The Effect of Calcium Ions on Carbon Suspensions[1]

H. PEPER [2] **and H. L. ROSANO,**[3] **Research and Development Division, Lever Brothers Company, Edgewater, New Jersey**

A high degree of dispersion of carbon black in water is obtained only in the presence of adsorbing long-chain, amphipathic molecules. Calcium ions flocculate these dispersions, but agglomeration can be prevented if anionic detergents are adsorbed on the carbon. Fine dispersions of carbon coated with a fatty acid or alcohol were maintained in the presence of calcium ions with detergents which coadsorb with the acid or alcohol monolayer. The significance of these results in regard to detergency theory is discussed.

THIS INVESTIGATION was undertaken in order to learn the conditions under which carbon black could be dispersed or flocculated in aqueous solutions. It is part of a program of study of the fundamentals of detergency. An assumption in this work is that, if soil particles do not flocculate in a solution, the factors that prevent particle-particle attachment will operate to some extent to prevent attachment to the fabric substrate. It is recognized that this is only a first approximation and a complete characterization of a detergent-fabric system would require knowledge of the nature of the fabric-water interface.

The stability of dispersions of a hydrophobic powder in water is generally considered to be principally controlled by the forces of electrostatic repulsion and Van der Waals' attraction as treated in the theory of Verwey and Overbeek (1). However there are cases of stable dispersions in which electrostatic repulsion does not appear to have a major effect. In these systems, resistance to flocculation is explained in terms of an entropy effect (2).

Several types of dispersing agents were investigated with respect to their ability to disperse carbon in water, the reaction of the dispersions to various concentrations of calcium chloride, and their influence on the electrokinetic potential of carbon particles in water and calcium chloride solutions.

The relative importance of electrostatic and nonelectrical factors in the stability of these carbon suspensions is then discussed in terms of the electrokinetic data and the chemical structure of the dispersing agents.

In another phase of this investigation the surface of the carbon was altered by preadsorbing a long-chain, aliphatic acid or alcohol. The response of these surface-modified carbon blacks to some of the same dispersing agents was studied in water and in calcium chloride solutions. The mechanism of interaction of the dispersing agents with the surface of the coated carbon was inferred from the results of experiments with a model system that consisted of insoluble monolayers spread at the air-water interface and penetrated from the water phase by dissolved dispersing agents.

The degree of dispersion of the carbon suspensions was estimated by measuring the opacity of the suspensions (3). The electrokinetic potential was determined by microelectrophoresis.

Experimental

A. *Materials.* The carbon black used in the dispersions was ELF 5 (Godfrey L. Cabot Company).

The water was prepared by double distillation, using a special all-Pyrex glass apparatus with a one-meter-long column having a spray trap at the top to insure against carry-over of undistilled liquid. The pot contained alkaline permanganate to oxidize organic contaminants. In the experiments with hexadecanoic acid-coated carbon it was essential to use doubly-distilled water in order to maintain a deflocculated system. Concentrations of calcium ion of the order of 10^{-5} molar were sufficient to produce substantial flocculation dispersions of this coated carbon.

The calcium chloride used was reagent grade. Sodium hexadecanoyl methyl taurate was prepared from distilled fatty acids, and the final product was recrystallized from ethanol. The hexadecanoic acid was Eastman White Label, and the hexadecanol was a middle fraction from a Podbielniak distillation apparatus (mp. 49.0°C.). The hexadecanol ethylene oxide condensate was an experimental sample from the General Aniline and Film Company and contained 14 moles of ethylene oxide per mole of hexadecanol. The product was a mixture of various chain-lengths, which formed clear water solutions at room temperature and in the calcium chloride solutions. The sodium dodecyl (propylene tetramer) benzene sulfonate was a commercial material substantially free of inorganic salts. Tetrasodium pyrophosphate and tetrasodium ethylene diamine tetra-acetate were also commercial materials.

