Ecological Behavior of Cationic Surfactants from Fabric Softeners in the Aquatic Environment

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ABSTRACT

The use of cationic surfactants in fabric softeners has reached considerable proportions in the Western industrialized nations during the last 10 years. In the Federal Republic of Germany alone, some 22,000 ton of cationic surfactants were marketed in 1981 for this specific purpose. The considerable share (12%) of total consumption which this class of surfactants accounts for is equivalent to a theoretical wastewater concentration of ca. 5 mg/L. Consequently, it raises questions concerning environmental behavior of this class of substances. The following factors are of substantial importance in this regard: acute and chronic toxicity in the aquatic environment; biodegradability under aerobic and anaerobic conditions; and the possibility of bioaccumulation in the aquatic organisms, particularly in fish. Basically, the ecological behavior of cationic surfactants, like that of distearyl dimethyl ammonium chloride (DSDMAC) and dialkyl imidazolinium salts (DAIC) which are mostly used, is determined markedly by their physicochemical properties, above all their strong adsorption on surfaces, e.g., on clay minerals or on activated sludge, thus leading to their elimination in water treatment plants and water courses. Of far-reaching consequence from the toxicological aspect is the fact that they form neutral salts with the anionic surfactants present in excess in domestic wastewater, thus leading to a considerable decrease in toxicity. Although adsorption and ion-exchange processes are primarily effective in elimination of cationic surfactants of the DSDMAC and DAIC types in wastewater treatment, there are significant indications on the basis of experiments that these substances are subject to extensive aerobic biochemical degradation. However, it appears that anaerobic degradation does not take place. Tests conducted so far on the bioaccumulation behavior, particularly on a laboratory scale, indicate that these substances practically do not accumulate in the edible parts of fish and thus no risks are being discerned at present as regards the residue situation.

INTRODUCTION

Cationic surfactants are used worldwide in numerous application ranges, such as disinfection, hydrophobizing, softening textile fabrics, obtaining antistatic effects, and corrosion protection.

In the past 10 years, particular cationic surfactants have been used to an increasing extent as fabric softeners, especially in Western Europe. West Germany is the number one consumer; annual per capita consumption is 0.33 kg, on the basis of the pure substance. At the same time, it is assumed that the consumption of cationic surfactants in West Germany has already reached a certain saturation limit, and that an increase in the next few years is no longer to be expected (1). Table 1 explains these ratios; it becomes apparent that consumption increases are quite possible in a few countries.

By way of comparison, ca. 39,000 tons of quaternary ammonium compounds were marketed in the USA in 1978. According to an estimate by Hull and Co., the consumption of cationics in fabric softeners was 72 million lb, consisting of 57.5 million lb of distearyl dimethyl ammonium chloride, 8.3 million lb of imidazolinium quats, and 6.2 million lb of amidoamine compounds. This is double the amount in 1971 (3). Cationic surfactants amount to ca. 7% of the total surfactant production in the USA (4). Worldwide, their share should be ca. 6%; this amount covers all application purposes (5). This relatively large increase in the share of cationic surfactants in the total consumption of surfactants is a major motive for discussion here (and lately within the EEC as well) of the behavior of this surfactant class in the environment. We start with the fact that, provided these substances are used according to their purpose, they mainly get into effluents and may add an additional load on the environment. The main theme is the effect on effluent treatment and the possible damaging effects on waters. When starting from a specific effluent amount of 200 L per capita per day, and in line with the corresponding theoretical calculations, the cationic surfactant concentration conditioned by softeners amounts to only ca. 4.5 mg/L in the untreated sanitary wastewater in West Germany. This corresponds to a chemical oxygen demand (COD) rise of ca. 10 mg/L.

These considerations have expressly not taken into account more recent developments of specialty chemicals in heavy-duty detergents for textiles: the cationic surfactants are added directly to these and make separate softening superfluous. Their effects on the environment must be thoroughly studied.

CHEMICAL MECHANISM OF CATIONIC SURFACTANTS

The chemical nature and structure of cationic surfactants point to a series of common properties that determine in the long run their physicochemical behavior, not only in their actual application but also in the environment. They have heteroatoms (that are generally positively charged) as solubility-forming groups; the main technical objective is achieved by the aliphatic N compounds with a quaternary ammonium as well as by similarly constructed alicyclic or aromatic cyclic systems, such as pyridine or imidazoline (6).

