Role of Detergent Builders in Fabric Washing Formulations

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ABSTRACT

The role of a detergent builder in fabric washing formulations is complex because the builder is multifunctional. The primary function of a builder is to counteract the detrimental effects of hardness ions (Ca^{2+} and Mg^{2+}) which arise in the wash solution not only from the tap water but also from the washload. The need to control the free hardness ion level to 0.1°FH is well established and is mainly required to release calcium bound soil and prevent further calcium soil interaction during the wash process. The most elegant way of doing this is with a sequestrant. Sodium triphosphate is the preferred material. Measurement of the equilibrium constants of sequestrants with $Ca^{2+}/Mg^{2+}/Na^{+}/H^{+}$ as a function of temperature and ionic strength allows prediction of free hardness ion levels over a wide range of conditions such as temperature, pH, water hardness, and dosage. Secondary functions such as specific adsorption effects are important, and a true builder will aid not only soil removal but alleviate soil redeposition.

A builder may be defined as a compound which, when added to a detergent product, extends and improves its cleaning properties. In this definition of a builder, first given by Jones, Hudson, and Parke in 1960, "cleaning" is the net amount of soil removed – that is, the total soil removed from the fabric minus that redeposited. The action of a builder, therefore, is to increase soil removal and to decrease soil redeposition. Only those materials which are involved in both processes are considered to be builders.

Sodium triphosphate (STP) is the main builder used in detergents. Indeed, such is the universality of its use, the term "building" is almost synonymous with the solution/adsorption properties of sodium triphosphate. This being the case, and with the knowledge that later papers in this conference will describe the properties of potential STP substitutes, I shall make specific reference to sodium triphosphate when describing the properties and functions of a builder.

The mechanism of building has been studied a great deal, but no one would claim to have a completely satisfactory theory of building. This is predominantly due to the fact that building is not the result of a single property but a combination of several effects. There are many variables in the washing process which are important in determining the relative contributions of these several effects. For example, soil found on textiles prior to washing is extremely variable in its composition, its physical state, and its location on and within fibers. Fabrics too are extremely variable in their composition, finish, and construction. Even the housewife may be considered as an uncontrollable variable in that it is she who determines the dosage, wash temperature, wash process, and so on. All of these variables play a part in determining the relative contributions of the several effects which constitute building.

However, from studies on the role of builders under a wide variety of conditions it is clear that for the detergency of cotton the primary function of a detergent builder is to counteract the detrimental effects of hardness ions in the detergency process.

Saying that the primary function of a builder is to counteract the detrimental effects of hardness ions (Ca^{2+} and Mg^{2+}) during the wash process is not quite the same as saying that the primary function is to soften the water although this is the mechanism we use to achieve the major part of the required function. In understanding the role of the builder, therefore, we need first to determine the source of the hardness ions, second to define the ways in which they interfere with the detergency process, and finally to examine the methods available to counteract this interference. In attempting to do this I shall refer to calcium ions although similar interactions, but to a lesser degree, also occur with magnesium ions. Additionally, the wash conditions used in illustration will be typically European.

First of all let us discuss the source of the hardness ions in the wash system. Hardness ions enter the wash liquor via the tap water *and* the washload. Therefore, the total amount of hardness ions that we need to counteract during the wash process is greater than that due to the tap water alone and the name *we* give to this effect is "hardening up."

How do calcium ions interfere with the detergency process? There have been a number of studies aimed at determining the free hardness ion level required in detergent systems to yield good detergency properties. For the soils encountered in the home a free calcium ion concentration of 10^{-5} moles per liter is generally considered to be required.

Figure 1 shows a schematic plot of detergent efficiency for an anionic surfactant system in which the free calcium ion is expressed as pCa which is, of course, $-\log_{10}[Ca^{2+}]$. When the free $[Ca^{2+}]$ is below 10^{-5} mol per liter, the wash result is good; when the free $[Ca^{2+}]$ is high enough to precipitate the anionic surfactant, the result is poor; and when the free $[Ca^{2+}]$ is intermediate, the wash result is only moderate.

To understand this we have to look at the various interactions that are occurring, and these are presented in a simple form in Figure 2.

The first interaction is well known – the precipitation of anionic surfactant by calcium ions with the subsequent reduced detergency efficiency. The level of free calcium ion below which this interaction does not take place depends on the type of anionic surfactant used and its co-actives, but typically a free calcium ion concentration of less than 3°FH is required. Replacement of an anionic surfactant by a nonionic surfactant which does not interact with calcium overcomes the surfactant precipitation problem, but experiment clearly shows that a nonionic surfactant requires building to the same free calcium ion concentration as the anionic surfactant although some detergency benefit from the nonionic is seen in the poor wash region.

