Detergent Building Action of Uncharged Polymers in Relation to Their Molecular Weights

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ABSTRACT

The detergency building action of water soluble uncharged polymers has been studied in relation to their molecular weights. Standard soiled cloths were used to evaluate detergency and results were obtained for detergent formulations without polyphosphate. The polymers examined were polyethylene glycols, polyvinyl alcohols and polyvinyl pyrrolidones. The building action is highly dependent on the molecular weight of the polymers, and only a small difference has been found between the chemical structures of the polymers examined. As the molecular weight decreases, the building action generally increases. For polyethylene glycol and polyvinyl alcohol, an optimum range of molecular weight was observed for maximum effectiveness. The building action of these polymers seems to be closely related to their ability to disperse soil particles in detergent solution. Data on suspension stabilities of titanium oxide, ferric oxide and kaolinite particles in the presence of polyethylene glycols are also included.

INTRODUCTION

In the previous papers (1,2) the importance in building action of alkalis, dispersants and sequestrants has been discussed from the results of detergency obtained from a variety of combinations of these components. It has been shown that these three builder components are indispensable in detergent formulations, and at their optimum combinations detergents exhibit soil removal efficiency comparable to the conventional detergent built with sodium polyphosphate. However, it should be noted that the building action of inorganic and organic compounds in a detersive system involves many phenomena that are related in a complicated way.

Polymers are often used as dispersants or flocculants for colloidal suspensions, depending on their molecular weights, and low molecular weight polymers are generally effective as dispersants (3,4). In the present work the building action of some water soluble uncharged polymers, which were used as dispersing agents, has been studied in relation to their molecular weights by formulating detergents with an alkali, a sequestrant and a polymer and without sodium tripolyphosphate. In connection with the building action of polyethylene glycol, the ability of this polymer to stabilize suspended colloidal particles has also been examined in this work.

EXPERIMENTAL PROCEDURE

Materials

The following polymers were used: polyethylene glycols, commercial samples from Sanyo Kasei Co. and laboratory-prepared samples; polyvinyl alcohols, commercial samples from Nippon Gosei Co. and fractionated samples therefrom; polyvinyl pyrrolidones, commercial samples from General Aniline and Film Co. and a fractionated sample therefrom. Fractionation of polymers was made by the ordinary method combining good and poor solvents (5). The approximate molecular weights of these polymers were taken from manufacturers' catalogs or determined with an Ostwald-type viscometer or a Hitachi-Perkin Elmer osmometer, Model 115. The sodium salt of β-naphthalene sulfonic acid-formalin condensate (degree of condensation about 6) and sodium alkylbenzene sulfonate (average alkyl chain C_{12}) were the same samples as those used in the previous work (6). Sodium nitrilotriacetate, carbonate and sulfate were of reagent grade. Titanium oxide and ferric oxide were

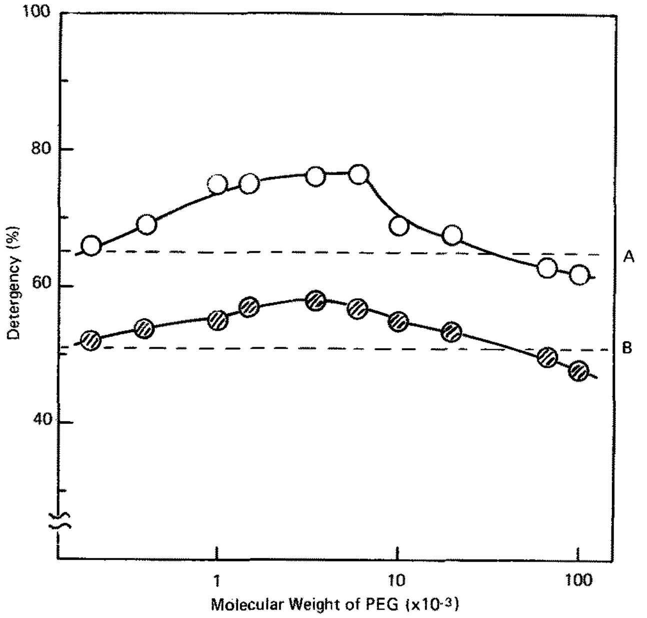

FIG. 1. The effect of molecular weight of polyethylene glycol (PEG) on detergency toward soiled cloths A (○) and B (⊕) at 0.20% detergent concentration. Broken lines indicate the detergency without PEG.