As a rule, cationic compounds with surface-active properties have at least one or two alkyl chains of 8-22 C atoms. The other alkyl groups are mostly short-chain substituents, such as methyl or benzyl groups. Compounds with alkyl fractions of C_8—C_{14} are appropriate and are preferred as disinfectants: with chain lengths exceeding

TABLE I

Consumption of Cationic Surfactants (1981) (2)

Country	Annual consumption (tons/year)	% Share of total surfactant consumption
European Economic Community	100,000	10
France	15,000	8
West Germany	27,000	10
Italy	9,000	4.7
United Kingdom	10,000	6.6

C_{14} (preferably C_{16}–C_{18}), the softening effect comes to the fore. Because of their positive charges, cationic surfactants have a strong affinity for negatively charged surfaces, to which their application as a softener or as a disinfectant is attributed.

The chain length of the fatty acid groups has a decisive effect on the water solubility; and water solubility is closely related to the type and range of activity. Accordingly (7), the water solubility of distearyl dimethyl ammonium chloride (DSDMAC) is 2.5 mg/L, whereas the surfactants used as disinfectants are almost completely water-soluble.

The anions of cationic surfactants are usually halogens, but also may be methylsulfate or dimethyl phosphate. At present, fabric softener preparations in Europe are nearly exclusively limited to ditallow dimethyl ammonium chloride, and more particularly mainly as DSDMAC, and dialkyl imidazolinium salts (DAIC).

At present, the share of DSDMAC alone is 90% in West Germany (20,000 tons/year). Consumption of DAIC has increased partly due to a better processibility: this is apparent in the fabric softeners marketed in 1982, that have 15–50% active substance.

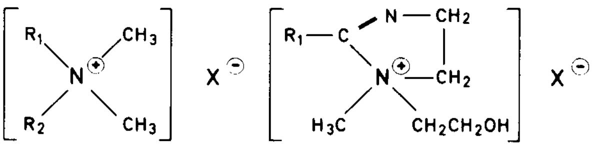
The structural formulas of both compound types are represented in Figure 1. Cationic surfactants of the DSDMAC-type are relatively stable chemically and do not change under washing conditions. In contrast with this, imidazolinium salts in aqueous solution are susceptible to hydrolysis; after a short time at pH values exceeding 8, a hydrolytic degradation of the imidazoline ring occurs, forming amide structures (Fig. 2) (8).

A particularly important property of cationics used in softeners — with regard to their environmental behavior — is determined by the electrically neutral salt formation, preferably with anionics: excess volumes of the latter are clearly found in wash liquor and in the effluent. Stoichiometric 6:1 ratios are common. The electrically neutral salts of linear alkylbenzene sulfonates and of DSDMAC and DAIC, that are most used in softeners, are largely insoluble in water and precipitate as 2:1 up to 1:2 complexes at rather high concentrations. Their formation can be established, among other things, by pursuing the conductivity ratios. The IR spectrum of an ABS-DSDMAC adduct is given in Figure 3. The functional bands of both initial components are easily recognizable. As a whole, one should start from the fact that the cationic surfactants used in softeners so far occur, as a rule, in the form of their electrically neutral salts in effluents and also in surface water. Contrary to this, the behavior of the short-chain cationic surfactants in this direction has not yet been studied and the question remains whether, here as well, formation of insoluble complexes takes place.

ANALYSES OF CATIONIC SURFACTANTS

Although there are several detection processes for cationic surfactants as pure substances, e.g., in detergent preparations, only a very limited number of analytical procedures are available for their determination in water and wastewater. At present, the Waters and Kupfer method is the main one. The particular difficulties with regard to the detection of cationic surfactants lie in the fact that cationics occur in very low concentrations, especially in surface waters, where many materials may interfere with their detection, and occur in various states and forms of bonds. In many cases, it is desirable to have a differentiating approach. Figure 4 illustrates this state of affairs.

This method is fundamentally based on colorometric determination of the adduct, or neutral salt formed between cationic surfactant and disulfine blue; analogously to the methylene blue active substances (MBAS) with the anionic surfactants. It is called disulfine blue active substance (DSBAS). In further analogy to MBAS, DSBAS is not specific for a particular cationic surfactant, but includes numerous surfactants of the quaternary ammonium and imidazolinium salts up to the protonated alkyl amines and aminoxides (9).