B. *Equipment.* Light transmission of the suspensions was measured with a Photomultiplier Microphotometer (American Instrument Company, Silver Spring, Md.). Light of wavelength 5200 Å was employed, and transmission was measured in a rectangular cell which provided an optical path of 2.5 cm. for the suspension.

The electrophoretic mobility of the particles was measured in a micro-electrophoresis apparatus of the type described by Northrop and Kunitz (4).

The monolayer penetration experiments were performed at constant area by a method (5,6) that essentially involved the spreading of a film of stearic acid under a surface pressure of 17 dynes/cm., followed by injection of surfactant beneath the film and by measuring the changes in surface pressure at definite time-intervals. The surface pressure was measured by the pull on a sand-blasted platinum plate. Complete wetting of the plate was readily ascertainable by visual observation. A rectangular Pyrex dish was used for the solutions on which the monolayers were spread. Careful cleaning of all the components of this apparatus was conveniently accomplished by flaming (platinum plate) or rinsing with a fresh solution of sodium dichromate in concentrated sulfuric acid (Pyrex dish). All of the detergents were used in the penetration experiments at a final concentration that gave a surface pressure of 17 dynes/cm. in the absence of an insoluble film. Sodium dodecylbenzene sulfonate was used at 4.22 x 10^{-5} molar concentration and sodium

---

[1] Presented at the American Chemical Society Meeting (Colloid Division), Miami, Fla., April, 1957).

[2] Present address Harris Research Laboratories Inc., Washington, D.C.

[3] Present address: School of Mines, Columbia University, New York.

hexadecanoyl methyl taurate at 1.25 x 10^{-5} molar. All solutions were 2 x 10^{-5} molar calcium chloride.

C. *Procedures.* The test dispersions were prepared by diluting a 0.5% stock dispersion to 0.01% in the solution that was examined. These diluted carbon black dispersions were agitated in 100-ml. glass-stoppered graduate cylinders by inverting 10 times by hand. Directly after this mixing procedure a portion was poured into the optical cell, and the percentage of transmission was read in the photometer. The more flocculated systems transmitted about 25% of the incident light, and the deflocculated suspensions obtained with coated carbons in ion-free water and in hexadecanol polyether solutions transmitted only a few tenths of 1% of the incident light. The validity of the assumption that finer dispersions were more opaque and the flocculated suspensions relatively transparent was obvious from visual inspection of the large number of suspensions observed. Of course, this assumption would be invalid for systems composed of flocs less than a few tenths of a micron in diameter, through which considerable light would be transmitted. The mild agitation used in this investigation did not produce submicron size particles. Reich and Vold (3) have established a semiquantitative relation between floc size and light transmission.

Carbon coated with hexadecanoic acid or hexadecanol was prepared by stirring 2% of carbon black in a .05% methanol solution of the acid or alcohol for 15 min. at room temperature. The carbon was filtered, and the dried filter cake was prepared as a 0.1% stock suspension by agitating in a Waring Blendor at 40 volts (6,000 r.p.m.) for 5 min.

The electrophoretic mobility of the carbon particles in a particular medium was obtained from the mean of 10 observations. The electrokinetic potential was calculated from the mobility using Smoluchowski's equation:

$$\zeta = \frac{4\ \pi\ \eta\ V}{D\ \ X}\ (9 \times 10^4)$$

Where η = viscosity of water (poises)
D = dielectric constant of water
V = particle velocity in cm./sec.
X = voltage gradient in volts/cm.

All experiments in this investigation were performed at 25 ± 1°C.

Results

A. *Properties of Dispersions of Carbon in Various Aqueous Solutions.* Figure 1 gives the percentage of light transmission of .01% carbon in water, solutions of an inorganic sequestering agent, and solutions of two surface-active materials as a function of calcium ion concentration. The carbon is highly flocculated in water and does not change appreciably with added calcium chloride. These dispersions, which transmitted 25% of the incident light, had a gray appearance and were composed of flocs ranging from 100–1,000 microns in diameter. The distance between individual flocs was large, which accounted for the gray appearance and the large amount of light that was transmitted. The 0.1% solution of tetrasodium pyrophosphate had only a slight effect toward reducing the floc size and increasing the turbidity of the suspension. As in the case of water alone, there was no change in turbidity with increasing calcium ion concentration.

