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Influence of porosity on the adsorption enthalpies of a non-ionic surfactant onto carbonaceous materials

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Abstract

The adsorption of a non-ionic surfactant (Triton X-100 (TX-100)) from aqueous solutions onto a set of carbon blacks and activated carbons has been compared by a calorimetric study. Different behaviours in the progress of the adsorption enthalpy as a function of surface coverage are obtained. However, irrespective of the nature of the carbon support, the process can be related to the same types of interactions since the evolution of adsorption enthalpy in these systems depends mainly on the porosity of the samples but not on the chemistry surface composition. The results at low coverage, indicate two kinds, at least, of adsorption behaviour: the first related to the adsorption of TX-100 in the narrowest pores with a suitable width, and the second on more open surfaces. In the narrowest micropores, the adsorption enthalpy can be twice that for a non-microporous surface as can be expected for slit-shaped micropores accommodating only one molecule. At higher coverage, the retention is due to interactions between surfactant molecules at the adsorbent-solution interface leading to the formation of interfacial aggregates. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption enthalpies; Porosity; Carbonaceous materials

1. Introduction

Adsorption from dilute aqueous solutions onto solid surfaces is becoming a highly attractive separation technique for many applications, such as waste-water treatment, liquid mixture separation and purification, or polar organic solutes recovery from biotechnology processes [1]. In particular, adsorption provides a technique of great interest to remove surfactants from municipal and industrial waste-water [2–5]. This purpose can be achieved by using adsorbents with a high adsorptive capacity and selectivity. This is the case of carbon blacks and activated carbons, which can be employed as adsorbents of non-ionic surfactants thanks to their high specific surface area and their high degree of porous structure [6].

The most commonly used non-ionic surfactants are composed of a polyethylene oxide chain to which a hydrophobic moiety, usually a hydrocarbon, is attached [7]. When aqueous solutions of such non-ionic surfactant are brought into contact with a solid surface without any spatial restriction, models of

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adsorption suggest that the arrangement of surfactant molecules in the adsorbed layer could progress from a horizontal to a vertical configuration as coverage increases [8]. In the case of a porous solid, it is expected some restrictions to the adsorbate orientation at the surface, as soon as the pore width and the molecular size are of the same order of magnitude.

A proper understanding of the mechanism of adsorption is essential in improving the efficiency of the above mentioned industrial process in the field of environmental pollution control. The interpretation of the adsorption mechanism is primarily developed from the study of the adsorption isotherm, since it is possible to get information about the solid capacity to retain a solute and, sometimes, about the arrangement of adsorbed molecules on the surface. However, in many cases, changes in the adsorption mechanism are not as clearly evidenced by adsorption isotherms as they could be by adsorption enthalpies, since these latter can be more sensitive to conformational changes in the adsorbed phase and usually offers an opportunity for studying directly the different types of interaction in the system. So, the combination of adsorption enthalpy, experimentally measured by microcalorimetry, and adsorption isotherms has been the method frequently employed in studies of the adsorption mechanism of surfactants adsorbing on solid surface from aqueous solutions [9–11].

We present in this paper a calorimetric study of the adsorption of the surfactant Triton X-100 (TX-100) onto a set of carbon blacks and activated carbons. The analysis of adsorption from solution results illuminates pore characterisations and allows to propose an interpretation of the adsorption behaviour of these systems.

2. Experimental

2.1. Materials

The carbonaceous materials employed in this adsorption study, with the abbreviation indicated in brackets, were six carbon blacks, Black Pearls 2000 (BP2000), Black Pearls 1300 (BP1300), Black Pearls 880 (BP880), Vulcan 6 (V6), Vulcan 3 (V3) and Sterling V (SV) and three commercial activated carbons, Panreac (P), Norit (N) and Darco (D). Some of the surface characteristics of these materials had been evaluated in previous works [12,13]: the nitrogen adsorption isotherm at 77 K were used to calculate the BET specific surface area accessible to N_2 (S_{BET}), the external or non-microporous surface (S_{ext}), the ratio of the external to the total BET surface area (S_{ext}/S_{BET}), the micropore (V_{mi}) and mesopore (V_{me}) volumes. These results are listed in Table 1.

