167. *The Effect of Graphitization on the Adsorption of Surfactants by Carbon Blacks.*

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Adsorption isotherms have been determined for an anionic and cationic surfactant (Aerosol OT and cetyltrimethylammonium bromide) on three carbon blacks, before and after graphitization.

The graphitized carbons present inert faces on which a monolayer can be deposited by physical adsorption. The density of packing at saturation depends to a minor degree on the nature of the counterion and the ionic strength of the solution.

The original carbons carry weakly acidic oxygen complexes, and these reduce the affinity of the surface for Aerosol. On the other hand, a bimolecular layer can be formed on these carbons from concentrated solutions containing salts, whereas no second layer formed from such solutions on the graphitized carbons.

The implications of these results for the structures of the adsorbed layers are discussed.

COMMERCIAL carbon blacks consist of spheroidal particles that contain, in addition to carbon, small proportions of oxygen, hydrogen, and involatile ash. The oxygen is chemically combined as " oxygen complexes " that are removable by heating to *ca.* 1000° in vacuum; the last of the hydrogen is not removed until *ca.* 2000°, and, finally, heating between 2500 and 3000° induces crystallization of the carbon. The particles change into irregular polyhedra, which, although not crystallographically perfect graphite, behave from the surface-chemical point of view like the inert basal planes of graphite.

The "original" carbons (*i.e.*, before graphitization) are not, however, inert. The oxygen complexes act as weak acid and, according to some authors, as weak bases also.[1] Some striking differences have now been observed between the affinity of the original and graphitized carbon blacks for surfactants.

EXPERIMENTAL

Materials and Methods.—The carbons used were kindly provided by Dr. W. R. Smith of Cabot Inc., U.S.A., and included " Spheron 6 " and its graphitized form " Graphon," which have been much studied by gas-adsorption techniques. The characteristics of the materials are summarized in Table 1. Graphitization, at approx. 2700°, was carried out by the manufacturers.

TABLE 1.

	Volatile content (%)	Ash (%)	Average particle diam. (Å)	Surface area (m.^{2}/g.)
Spheron 6	5·0	0·07	250	113·2
Graphon	0·08	0·01	250	94·2
Sterlin FT (original)	0·5	0·07	2000	14·1
Sterling FT (graphitized)	0·06	0·02	2000	13·3
Sterling MT (original)	<1	0·07	4720	7·9
Sterling MT (graphitized)	0·04	0·04	4720	6·9

The surface areas quoted were kindly checked by Dr. E. Redman (Morganite Research Ltd., London) by nitrogen adsorption.

The surfactants employed were Aerosol OT (sodium diethylhexylsulphosuccinate) and cetyltrimethylammonium bromide. The samples used gave no minimum in the surface tension–concentration curve, indicating absence of highly surface-active impurities. Concentrations of their aqueous solutions were determined by the methods of Barr, Oliver, and Stubbings [2]

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[1] Cf. R. N. Smith, *Quart. Rev.*, 1959, **13**, 287.

[2] T. Barr, J. Oliver, and W. V. Stubbings, *J. Soc. Chem. Ind.*, 1948, **67**, 45.

and Hillenbrand, Sutherland, and Hogsett,[3] respectively, which were accurate to ±1%, except below 0·1 mmole/l., for which region surface tension measurements by the equilibrium plate method were used to determine the concentration of surfactant left in solution. The Li,Cs, and Ag forms of Aerosol OT were prepared by ion exchange with resins.

The presence of acidic or basic character in the carbons was investigated by potentiometric titration with 0·1N-sodium hydroxide and hydrochloric acid in presence of 0·01N-sodium chloride, by use of a hydrogen electrode, a potentiometer sensitive to m ±0·1v, and a motorized piston microburette for supplying accurate small additions of titrant. Suspensions were stirred by bubbling nitrogen in an enclosed vessel to exclude carbon dioxide. The amount of acid or alkali bound by the carbon was obtained from the difference of the e.m.f.–volume curves, with and without carbon present.

Adsorption determinations were carried out in stoppered flasks shaken in an air thermostat at 25° ± 1°; adsorption was virtually complete within 1 hr., but not less than 2 hr. was allowed.