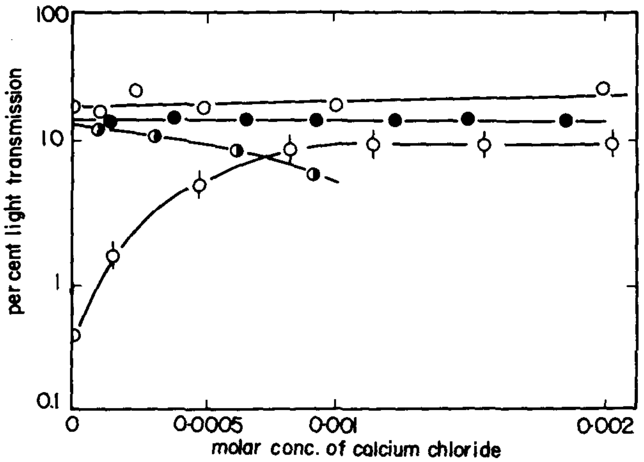

FIG. 1. Flocculation of .01% carbon suspensions (indicated by percentage of light transmission) as a function of Ca^{++} concentration in solutions of various dispersing agents. ○—water; ●—3.8 x 10^{-3} molar tetrasodium pyrophosphate; ◐—5 x 10^{-3} molar sodium dodecylbenzene sulfonate; ⌽—5 x 10^{-3} molar hexadecanol-ethylene oxide adduct.

The 5 x 10^{-3} molar solutions of the two surface-active materials showed widely-different results both in ability to disperse carbon in Ca^{++} free water and with increasing concentrations of Ca^{++}. Sodium dodecylbenzene sulfonate had only a very slight effect in Ca^{++} free water, but the dispersion of particles of carbon became finer with increasing Ca^{++} concentration, as indicated by the increasing opacity of the dispersion. The hexadecanol polyether solution produced an extremely fine dispersion, which transmitted only a few tenths of 1% of the incident light. Qualitatively this dispersion differed enormously in appearance from those which transmit about 10% of the light beam. The fine dispersion which transmits in the 0.1% range has a jet black appearance while those which transmit 2–15% have the appearance of various degrees of gray. The dispersion in the nonionic detergent solution is flocculated severely in 10^{-3} molar calcium ion solution however, indicating a sharp sensitivity to electrical effects.

The results in Figure 1 show that only the surface-active, organic substances have a substantial effect on dispersing carbon. Since the hydrocarbon portion of the detergent molecule probably adsorbs on the nonpolar carbon surface, it would appear that this mechanism is required for dispersing the hydrophobic carbon in water.

The electrophoretic mobilities of carbon particles dispersed in these solutions were determined; the calculated *zeta* potentials are plotted against the molar calcium ion concentration in Figure 2. In pure water the carbon has a negative charge, which is reduced with increasing concentrations of calcium chloride, as might be expected from a divalent counter-ion. In a solution of sodium pyrophosphate the negative potential of the carbon particles is increased from 50 to 70 millivolts, and this value remains approximately constant with the added calcium chloride until there are about equimolar concentrations of calcium ions and pyrophosphate ions. In sodium dodecylbenzene sulfonate solution the negative potential of the dispersed carbon is higher than in pure water, and the addition of calcium chloride increases it further. The latter effect may result from increased adsorption of organic sulfonate ions by a salting-out effect, which overcomes

