The Stability of Sodium Hypochlorite in the Presence of Surfactants

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Studies were made on the stability of NaOCl at 40°C in the presence of sodium alkanesulfonate or alkylarenesulfonate anionic surfactants, and in the presence of a nonionic surfactant, *N*-octylpyrrolidinone. The results were compared with NaOCl stability in the absence of additives and in the presence of nonsurfactant short-chain sodium alkylbenzenesulfonates. The data indicated that the rate of NaOCl loss is greatly dependent upon the pH of the solution, even at alkaline pHs. At initial pHs below 11, in the absence of additive, there is significant disproportionation of OCl^- to ClO_3^- and Cl^-, accompanied by decrease in the pH of the solution, within a period of several days. Even at an initial pH of 11.3, in the presence of the surfactants investigated, there is significant disproportionation of OCl^- and decrease in the pH of the solution in the first several days. When the initial pH of the solution is 13.5, there is no significant decrease in pH of the solution for at least two months in the presence of the surfactants studied. NaOCl stability in the presence of surfactant decreases in the order: sodium linear alkanesulfonate > sodium linear alkyldiphenylethersulfonate > sodium linear alkylbenzenesulfonate >> *N*-octylpyrrolidinone. Stability was greater in the presence of linear alkylarenesulfonates than in the presence of branched alkylarenesulfonates. It is suggested that the differences in stability observed are due to the greater ease of oxidation of tertiary carbon atoms compared to primary or secondary atoms.

KEY WORDS: **Alkanesulfonate, alkylarenesulfonate, alkylbenzenesulfonate, alkyldiphenylethersulfonate, anionic surfactants, bleach stability, *N*-octylpyrrolidinone, nonionic surfactant, sodium hypochlorite stability, stability.**

The presence of sodium hypochlorite in detergent compositions adds an important bleaching property to the product. However, many organic functional groups, notably primary or secondary hydroxyl groups present in many surfactant structures, are readily oxidized by sodium hypochlorite. This severely limits the types of surfactants that can be used in such compositions. In spite of a number of patent references (1–4), the chemical literature contains few (5,6) systematic studies of the effect of surfactant structure on sodium hypochlorite stability. Our interest in the problem was heightened by data indicating that in some cases there seemed to be no rational explanation for the effects observed. As a result, an investigation was initiated in an attempt to explain some of the relationships between hypochlorite stability and surfactant chemical structure.

EXPERIMENTAL PROCEDURES

Materials. All surfactants investigated were commercial materials, used as received, with the exception of LAS2, a water-white, specially purified grade of sodium linear dodecylbenzenesulfonate based on 1-dodecene (courtesy of Dr. Michael F. Cox, Vista Chemical, Ponca City, OK). The other surfactants investigated were: C_{12}DPES—sodium branched dodecyl diphenylether disulfonate (Dowfax 2A1-Dow Chemical, Midland, MI); C_{10}DPES—sodium linear decyl diphenylether disulfonate (Dowfax 3B2-Dow Chemical); C_{12}LAS—sodium linear dodecylbenzene sulfonate (C-550LAS—Vista Chemical); C_8SAS—sodium linear *sec*-octanesulfonate (Bio-terge PAS-85-Stepan, Northfield, IL); C_{12}SAS—sodium linear *sec*-dodecanesulfonate and C_{14}SAS—sodium linear *sec*-tetradecanesulfonate, both courtesy of Dr. Michael F. Cox, Vista Chemical; CS—sodium cumenesulfonate (Rutgers-Nease, State College, PA); and C_8Py—*N*-octylpyrrolidinone (ISP, Wayne, NJ). In addition, the following reagent-grade chemical compounds were investigated: *p*TS—sodium *p*-toluenesulfonate; C_{12}S—sodium dodecanesulfonate; and *m*XS—sodium *m*-xylenesulfonate. The NaOCl used was a commercial household bleach.