Quaternary Ammonium-Type Imidazolinium-Type

FIG. 1. Basic types of cationics used as fabric softeners.

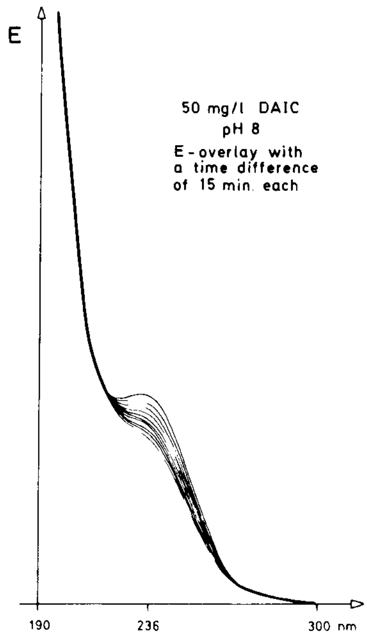


FIG. 2. Hydrolytic degradation of DAIC at pH 8.

Various cationic surfactants clearly show varying molar extinction coefficients, so that drawing representative calibration plots becomes a problem. So far, there has been no agreement as to a generally binding calibration standard, such as, e.g., DSDMAC. The application of the Waters and Kupfer method that was considerably modified and improved by Osburn — particularly concerning the sample pretreatment including stabilization and extraction — enables detection up to ca. 80 μg/L.

The thin layer chromatographic method (10) uses the same pretreatment steps as the one according to Wickbold: although its detection limit of 2 μg/L makes it clearly more sensitive, it requires considerably more time as well. The quantitative evaluation of the chromatograms after coloring with Dragendorff-reagent is done with a densitometer.

More recent developments in analyses of cationic surfactants uses liquid chromatography (HPLC) while using conductometric detectors (11). This makes it possible to determine aromatic and alicyclic cationic surfactants side by side in the microgram range. The practical detection limit is at 2 ppb. Essential characteristics of this method are the use of a separating column, without additional suppressor column (SCIC), and the use of nonaqueous elution agents such as chloroform or methanol. A series of extraction and evaporation steps also are part of the process.