RESULTS

Acid–Base Properties.—Judged by the small pH-shift on placing the carbons in neutral 0·1N-sodium chloride, Spheron 6 is " acidic " and the Sterlings and all the graphitized carbons are " basic " in character. Titratable water-soluble impurities are small in amount compared with the amount of acid that is taken up on titration of the ungraphitized carbons (and are not related to the presence of tarry matter that can be extracted with benzene).

Spheron 6 behaved as a very weak poly-acid, no saturation being reached at pH 11·5, at which point alkali amounting to about 0·1 m.equiv./g. of carbon had been combined. (This corresponds to only 1/30th of the oxygen complexes present in this carbon). By comparison, the graphitized carbons had negligible base-binding capacity—only around 5 μequiv./g., even for Graphon.

The alkaline reaction shown by several of the materials did not appear to indicate the presence of important amounts of bound basic groups on the surface of the carbon. Sterling MT was investigated in detail. The original carbon required about 10 μequiv./g. to bring it to pH 2·7, but about half of this quantity could be accounted for by soluble impurities; further, on back-titration after acidification about 5 μequiv./g. less alkali was needed to restore the pH, suggesting loss of carbon dioxide.

It was therefore concluded that the alkaline reaction of Sterling MT was due to its inorganic-ash content. Indeed, if the 0·07% ash were assumed to be calcium carbonate, this would approximately account for the results. Any true acid-binding by the carbon surface must be less than 1 μequiv./g. at pH 6, rising to not more than 5 μequiv./g. at pH 2·7. Both original and graphitized Sterling MT were found to be negatively charged in electrophoresis in media of pH 6—11, but became positively charged at pH 3.

As the adsorption of detergent was studied with neutral solutions, it can be assumed that the original carbons carried significant amounts of oxide complexes of weakly acidic type (presumably phenolic in character) while the graphitized carbons were virtually free from them (*e.g.*, the amount of surfactant adsorbed on Graphon was of the order of 300 μequiv./g. compared with 5 μequiv. of titratable acid capacity).

Adsorption of Surfactants.—Adsorption isotherms for the pure surfactants from water are summarized in Figs. 1 and 2. Adsorption is reversible over the experimental range.

All the isotherms are of the general " Langmuir " form, with a long plateau. The data conform approximately to the Langmuir isotherm within experimental accuracy but detailed analysis is not justified, firstly because the data at low concentrations are not precise enough, and secondly because high coverage is reached only at concentrations above the critical micellar concentration, where activities are not proportional to concentrations.

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[3] E. F. Hillenbrand, W. W. Sutherland, and J. N. Hogsett, *Analyt. Chem.*, 1951, **23**, 606.

The plateau commences at, or a little above, the critical micellar concentration (c.m.c.); thereafter the adsorption continues to rise slightly, showing that the activity of the adsorbate is also increasing somewhat and that micellization is different in character from phase separation.

It is evident that the graphitized carbons have a lower capacity per unit weight *but a higher affinity* for the surfactants than have the original carbons. For example, the point of $\frac{3}{4}$ saturation is at about 0·3 mmole for the former and about 0·9 mmolar for the latter. Dividing the N_2-area by the amount of Aerosol adsorbed at " saturation " (taken as the value at 9 mmole/l.) gave the following N_2-areas (in Å^2) per molecule:

	Spheron	Sterling FT	Sterling MT
Original carbon	89	71	75
Graphitized	78	69	71

These figures show a slightly closer packing on the graphitized carbons.

Adsorption from Solutions containing Salts and Various Counterions.—Addition of sodium chloride to an anionic surfactant not only increases the activity of solute by common-ion effect, but also reduces the c.m.c. by electrostatic screening of double-layer repulsion (reduction of $1/\kappa$, the inverse Debye thickness), and may be expected to facilitate adsorption by both effects. Fig. 3 shows results obtained with lithium, sodium, cæsium, and silver forms of Aerosol OT in the presence of 0·01N-simple electrolyte with the same cations, the substrate being *graphitized* Sterling MT. It is evident again that these systems still show physical monolayer adsorption, the plateau being reached slightly above the c.m.c. in each case; but it is significant that the level of " saturation " adsorption is different. The addition of sodium chloride reduces the area per molecule from 70 to 66 Å^2. The other