Determination of OCl^- stability. Stability of OCl^- was determined in 1% (w/w) aqueous solutions of surfactant with an initial NaOCl concentration of approximately 2.3% (w/w) in either colorless glass or opaque brown plastic containers. Solutions were maintained at 40 ± 1°C. The percentage of NaOCl in the solution was measured by iodometry (7). A 5-mL sample of the test solution was diluted with 20 mL of distilled water and 2 g of KI and 10 mL of 1 N H_2SO_4 were added. The solution was titrated with 0.1 M sodium thiosulfate that had previously been standardized against potassium iodate under similar conditions, and starch indicator was used.

Determination of ClO_3^- content. After complete loss of OCl^- (8), a 5-mL sample of the test solution was placed in a 250-mL glass-stoppered Erlenmeyer flask. Twenty-five mL of 0.2 M KI solution was added, then 50 mL of conc. hydrochloric acid. The solution was mixed well and allowed to stand in the dark for 15 min. Five mL of $CHCl_3$ was added and the solution was titrated with standard 0.1 M KIO_3, with shaking, until complete disappearance of the iodine color from the $CHCl_3$ layer. The following equations pertain:

$$ClO_3^-(IO_3^-) + 6\ I^- + 6\ H^+ \rightarrow 3\ I_2 + Cl^- + 3\ H_2O \qquad [1]$$

$$ClO_3^-(IO_3^-) + 3\ I_2 + 6\ H^+ + 5\ Cl^- \rightarrow 6\ ICl + 3\ H_2O \qquad [2]$$

$$ClO_3^-(IO_3^-) + 3\ I^- + 6\ H^+ + 2\ Cl^- \rightarrow 3\ ICl + 3\ H_2O \qquad [3]$$

Twenty-five mL of the same 0.2 M KI, treated with 50 mL of conc. hydrochloric acid under the same conditions, was titrated with the standard 0.1 M KIO_3 in the presence of 5 mL of $CHCl_3$. The difference in titration values of KI and test solutions was used to calculate the ClO_3^- content of the test solution. Proton nuclear magnetic resonance (NMR) spectra were obtained either on a Varian T-60 (Palo Alto, CA), or an IBM 250 AF (Danbury, CT) Fourier Transform NMR Spectrometer.

RESULTS AND DISCUSSION

Effect of pH. It is well known that OCl^- in aqueous solution can decompose by the reactions:

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$$2\ \mathrm{OCl}^- \rightarrow 2\ \mathrm{Cl}^- + \mathrm{O}_2 \qquad [4]$$

$$3\ \mathrm{OCl}^- \rightarrow 2\ \mathrm{Cl}^- + \mathrm{ClO}_3^- \qquad [5]$$

and that the rates of these reactions are markedly influenced by concentration, pH, temperature, added salts and photolysis (9). To draw valid conclusions regarding the effect of various surfactant structures on OCl^- stability, it is necessary to keep these variables constant and to minimize OCl^- self-decomposition by reactions [4] and [5]. A complication is that the pH of NaOCl solutions decreases when NaOCl decomposes by either of the above reactions, because OCl^- (K_a of HOCl $= 3 \times 10^{-8}$) (9) is much more basic than Cl^- or ClO_3^-. Since HOCl decomposes much more rapidly than OCl^- (9), this will accelerate the rate of self-decomposition of OCl^- (Fig. 1). ClO_3^- determination in the NaOCl solutions with initial pHs of 9.0 or 10.0, after all the OCl^- had decomposed, showed that almost all had reacted in accordance with equation [5], above, to form ClO_3^- (and presumably Cl^-). Only when the pH of the NaOCl solution is >11, is there little self-decomposition of the OCl^- and the pH of the solution remains essentially constant (for at least 45 days). Consequently, all stability studies in the presence of surfactant were done at pH values above 11.

Effect of container. To determine whether photolysis or the nature of the container surface might play a role in the decomposition of NaOCl, initial experiments were conducted both in colorless glass (CG) and in opaque brown plastic (OBP) containers in a lighted room. Data are presented in Table 1.

It is apparent from the data that NaOCl stability in both types of containers is similar, both in the absence or in the presence of added surfactant. It would therefore seem that, under these conditions, NaOCl decomposition due to photolysis is not a significant factor, nor is the difference in the container surface significant.