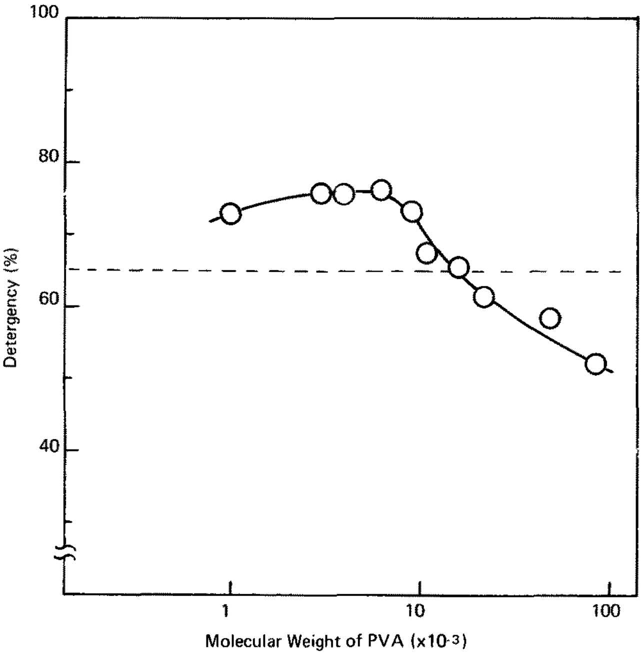

FIG. 2. The effect of molecular weight of polyvinyl alcohol (PVA) on detergency toward soiled cloth A at 0.20% detergent concentration. Broken line indicates the detergency without PVA.

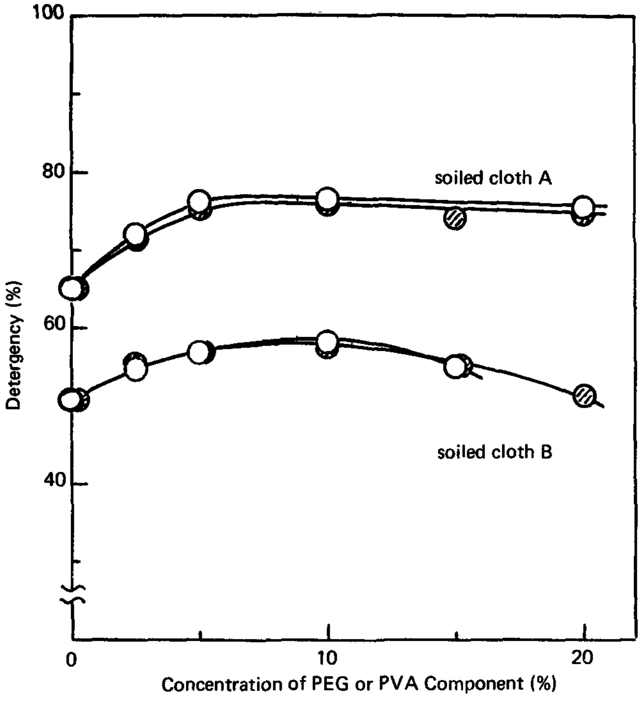

FIG. 3. The effect of concentrations of polyethylene glycol (○) with a mol. wt. of $3.5\mathrm{x}10^3$ and polyvinyl alcohol (⊕) with a mol. wt. of $4.0\mathrm{x}10^3$ on detergency toward soiled cloths A and B at 0.20% detergent concentration.

the same samples as those used in the previous work (6) and kaolinite was obtained from Wako Pure Chemicals Co.

Laundering Experiments

Two different types of soiled cloths were used. Soiled cloth A was prepared with a polyester-cotton blend of 60:40 and an artificial soil composed of bentonite clay, carbon black, lanolin, oleic acid and beef tallow (72:8:8:6:6). Soiled cloth B was prepared with cotton and an artificial soil composed of carbon black, cotton seed oil, beef tallow, cholesterol and paraffin (2.5:57.5:20:10:10). Details of these soiled cloths have already been described (1,2). Laundering experiments were carried out at 25 C at 0.2% detergent concentration in the same way as reported previously (1). The hard water used was one containing calcium and magnesium ions in a mole ratio of 2:1 having a total hardness of 72 ppm as calcium carbonate. Soil removal efficiency was determined by reflectance measurement and the result was expressed as per cent detergency (7).

Suspension Stability Measurements

The relative sedimentation volumes for titanium oxide, ferric oxide and kaolinite particles in suspensions (1.0 g of solid particles/30 ml water) containing 0.05% polyethylene glycol (PEG) adjusted to pH 9.0 $\sim$ 9.2 with sodium hydroxide, were determined in the same way as reported elsewhere (6), the relative sedimentation volume being defined as a ratio of sedimentation volume of particles in a sample solution to that in water.

