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Abstract

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The Effect of Phosphates and Polyphosphates on the Solubilizing Ability of Detergents

It is known that solutions of detergents, above the critical concentration of micelle formation, are two-phase systems, the dispersed phase of which consists of associates of individual molecules called micelles ($^{1-5}$). The micelles are in a mobile reversible equilibrium with the nonassociated part of the molecules and ions of the detergents in solution. Their oleophilicity is affected by changes in temperature and in the parameters of the dispersion medium.

The micellar structures of detergents and the dispersion medium of a colloidal solution change greatly under the influence of electrolytes and polar organic substances, which in practice are called active additives (^{6,7}). Active additives play an important role in the formation of micellar structures in solutions, determining many of their practically important properties. At present it is generally accepted that without active additives it is impossible to obtain a high-quality detergent based on known synthetic surface-active substances (^{7,12}).

In connection with the need to replace food fats used for technical purposes with synthetic products, it is necessary to determine the influence of various factors on the oleophilic properties of micellar structures formed in detergent solutions, so as to obtain them with the required effectiveness. The mechanism of action of active additives on the colloid-chemical properties of detergents has still not been sufficiently clarified. The theoretical foundations for increasing their effectiveness by means of additives of various electrolytes and polar substances have not been developed (^{10}). Active additives in detergent formulations are selected mainly empirically. It is known that condensed phosphates have found wide application as active additives to synthetic detergents (^{4,7,12}). Using objective methods, the comparative effectiveness of additives of phosphates and polyphosphates to various synthetic substances has not yet been studied. The methods used in practice for determining surface activity and for test washings often give contradictory results (^{7,9}).

Characteristic and specific properties of detergents are the critical micelle-formation concentration and the solubilizing ability of their solutions (^{8,9}). Factors influencing these properties will change the lyophilicity of the detergent solution. It may be expected that phosphate additives shift the equilibrium in a detergent solution toward the formation of more oleophilic micellar structures

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

possessing enhanced detergent and solubilizing ability. To test this assumption, a special investigation was carried out to determine the influence of phosphates and polyphosphates on the solubilization of hydrocarbons in soap solutions.

Experimental data on the limiting solubilization of toluene and heptane in $0.1M$ solutions of sodium laurinate and sodium naphthenate in the presence of various amounts of phosphates and polyphosphates are given in Figs. 1–3. The solubilization was determined by the direct volumetric method described earlier (^{11}).

From consideration of the curves of the dependence of the effects of toluene solubilization on additions of increasing amounts of sodium hexametaphosphate, tripolyphosphate, pyrophosphate, and phosphate, it is evident that all the phosphates studied increase the solubilizing ability of sodium laurinate solutions (Fig. 1). However, a large difference is observed in the increase of the solubilization effects depending on the number of phosphorus atoms contained in the molecules of the phosphates added. Thus, for example, when 0.5 mole of sodium phosphate and hexametaphosphate per 1 mole of soap is added to the solution, the solubilization of toluene in the solution increases, respectively, by 1.3 and 4.76 times

Fig. 1. Curves of the dependence of the effects of solubilization of toluene in a 0.01 *M* solution of sodium laurinate on additions of phosphates: **1** –hexametaphosphate, **2** –tripolyphosphate, **3** –pyrophosphate, and **4** –sodium phosphate

Fig. 2. Curves of the dependence of the effects of solubilization of heptane in 0.1 *M* solutions of sodium laurinate on additions of phosphates: **1** –hexametaphosphate, **2** –tripolyphosphate, **3** –pyrophosphate, and **4** –sodium phosphate

(Fig. 1, curves 1, 4). Additions of pyrophosphate and tripolyphosphate occupy an intermediate position in their influence on the solubilization effects. An analogous regularity in the increase of solubilization in sodium laurinate solutions is also observed for heptane under the influence of additions of sodium phosphates (Fig. 2). In a 0.1 *M* solution of sodium laurinate, in the absence of phosphate additions, about 0.13 mole of heptane per mole of soap is solubilized. With additions of 0.5 mole of phosphate and hexametaphosphate, the solubilization of heptane in the same soap solution increases, respectively, to 0.19 and 0.77 mole per mole of soap, or by 1.4 and 5.9 times. From comparison of the experimental data it is evident that additions of the phosphates studied enhance the solubilization of heptane in the soap solution more strongly than that of toluene. In studying the solubilization of heptane in 0.1 *M* solutions of sodium naphthenate (molecular weight 270) in the presence of increasing amounts of sodium phosphate and hexametaphosphate, higher solubilization

Fig. 3. Curves of the dependence of the heptane solubilization effect in 0.1 M sodium naphthenate solutions (molecular weight 270) on phosphate additives: 1—hexametaphosphate and 2—sodium phosphate

Figure 2: Fig. 3. Curves of the dependence of the heptane solubilization effect in 0.1 M sodium naphthenate solutions (molecular weight 270) on phosphate additives: 1—hexametaphosphate and 2—sodium phosphate

effects were observed in comparison with the corresponding sodium laurinate solutions at equal phosphate additions. This phenomenon indicates that electrolyte additions act differently on the oleophilic properties of detergents with unlike structures of the hydrocarbon radicals. When 0.5 and 1.0 mole of sodium phosphate are added to a sodium naphthenate solution, the solubilization of heptane increases by 1.7 and 2.4 times. Addition of the same amounts of sodium hexametaphosphate causes an increase in the solubilization of heptane by 5.7 and 19.8 times, respectively (Fig. 3).

In terms of their ability to increase the solubilizing effectiveness of detergent solutions, the phosphates studied are arranged in the following decreasing order: hexametaphosphate > tripolyphosphate > pyrophosphate > sodium phosphate.

Phosphates exert an influence on the solubilizing capacity of soap solutions analogous to that of alkaline electrolytes (6). Tripolyphosphate and hexametaphosphate increase the solubilizing capacity of soap solutions more sharply than do phosphates and other electrolytes. This is connected with the fact that condensed phosphates, which are high-molecular inorganic compounds, not only soften water, acting like ion exchangers (13), but are also capable of forming polymeric anions and associates of a colloidal degree of dispersion. Polyphosphates, being adsorbed on the surface of associates of detergents, apparently form mixed soap-polyphosphate micelles, in which the energy of repulsion of like-charged hydrophilic groups is reduced, as a result of which their dimensions increase. This is accompanied by an increase in the oleophilicity of the system and an increase in the solubilization of hydrocarbons in solutions of detergents containing polyphosphate additives. The action of polyphosphates in the washing process is more complex than is currently assumed. The increased effectiveness of detergents containing polyphosphates is explained not only by the fact that they disperse particles of mineral soils and bind, into a water-soluble complex, the calcium and magnesium ions that determine water hardness (12, 13); a more important property of polyphosphates, not discussed in the literature, is that they shift the oleophilicity of micellar structures into the optimum region, causing a change in the bulk properties of detergent solutions and thereby sharply increasing their solubilizing capacity and practically important properties.

Fig. 3. Curves of the dependence of the heptane solubilization effect in 0.1 *M* sodium naphthenate solutions (molecular weight 270) on phosphate additives: 1—hexametaphosphate and 2—sodium phosphate

This study has shown the possibility of regulating the degree of colloidality of detergent solutions by means of phosphates and other active additives and of obtaining detergent-active additive-water systems with predetermined properties. The action of phosphates and polyphosphates on micellar structures of soaps is equivalent to lengthening the hydrocarbon radicals of detergents and obtaining their more oleophilic homologues.

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