NaOCl stability in the presence of surfactants and nonsurfactant alkylbenzenesulfonates (initial pH ~ 11.3). Figure 2 shows plots of percentage NaOCl remaining as a function of time for aqueous solutions with an initial NaOCl concentration of approximately 2.3%, a surfactant or alkylbenzenesulfonate concentration of 1% and an initial pH of about 11.3, contained in either brown opaque plastic or colorless glass bottles at 40°C. None of the surfactants tested has a nominal chemical structure with a readily oxidized group (*e.g.*, primary or secondary hydroxyl).

It is apparent from the data that, under these conditions, every surfactant tested decreased the stability of the NaOCl, in some cases markedly. In addition, the following conclusions regarding structural effects can be drawn: (i) NaOCl is more stable in the presence of alkanesulfonate-type surfactants ($C_{12}S$, $C_{14}SAS$) than in the presence of alkylarenesulfonate-type surfactants ($C_{10}DPES$, $C_{12}LAS$); (ii) NaOCl is more stable in the presence of alkylarenesulfonates that do not form micelles (*p*TS, CS, *m*XS) than in the presence of micelle-forming ones; (iii) in the presence of a nonionic surfactant of the *N*-alkylpyrrolidinone type (C_8Py), in spite of the absence of easily oxidized groups (*i.e.*, primary or secondary hydroxyls), all of the NaOCl was lost in a few days. It

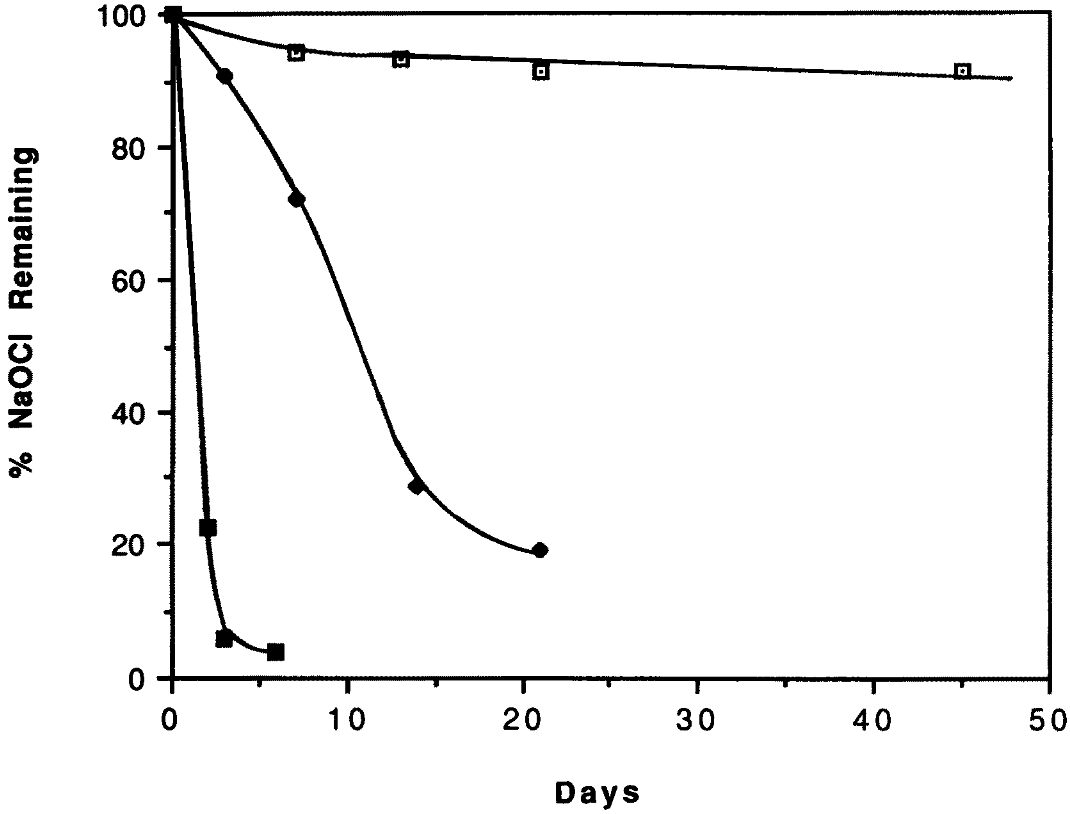

FIG. 1. Self-decomposition of NaOCl (initial conc. about 2.3%) at 40° at various initial pHs: ■ initial pH 9; ◆ initial pH 10; □ initial pH 11.3.

