

The Chemistry of Detergency*

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DETERGENCY is one of many chemico-mechanical processes which have great technological importance. Here, as in the separation of minerals, emulsification of liquids, grinding of solids, or wetting of textiles, the complicated interactions among the chemical and mechanical variables have interfered with the interpretation of experiments.

From the standpoint of designing and selecting detergents, it seems profitable to try to isolate the essentially chemical aspects of the problem from the mechanical considerations which are also involved. This appears to have been realized by Spring (1) in 1909, who discussed the process of detergency in terms of a chemical or pseudo-chemical reaction between the dirt and the detergent. More recently, McBain (2) elaborated on this idea but does not seem to have exploited it very much, particularly with respect to solid soil. Others have performed experiments which are also relevant, but their ideas have not been explicitly formulated in chemical terms, nor were their experiments very comprehensive.

The chemical variables in the detergency process are the nature of the fibers of the fabric, the nature of the dirt, the nature of the detergent, and the composition of the detergent solution. These are the variables in the system which are of special interest for the design and selection of detergent compounds.

Among the essentially non-chemical considerations which we would like to avoid for the purposes of this study are questions of the structure of the fabric being washed, the size and shape of the dirt particles, the distribution of the dirt in the fabric, and agitation. While these are obviously important practical considerations, they are, to some extent, independent of the chemistry of the process.

Resolution of the washing process into chemical and mechanical phases is so important to understanding detergency that even if very difficult experiments were involved, they should be tried. It appears from our work and that of others, however, that rather simple experiments can be used. Furthermore, these give some insight into the process of detergency which is inaccessible from washing studies.

Three types of experiments will be briefly described and one of these will be elaborated to some extent.

The first experiment gives some indication of the operation of the chemical factors in detergency. A single cotton fiber is placed in a drop of an aqueous suspension of a selected finely divided carbon and observed under a microscope. It may be seen that while the carbon particles bounce indifferently off one another in the course of their Brownian movements, when they collide with the fiber they remain attached. In a short time a conspicuous concentration of the carbon particles on the fiber may be noted. When a proper amount of soap is added to the suspension, the carbon particles do not stick to the fiber. As far as we know, systematic experiments of this type with a variety of soaps, soils, fibers, and solution compositions have never been reported.

Another type of experiment which is similar in principle can also be easily performed. Spring (1) and McBain (3) have both reported that when aqueous suspensions of finely divided carbon are poured onto a filter paper clear water comes through. If, however, soap is added to the suspension, some of the carbon passes through the filter. This can reasonably be interpreted in terms of adhesion of the carbon to the paper fibers. If they stick, the effective pore size is reduced and no carbon passes. If they do not stick, the effective pore size of the filter is larger. While McBain (3) has reported many experiments of this kind, the range of variables covered is quite limited.

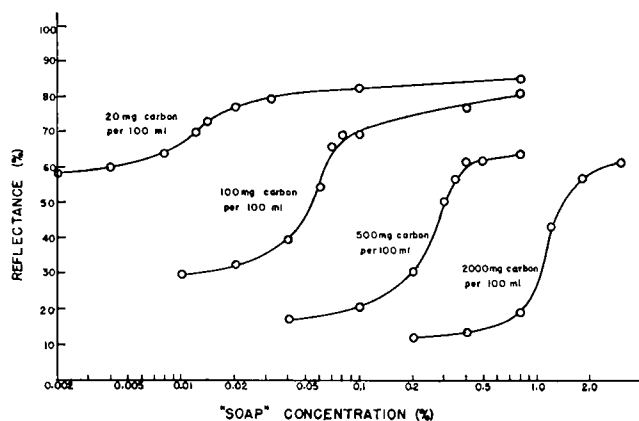


FIG. 1. Whiteness retention.

A third experiment in the same general class involves the exposure of a piece of clean fabric to a dirt suspension. When a cotton fabric is shaken in an aqueous suspension of carbon, it becomes quite dirty. However, if the suspension contains a proper amount of soap, the fabric remains clean. Spring (1), Carter (4), Powney and Noad (5), and Vaughn and Vitton (6) have reported on experiments of this kind.

It is notable that here one of the conditions encountered in actual laundry practice is simulated. That is, in the laundry dirty cloth is exposed to clean detergent solution and it is hoped to obtain clean cloth and dirt in suspension. A good rating in this whiteness retention test is therefore a necessary condition for good detergency.

A number of these whiteness retention tests have been conducted in our laboratory. The results show good precision. The tests are easily and rapidly done and the variables are easily controlled. The amount of dirt picked up by the fabric is estimated by reflectance measurements.

In addition to the usefulness of whiteness retention data for predicting the outcome of washing trials, they also illuminate certain features of the mechanism of detergency. Let us consider a series of whiteness retention experiments involving different amounts of finely divided carbon soil and various concentrations of detergent. In these experiments

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4 x 4" squares of cotton sheeting were placed in pint bottles containing 100 ml. of soil suspension and shaken for 1 minute by hand. The cotton was then removed, rinsed in clean water, ironed, and its reflectance noted.

