The Relation Between the Deflocculating and Frothing Powers of Soaps

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THE power of a soap solution to yield a froth is frequently regarded as an indication of its probable deflocculating, emulsifying or detergent power.

Experiment 1. The writer[1] has previously described a "graphite test" for detergent efficiency, based upon the formation of white froth when a soap solution is shaken with standardized flake graphite. He[2] also has presented data afforded by the "carbon black test," which depends upon estimation of the relative powers of various soap solutions to carry carbon black through filter paper. In the present experiment the essential features of both tests have been combined into one, in order to secure a direct comparison between frothing and deflocculation. Carbon black was made the sole test-substance. Tubes of soap solution were prepared, charged with carbon black and agitated in the constant temperature bath exactly as in the carbon black test except that the final agitation was continued for only thirty minutes. Next, each tube was removed, vigorously shaken for 5 seconds, returned to the carrier in the bath, left at rest for 2 minutes and then observed for the presence of a crescent of white froth, as was done in the graphite test. Finally the contents of all the tubes were filtered through papers standardized to pass 10 cc. water from 20 cc. within 14 to 18 seconds and the filtrates were colorimetrically compared with the Co-Ni-Cu standard to determine their "color ratios" in the manner described for the execution of the carbon black test. That is. the observations upon froth were interpolated between two successive steps of the carbon black test. By the "color ratio" of a filtrate is meant the ratio of the color of a solution of that filtrate (originally 7 cc.) made to a volume of 100 cc. compared with the color of the same Co-Ni-Cu standard as employed in the previously published work.

The soaps employed were sodium and potassium stearates. All solutions tested were made 0.02N in excess alkali, both to exclude any possible effects from free fatty acid or acid soap and because experience with the graphite test had indicated that at the temperatures and concentrations to prevail in the experiment such an alkaline sodium stearate contains but little colloidal soap while such an alkaline potassium stearate may be highly colloidal inasmuch as, in contrast to the sodium soap, it does not readily deposit crystals.

In Figure 1 are given color ratio-concentration curves for alkaline sodium stearate (Curve I) and alkaline potassium stearate (Curve II) with naked carbon black at 24° C. Points on the curves at which the characteristic white crescent of froth appeared are marked with circles; points at which the crescent was absent are indicated by

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[1] Ind. Eng. Chem. *17*, 461, 1187 (1925).

[2] Ind. Eng. Chem. *18*, 1313 (1926), Jour. Oil & Fat Ind., *4*, 15 (1927).

dots only. The results of the two tests, froth and deflocculation, were

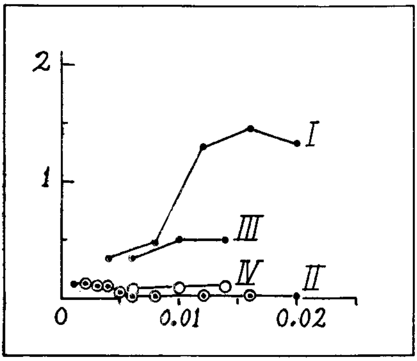

Fig. 1
Alkaline Sodium and Potassium Stearates at 24° *C. in Experiments* 1 *and* 2.
Horizontal—Normality of soap.
Vertical—"Color ratio" of filtrate.
Curve I—Naked carbon black with sodium soap in Experiment 1.
Curve II—Naked black with potassium soap in Experiment 1.
Curve III—Oiled carbon black with sodium soap in Experiment 2.
Curve IV—Oiled black with potassium soap in Experiment 2.

completely contradictory. Sodium stearate yielded no white froth in spite of its notable deflocculating

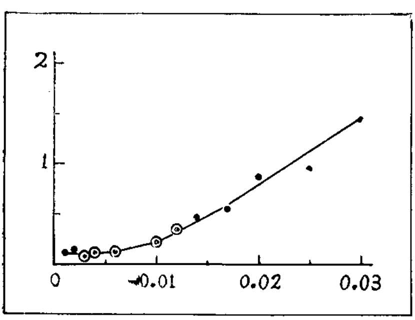

Fig. 2
Alkaline Sodium Stearate with Naked Carbon Black at 60° *C. in Experiment* 3.
Horizontal—Normality of soap.
Vertical—"Color ratio" of filtrate.

power; potassium stearate, with insignificant deflocculating power, showed a strongly conspicuous crescent of white froth over a wide range of concentration.

Experiment 2. The procedure of Experiment 1 was repeated with oiled carbon black made, as described in previously published work, from 5 parts by weight of carbon black and 1 of medicinal mineral oil, with similar results, the data being also given in Figure 1, as Curves III and IV.