TABLE 1

NaOCl Stability in Colorless Glass (CG) and in Opaque Brown Plastic (OBP) Containers (40°C; initial NaOCl conc., 2%)

		% NaOCl Remaining			
		Initial pH 11.3		Initial pH 13.5	
Compound	Time (days)	CG	OBP	CG	OBP
Blank	21	93	91		
C_{10}DPES	3	0	9	—	—
	20	0	0	89	89
C_{12}DPES	20	0	0	89	86
LAS	6	0	3	—	—
LAS2	7	53	59	—	—
C_{12}SAS	7	73	78	90	89
*p*TS	7	95	93	—	—
	21	—	—	92	93
C_{12}S	7	91	92	—	—

should be noted that C_{12}S and C_{12}LAS were not completely soluble in the NaOCl solution, which may account for the somewhat greater stability of NaOCl in their presence, compared to that in C_{10}DPES.

Measurement of the pH of the solutions showed that the loss of OCl^- due to the presence of the surfactant was accompanied, as in the absence of surfactant at initial pHs of 9.0 and 10.0 (Fig. 1), by significant decrease in the pH of the solution. The pH decreased to about 7 in most cases when all the OCl^- had reacted (as would be expected from the replacement of basic OCl^- by neutral Cl^- or ClO_3^-). This would produce self-decomposition of the OCl^-, as discussed above, and complicate interpretation of the results. Analysis of the solutions for ClO_3^- concentration when OCl^- no longer remained (OCl^- interferes in the method used for ClO_3^-) showed that, depending upon the nature of the surfactant present, 15–45% of the OCl^- had disproportionated to ClO_3^- (and Cl^-) in accordance with equation [5]. Consequently, additional NaOH (3%) was added to the solutions in all subsequent studies to maintain a pH high enough to minimize this self-destruction of OCl^-. The pH determinations on these solutions in the absence and presence of surfactants showed no significant decrease in pH (<0.3 pH unit) over the period of the investigation. The decrease in self-decomposition of the OCl^- at this higher pH was shown by ClO_3^- analysis on C_8Py after total loss of OCl^-. At an initial pH of about 11.3, 44% of the NaOCl disproportionated to ClO_3^- and Cl^-, whereas at an initial pH of 13.5, only 14% was found to disproportionate in this fashion.

NaOCl stability in the presence of surfactants plus 3% added NaOH (initial pH, 13.5). The much greater stability of NaOCl in the presence of all of the surfactants investigated at initial pH of 13.5 (Fig. 3 and 4), rather than about 11.3 (Fig. 2) confirms the importance of the pH of the solution in determining the rate of loss of OCl^-, even at initial alkaline pHs. It also suggests an explanation for the observed much more rapid loss of NaOCl in the presence of micelle-forming alkylarenesulfonates than in the presence of nonmicelle-forming alkylarenesulfonates (*e.g.*, LAS *vs.* CS). The pH at the surface of highly negatively charged anionic micelles is known to be con-