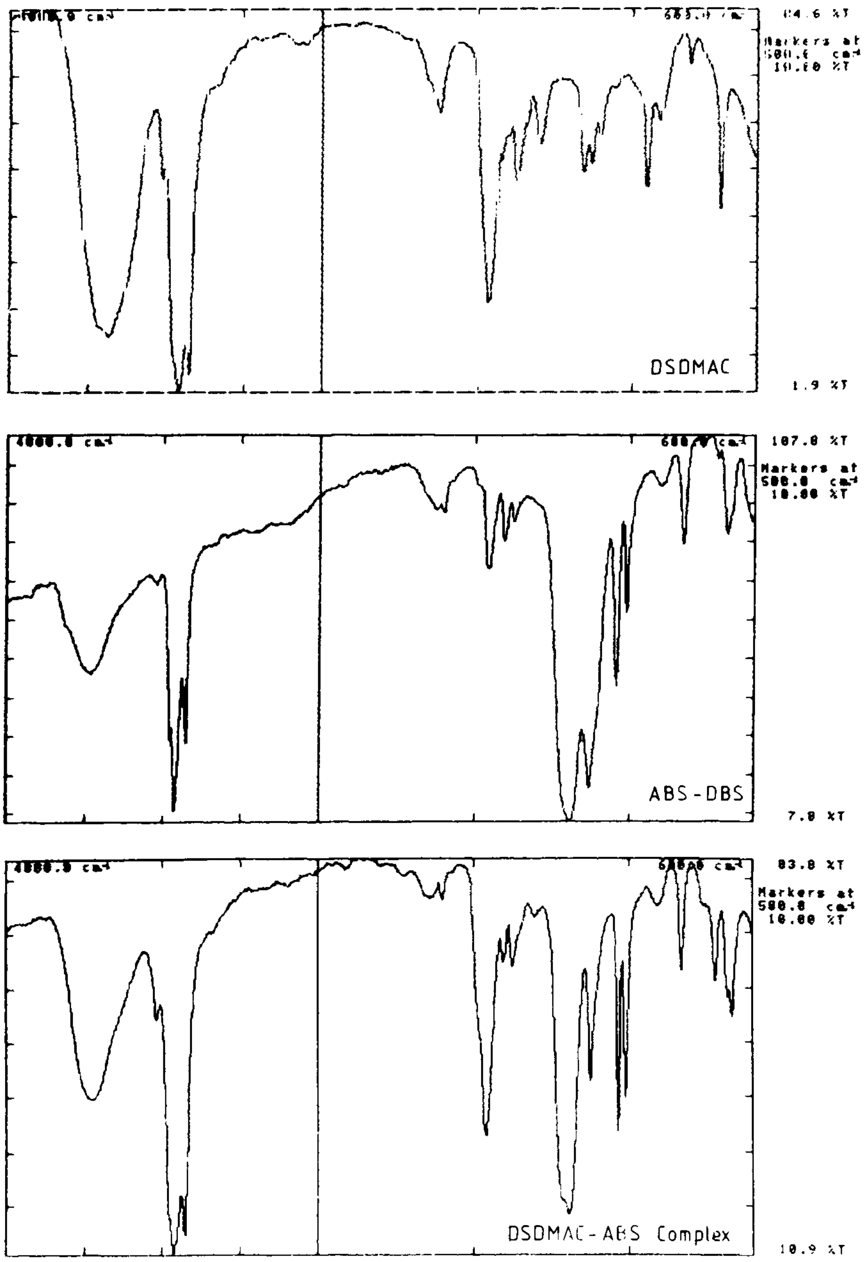


FIG. 3. Infrared spectra of DSDMAC, ABS/DBS and a DSDMAC-ABS complex (neutral salt).

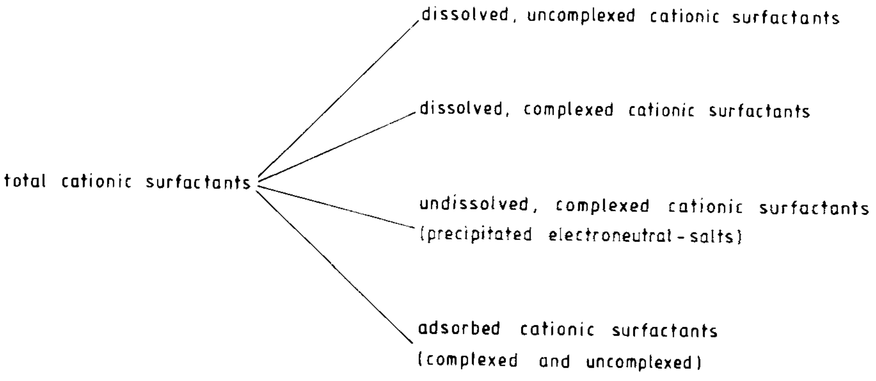


FIG. 4. Binding forms of cationics in the aquatic environment.

Recent progress has also been made in the determination of cationic surfactants in sludges or biomass; more accurate statements can be given about the distribution of these substances in the environment, and an answer can also be given now to inquiries about real biodegradation. Up to now, it has been rather difficult to determine load balances in treatment plants and in lab degradation tests, generally using radioactively marked substances. In this method, the dried organic solids, such as activated sludge, are hydrolyzed with hydrochloric acid at 150 C, and the cationic surfactants are complexed with disulfine blue. The DSBAS is extracted with chloroform, converted in methanol and subsequently cleaned on an ion-exchange column. A two-phase titration is the last step. The recovery rate is indicated to be 85% (12). On the whole, one may assume at present that several analytical methods with sufficient detection limits are available for the determination of cationic surfactants. All methods are characterized by the relatively long time required. This is especially due to the extensive cleaning and separation steps.