The studied surfactant was the non-ionic TX-100, supplied by Fluka (surfactant content higher than 99%). TX-100 is an octylphenol polyoxyethylenic surfactant having an average number of ethoxy units around 9.5 (an average molar mass of 624 g mol^{-1} was chosen for the calculations) [14]. Its critical micelle concentration (CMC) in water at 20°C is 3.0×10^{-4} mol l^{-1} [15]. Water for solutions was distilled and deionised (Milli-Q Plus, Millipore).

2.2. Batch calorimetry

Calorimetric measurements were made with a Tian–Calvet type microcalorimeter, by the standard "batch method" [16]. In this method, the solid (0.1 g

Table 1
Surface characteristics of the carbon blacks and the activated carbons, taken from [12,13], and their maximum adsorption capacities of TX100, taken from [18,19]

Sample	S_{BET} (m^2 g^{-1})	S_{ext} (m^2 g^{-1})	S_{ext}/S_{BET} (%)	V_{mi} (cm^3 g^{-1})	V_{me} (cm^3 g^{-1})	X_m (mmol g^{-1})
BP2000	1443	915	63	0.271	0.90	1.95
BP1300	511	358	70	0.078	0.64	0.713
BP880	224	192	86	0.016	0.63	0.442
V6	114	104	91	0.004	0.22	0.295
V3	80	77	96	0.001	0.15	0.188
SV	37	35	95	0.001	0.05	0.096
P	852	210	25	0.36	0.22	0.521
N	678	195	29	0.29	0.21	0.392
D	611	276	45	0.25	0.41	0.476

in all cases) was kept in suspension in the sample cell (20 ml) by means of a magnet-driven propeller with a slow–fast reciprocating motion. The reference cell was prepared identical to the sample cell with the exception of the solid. When the thermal equilibrium was reached, a small volume (0.25 ml) of a stock solution of surfactant (1.0×10^{-2} mol l^{-1}) was introduced into the sample cell, via a volumetric pump. Some of these surfactant molecules were adsorbed. The thermal effect induced by this process and the dilution of the injected surfactant solution was recorded. Once the calorimeter signal had returned to the baseline, another injection was carried out. Each new injection increases the surface coverage of the adsorbent. The experiment was fully computerised and it was carried out until the surface coverage of the adsorbent reaches a value of around 1. The correction term, due to dilution and demicellisation was determined in a blank experiment in which the same stock solution was injected into the calorimeter cell containing only pure water. All experiments were done at 20°C.

To extract from the calorimetric results the adsorption contribution, the adsorption isotherm must be known in order to determine the amount of surfactant adsorbed during the calorimetric experiment [17]. Therefore, the adsorption isotherms were previously measured under the same experimental conditions as those used for the calorimetric experiments [18]. From the amount adsorbed and the thermal effect corrected from the dilution contribution, the differential molar enthalpy of adsorption, Δh_{ads}, was calculated and plotted as a function of coverage, θ. The Δh_{ads} is the variation of enthalpy when 1 mol of solute is transferred from the equilibrium solution to the interface (i.e. the equilibrium solution is the reference state).

3. Results and discussion

The relevant isotherms of TX-100 onto the set of carbon blacks and activated carbons at 20°C, have already been carried out and published [18,19]. For the sake of clarity, only samples V3 and D are presented in Fig. 1, since the other samples showed a similar behaviour. This similarity suggests a similar mechanism of TX-100 adsorption. All of the adsorption isotherms of TX-100 consist of two distinct parts. The initial section, corresponding to the lowest