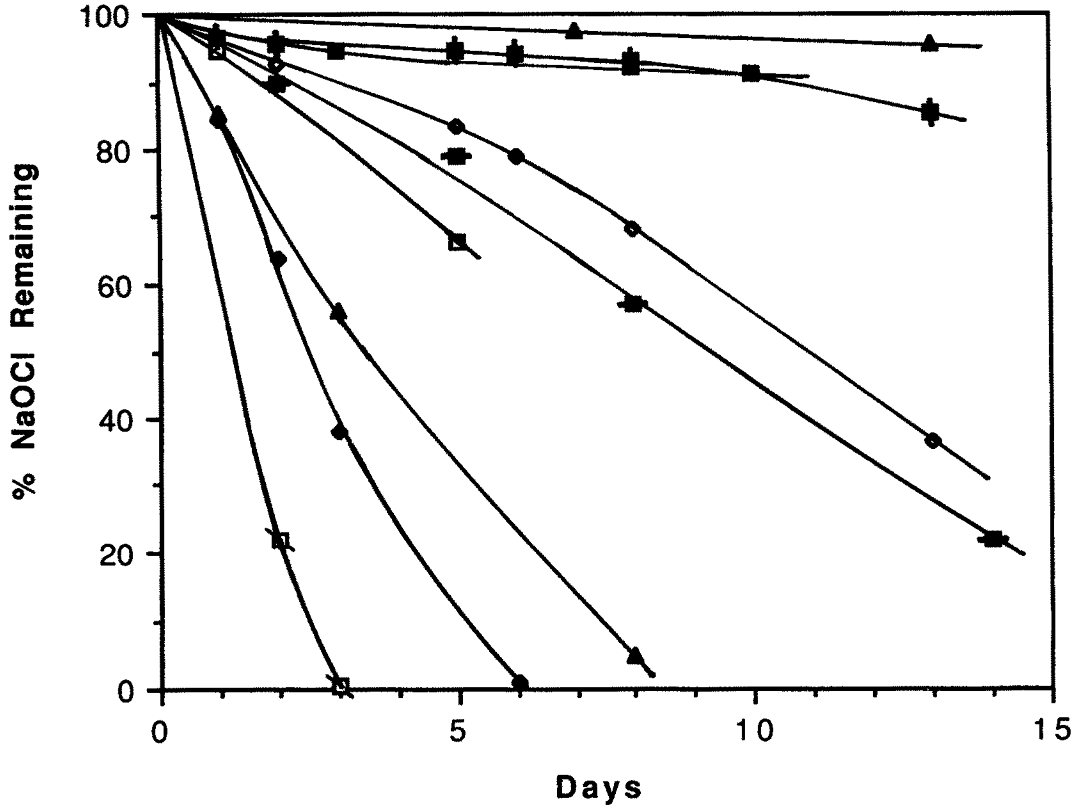

FIG. 2. Stability of NaOCl (initial conc. about 2.3%) at 40°C in the presence of 1% surfactant or short-chain alkylbenzenesulfonate at an initial pH of about 11.3: ▲ None; ■ C_{12}S; ✚ *p*TS; ◇ C_{14}SAS; -■-CS; □ *m*XS; ▲ C_8Py; ◆ C_{12}LAS; ⌧ C_{10}DPES.