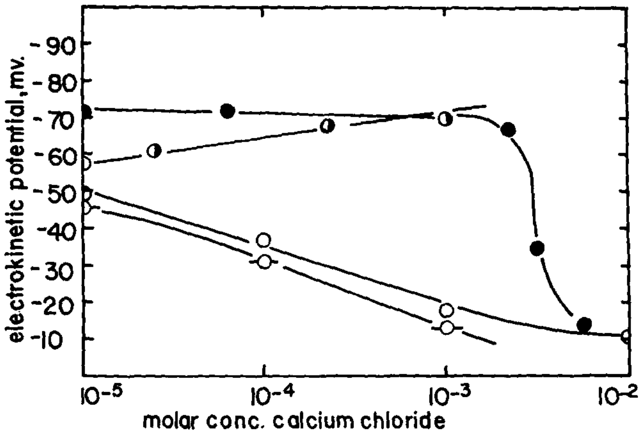

FIG. 2. The effect of Ca^{++} concentration on the electrokinetic potential of carbon in solutions of various dispersing agents. ○—water; -○-—5 x 10^{-3} molar hexadecanol ethyleneoxide adduct; ◑—5 x 10^{-3} molar sodium dodecylbenzene sulfonate; ●—3.8 x 10^{-3} molar sodium pyrophosphate.

the tendency of the calcium ions to decrease the potential. The nonionic, hexadecanol, polyether has only a small effect on the electrokinetic properties of the carbon; there is however a small decrease in charge, but qualitatively the *zeta* potential-calcium ion concentration relationship is the same as in the absence of surfactant, that is, the potential decreases with increasing calcium ion concentration.

A comparison of the light transmission data of Figure 1 with the *zeta* potential data in Figure 2 shows some correlation between high potential and degree of dispersion for the surface-active materials but not with the inorganic phosphate. The degree of dispersion of carbon in sodium dodecylbenzene sulfonate increases with the increasing calcium ion concentration, and there is a corresponding increase in the negative potential. The relationship is not so straight-forward in the case of the nonionic hexadecanol polyether. In water free of calcium ions there is an enormous increase in the degree of dispersion in the presence of hexadecanol polyether despite a slightly smaller *zeta* potential. However flocculation of this dispersion by the addition of calcium chloride is accompanied by a decrease in the electrokinetic potential, indicating that electrical effects are of some importance in this system.

These results suggest that the adsorption of amphipathic molecules on the hydrophobic carbon is a necessary condition for dispersion in water, but at least a minimum level of electrical repulsion must be maintained for stability. On the other hand, in the absence of adsorbed long-chain amphipathic molecules, even a high level of charge (as in the case of the pyrophosphate) is insufficient to produce a high degree of dispersion.

B. *Dispersions of Coated Carbon.* In the next experiments the surface of the carbon particles was coated with hexadecanoic acid or hexadecanol by stirring carbon black in a methanol solution of the acid or alcohol, then filtering and drying the coated, high-surface-area solid. The resulting material was dispersed in distilled water with a Waring Blendor. The dispersions obtained were extremely fine as compared with uncoated carbon. The carbon black which had been coated with hexadecanoic acid gave dispersions similar to those obtained with uncoated carbon in a solution of hexadecanol polyether. A coating of hexadecanol also gave fine dispersions, but these were somewhat coarser than those obtained with the hexadecanoic acid coating. The light transmission results of these experiments, also of those in which various amounts of calcium chloride were added to hexadecanol-coated carbon suspensions, are shown in Figure 3. Although the carbon which had been coated with the C_{16} acid gave finer dispersions in pure water, it was more severely flocculated by calcium chloride than the C_{16} alcohol-coated carbon. In a solution of sodium ethylene diamine tetra-acetate (EDTA) the acid-coated carbon remains as a fine dispersion with increasing concentration of calcium chloride up to approximately the point of molar equivalence of calcium chloride and EDTA. By itself EDTA does not disperse carbon, but if the carbon has been previously coated with fatty acid, flocculation is avoided, presumably by the sequestration of calcium ions. The acid-coated carbon was so sensitive to dissolved ions that ordinary house-distilled water caused flocculation. Only the specially-prepared, double-distilled water produced deflocculated acid-coated carbon.