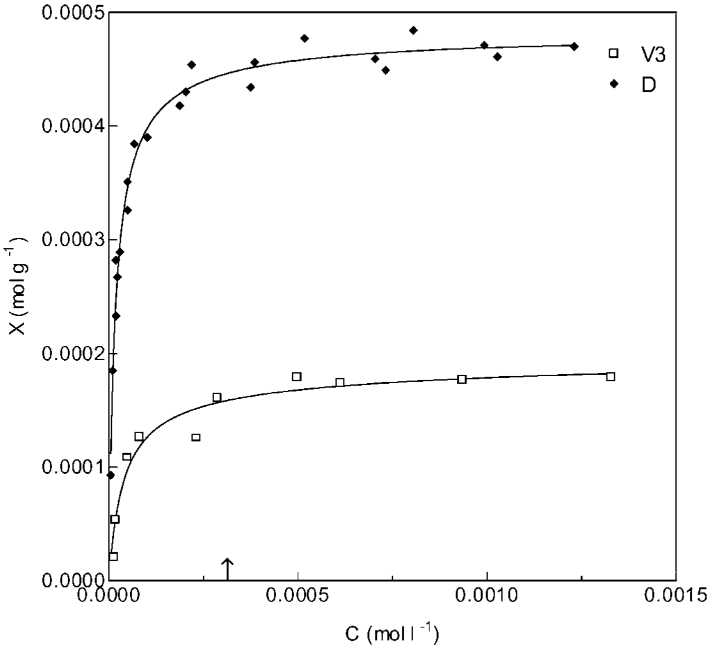

Fig. 1. Adsorption isotherms of TX-100 onto samples V3 and D at 20°C.

equilibrium concentrations (C) where a sharp increase of amount adsorbed (X) was observed, indicated a high affinity of TX-100 for the carbon blacks and the activated carbons surfaces. In the second part of isotherms, X remains approximately constant in all cases. This plateau appears at the CMC or slightly before (marked with arrow in Fig. 1). This plateau value has be taken as the maximum adsorption capacity of the solids (X_m) and allows defining θ, by the ratio of the amount adsorbed at a given equilibrium concentration to this maximum amount adsorbed. The X_m-values obtained are reported in Table 1 and they vary from 1.95×10^{-3} to 0.96×10^{-4} mol g^{-1} and from 5.21×10^{-4} to 3.92×10^{-4} mol g^{-1} for the carbon blacks and the activated carbons, respectively.

The analysis of the calorimetric data concerning the adsorption of TX-100 requires its dilution enthalpies at the working temperature. Fig. 2 shows the differential dilution enthalpies of TX-100 at 20°C as a function of the final concentration (obtained after dilution of a stock solution at 1.0×10^{-2} mol l^{-1}). This graph shows two plateaux separated by a step around the critical micelle concentration. The first plateau, obtained for final concentrations below the critical micelle concentration, corresponds to the dilution and destruction of micelles. This indicates that monomer dilution is negligible. The second plateau above the CMC is mainly due to micelles dilution. This is in fact a pseudo-plateau. At a theoretical final concentration equal to that of the stock solution, a zero-value should be reached because the concentration is the same in the stock solution and in the calorimetric cell. The height of the step allows deriving an endothermal micellisation enthalpy of 8 kJ mol^{-1}, in agreement with [20,21].

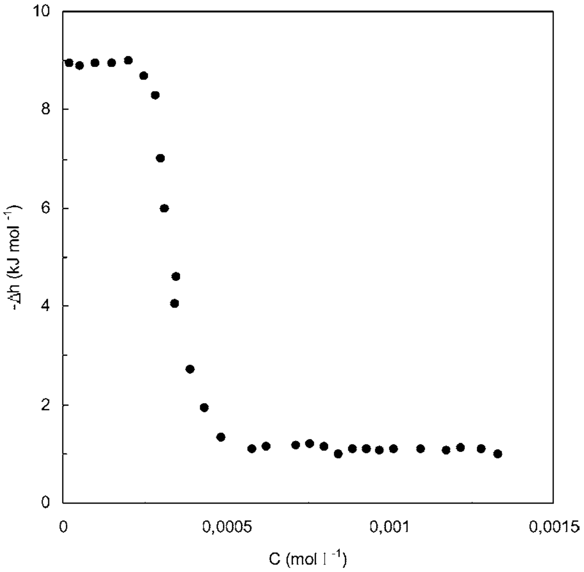

Fig. 2. Dilution Enthalpies of TX-100 at 20°C vs. final concentration after dilution from an initial concentration of 1.0×10^{-2} mol l^{-1}.