PHYSICOCHEMICAL BEHAVIOR

Cationic surfactants concentrate on surfaces by chemisorption, and their electrochemical nature causes them to adsorb at negatively loaded binding sites. They have a high affinity to some textile fabrics (cotton, cellulose fibers), but also to mineral and biological surfaces. Particularly intensive correlations occur with clay minerals, soil colloids, humic substances and water sediments, to which they are partly bound irreversibly. With the clay minerals, or phyllosilicates, of the montmorillonite, kaolinite or illite type, there is not only a binding at the outer surface, but also an inclusion into the sheet clearances. According to Weiss (13), the cationic exchange capacities amount to 60–140 mval/100 g. One must assume that the cationic surfactants incorporated in the sheet lattice clearances are no longer accessible to a biological attack by bacteria. The various types of cationic surfactants used as softeners show particular differences with regard to their exchange isotherms, in that DSDMAC is somewhat better bound than C_{18}-DAIC. Examinations (3) show that the adsorption coefficients are stable over a relatively broad concentration range. In case anionic surfactants are present, the sorption capacity is lowered. However, when dealing with processes in sewage plants and waters, its sorption at biological surfaces, e.g., bacteria, is as important as essential components of activated sludge or biofilter film. Extent and time-dependence of cationic surfactant fixation in living and sterilized activated sludge is represented in Figure 5. It can be seen that the DAIC is bound by activated sludge to a considerable extent within 30 min, and has already reached an approximate equilibrium state. As there is no significant difference in the sorption capacity of both sludges, it must be assumed that, in the first place, a purely physicochemical process becomes active in the elimination of the cationic surfactant. This is fully confirmed by a series of more recent examinations (3, 14).

The substantial capacity of the cationic surfactants to occupy negatively loaded binding sites at activated or inactivated material means that this will affect heavy metal sorption which are in competition, in that biological treatment processes especially are involved. It is known that activated sludge in particular has a very high capacity to eliminate heavy metals. Research by Huber (1) and Beveridge and Pickering (15) showed that the sorption of heavy metals to clay minerals and activated sludge is hindered to a considerable extent (competitive adsorption for surface sites), when cationic surfactants are present. So far, there has not been extensive examination on the importance of this process for the operational practice of sewage plants.

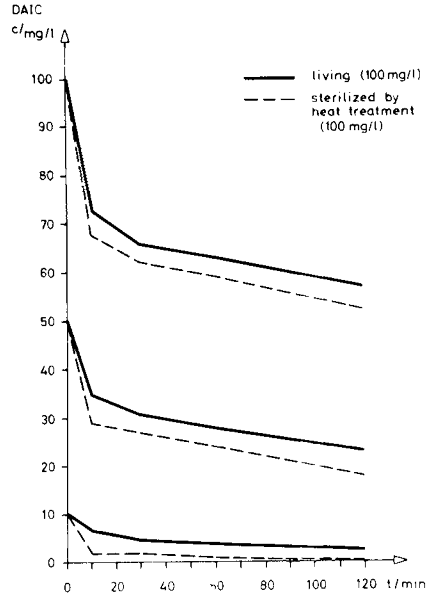


FIG. 5. Adsorption of DAIC to activated sludge.

The behavior of cationic surfactants in the environment is also affected by their photochemical stability. Neufahrt (16) showed that especially shortwave ultraviolet light is able to bring about partial or complete oxidization of DSDMAC, as well as of alkyldimethylammonium chloride after induction periods of 16–72 hr. The residual products after a rather short exposure time are biodegradable. The detection of photochemical instability is particularly important when making an agricultural evaluation of sewage sludges containing cationic surfactants because, as a rule, a longer exposure to light may occur.

ACUTE AND CHRONIC TOXICITY TO AQUATIC ORGANISMS

The acute and chronic toxicity to aquatic organisms is an essential criterion in the evaluation of the environmental compatibility of chemical substances. The LC_{50}-48^h values of the cationic surfactants applied in fabric softeners have been relatively well examined in various fish species. With LC_{50}-48-96^h values of 0.6–2.6 mg/L, these cationic surfactants belong to the environmental chemicals that have relatively high toxicity. Due to this, they are more toxic on average than the majority of anionic and neutral surfactants used in detergents for textiles. Daphnia magna, with LC_{50}-48^h values of 0.16–1.06 mg/L appears to be particularly sensitive to DSDMAC as well as to other cationic surfactants. The algistatic concentrations in the 5-day test are in the $>$ 0.1–1.0 mg/L range.

Kappeler (17) used an invertebrate and a fish species to determine the NOEC (no-observed-effect-concentration) values under chronical, or partly chronical, conditions. Depending on the test conditions, they vary between 0.05 and 0.5 mg/L.