The results are shown in Figure 1. One of the implications of these data is that there is a critical concentration of soap, or possibly a critical range of concentration, above which the cloth is recovered almost perfectly white and below which it is quite black.

Secondly, this critical concentration depends on the amount of dirt which is present. When this critical concentration of soap is plotted against the amount of dirt (Figure 2), a linear relationship is observed and the intercept of the line seems to be exactly zero.

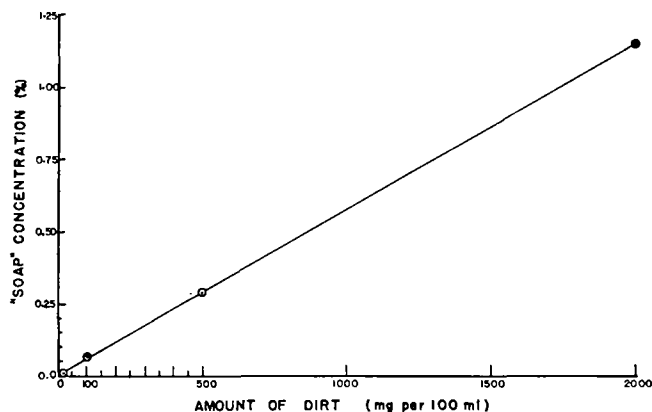


FIG. 2. Critical "soap" concentration.

The linear character of this relationship suggests that the interaction between the dirt and the soap is stoichiometric and might be dealt with by the usual chemical methods. The zero intercept indicates that in these experiments the cotton does not participate in the reaction since the same amount of fabric is used in all of the trials.

Another implication of the zero intercept is that micelle formation is not essential to detergency. If it were, the intercept would be expected at the critical concentration for micelles for the particular soap.

The data shown were obtained using Triton N-100 and carbon. Similar experiments were done with other detergents and soils. Their general behavior was quite similar. One of the differences among the various detergents, however, is their combining proportion with respect to various kinds of dirt. That is, different slopes are shown in graphs of critical soap concentration against amount of dirt (Figure 2). Materials which show low combining weights are, of course, effective at lower concentrations (i.e., if the volume of solution is held constant).

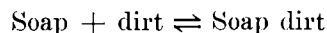
Spectacularly low combining weights for finely divided carbon are shown by certain polymeric detergents and high molecular weight materials like carboxy methyl cellulose. It is possible that this is due to the fact that these large molecules do not have access to as much of the highly convoluted surface of the carbon as do the smaller molecules.

A second difference among the various detergents which may be noted are changes in the slope of the curves of whiteness retention plotted against deter-

gent concentration for any amount of dirt (Figure 1). These differences may be related to the equilibrium constant for the soap-dirt reaction as will be shown later.

In addition to the combining proportions and slope a third consideration which must be introduced is the quality of the complex formed between soap and dirt as a dirt. When the whiteness retention above the critical soap concentration is very nearly 100%, it is clear that the complex is quite ineffective as a dirt. In some cases, however, the whiteness retention-concentration curves level off at much lower reflectances. In these situations the dirtiness of the complex must be considered.

When the dirtiness of the complex can be neglected some very simple, heuristic, equilibrium calculations can be made. Consider the reaction



$$K = \frac{[\text{soap, dirt}]}{[\text{Soap}][\text{dirt}]}$$

For known initial soap and dirt concentrations the value of K permits the amount of uncombined dirt to be calculated.

By means of a separate group of experiments (Figure 3) the relationship between the amount of free dirt in the solution and the reflectance of the exposed cloth can be determined. Using this graph, a theoretical curve can be computed for the relationship between whiteness retention and soap concentration for any value of K . These theoretical curves (Figure 4) look very much like the experimental curves some of which were shown in Figure 1.

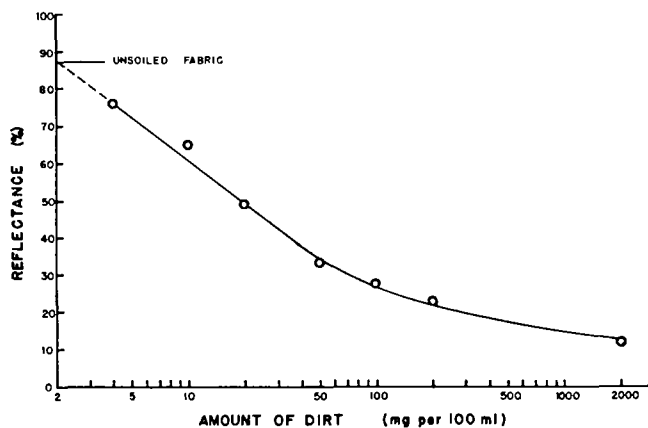


FIG. 3. Whiteness retention without "soap."

The arguments on which these equilibrium calculations are based are admittedly very precarious. The good agreement with experiment is, however, provocative. The reaction between soap and dirt could have been studied much more directly by means of adsorption experiments. The measurements reported here, however, have a more immediate and obvious connection with the process of detergency. The data are very easily obtained and this makes it practical to examine a wide range of the variables: fabric, soil, and detergent solution.