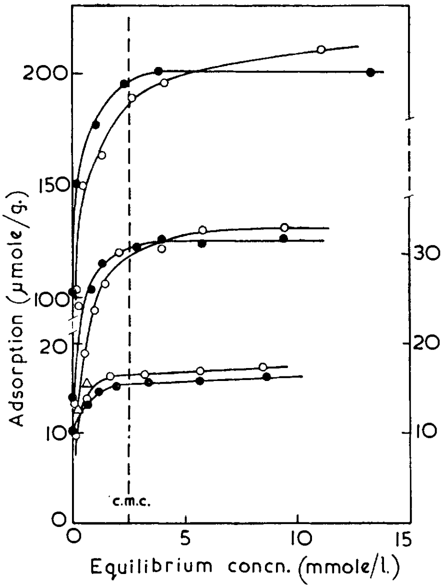

FIG. 1. Adsorption isotherms for Aerosol OT from water.

○, Original carbon; ●, Graphitized carbon; upper pair of curves, Spheron 6; middle pair, Sterling FT; bottom pair, Sterling MT (△, desorption).

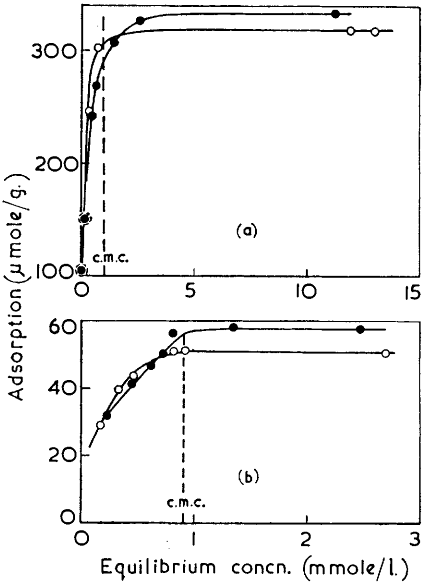

FIG. 2. Adsorption isotherms for cetyltrimethylammonium bromide from water.

○, Original carbon; ●, Graphitized carbon; (a) Spheron 6; (b) Sterling FT.

curves correspond to 72, 66, and 61 Å^2 per molecule for the lithium, silver, and cæsium forms.

The c.m.c. values for Aerosol OT in 0·01N-salt solutions were determined from measurements of the surface tensions, γ (made by the vertical plate method). Results have been recorded elsewhere.[4] Graphs of γ versus $\log c$ for constant concentration of simple salt showed sharp intersections of linear portions at the following c.m.c. values (in mmole l.$^{-1}$); Na (in absence of salt) 2·5; Na (+0·01N-NaCl) 1·3; Ag (+0·01N-AgNO$_3$) 1·1; Cs (+0·01N-CsCl) 0·9. This corresponds to increasing ion-pairing (or Stern adsorption) in the order $Na^+ < Ag^+ < Cs^+$, which is the order of decreasing hydrated ionic radii. The parallel between physical monolayer adsorption and micellization in these systems is noteworthy.

The adsorption isotherms obtained with the *original* carbons in Aerosol +0·01N-salt solutions proved to be remarkably different from those for the graphitized carbons (cf. Fig. 4, which is exactly comparable with Fig. 3). Instead of reaching a plateau, the curves for sodium, silver, and cæsium rise again and pass through a maximum which corresponds approximately to a *bimolecular layer*. In each case there is a distinct shoulder where the first layer is completed. With lithium the onset of the second layer would evidently be at surfactant concentrations beyond the range studied. The case of sodium is particularly clear in proving again that the thermodynamic activity of the surfactant increases with increasing concentration in the region above c.m.c., for the second layer does not begin to form until 3 × c.m.c. is reached.