Experiment 3. The same method of procedure with naked black as

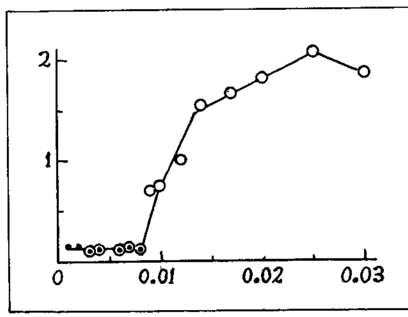

Fig. 3
Alkaline Potassium Stearate with Naked Carbon Black at 40° *C. in Experiment* 3
Horizontal—Normality of soap.
Vertical—"Color ratio" of filtrate.

in Experiment 1 was applied to alkaline sodium stearate at 60°C. and to alkaline potassium stearate at 40°C., with one added step. After collection of each filtrate the cylinder containing it was placed in a bath at the original temperature for at least 30 minutes, then stoppered, vigorously shaken for 5 seconds, left at rest 2 minutes and then observed to determine whether a white froth, covering the whole surface, still persisted. From the two observations on froth, one before and one after filtration, some idea could be gained of the quantity of soap held back by the filter paper. The results are given in Figures 2 and 3. Blank circles indicate white froth both before and after filtration; simple dots indicate absence of froth at both stages while a dot surrounded by a circle indicates that white froth was apparent before filtration but not

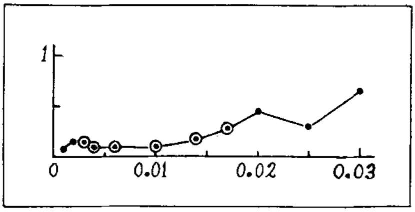

Fig. 4

Alkaline Sodium Stearate with Oiled Carbon Black at 60° *C. in Experiment* 4.

Horizontal—Normality of soap.
Vertical—"Color ratio" of filtrate.

after. This significance attaches to the signs in Figures 1 to 4, but not to those in Figures 5 to 7.

Experiment 4. Alkaline sodium stearate was tested in the same way

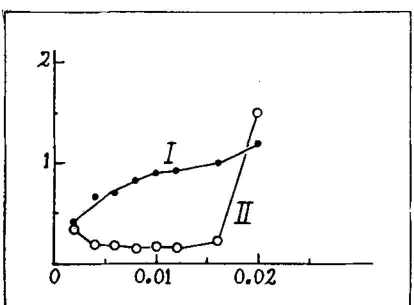

Fig. 5

Alkaline Sodium and Potassium Stearates with Naked Carbon Black at 24° *C. in Experiment* 5.

Horizontal—Normality of soap.
Vertical—"Color ratio" of filtrate.
Curve I—Sodium Stearate.
Curve II—Potassium stearate.

at 60° C. against oiled carbon black with the results shown in Figure 4.

The above data clearly show that at best the first appearance of the characteristic white froth with increasing soap concentration marks only incipient deflocculating power. With sodium stearate the range over which white froth was evident was very short and came to its upper limit at a point where the soap had reached a concentration

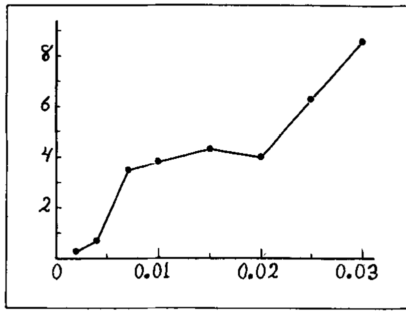

Fig. 6

Alkaline Potassium Stearate with Naked Carbon Black at 37.5° *C. in Experiment* 6.

Horizontal—Normality of soap.
Vertical—"Color ratio" of filtrate.

only sufficient to exert a fraction of its potential deflocculating power.

Experiment 5. In the carbon black test the filtering medium is not simply the paper but is largely constituted by a layer of carbon black which becomes deposited on the paper. In general the solutions of sodium stearate were of low viscosity, filtered rapidly and were still coming through strongly colored when the 7 cc. of filtrate was completed, while the solutions of potassium stearate often were very sluggish and cleared completely long before 7 cc. had passed the filter. Accordingly, to avoid filtration, tests with naked black were started as in Experiment 1 but agitation after addition of carbon black was continued for 40 minutes and then the tubes were shifted to an upright position in the bath and left at rest at 24° C. for 24 hours. Then 5 cc. from each was pipetted from a point approximately halfway between froth and sediment, diluted, and colorimetrically examined. The results are given in Figure 5. In this case the "color ratio" is based upon a solution of the 5 cc. of liquid made to a volume of 100 cc. The results of this experiment corroborate those of Experiment 1, that is, the sodium stearate appeared a decidedly more powerful deflocculant at 24° C. than the potassium stearate. The sudden rise in the apparent deflocculating power of potassium stearate at 0.02 N was evidently due merely to prevention of settling by incipient gelatinization of the soap. The carbon black in this filtrate could be seen, after dilution, to consist mostly of large particles, soon subsiding.