Figs. 3 and 4 show the differential molar adsorption enthalpies of TX-100 ($-\Delta h_{ads}$) as a function of coverage (θ), onto the carbon blacks and the activated carbons, respectively. Fig. 3 indicates that the differential molar enthalpy of adsorption follows the same general trend with θ for the six carbon blacks: a highly exothermal effect at lowest coverages, which emphasises the strong initial adsorption of TX-100 obtained from adsorption isotherms, followed by an endothermal one and, finally, as the coverage approaches unity, it tends to a value close to zero. Despite that similarity, it can be distinguished two different behaviours at very low surface coverage depending on the sample (Fig. 5). The differential enthalpy values extrapolated at zero coverage, $(\Delta h_{ads})_{\theta=0}$, are: around -144 kJ mol^{-1} for BP2000, BP1300 and BP880, and approximately one-half of that value (-74 kJ mol^{-1}) for V6, V3 and SV. Two groups of carbons are, thus, defined: BP2000, BP1300, BP880 on one side and V6, V3 and SV on the other side.

From Fig. 4 it can be seen that the enthalpic curves for the activated carbons are of two types. The first one corresponds to sample D, which presents a similar general trend of $-\Delta h_{ads}$ with θ to that the carbon blacks. The second one corresponds to the samples P and N for which, although the low coverage enthalpy values reach similar values to those of the sample D (Fig. 6) or of the Black Pearls set (Fig. 5), $-\Delta h_{ads}$ decreases less drastically with θ than the other samples, and so the values are exothermal at all coverages. This behaviour obtained for samples P and N is very close than those found by Partyka and co-workers who also studied the adsorption of TX-100 onto activated carbon [22,23].

It is known that at the lowest equilibrium concentrations, adsorption takes place preferentially on the most energetic sites of the surface. Then the $-\Delta h_{ads}$-values obtained at very low coverage, can be attributed to the adsorption of surfactant molecules on these

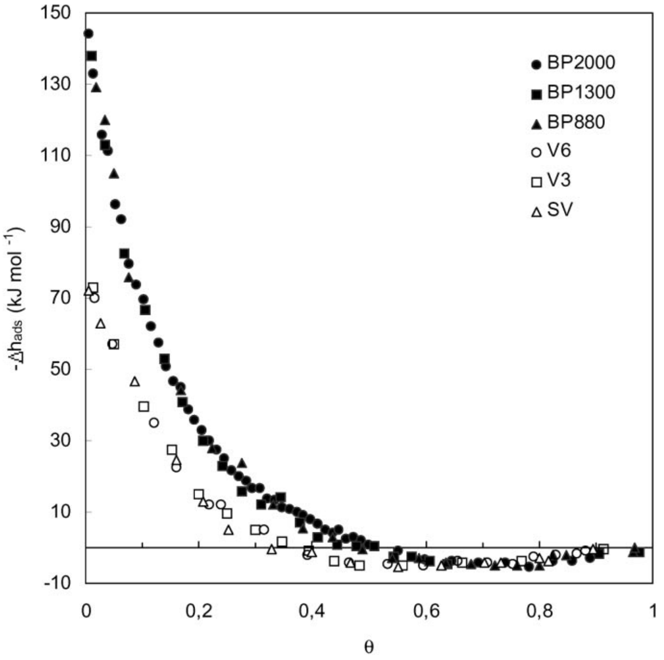

Fig. 3. Differential enthalpies of adsorption of TX-100 vs. coverage onto carbons blacks at 20°C.