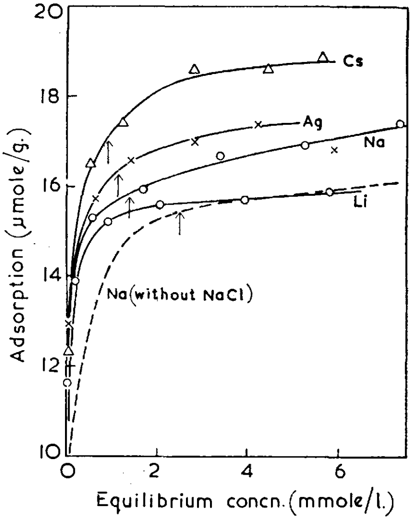

FIG. 3. Adsorption isotherms for different salt forms of Aerosol OT from 0·01M-solution of added electrolyte with a common cation, on to *graphitized* Sterling MT (arrows mark c.m.c.).

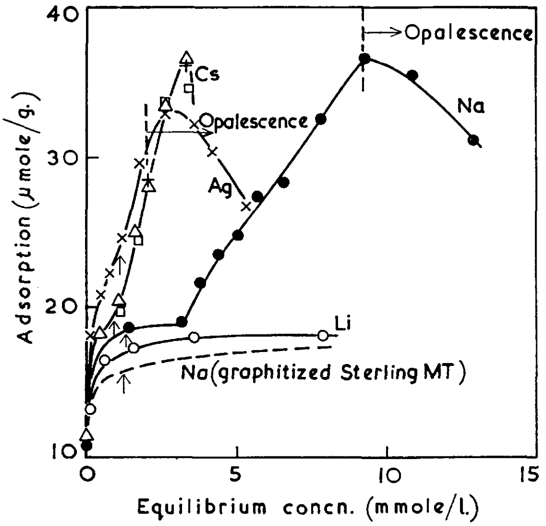

FIG. 4. Adsorption isotherms for different salt forms of Aerosol OT from 0·01M-solution of added electrolyte with a common cation, on to original (non-graphitized) Sterling MT. (On graph for Cs: △ untreated carbon; □ treated for removal of ash; + treated for removal of tar—see text).

DISCUSSION

Polarity of the Surfaces.—It seems likely that the original carbon blacks are completely covered with " oxygen complexes " (the amount of oxygen being of the required order) while the graphitized carbons are chemically inert over the exposed basal planes, and carry

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[4] F. Z. Saleeb, Ph.D. Thesis, Univ. of London, 1962.

oxygen complexes only at the edges of the crystallites. As the larger graphitized carbons are the better crystallized, these materials provide almost ideal inert solid substrates for study of physical adsorption. Smith,[5] Kiselev *et al.*,[6] and other workers, have demonstrated from gas-adsorption data the molecular uniformity of the surfaces of these materials. Young, Chessick, Healey, and Zettlemoyer[7] have shown that only $\frac{1}{1500}$ of the surface sites on Graphon are polar; the proportion is presumably even smaller for the graphitized Sterlings.

Structure of the First Layer.—There is no doubt that, with both types of carbon, saturation from salt-free detergent solution corresponds to a monolayer physically adsorbed with polar groups outward. The orientation, expected theoretically, was confirmed by wetting characteristics, electrokinetic potentials (reported elsewhere[8]), and colloidal stability. The areas found with the two graphitized Sterlings agree with the value of 70 Å^2 per molecule arrived at by Abram[4] from a molecular-scale model of Aerosol OT in an unstrained configuration with the molecule oriented vertically. The larger apparent areas occupied by Aerosol on Spheron and Graphon are probably due to molecular roughness or porosity of these surfaces, nitrogen being able to penetrate where Aerosol cannot. (Spheron is less perfectly crystallized by heating than the Sterlings.)

It is clear that adsorption in this system is due mainly to physical surface-activity. The basal planes of graphite are non-polar, and adsorption of surfactant is due to escape of the non-polar group from the water phase. The hydrophobic carbons were all rendered hydrophilic by adsorption of surfactant to the extent of about 85% of saturation. The weaker binding on to the original carbons can be ascribed to the presence of polar groups—the oxygen complexes—on the carbon.

Results obtained with cetyltrimethylammonium bromide (c.t.a.b.) (Fig. 2) are simiar to those with Aerosol, saturation being reached at an equilibrium concentration slightly above the c.m.c. This already suggests mainly physical adsorption. In addition, electrophoretic measurements on graphitized Sterling MT showed that even in 0·17 mmolar solutions of the cationic surfactant (1/5th of the c.m.c.) this carbon is strongly positively charged, whereas all the carbons were negative in pure water or in Aerosol solutions. Therefore, the bulk of the monolayer of surfactant is physically adsorbed with ionic groups outwards.