Two essential circumstances must be observed in rating effective toxicity in effluents and surface waters of cationic surfactants used in fabric softeners:

– the electrically neutral salt formation of the anionic surfactants present in excess; with DSDMAC and DAIC, it leads to considerable decrease of toxicity. Electrically neutral salts from DSDMAC and LAS, for example, are on average one-sixth as toxic as DSDMAC. One may assume that this process begins in the washing machine, where both surfactant groups meet in the prewash. This process of mutual detoxification of anionic and cationic surfactants is probably based on a precipitation of electrically neutral salts and less on a change in electrochemical behavior, such as extensive loss of surface activity. Other substances that frequently occur in waters have a similar detoxifing effect on DSDMAC. These substances include, among others, fulvic acid and lignin. In the case of binding to lignin compounds, the toxicity of DSDMAC with regard to Daphnia is decreased by a factor of 32 (18).

- the strong affinity of the cationic surfactants to the inorganic and organic suspended matters in effluents and surface waters. They are inactivated through adsorption at their surfaces.

BIOACCUMULATION

Besides toxicity and biological degradability, the bioaccumulation behavior is another important parameter of the environmental compatibility of a substance. The quantity to be measured is the so-called BCF value, which is defined as a quotient from the average concentration of the substance in question in the test solution, or test water, and from its average concentration in the test organism, e.g., fish. According to research by Kappeler, (17) and Holman, DSDMAC only has a low bioaccumulation potential in fish (Lepomis, Cyprinus). With 0.02 mg/L concentrations in the environment, and with a 49-day exposure time, less than a 5-fold enrichment was found in the edible parts of fish.

The BCF value in the nonedible parts of fish was 260: this corresponds to an average value of 32. It is rather remarkable that, when using river water, lower bioconcentrations are measured. According to P&G research, DAIC behaves in a similar way; with Lepomis it shows a BCF value of 10.

On the basis of this generally low bioaccumulation capacity of the cationics used in laundry softeners at present, no risk is detected for the fish themselves or for their use as food. So far, nothing indicates that, in water, biomagnification would occur through the food chain.

BIODEGRADATION

In the series of criteria taken into consideration for the characterization of the environmental behavior of chemical substances, biodegradation comes first. Detailed examinations of the biological decomposition behavior under aerobic and anaerobic conditions were thus made with various cationic surfactants. Such examinations included laboratory tests as well as treatment plant tests on a technical scale.

Aerobic Degradation

Because of the specific behavior of cationic surfactants and their high affinity to negatively loaded surfaces, the common degradation tests (e.g., according to OECD specifications) have the basic problem of distinguishing between elimination through sorption processes of a physiochemical nature, and actual biochemical degradation.

In addition to this, one must consider an overlap of both mechanisms. There is the particular importance here of tests with radioactively marked cationic surfactants, in that the completeness of the decomposition can be ascertained through the CO_2 release.

Sullivan (personal communication) Holman and Krzeminski (19) have established clear proof for biodegradation of the cationic surfactants, and particularly of DSDMAC and DAIC applied in softeners. Afterwards, these compounds are basically accessible to primary and ultimate degradation, Janicke et al (20) and Gerike (21) reached largely similar conclusions; using the OECD confirmatory test and additionally coupled units, mass balancing made it possible to distinguish which DSDMAC shares are decomposed and which are only adsorbed.

According to research by Games et al. (3), these statements also apply to octadecyl trimethyl ammonium chloride (OTAC) and dioctadecyl dimethyl ammonium chloride (DODAC). In laboratory tests, they are adsorbed on activated sludge within 30 min at concentrations of 0.1–20 mg/L, and they are subjected to a primary degradation with a 2.5-hr half-life. No formation of metabolites was observed in the cationic surfactants that were marked radioactively in the decomposition test. The complete degradation requires more time: half-life for this amounts to 28–40 hr. OTAC, like DSDMAC, is detoxified through anionic surfactants (LAS) through a formation of insoluble electrically neutral salts, in that these are more degradable than pure OTAC.