RESULTS AND DISCUSSION

Effect of Polymer Molecular Weight on Detergency

Figure 1 shows the effect of the molecular weight of PEG on detergency toward soiled cloths A and B at 0.20% detergent concentration. The detergent was formulated with 20% sodium alkylbenzene sulfonate, 5% PEG, 5% sodium nitrolotriacetate, 5% sodium carbonate and 65% sodium sulfate. In this model of detergent formulation, sodium nitrilotriacetate was purposely used as a sequestrant to examine the building effect of polymers. The soil removal efficiency of the detergent without PEG was 65% for soiled cloth A and 51% for soiled cloth B (indicated by broken lines). As seen in Figure 1, the effect of PEG on detergency depends on its molecular weight and there appears to be a maximum detergency around molecular weights of $1.0\mathrm{x}10^3 \sim 8.0\mathrm{x}10^3$. The detergency at the maximum is comparable to the detergency obtained by a typical, commercial detergent (2) built with sodium tripolyphosphate. The molecular weight dependencies of detergency for soiled cloths A and B are similar. However, the builder effect of PEG on soiled cloth A is higher in magnitude.

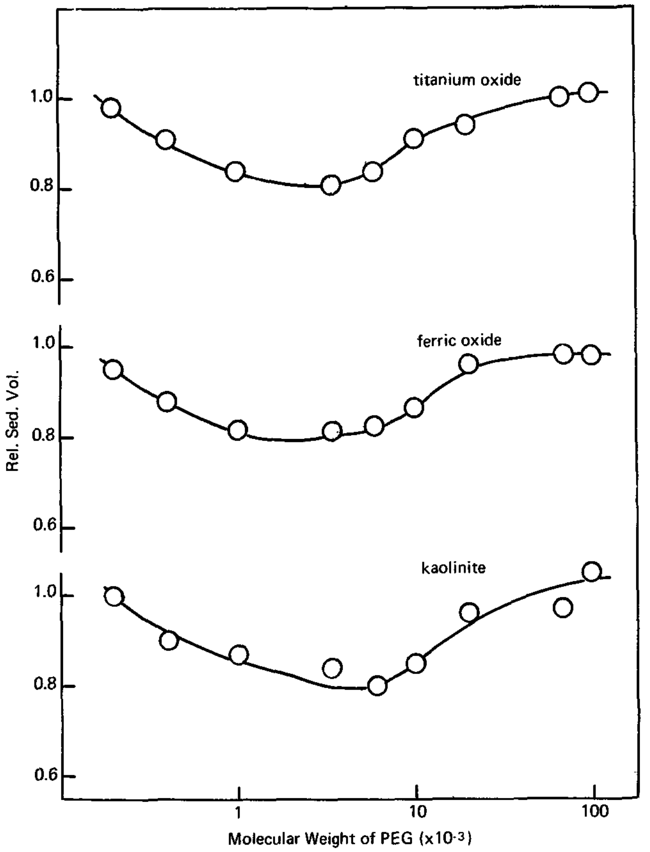

FIG. 4. The effect of molecular weight of polyethylene glycol (PEG) on the relative sedimentation volumes of titanium oxide, ferric oxide and kaolinite suspensions at 0.05% PEG concentration at pH 9.0$\sim$9.2.

Figure 2 shows the effect of the molecular weight of polyvinyl alcohol (PVA), with a saponification degree of >95%, on detergency toward soiled cloth A. Addition of PVA with molecular weights of $1.0\mathrm{x}10^3 \sim 9.0\mathrm{x}10^3$ enhances the detergency as observed in PEG, and PVA with molecular weights higher than $1.0\mathrm{x}10^4$ yields reduced detergency. These results indicate that there is an optimum molecular weight of polymer for a detergent builder component.

An increase in detergency on addition of PEG or PVA with a relatively low molecular weight would be ascribed essentially to their adsorption onto soil particles or cloth or both. Adsorption of polymer molecules onto soil particles will result in repulsive force from the decrease in entropy obtained when such polymer-adsorbed particles approach each other (8). The building action of these polymers may be partially understood by this mechanism. On the other hand, the negative builder effect was observed for the above two polymers with relatively high molecular weights. The number of segments adsorbed on a soil particle per polymer molecule will not increase appreciably with molecular

TABLE I

Builder Effect of Polymers[a] on Detergency Toward Soiled Cloth A at 0.20% Detergent Concentration[b]

Samples[c]	Molecular weight of monomer unit	Detergency, %		
		Low mol. wt.	Medium mol. wt.	High mol. wt.
Polyvinyl pyrrolidone	111	77.5(—[d])	71.6(1.0x10^4)	57.0(1.5x10^5)
Carboxymethyl cellulose	205	—	70.0(—[e])	60.6(6.0x10^4)
Naphthalene sulfonic acid-formalin condensate	242	75.4(1.5x10^3)	—	—

[a] 5% on the basis of detergent composition.