The second interaction is that in which calcium ions can destabilize the removed soil by a colloid destabilization mechanism, and this results in soil redeposition. The free calcium ion concentration required to prevent this depends on the nature of the soil, but free calcium ion levels below

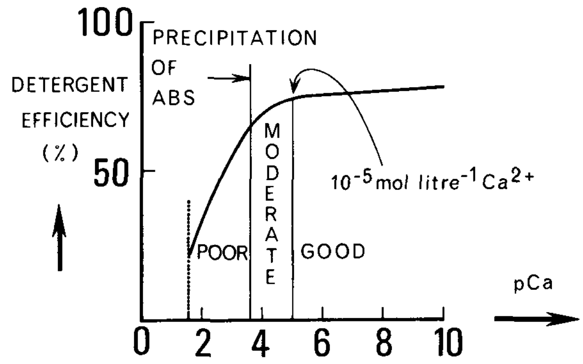

FIG. 1. Schematic diagram of detergent efficiency with $-\log_{10}[Ca^{2+}]$.

$$1.\ Ca^{2+}_{Tap} + ABS \rightarrow Ca(ABS)_2 \downarrow$$

$$2.\ Ca^{2+}_{Tap} + SOIL_{Rem} \rightarrow REDEPOSITION$$

$$3.\ Ca^{2+}_{Tap} + SOIL_{Fabric} \rightarrow Ca\,SOIL$$

FIG. 2. Calcium interactions.

3°FH have been found to result in a reduced destabilization effect.

Interaction 3 is that of hardness ions combining with the soil on the fabric and can be illustrated with reference to a common soil found on fabrics – a particulate/sebum mixture. Sebum, the sebaceous secretion of the skin, is a complex and variable mixture of free fatty acids, glycerides, fatty alcohols, squalene, and other minor components. At normal wash pH's (about 9.5) these fatty acids can ionize. This process is helpful in promoting soil removal since these fatty acids are then effectively soaps which not only are easily released from the fabric but which can also assist the surfactant in emulsification and removal of nonpolar components. However, this ionization allows hardness ions to interact with the free fatty acids and form a calcium/soil complex which is difficult to remove and which also acts as a barrier to surfactant penetration of the oily soil.

There is one further interfering effect of calcium ions and this is due to calcium ions associated with the soil before the wash process commences. The calcium may be part of the soil itself, for example in clays, or it may be the result of the interaction of calcium with soil as just described but in previous washes performed under nonoptimum conditions or during the rinse process. An important function of the builder is to abstract the calcium from these "calcium bound soils." Sodium triphosphate is particularly effective at abstracting calcium from this type of soil by an adsorption/desorption process. However, even a sequestrant with a high affinity for calcium such as STP cannot solubilize the calcium salts of the higher chain length fatty acids such as stearate. But by abstracting the calcium from the lower chain length members the calcium salts of the high chain length fatty acids can be removed by a loosening effect at a *rate,* and this is important, which is effective in the time of the wash. It is this interaction with soil during the wash process and

SEQUESTRATION	– Soluble Complex eg. STP, NTA and CMOS
PRECIPITATION	– Insoluble Complex eg. Soap and $NaCO_3$
ION EXCHANGE	– Insoluble Complex eg. Organic ion exchangers and aluminosilicates

FIG. 3. Water softening.

EQUILIBRIUM	$LOG_{10}K$
$Ca^{2+} + P_3O_{10}{}^{5-} \rightleftharpoons CaP_3O_{10}{}^{3-}$	7·55
$Na^{+} + P_3O_{10}{}^{5-} \rightleftharpoons NaP_3O_{10}{}^{4-}$	2·85
$H^{+} + P_3O_{10}{}^{5-} \rightleftharpoons HP_3O_{10}{}^{4-}$	9·57
$Ca^{2+} + NaP_3O_{10}{}^{4-} \rightleftharpoons CaNaP_3O_{10}{}^{2-}$	6·10
$Ca^{2+} + HP_3O_{10}{}^{4-} \rightleftharpoons CaHP_3O_{10}{}^{2-}$	4·86

FIG. 4. Stability constants at 60 C for $Ca^{2+}/Na^{+}/H^{+}/P_3O_{10}{}^{5-}$ system (μ=O).

the abstraction of calcium bound soil which require the free calcium ion to be less than 10^{-5} mol per liter.

The method used to counteract these interactions is simply to provide lower free energy sites for the Ca^{2+} ions than those of soil and surfactant – this is essentially water softening.

Water can be softened by three processes shown in Figure 3; sequestration, precipitation, and ion exchange. STP, NTA, and CMOS are examples of builders which form soluble complexes although STP can act as a precipitant builder under certain conditions. Soap and sodium carbonate are well-known examples of precipitant builders used, and synthetic organic resins and aluminosilicates are examples of ion exchangers.

Of these three methods the most elegant way is that of forming a soluble complex since the formation of an insoluble species yields a potentially depositing system. As I mentioned earlier, the preferred material is STP, and I would like now to illustrate how the measurement of its thermodynamic equilibrium constants with calcium ions, hydrogen ions, sodium ions and their mixed complexes allows, if their variation with ionic strength is known, the prediction of the extent of water softening over a wide range of conditions of water hardness, pH, temperature, and product dosage.