Experiment 6. The results of a similar experiment with potassium stearate at 37.5° C. are given in Figure 6.

Experiment 7. Turning from the discouraging data on the incipient appearance of white froth as an index of deflocculation, observations were undertaken on the volume and persistence of froth. Tubes were selected to hold 20 cc. liquid at the same level. These were charged with alkaline potassium stearate and naked carbon black as in the preceding experiments except that before the carbon black had been added the contents of the tubes were mixed only very gently, to avoid the formation of froth. After the carbon black had been introduced the tubes were agitated at 30 r.p.m. for 30 minutes, left at rest for 15 minutes at an angle of 45° in the carrier, then held upright and the height of the froth measured, each tube being immediately returned to the bath. After these measurements had been completed each tube was removed, shaken vigorously for 5 seconds and returned to the carrier for 15 minutes, after which the froth was again measured. Results are given in Figure 7. Points above the 8 cm. level indicate that the tubes were filled completely with froth up to the stopper. The results of the experiment indicate that, in a general way, this soap was a more powerful frothing agent, as it was a deflocculant, at 40° C. than at 24° C. But it is important to note how greatly the character of the shaking, whether gentle or violent, affects the results. At certain points the more violent the shak-

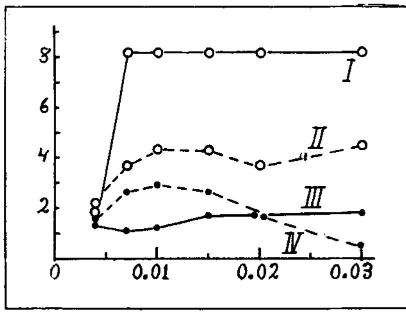

Fig. 7

Alkaline Potassium Stearate with Naked Carbon Black in Experiment 7.

Horizontal—Normality of soap.

Vertical—Height of froth in centimeters.

Curve I—At 40° *C. after gentle agitation.*

Curve II—At 40° *C. after violent shaking.*

Curve III—At 24° *C. after gentle agitation.*

Curve IV—At 24° *C. after violent shaking.*

ing, the more copious the froth; at other points the froth produced by gentle agitation becomes broken down by more vigorous shaking.

Discussion

It appears that the active frothing agent in a soap solution, like the active deflocculating agent, must consist either of simple soap anions or of simple soap molecules. The evidence from these experiments seems against colloidal soap playing a direct part in frothing any more than it does in deflocculation. In concentrations sufficiently high to effect incipient gelatinization colloidal soap may mechanically retard the escape of air bubbles or the subsidence of particles but this effect is neither a true frothing nor true deflocculation.

Evidently frothing and deflocculation are concomitant, not sequent, phenomena. With increasing concentration of soap both begin together and both become intensified in a roughly parallel manner. But the parallelism is so rough and the volume of the froth is so affected by the manner in which it is produced that the relative copiousness or persistence of the froths yielded by two different soaps would appear to offer but a slender basis for judging their probable deflocculating power. With still further increased concentration frothing power may diminish like, but not necessarily parallel with, deflocculating power, while in other cases the froth may change from white to black because the carbon black, although largely deflocculated, is preferentially attracted into the froth. The "graphite test" therefore possesses two points of obvious weakness. In the lower range of concentration it reveals only incipient deflocculating power and nothing at all respecting the maximum potential deflocculating powers of different soaps. In the higher range of concentration it fails to distinguish entire loss of deflocculating power from a mere transference of particles to the froth.

The principal drawback to the "carbon black test" is the operation of filtration. Different lots of papers from the same manufacturer may vary so much that it is often a tedious undertaking to sort out enough papers of the particular porosity desired in an experiment. Perhaps settling may replace filtration with advantage. But then it will become necessary not to be misled by the tendency of an incipiently gelatinized soap to mechanically retard settling. At any rate it appears that the carbon black method, whether with naked or oiled black, filtration or settling, offers the best prospects for an adequate laboratory investigation of the characteristic and essential properties of soaps.

Summary

In order to determine directly the relation between frothing and deflocculation the essential features of the "graphite test" and other frothing tests were combined with the "carbon black test," and a possible modification of the latter was suggested.

It appears that frothing and deflocculation are concomitant, not sequent, phemonena, and that both are due to a similar mechanism. But the parallelism between the two appears so poor that no test for frothing power, whether utilizing the froth in a qualitative or quantitative way, deserves much confidence as an indication of probable deflocculating power.