WHY DOES SOAP CLEAN?

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Why does soap clean? This question is not put as a rhetorical one, nor yet in the thought that the writer has a satisfactory answer, for full well he is aware that there does not appear to be unanimity of opinion among scientists as to the how and the why of the detergent action of soap. An adequate theory which pictures fully the functioning of soaps is still wanting. In view of this situation an answer submitted as a review of sundry theories suggests a discreet, although not a valiant, retreat from the self-imposed difficulty in which the questioner finds himself.

As a direct result of Chevreul's studies over a century ago, on the chemical nature of the fatty oils, empiricism in soap making gave way to scientific method; rule-of-thumb procedures were replaced by operations which are governed by the laws of mass action, the phase rule, and the chemistry of the colloidal state. For some eight decades following Chevreul's discovery the view was held by many that soaps are fatty acid-salts containing "water of constitution" and that when dissolved in water solutions like those of any normal electrolyte result. This view later required modification, however, when it was observed that soaps in solution are in reality mixed systems, that is solutions of soap-in-water admixed with solutions of water-in-soap. Alexander cautions that soaps should be regarded not as compounds of fatty acids having chemically combined a definite amount of water, but rather as adsorption products whose composition depends upon the environment in which the fatty acid salts find themselves at the moment of the finishing operation. From which it follows that a soap may exist in the form of a sol-sol, a sol-gel, or a sol-curdled gel. That soaps are colloidal in nature was suggested as early as 1880, yet this observation remained unnoticed for fifteen years. McBain regards soaps as "colloidal electrolytes," salts in which one of the ions has been replaced by a heavily charged, heavily hydrated "ionic micelle" which exhibits a high conductivity.

In the not-inconsiderable literature on the detergent action of soap, there may be found several theories offered in explanation of this phenomenon. Some are of historical interest only and are now obsolete, others are merely the result of an expansion or a modification of views once expressed by a predecessor, whereas still others appear rather successfully to have withstood the scrutiny of criticism.

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Chevreul observed that when soaps are acted upon by water hydrolysis to free alkali and an acid salt of the fatty acid occurs. He then assumed that the dirt particles adhere to the surface film of the fatty substance, the latter in turn being saponified by the free alkali of the soap solution with the result that the dirt particles, being thereby released, are suspended in the suds. Of this theory says Elledge (1932), "The fallacy concerning the behavior of the dirt and the quantitative effect of the alkali liberated by hydrolysis seems not to have been detected for a period of nearly one hundred years." In fact, during this entire period it seemed to be the current opinion, with perhaps a few exceptions, that detergent action was directly traceable to the alkali of hydrolysis as the active agent. Among the dissenting views was that of Hirsch (1898) who showed that fatty oils are not more readily emulsified than are various other organic liquids, from which observation he concluded that emulsification must be due to the soap itself and not to any alkali present. The illuminating investigation of Hillyer (1903) supported this observation. Hillyer also took the position that whatever alkali might result from the hydrolysis of the soap did not have the property of wetting oily material as does soap. Lubrication of texture and impurities also entered the picture as he saw it. All of which he explained, apparently without knowledge of similar views suggested by Donnan (1899), on the basis of the parallelism of low surface tension and emulsification, that is, it is a function of the lowering of the oil-water interfacial tension. His own words are, "The low cohesion of the soap solutions and their strong attraction, adhesion or affinity to oily matter—together cause the low surface-tension between soap solution and oil."

It was during this period that the concept of Brownian movement of the soap particles as an explanation of detergency was suggested. Jevons (1878), one of its proponents, said in substance, "One may picture the phenomenon as though the suspended particles hurl themselves against the dirt particles loosening and washing them away." Of this it may be said that it requires considerable stretch of the imagination to accept as an explanation what is in reality a description.

A theory of lubrication of texture and impurity to the end that the removal of the latter be facilitated also received some attention. Of this hypothesis Fall (1927) said, "This might be considered as the action of the soap in forming non-adhesive colloidal sorption compounds with tissue and impurities due sometimes to acid soap, but more often to soap itself and capable of remaining in stable suspension."

Toward the end of the first decade of the present century the mass of evidence which began to accumulate on the subject lent convincing support to a theory which is postulated upon the colloidal properties of soaps. It has survived and appears now to have been accepted in the main as offering an explanation of the vexing question of the detergent action of soap. Fundamentally, this theory states that the detergent action of soap is due to its ability as a colloid to produce deflocculation. Then, too, there is a preferential absorption of the dirt by soap relatively to the skin or textile. Elledge (1932) summarizes the distinctive characteristics of the colloid theory as follows: the ability of a soap to wet a surface, to disperse and suspend small solid particles and droplets of a liquid which is immiscible with water and to lubricate surfaces and dirt particles is a function of its property of materially lowering the surface tension of solutions. Within certain ranges of soap concentration, added alkali will further lower the surface tension.

Fourteen years ago McBain (Third Report on Colloid Chemistry, British A.A.A., 1920, p. 27) summarized the then known factors in the detergent action of soap. They are still valid today. Besides the obvious necessity of having the soap in solution these are, as expressed in his own words, the "power of emulsification which goes parallel with low surface tension and the formation of surface films; wetting power which like the last, is ascribable to the undecomposed soap itself; the action of soap in forming non-adhesive colloidal sorption compounds with tissue and impurities due sometimes to acid soap, but more often to soap itself and capable of remaining in stable suspension; and it is essential in all cases that the soap should be in colloidal form." His suggestion that the existing fragmentary work in any one case be completed and co-ordinated by quantitative studies is still pertinent.