Figure 4 shows the main equilibria in $Ca^{2+}/Na^{+}/H^{+}/P_3O_{10}{}^{5-}$ system for the condition where the concentration of sodium triphosphate is greater than the total concentration of calcium in the mixture. The stability constant of the $CaNaP_3O_{10}{}^{2-}$ complex is about 1½ units less than that of $CaP_3O_{10}{}^{3-}$ and this is important in determining free calcium ion levels in wash systems because of the high concentration of sodium ions present under normal product usage conditions. The stability constant of $CaHP_3O_{10}{}^{2-}$ complex is much lower than $CaP_3O_{10}{}^{3-}$, but at pH's above 9 this is relatively unimportant in determining free calcium ion levels. However, knowledge of these constants alone is not sufficient to allow the prediction of free calcium ion levels – their variation with ionic strength is required.

The log stability constants of the three complexes $CaP_3O_{10}{}^{3-}$, $CaNaP_3O_{10}{}^{2-}$, and $CaHP_3O_{10}{}^{2-}$ are plotted against the Davies function $\sqrt{I}/(1+\sqrt{I})-0.2I$ in Figure 5. The plots give straight lines which do not have the gradient predicted by the Davies equation. The reduction in the affinity for calcium of the three anions with increasing ionic strength can clearly be seen. Thus, for triphosphate the interaction with sodium ions and the reduced calcium binding with ionic strength impose a limit to the free calcium ion lowering that can be achieved with STP built products. However, for virtually all conditions the free

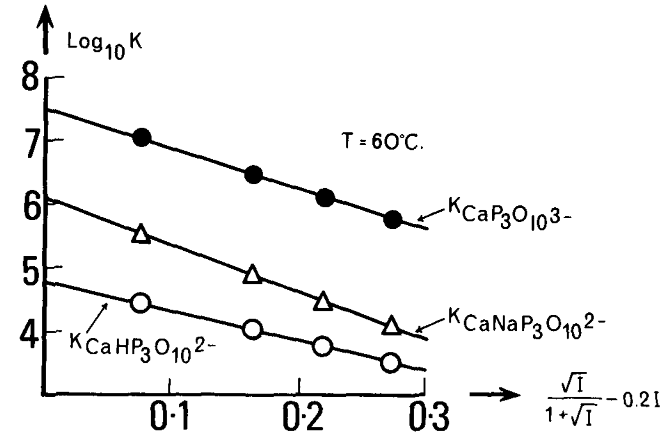

FIG. 5. Variation of $\log_{10}K$ with ionic strength.

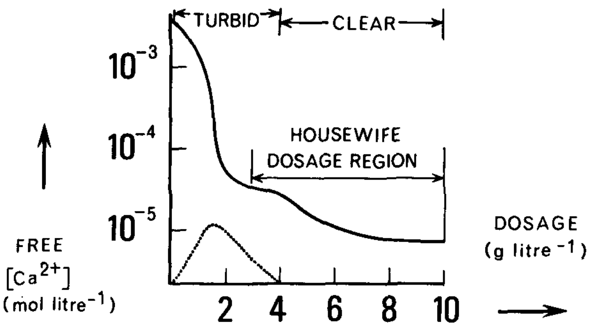

FIG. 6. Calculated free Ca^{2+} concentration for STP built product.

$[Ca^{2+}]$ attained with STP built products is sufficiently low.

The calculated free calcium ion concentration of a STP built product as a function of product dosage for a model formulation containing 35% sodium triphosphate in 40°FH water, pH = 10.0, and a temperature of 60 C is shown in Figure 6. At low dosages (less than 4 g/liter) the free calcium ion level is controlled essentially by the insoluble precipitate $Ca_5(P_3O_{10})_2$ and the equilibrium between this and the soluble complex $CaP_3O_{10}{}^{3-}$. The dashed curve at the bottom left hand corner of the diagram shows (not to scale) the weight of $Ca_5(P_3O_{10})_2$ produced. At higher dosages the free calcium ion level is essentially determined by the stability constants of $CaP_3O_{10}{}^{3-}$ and $CaNaP_3O_{10}{}^{2-}$ complexes. Determination of the free calcium by an ion electrode results in excellent agreement between predicted and measured values. The housewife dosage region is quite extensive, and some housewives do not attain the optimum free calcium ion level of 10^{-5} mol per liter. It is important to note that in the practical situation the curve is displaced to the right and higher dosages are required to reduce the free $[Ca^{2+}]$ to the optimum level. This is mainly because (a) hardness ions are introduced into the wash system with the load as described earlier, (b) in some machines not all the builder reaches the wash system, and (c) sodium triphosphate "breaks down" during processing of the powder and this reduces its concentration in the wash system.

There are a number of important secondary functions of a builder. A builder should have some removed soil stabilization properties. The removal of hardness ions from solution to eliminate their flocculating effect has been previously noted. However, experiments in distilled water show that various builders differ in their ability to stabilize soil. For example, sodium triphosphate is particularly good at stabilizing clay soils by an adsorption process which increases the zeta potential. Specific adsorption onto soil and substrate is also a contributing factor in the detergency process due to the repulsive forces produced. For the builder to have buffer capacity in the detergent pH range is advantageous but this can be supplied by other materials such as alkaline silicate.