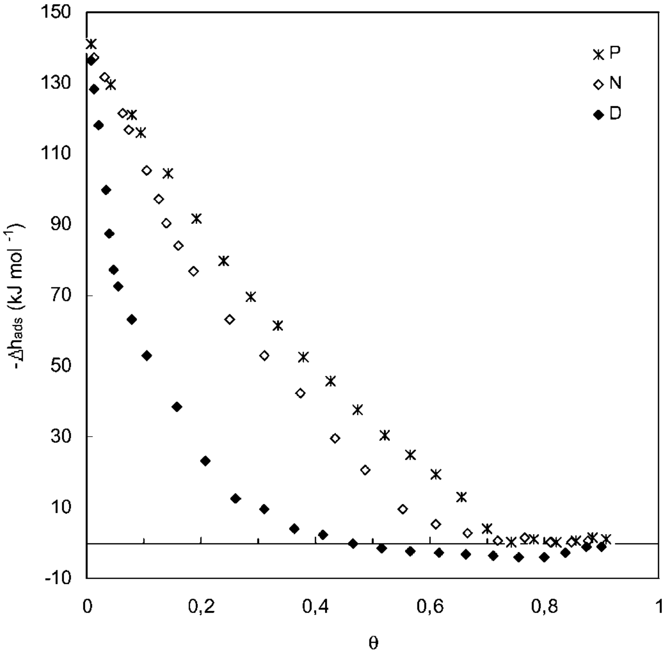

Fig. 4. Differential enthalpies of adsorption of TX-100 vs. coverage onto activated carbons at 20°C.

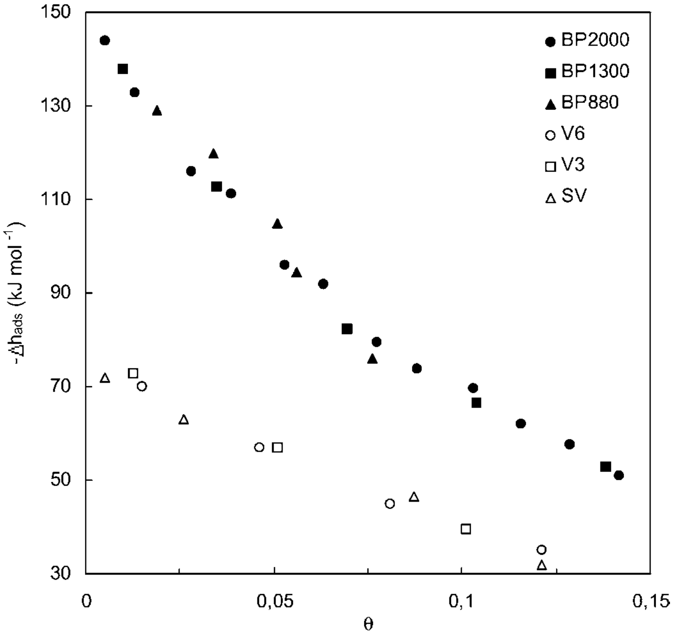

Fig. 5. Differential enthalpies of adsorption of TX-100 onto carbon blacks: low coverage range.

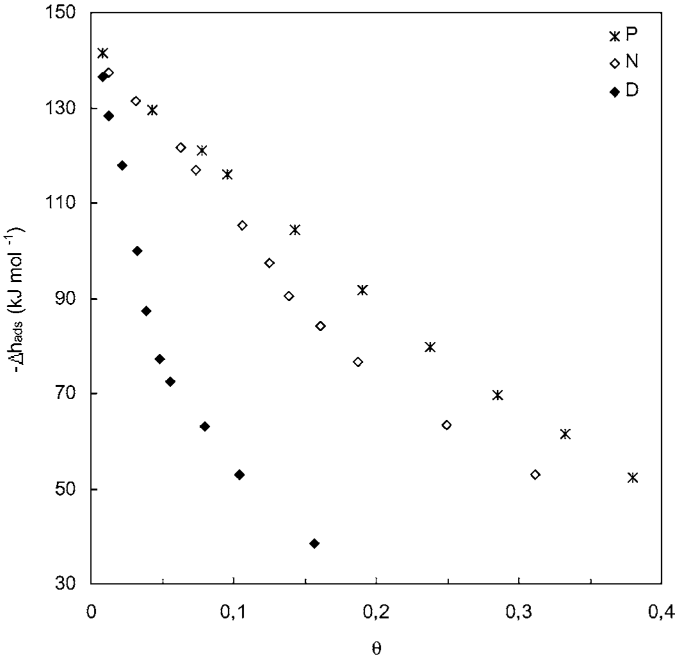

Fig. 6. Differential enthalpies of adsorption of TX-100 onto activated carbons: low coverage range.

most energetic sites, which, for these systems, could be related to either the narrowest micropores or the most energetic surface groups.