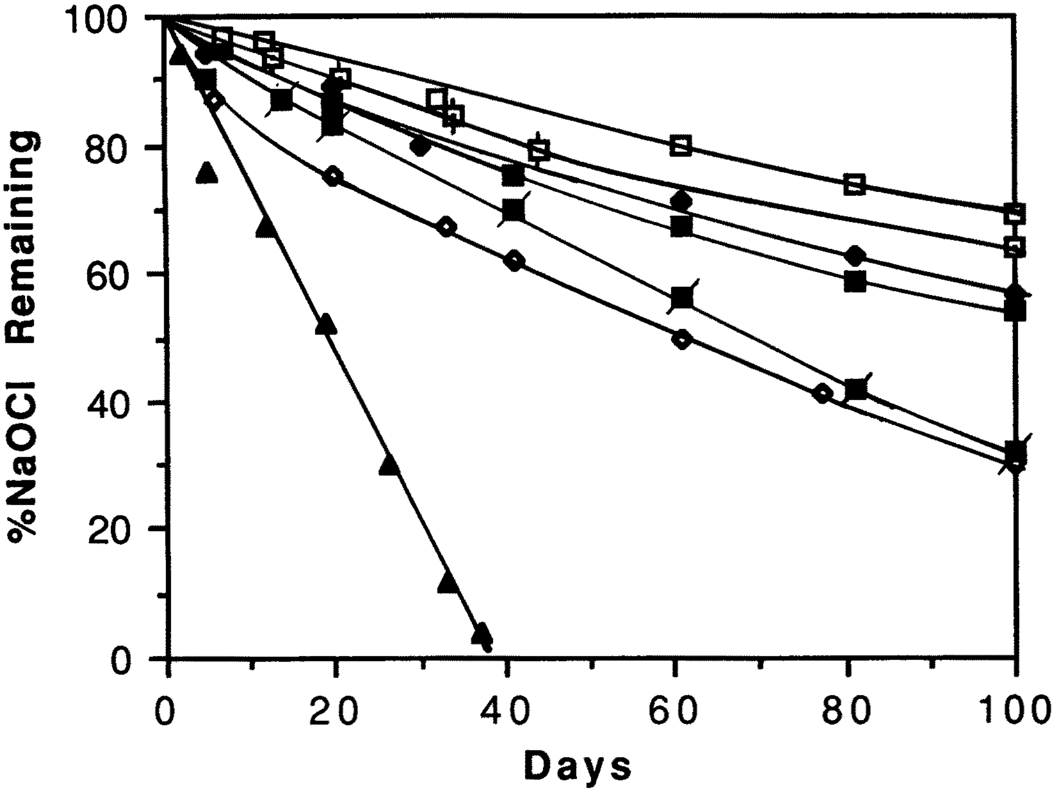

FIG. 3. Stability of NaOCl (initial conc. about 2.3%) at 40°C in the presence of 1% surfactant and 3% added NaOH (initial pH, 13.5). Surfactant: □ None; ⊞ C_{14}SAS; ◆ C_{10}DPES; ■ C_{12}DPES; ▨ C_{12}LAS2; ◇ C_{12}LAS; ▲ C_8Py.

siderably lower than in the bulk phase (10), and therefore the presence of anionic micelles can be expected to increase the rate of NaOCl decomposition. That is, the OCl^- self-decomposition is an anionic micelle-catalyzed reaction. When the pH of the solution is raised to the point where such self-decomposition of OCl^- is minimized, the difference in stability of NaOCl in the presence of alkylarenesulfonate capable and incapable of forming micelles is decreased considerably (*p*TS *vs.* C_{10}DPES, Fig. 4).

However, the other effects noted above at an initial pH of about 11.3 are again seen here: (i) NaOCl is much more stable in the presence of the various sodium alkylarene- and alkanesulfonates than in the presence of *N*-octylpyrrolidone; (ii) NaOCl is more stable in the presence of long-chain sodium alkanesulfonate-type surfactants (C_{12}SAS, C_{14}SAS) than in the presence of sodium alkylarenesulfonates (C_{10}DPES, C_{12}DPES, LAS, LAS2), although the difference between them is diminished at the higher pH. The presence in the latter of benzylic carbon atoms that are more easily oxidized than the methylene carbon atoms in the alkyl chains of the former may account for this. A number of other structural effects are noteworthy: (i) the greater stability of NaOCl in the presence of linear alkyldiphenylethersulfonate (C_{10}DPES) than in the presence of linear alkylbenzenesulfonates (LAS, LAS2); (ii) the greater stability of NaOCl in the presence of a linear alkyldiphenylethersulfonate (C_{10}DPES) than in the presence of a branched alkyldiphenylethersulfonate (C_{12}DPES). The former effect still remains unexplained; the latter effect may be due to the greater ease of oxidation by OCl^- of tertiary carbon than of primary or secondary carbon atoms in the alkyl chain. Evidence for this is the greater stability of NaOCl in the presence of sodium *p*-toluenesulfonate (*p*TS), which contains only a primary carbon (methyl group), than in the presence of sodium *p*-isopropylbenzenesulfonate (CS), which contains a tertiary carbon atom (Fig. 4).