The area of saturation was approximately 40 Å^2 per molecule on the graphitized carbons. This corresponds to the bulky trimethylammonium headgroup, rather than the cetyl paraffin chain. On the original Spheron cetyltrimethylammonium bromide packed to only 67% of this density. This suggests again that interaction with pre-existing polar groups restricts the freedom of packing of the surfactant. On the other hand, the affinity of the original carbons for this cationic surfactant is not less than that of the graphitized carbons (as was the case for the anionic agent); indeed, it appears to be slightly greater. This suggests that some degree of salt formation occurs between the cationic surfactant and the anionic oxygen complexes. It may be that a small proportion of the cationic molecules are anchored firmly in " reverse orientation " (*i.e.*, chemisorbed with chains outermost), while the majority then fill in as best they can by physical adsorption in the spaces left.

Summarizing, it can be concluded that a physically adsorbed and almost close-packed monolayer is formed from solutions at concentrations from 1·5 up to at least 4 times the c.m.c. if the substrate is non-polar; but when polar groups are present the packing is less close. Of course, additions of solute above the c.m.c. do not greatly increase the activity.

It is evident that " saturation " on these non-polar surfaces is not determined by rigid close-packing of the paraffin chains. In the Aerosol OT molecule these chains are double ethyl-hexyl groups and therefore appreciably compressible. The level of the plateau is

[5] M. H. Polley, W. D. Schaeffer, and W. R. Smith, *J. Phys. Chem.*, 1953, **57**, 469.

[6] A. A. Isirikyan and A. V. Kiselev, *J. Phys. Chem.*, 1961, **65**, 601.

[7] G. J. Young, J. J. Chessick, F. H. Healey, and A. C. Zettlemoyer, *J. Phys. Chem.*, 1954, **58**, 313.

[8] F. Z. Saleeb and J. A. Kitchener, 4th Int. Congress of Surface Activity, 1964, to be published.

therefore dependent on the thermodynamic activity of the solution and the activity coefficient of the adsorbed monolayer. Both are significantly affected by the nature of the counterion.

The surface-tension measurements provided data for calculation, *via* the Gibbs equation, of the adsorption of the surfactant at the air–water interface for comparison. The areas per molecule below the c.m.c. were 75 Å^2 for the sodium and silver forms and 71 Å^2 for the cæsium form. These figures also indicate the influence of counterion on the packing of the monolayers, but the areas are significantly greater than those for saturated monolayers on carbon. The adsorption at the air–water interface appears to be constant from 0·3 × c.m.c. up to the c.m.c., as has been noted with other surfactants by van Voorst Vader,[9] whereas adsorption on the carbons was highly dependent on concentration over this range, and saturation was not reached until distinctly higher concentrations than the c.m.c. were reached.

Origin of the Adsorption Maxima.—The occurrence of *maxima* in the isotherms was traced to the onset of a phase change in the solutions. All solutions around the maxima tended to develop a bluish haze *very slowly*. No actual precipitate ever formed. The new phase was presumably a stable, colloidal emulsion of mesomorphic type, for no crystalline phase can be obtained from concentrated solutions of Aerosol OT. The maxima actually correspond to " equilibrium " adsorption from super-saturated solutions. For example, a faint opalescence, detectable in an absorptiometer with blue light, was first noted at 9·2 mM with Na-Aerosol (+0·01N-silver chloride) and at 2·0 mM with Ag-Aerosol (+0·01N-silver nitrate), whereas the maxima occurred at 10 and 2·8 mM, respectively. The haze disappeared on warming the solution and slowly formed again, apparently reversibly, on cooling. Transparent solutions remained so indefinitely. The Li-Aerosol remained clear at all concentrations studied and gave no second layer on the isotherm. These various observations all support the conclusion that the opalescence was, indeed, separation of a new phase of the Aerosol salt, not an artefact arising from hydrolysis, etc.