The difference in the degree of dispersion between the acid-coated and alcohol-coated carbon may be caused by electrostatic repulsion that results from a slight ionization of the carboxyl groups. This interpretation is reinforced by the higher degree of flocculation that is induced upon the acid-coated system than that for the alcohol-coated powder by the addition of calcium chloride. Flocculation of the car-

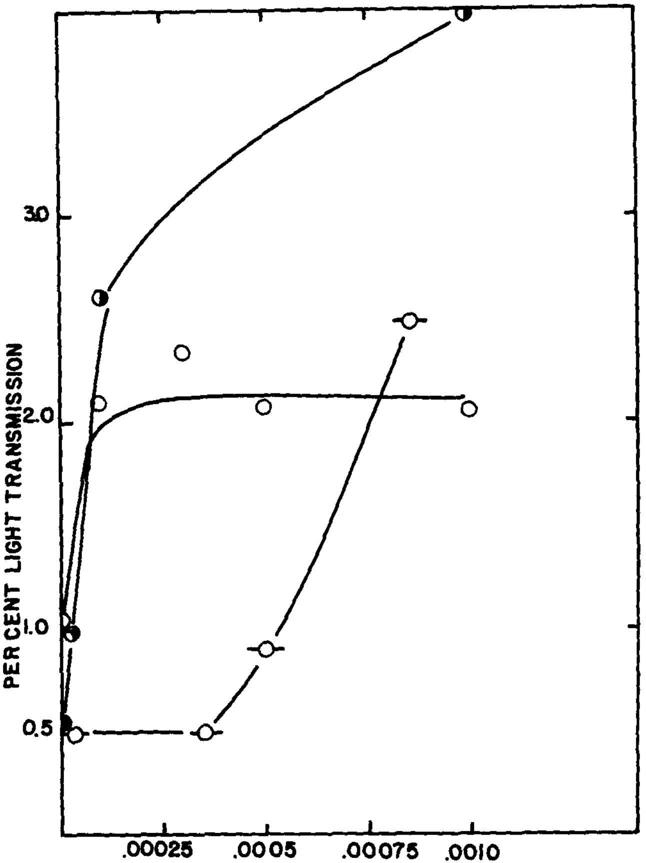

FIG. 3. The flocculation of 0.01% coated carbon suspensions (as indicated by percentage of transmission) as a function of Ca^{++} concentration. ◑—hexadecanoic acid-coated carbon; -○-hexadecanoic acid-coated carbon in a 5.2 x 10^{-4} molar solution of tetrasodium ethylenediaminetetra-acetate; and ○—hexadecanol-coated carbon.

boxyl-covered particles can take place by two mechanisms: reduced repulsion between particles by compression of the electrical double layer by the calcium ions and cross-linking of particles on account of salt formation by the divalent calcium ions. On the other hand, only the electrical effect can operate in the case of the nonreactive, alcohol-coated particles. The high degree of flocculation observed in the acid system may then be caused by a cross-linking phenomenon that results from calcium salt formation with ionized carboxyl groups. The detailed interpretation of flocculation by calcium soap formation may however be more subtle than the suggested cross-linking. Wolstenholme and Schulman (7) have shown that metal soap monolayers are strongly condensed in a pH region where the corresponding metal monohydroxide exists. Their explanation for the cohesive strength of these monolayers is that a hydrogen-bonded network is formed among the -OH groups attached to the metal ions. If this phenomenon operated on the acid monolayer that covers the dispersed carbon, the ensuing solidification of the film would cause a decrease in randomness of the orientation of the polar head groups, thus negating the entropic repulsion effect.