Additional evidence is presented by the changes in the proton NMR spectrum of sodium *p*-cumenesulfonate after reaction with NaOCl. Initially, the spectrum shows the expected pair of doublets centered at δ 6.5 and 6.8 due to the aromatic protons, a multiplet at δ 2.9 for the tertiary carbon hydrogen, and a doublet centered at δ 1.2 for the primary carbon (methyl) hydrogens. After reaction with the NaOCl, the spectrum shows no peak in the region around δ 2.9, indicating complete loss of the tertiary carbon hydrogen. In addition, the methyl hydrogen peak is now a singlet and is centered at δ1.6, rather than at δ 1.2, as would be expected from the removal of the hydrogen from the adjacent tertiary carbon atoms and its replacement by a more electrophilic atom. Our investigations are continuing.

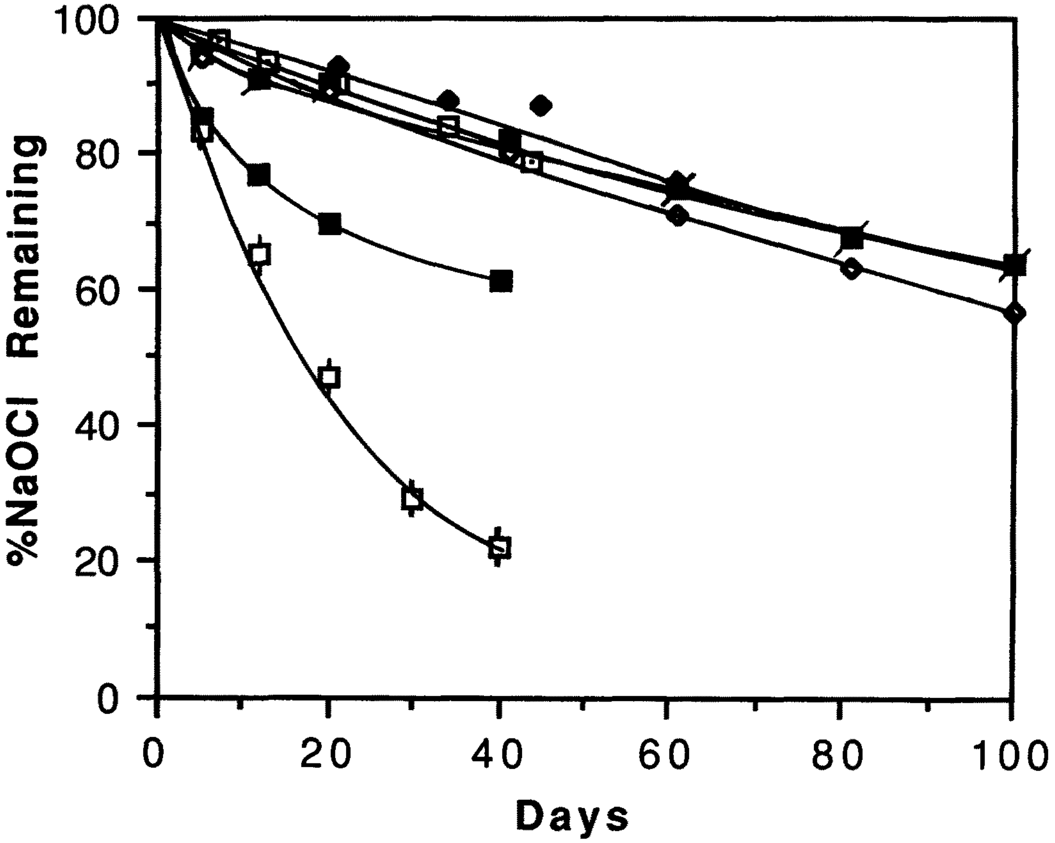

FIG. 4. Stability of NaOCl (initial conc. about 2.3%) at 40°C in the presence of 1% surfactant or short-chain alkylbenzenesulfonate and 3% added NaOH (initial pH, 13.5): ⊡ None; ◆ *p*TS; ■ C_{12}SAS; ◇ C_{10}DPES; ■ C_8SAS; ⌑ CS.

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