not be forgotten that the evaluation of A_{m3} is made by taking the BET surface area, an important part of which is localized in micropores inaccessible to SDS. This model is also compatible with the results obtained for the carbons BP2000 and SV characterized by the lowest values of A_{m3}, despite having a similar micropore–mesopore relation, or even lower than BP1300. However, since both BP2000 and SV are very macroporous, the access of the adsorbate towards the mesopores and its retention would be favored.

This important role played by meso- and macroporosity in the first adsorption process can be understood taking into account the ionic nature of the surfactant employed. The presence of the retained ions would impede access towards more internal positions of the adsorbent due to repulsive interactions, and consequently the more open the carbon surface, the easier the adsorption.

The second adsorption mechanism that can be assumed in these systems is that represented by curve 2. The lowest $A_{2,\max}$ values correspond to the most macroporous samples. This result is to be expected based on the argument given for the first adsorption process, since once the most energetic sites have been blocked, adsorption progresses on the surface of the macropores.

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