Next the dispersing power of two anionic detergents toward hexadecanoic acid and hexadecanol-coated carbon in the presence of calcium chloride was investigated. The results are shown graphically in Figure 4 as percentage of light transmission *vs.* calcium chloride concentration. In a 10^{-3} molar solution of sodium dodecylbenzene sulfonate, hexadecanoic acid-coated carbon is severely flocculated by calcium chloride. The same concentration of sodium hexadecanoyl methyl taurate has a substantial effect in preventing flocculation by the calcium salt. Both of these anionic surfactants are extremely effective in preventing flocculation of the carbon that is coated with hexadecanol.

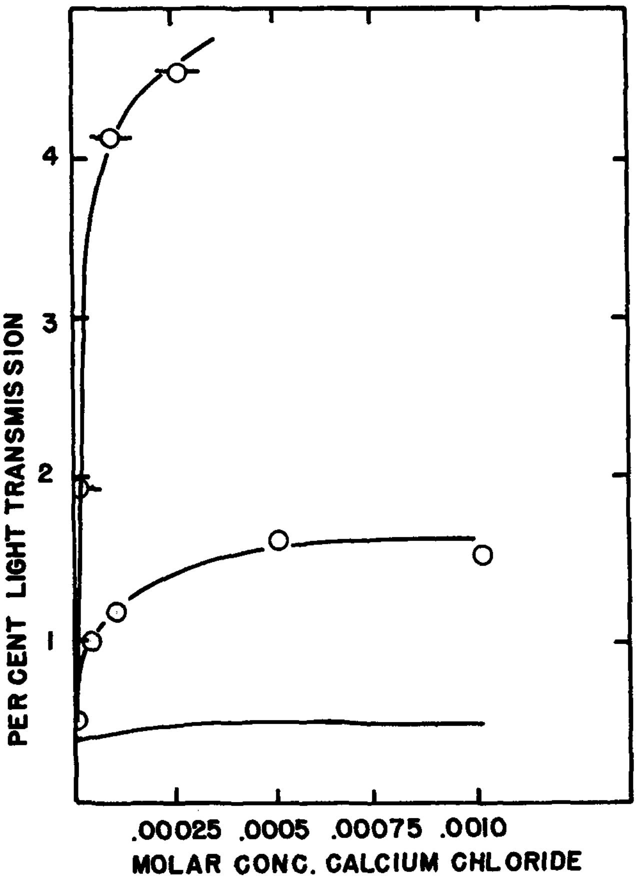

FIG. 4. The flocculation of .01% carbon suspensions by Ca^{++} as indicated by the percentage of light transmission. -○- — hexadecanoic acid-coated carbon in 10^{-3} molar sodium dodecylbenzene sulfonate; ○—hexadecanoic acid-coated carbon in 10^{-3} *molar sodium hexadecanoyl methyl taurate*; —— —hexadecanol-coated carbon in the same detergent solutions.

It has been demonstrated that the hydrophobic carbon black is a highly flocculated powder in water (Figure 1), but when the powder has been previously coated with a 16-carbon atom fatty acid or alcohol, a fine dispersion is obtained (Figure 3). This suggests that the long-chain acid and alcohol molecules are oriented on the carbon surface with their polar groups facing outward, thus rendering the surface hydrophilic with a small particle-water interfacial energy. Assuming this picture of the acid or alcohol-coated carbon surface, the detergent ions must penetrate the acid or alcohol monolayer to adsorb on the coated powder. A model system was chosen to examine the penetration phenomenon. This consisted of insoluble monolayers spread on water and penetrated by dissolved detergents.

The penetration of insoluble monolayers at the air-water interface by soluble detergents has been studied extensively by Schulman and others (8,9,10,11,12).