Carbon blacks and activated carbons can be solids very different from a textural and chemical point of view, however, the similarity of behaviour seen in Figs. 5 and 6 at the lowest coverage ratios and in the value of $(\Delta h_{\mathrm{ads}})_{\theta=0}$ irrespective of the nature of the carbon support (activated carbon and Black Pearls series) indicate that the interaction between the adsorbate and the carbons are the same type in both cases. This fact is a clear indication that the adsorption of TX-100 at low coverages involves similar adsorption surface centres.

To elucidate which of the above mentioned contributions predominates for our systems, the carbonaceous materials were characterised in terms of surface chemistry and porosity. In the previous characterisation works [12,13], a difference was found of surface chemical nature between the carbon black and the activated charcoals, but no difference between the samples of the same sets. Despite some differences found in the surface densities of these functional groups from one sample to the other in a given set of solids, there is no correlation with the two groups of samples evidenced by calorimetric results at low coverage. This fact suggests that the chemistry surface does not play a key role in distinguishing between the adsorption onto activated carbons and carbon blacks nor among the samples of each group. As a consequence, the different values of $(\Delta h_{\mathrm{ads}})_{\theta=0}$ have to be connected with another characteristic of the adsorbents than the surface chemistry.

Gas adsorption results [12,13] indicate that Black Pearls and activated carbons, possess a porosity which includes mainly micropores. On the other side, V6, V3 and SV are samples with a high external surface area, mesopores and an almost negligible microporous volume (see Table 1). As a consequence, it can be stated that adsorption at low coverage on samples V6, V3 and SV takes place on the most energetic sites of the surface, but these sites are not located inside micropores.

It is interesting to analyse the behaviour of the Black Pearls and activated carbons groups at very low coverage. The Black Pearls have a well developed microporosity and their values of $(\Delta h_{\mathrm{ads}})_{\theta=0}$ is ca. twice that for V6, V3 and SV. This suggests that the beginning of adsorption occur on the most energetic sites of the Black Pearl surface, which can be similar to that of the non-microporous samples from a chemical point of view, but is probably located inside the microporosity. If a molecule is adsorbed into a slit-shaped pore whose width is close to the solute size, it interacts simultaneously with both of the micropore walls, leading to an adsorption enthalpy twice that for molecules adsorbed on a more open surface [24,25]. The very high enthalpies at low coverage (-144 kJ mol^{-1}) could correspond to a surfactant molecule in a flat conformation in a slit-shaped micropore having a width close to that of an alkyl chain. This enhancement of adsorption energy due to micropores is expected to decrease progressively with an increase of micropore width, i.e. when coverage increases. As shown in Figs. 3 and 4, as coverage increases $-\Delta h_{\mathrm{ads}}$ decreases in all cases until the same range as adsorption enthalpies for the non-microporous samples, although it can be seen that this value is reached at different coverage ratio depending on the sample, ca. 0.1 for Black Pearls and D, 0.2 for N and 0.3 for P.

Adsorption of non-ionic surfactants on open hydrophobic surfaces is suggested to evolve from an horizontal arrangement of adsorbed molecules to a more or less vertical orientation, by the displacement of the hydrophilic tails from the surface by the hydrophobic chains of the newly adsorbed molecules [8]. This progressive displacement to a more tilted disposition would lead to a less and less exothermal contribution of the adsorbent–adsorbate interaction [26]. Also, the increasing coverage allows the hydrocarbon chains of adsorbed molecules to interact between them, which is associated with an endothermic process [27].

As coverage increases, the differential adsorption enthalpies for these samples become positive at a coverage ratio between ca. 0.35 and 0.50, depending on the sample. However, sample P and N show a different behaviour: the exothermic effect continues being observed until θ is ca. 0.8, after which the differential enthalpies reach values close to zero. The rate of the evolution with coverage of the differential adsorption enthalpy in the range between –74 and 6 kJ mol^{-1} is higher for the Black Pearls and D samples than for the non-microporous samples. For the non-microporous samples, this behaviour is the reflection of both the decrease of the adsorbing sites energy and the conformational changes of the adsorbed molecules. These arguments are also valid for the microporous samples, but the enlargement of the microporosity gives an additional contribution that could cause the steeper slope observed in this range.