[b] Detergency without polymer, 65%.

[c] Number in parentheses indicates approximate mol. wt.

[d] Fractionated sample from PVP, mol. wt. 1.0x10^4.

[e] Fractionated sample from CMC, mol. wt. 6.0x10^4.

weight (9). If the remaining segments, which are not adsorbed on the particle and extend into the water medium, are greater than is necessary for dispersing action by the entropy reduction of the polymer, they will promote flocculation by either or both of two ways: (a) the extended segments of a polymer molecule are adsorbed onto one or more additional particles thus forming a polymer bridge, or (b) the extended segments of one polymer molecule interact with the extended segments of other similarly adsorbed molecules thus bridging by a polymer-polymer interaction (10). The lowering of detergency observed on addition of high molecular weight polymers would be explained by this mechanism of flocculation. Therefore, the ability of polymers to function as a detergent builder is primarily confined to their molecular weights.

The building action of a polymer is also influenced generally by its concentration in detergent. Figure 3 shows the effect of the concentration of PEG with a molecular weight of 3.5x10^3 or PVA with a molecular weight of 4.0x10^3 on detergency toward soiled cloths A and B. The formulation of the detergent was the same as that described in Figure 1 except for the concentration of the polymer component with which the concentration of sodium sulfate was balanced to bring the total to 100%. The detergency for soiled cloth A reaches its highest value with about a 5% addition of PEG or PVA and shows no further increase with concentration. The detergency toward soiled cloth B, on the other hand, reaches to a maximum around a concentration of 10%, then decreases gradually with concentration. The lowering of the building action observed for soiled cloth B in the region of high concentrations may be interpreted as showing that the polymer acts as a flocculant rather than a dispersant under such high concentrations. In general, the dispersing action of a polymer-type dispersant depends on its concentration and it behaves like a flocculant when the concentration is increased (11).

Up to this point, attention has been directed to PEG and PVA. Three samples of different molecular weights of polyvinyl pyrrolidone (PVP) were also examined. It is evident from the results shown in Table I that PVP with low molecular weight promotes soil removal efficiency, as observed for PEG or PVA, and PVP with high molecular weight is ineffective in this respect. For comparison, samples of sodium carboxymethyl cellulose (CMC), which is an organic builder widely used for prevention of soil redeposition, were also examined. It is interesting to note that CMC, especially CMC with high molecular weight, is ineffective as a builder component at the high level of concentration examined here. On the other hand a commonly used dispersant, sodium salt of β-naphthalene sulfonic acid-formalin condensate, is effective and actually promotes detergency.

Effect of PEG Molecular Weight on Suspension Stability

As discussed above, the effectiveness of the polymer as a builder component may be ascribed primarily to its ability to disperse soiled particles in detergent solution. In the present experiment, the relative sedimentation volumes, SV_{rel}, of three different types of solid particles in the solutions of PEG with different molecular weights were determined as a measure of the dispersing ability of the polymer or the suspension stability in the presence of the polymer. It is known that sediments of flocculated suspensions are usually much more voluminous than those of stable suspensions of the same concentration (12). Figure 4 shows the effect of the molecular weight of PEG on the values of SV_{rel} for titanium oxide, ferric oxide and kaolinite suspensions at 0.05% PEG concentration. As seen in Figure 4, the curves of SV_{rel} vs. molecular weight for these suspensions are concave upwards, indicating that there is an optimum molecular weight for dispersion of these particles and the suspensions are relatively stable at molecular weights of 1.0x10^3 ~ 1.0x10^4. This range of molecular weight nearly corresponds to the range in which PEG is effect as a building component.

The values of SV_{rel} for these suspensions obtained at the optimum molecular weight become much lower if sodium alkylbenzene sulfonate is added to the suspensions. Namely, the suspension stability increases in the presence of the surfactant. For example, SV_{rel} for titanium oxide suspension containing 0.05% additive(s) is 0.81 with PEG (mol. wt. 3.5x10^3) alone, 0.54 with the surfactant alone, and 0.41 with PEG and the surfactant (1:1). In accordance with other work (13) on mixed solutions of polymers and surfactants, this results suggests that PEG makes a kind of complex with the surfactant by which the dispersion of soiled particles is promoted, thus enhancing soil removal efficiency.

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