The insoluble monolayer that is being penetrated can be a barrier against adsorption, or, in situations where strong interactions occur between the penetrating detergent and the insoluble monolayer, it can enhance adsorption. Branching in the aliphatic portion of the penetrating detergent (7) and condensation of fatty acid monolayers by calcium ions (6) are factors which can sharply limit penetration. In order to learn if a more detailed analogy might exist between the penetration of fatty acid or alcohol monolayers at the air-water interface and the dispersion of carbon coated with these substances, constant area monolayer penetration experiments were performed. The changes in surface pressure with the time of octadecanoic acid or octadecyl alcohol monolayers spread on dilute calcium chloride solutions and penetrated by sodium dodecylbenzene sulfonate or sodium hexadecanoyl methyl taurate are shown in Figure 5. Eighteen-carbon atom molecules were used to avoid dissolution of the monolayer. The octadecanoic acid film is only slightly penetrated by sodium dodecylbenzene sulfonate, as indicated by the small increase in surface pressure. Under similar conditions octadecanol undergoes strong penetration by the alkylbenzene sulfonate. The data in Figure 5 show further that octadecanoic acid undergoes a large increase in surface pressure because of penetration by the straight-chain, hexadecanoyl taurate.

The relatively large resistance to penetration of the acid film compared with the alcohol is probably caused by a combination of the following cohesive forces: stronger hydrogen bonding among the carboxyl groups than the hydroxyls and calcium soap formation. The weaker penetration by the branched alkylbenzene sulfonate is probably associated with steric effects, *i.e.*, Van der Wals' interaction is inhibited between the straight hydrocarbon chains of the insoluble monolayer and the branched alkyl structure of the sulfonate.

The results of the penetration experiments suggest an explanation for the high degree of dispersion of

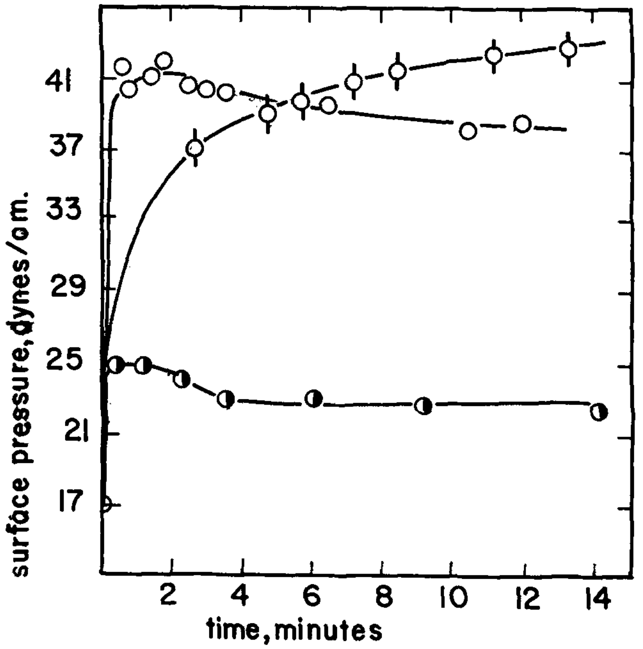

FIG. 5. The penetration at constant area of monolayers of octadecanoic acid and octadecanol by dissolved detergents, showing an increase in surface pressure with time. ◑—octadecanoic acid monolayer penetrated by sodium dodecylbenzene sulfonate (4.22×10^{-5} molar); ○—octadecanol penetrated by sodium dodecylbenzene sulfonate; and ⦶—octadecanoic acid penetrated by sodium hexadecanoyl methyl taurate (1.25×10^{-5} molar).

the long-chain, alcohol-coated carbon which persists at high concentrations of calcium chloride in solutions of the two anionic detergents. The dissolved surface-active agents penetrate the hexadecanol monolayers on the carbon particles, producing a negatively-charged surface which is not neutralized by calcium ions. A substantiation of this interpretation is found in the electrokinetic data with dodecylbenzene sulfonate (Figure 2), which show an increase in charge with the increasing calcium ion concentration. When hexadecanoic acid is adsorbed on the carbon, the alkylbenzene sulfonate cannot protect the system from flocculation by the calcium chloride because the calcium soap film which is formed cannot be penetrated by the branched hydrocarbon structure of the dissolved detergent. The straight-chain taurate gives some protection against flocculation, probably because of penetration of the calcium-soap film. The effect is not as large as in the alcohol-coated carbon, presumably because some of the flocculating tendency of the calcium soap remains.