At coverage around 0.6 the endothermal effect observed in these cases gets values close to the micellisation enthalpy of TX-100 [20,21]. Below the CMC, the only species in solution are monomers. The observed endothermal effect is compatible with a surface aggregation process similar to bulk micelle formation. Accordingly, we can assume that above coverage 0.6, surfactant molecules are adsorbed by hydrophobic interactions with molecules already fixed on the solid surface, leading to the formation of interfacial aggregates. The shape of these aggregates is probably hemispherical or hemicylindrical as suggested by AFM results [28]. It is likely that this process has to take place on the external surface or inside pores wide enough to accommodate these aggregates. The porosity analysis shows that all these samples are the solids with the highest values of the ratio of external to BET surface area ($S_{\mathrm{ext}}/S_{\mathrm{BET}}$).

According to the previous assumptions, if the endothermic transition can be related to the aggregation process on an open enough surface, the coverage at which the formation of aggregates happens should depend on the textural characteristics of the samples. This is evidenced by the comparison of the values of $S_{\mathrm{ext}}/S_{\mathrm{BET}}$ shown in Table 1 with the coverage at which the endothermal transition takes place (see Figs. 3 and 4). As expected, this coverage is higher for the set of the most microporous of these samples (BP2000, BP1300, BP880 and D) which have the largest proportion of micropores as indicate by the lowest values of the corresponding $S_{\mathrm{ext}}/S_{\mathrm{BET}}$ ratio.

As it can be seen in Fig. 3 for these solids, a further increase of the equilibrium concentration leads to differential enthalpy values less endothermic. In this region ($\theta > 0.8$), the surface is almost completely covered and the bulk concentration is nearly equal to the critical micelle concentration. The adsorption enthalpy corresponds to the transfer of a surfactant molecule from a solution containing micelles to the interface. Consequently, if we assume the above mechanism, the net enthalpic effect in this coverage range decreases because aggregates are energetically similar in solution and at the interface. This evolution is due to the fact that adsorption enthalpies are here referred to the equilibrium solution. When the reference state is chosen at infinite dilution, the enthalpy of adsorption stay equal to the micellisation enthalpy until coverage 1 [20,29].

Finally, it can be seen from Fig. 4 that for the samples P and N, the formation of the aggregates is not as clear as for the other sample, because the endothermal effect is not evident. It is probably due to the fact that samples P and N are the solids with the lowest values of the ratio of external surface area: they are more microporous than mesoporous (Table 1). It is then expected that the interactions between adsorbed molecules meet some steric hindrance.

4. Conclusions

The analysis of adsorption enthalpy of TX-100 from aqueous solutions onto activated carbons and carbon blacks allows us to propose the following interpretation of the adsorption behaviour of these systems. At very low coverages ratios, the enthalpy is exothermic and very high for the all cases; then adsorption is related to the adsorption in the narrowest pores. For the microporous samples this interaction leads to an adsorption enthalpy twice that on more open surfaces.

Beyond this phase, an exothermic effect continues to be observed that results from two kinds of interactions: while the less energetic sites are filled simultaneously the molecule of surfactant interacts with the solid surface and laterally with the hydrophobic chain of the molecules already adsorbed; this last effect is endothermic and for carbons with the highest values of the ratio of external surface (carbon blacks and D) becomes dominant as soon as the coverage increases. In these cases an approximate endothermic plateau is observed and followed beyond a degree of coverage about 0.6 by a rise in the endothermic effect. It is likely that this surface aggregation mechanism will occur when the surface is enough open, because the aggregate size, which is probably close to the micelle or the half-micelle size, is of the same order as a mesopore.

For the samples P and N the endothermic transition is not found but at coverage over 0.8 the enthalpy becomes zero. This fact is in agreement with the lower ratio of external surface area found for these samples from nitrogen adsorption. The surface is mainly developed in micropores where the aggregation is more or less prevented.

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