Whereas research done so far on the decomposition of cationic surfactants mainly started from the common laboratory tests, Larson and Vashon (14) have recently tested adsorption and decomposition of monoalkyl- and dialkyl cationic surfactants with longer chains. Conditions under which they were tested corresponded to those in a body of water or in a treatment plant. It appeared that elimination of the cationic surfactants examined will occur sooner under natural conditions, because a strong fixation to water sediments occurs without the bioavailability being essentially affected.

According to examinations by Topping and Waters (22) and Kupfer (23) in sewage plants in Germany, the United Kingdom and Belguim, DSDMAC and DSBAS are eliminated up to 95% in trickling filters as well as in activated sludge plants. From a purely mathematical viewpoint, outlet values of 0.23 mg/L can be expected, while considering the consumer habits in West Germany, i.e, a total consumption of ca. 20,000 tons/year of DSDMAC and a 95% elimination of sewage plants with biological treatment. However, due to circumstances that are not yet fully clarified, the outlet concentrations measured are partly still lower with 0.02–0.16 mg/L DSBAS: the DSDMAC percentage amounts here to ca. 50%.

When assuming that the reference value is 0.23 mg/L, and that the effluent is diluted 7 times in the receiving water, a concentration of 0.032 mg/L results. According to the examinations available so far, this concentration is clearly exceeded in flows in West Germany that receive effluents, as is shown by the following: Main near Frankfurt, 0.005–0.02 mg/L DSBAS; Rhine and affluents, 0.019 mg/L DSDMAC. It is assumed that the entire dissolved DSBAS or DSDMAC fraction is complexed with the anionics that are generally present in the waters, and is thus only conditionally available.

ANAEROBIC DEGRADATION

The question of anaerobic decomposition of cationic surfactants is particularly important, because

- a 20–40% elimination is already achieved in the primary treatment through the adsorption to sewage sludge; as a rule, this sludge is subjected to a sludge digestion, without previous action of aerobic decomposition processes; and
- when dealing with agricultural sewage sludge utilization, it is essential not to put any further hazardous substances into the soil.

From a purely mathematical viewpoint, and when taking as a basis a crude effluent concentration of 4.5 mg/L for

DSDMAC in Germany, and assuming that there is complete adsorption at the crude effluent sludge, DSDMAC in sludge should be ca. 1.6% (related to dry weight). It appears from all examinations made so far on the behavior of cationic surfactants and their electrically neutral salts under anaerobic conditions such as e.g., sludge digestion, that, contrary to the relatively easy aerobic decomposition, they appear to be persistent here and do not degrade. At the same time, the question is thus raised with regard to their toxicity towards microorganisms that normally dominate the biochemical processes in sludge digestion or other anaerobic effluent processes. Further studies (22) on anaerobic sludge digestion, when having DSDMAC contents of digested sludge up to 2.5%, is not inhibited. According to Janicke et al. (20), electrically neutral salts of DSDMAC and LAS do not affect the anaerobic sludge treatment either, when they appear at concentrations up to 67 mg/L TS and at digestion times of 70-80 days. In general, one may assume that the cationic surfactants used in fabric softeners, including their neutral salts, are not biodegradable under anaerobic conditions and that, at the same time, when occuring at concentrations that are possible in practice, they do not inhibit the anaerobic wastewater or sludge treatment processes.

The present knowledge about environmental properties of cationic surfactants used in fabric softeners has not given the EEC or West Germany cause to draw up legal specifications on their minimum degradability, as is the case for anionic and nonionic surfactants. However, new shorter-chain cationics that are used as specialty chemicals in some new heavy-duty powders have different properties and might require a different environmental analysis. Their solubilities and the fact that they do not complex with LAS raises some questions about their toxicity. Their fate, however, is governed by a very high and rapid biodegradability.