It is surprising that only bimolecular layers were formed, the solid not serving as " nucleation " substrate for the mesomorphic phase. This is shown by the fact that adsorption from solutions at higher concentrations, where supersaturation has presumably been relieved to an increasing extent by phase separation, was actually reduced.

Structure of the Bimolecular Layers.—The most significant feature of these results is that bimolecular layers could be formed only on the original carbons, never on the graphitized carbons, even from super-saturated solutions or opalescent solutions carrying colloidal surfactant phase. As the adsorbed layer on graphite is physically held and virtually close-packed with association of counterions, it presumably possesses the conventional structure with paraffin chains all oriented neatly towards the solid and ionic head-groups exposed to the solution.* It follows that the lower component of the bimolecular layer on the original carbons must differ from this in some way, for it *does* accept a second layer. The top component presumably has the conventional structure with ionic groups outwards, though it is less stably anchored than the single monolayer on graphite, requiring higher concentrations for its formation.

One possibility is that the basal layer of the bimolecular coating on the original carbon is in " reverse orientation " (non-polar groups outermost) brought about by salt formation with the surface; in fact, Aerosol OT has been used as a flotation collector for fluorite.[10]

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* Since no second monolayer or deposit of mesomorphic phase will form on top of well-oriented ionic monolayers the mesomorphic phase (at least in Aerosol OT) does *not* consist of a pile of parallel bimolecular leaflets. It may be the cylindrical micellar structure suggested for the " middle soap " phase of soaps by Luzatti *et al.*[10a]

[9] F. van Voorst Vader, *Trans. Faraday Soc.*, 1960, **56**, 1067.

[10] K. L. Sutherland and I. W. Wark, " Principles of Flotation," Australian Inst. Min. Met., Melbourne, 1955, p. 291.

[10a] Luzatti, Müstacchi, and Skoulios, *Discuss. Faraday Soc.*, 1958, **25**, 43.

As the present work has thrown doubt on the existence of basic carbon–oxygen complexes, the possibility of reaction between Aerosol and the basic constituents of the ash was considered. However, in contrast to the results of Vold and Sivaramakrishnan,[11] acid-treatment of Sterling MT with 4N-hydrochloric acid for 5 hr. on a steam-bath, which reduced the ash from 0·07 to <0·01%, had no significant effect on the adsorption isotherm (Fig. 4). Furthermore, there was no significant rise of pH when Aerosol was adsorbed (in absence of carbon dioxide), as there would have been if an appreciable proportion of the first monolayer were reacting with basic groups. Nor was the presence of a trace of tarry matter in the original carbons responsible for the second layer, for Soxhlet extraction with benzene to remove the tar also had no effect on the adsorption (Fig. 4). (The carbon remained predominantly hydrophobic after extraction, despite the presence of polar acidic oxygen complexes).

As a further check on the state of the first layer, electrophoretic mobilities of Spheron 6 and its graphitized form, Graphon, in pure Aerosol solutions were determined. The latter carbon moved about 12% the faster (over the range of 50—100% of a monolayer), but this presumably corresponds to the slightly stronger adsorption (at low coverage) on Graphon (Fig. 1). It appears that the two surfaces must carry very similar electrical double-layers, with the *majority* of the molecules oriented with polar groups outwards.

As the surface of the original carbons is known to be heterogeneous in character and partly polar,[6] the simplest hypothesis to explain the above facts is to suppose that the polar groups militate against adsorption of non-polar chains, without, however, entirely preventing it. Thus, the first layer may contain a small proportion of surfactant molecules chemisorbed in reverse orientation, while the majority are oriented normally. But, when a second layer is present, some, at least, of the first layer overturn to minimize the energy of the whole sandwich, for the polar (but not ionic) oxygen complexes offer a less unfavourable environment for the head-groups than do the hydrocarbon tails of the outer layer.

We thank Dr. W. R. Smith of Cabot Inc., U.S.A., for gifts of the carbons, original and graphitized; and the National Research Centre, Cairo, U.A.R., for award of study leave to F. Z. S.

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[*Received, March* 17*th*, 1964.]

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[11] R. D. Vold and N. H. Sivaramakrishnan, *J. Phys. Chem.*, 1958, **62**, 984.