Practical experience (13, 14, 15) has shown that free calcium ions have an important effect in limiting the effectiveness of a washing solution and that satisfactory results generally depend upon removing these ions by precipitation or sequestration. The extreme susceptibility of fatty acid-coated carbon black suspensions to flocculation by free calcium ions suggests that this or some other similar soil system may be of fundamental importance in common detergency problems. A simple artificial soil of this kind should be evaluated in fabric detergency tests, and if the results correlate with practical experience, this might result in considerably simplified means for further fundamental detergency investigations as well as improved evaluation procedures.

Conclusions

The results of this investigation show that the hydrophobic powder, carbon black, cannot be dispersed in water by increasing the charge on the particles by the addition of a salt which is not surface-active. Varying degrees of dispersion of carbon black in water are obtained in the presence of organic detergents, and the resistance to flocculation by the addition of calcium chloride depends on the ability of the adsorbed detergent to maintain a relatively large charge on the dispersed particles. If the surface of the powder is modified by previously adsorbing a water-insoluble, amphipathic substance, such as hexadecanoic acid or hexadecanol, fine dispersions are obtained in pure water. Extreme flocculation of these dispersions occurs in the presence of calcium chloride, especially with the acid-coated carbon, apparently because of a combination of the effects of calcium ions that reduce the charge of the electrical double layer and form a condensed calcium soap film on the particles. Dissolved anionic detergents inhibit the effect of calcium ions entirely in the hexadecanol-carbon system and are either moderately or not at all effective in the hexadecanoic acid-carbon system. The degree of the stabilizing effect of the organic detergent in the coated carbon system correlated with its ability to penetrate a long-chain carboxylic acid or alcohol monolayer at the air-water interface.

The entropic repulsion resulting from the adsorption of long-chain molecules appears to be a necessary but insufficient condition for dispersing carbon in water. A minimum level of electrical repulsion must be maintained in combination with the effect of the adsorbed long-chain molecules in order to prevent flocculation.

REFERENCES

1. Verwey, D.J.W., and Overbeek, J.T.G., "Theory of the Stability of Lyophobic Colloids," Elsevier, Amsterdam, 1948.
2. Mackor, E.L., J. Colloid Sci., *6*, 492 (1951).
3. Reich, I., and Vold, R.D., J. Phys. Chem., *63*, 1497 (1959).
4. Northrop, J.H., and Kunitz, M., J. Gen. Physiol., *7*, 729 (1925).
5. Peper, H., J. Colloid Sci., *13*, 199 (1958).
6. Goddard, E.D., and Schulman, J.H., J. Colloid Sci., *8*, 309 (1953).
7. Wolstenholme, G.A., and Schulman, J.H., Trans. Faraday Soc., *46*, 475 (1950).
8. Schulman, J.H., and Hughes, A.H., Biochem J. (London), *29*, 1243 (1935).
9. Matalon, R., and Schulman, J.H., Trans. Faraday Soc., *43*, 479 (1947).
10. Matalon, R., J. Colloid Sci., *8*, 53 (1953).
11. Schulman, J.H., and Rideal, E.K., Proc. Roy. Soc. (London), *B122*, 29 (1937).
12. Schulman, J.H., and Stenhagen, E., Proc. Roy. Soc. (London), *B126* (1938).
13. Vitale, P.T., J. Am. Oil Chem. Soc., *31*, 431 (1954).
14. Ross, J., Vitale, P.T. and Schwartz, A.M., *ibid.*, *32*, 200 (1955).
15. Harris, J.C., Textile Research J., *29*, 99 (1959).

[Received April 20, 1959]