REFERENCES

1. Huber, L., Tenside Deterg. 19:178 (1982).
2. Capridene, R., I.R.CH.A, D.8470.
3. Games, L.M., Z.E. King and R.J. Larson, Environ, Sci. Technol. 16:483 (1982).
4. Sivak, A., M. Goyer, J. Perwak and P. Thayer, Solution Behavior of Surfactants, Vol. I., Plenum Publishing Corp., New York, 1982.
5. Lienado, R.A., and T.A. Neubecker, Anal. Chem. 55:93R (1983).
6. Täuber, G., and A. May, Tenside Deterg. 19:150 (1982).
7. Kunieda, H., and K. Shinoda, Phys. Chem. 82:1710 (1978).
8. Schut, J., Tenside Deterg. 19:155 (1982).
9. Osburn, Q.W., Analytical Method for a Cationic Fabric Softener in Waters and Wastes, Procter & Gamble Company, Technical Center, 1982.
10. Michelsen, E.R., Quantitative Determination of Quaternary Ammonium Bases (QAB) in Water and Wastewater by Thin Layer Chromatography, preprint from J. Chromatogr. (1978).
11. Wee, V.T., and J.M. Kennedy, Anal. Chem. 54:1631 (1982).
12. Neufahart, A.M., H.M. Eckert, M. Kellner and K. Lötsch, Aspect of the Environmental Safety of DSDMAC, 6th report on tracer studies on sewage sludge and carp (*Cyprinus carpio*) CED Congress, Madrid, 1978.
13. Weiss, A., Tenside Deterg. 19:157 (1982).
14. Larson, R.J., and R.D. Vashon, Dev. Ind. Microbiol. 24 (1983).
15. Beveridge, A., and W.F. Pickering, Water Res. 17:215 (1983).
16. Neufahrt, A.M., K. Lötsch, D. Pleschke and G. Spaar, A New Method to Determine the Biodegradation of PRAPAGEN WK under Activated Sludge Conditions, Int. Bericht, Hoechst AG.
17. Kappeler, T.U., Tenside Deterg. 19:169 (1982).
18. Waters, J., Ibid. 19:177 (1982).
19. Krzeminski, S.F., J.J. Martin and C.K. Brackett, Household Pers. Prod. Ind. 10:22 (1973).
20. Janicke, W., and G. Hilge, Tenside Deterg. 16:117 (1979).
21. Gerike, P., Ibid. 19:162 (1982).
22. Topping, B.W., and J. Waters, Ibid. 19:164 (1982).
23. Kupfer, W., Ibid. 19:158 (1982).

Organoclay Rheological Additives: Past, Present and Future

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ABSTRACT

Rheological or flow properties have important implications in many and diverse applications. Often, an additive is used to impart the desired flow behavior. Among these, organoclay products, formed by the reaction of organic cations with smectite clays, are the most widely used additives for solvent-based coatings. The cation – usually a quaternary ammonium salt – used will influence the performance of the resultant organoclay. Criteria to consider in the choice of a cation are molecular size, compatibility with the fluid in which the organoclay is to be used, stability and reactivity. To form a stable organoclay product, the organic cation must contain at least one long-chain alkyl group. Othr groups attached to the cation may be divided into two categories: "filler" groups serve to complete the tetrahedron around the nitrogen, whereas "active" groups contribute beneficially to the performance of the organoclay. Our study of the structure/property relationships has led to the development of new additives described here. These are superior, particularly in terms of use, while providing the same excellent rheological control offered by earlier additives.

INTRODUCTION

The control of rheology, or flow behavior, has application in products ranging from foods to lubricants to paints and other coatings. Often, seemingly contradictory flow behaviors are desired under different conditions. At times, low viscosity at low shear and high viscosity at high shear is desired. Examples of such behavior may be found in the automatic transmission of your car; under low shear conditions, this transmission fluid has very low viscosity, but under the high shear conditions that the fluid experiences while driving, the fluid behaves more like a solid . Water, also, under high shear conditions will assume the properties of a solid, which is partially responsible for the action of boat propellers.

More often, the opposite type of flow behavior is desired; i.e., high viscosity under low shear conditions, and low viscosity under high shear conditions. Lubricating greases, for example, must be sufficiently fluid to maintain coverage of the moving and contacting parts, but thick enough to remain in the bearing. Paints exhibiting this type of flow behavior apply easily, while being more resistant to pigment settling and allowing application of a thick film without sagging.

The rheologist has described several basic types of flow behavior (1), the most important of which are:

- Newtonian flow, in which the viscosity of the fluid is independent of the applied shear (Fig. 1a);
- pseudoplasticity, in which the viscosity of the fluid is a function of the applied shear. The viscosity of a pseudoplastic fluid decreases reversibly as the shear increases (Fig. 1b);
- dilatancy, which is basically the opposite of pseudo-