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# The effect of froth stability and wettability on the flotation of a xerographic toner

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*Abstract*: The Separation of ink and pulp fibers in recycled paper is primarily achieved by flotation methods. Xerographic toners from photocopiers and laser printers are known to cause problems in flotation deinking. Wettability and froth stability are two important factors which determine the floatability of xerographic toners. The floatability is investigated for a selected toner using a cationic, a nonionic, and an anionic surfactant. At low surfactant concentrations the froth is too unstable to support flotation, whereas at high surfactant concentrations the toner is rendered hydrophilic by adsorbed surfactant molecules and does not stick to air bubbles. Consequently, a maximum in flotation response is found at an intermediate surfactant concentration near the critical micelle concentration. Cationic, nonionic, and anionic surfactants all adsorb with their hydrocarbon tails on the toner surface. By choosing appropriate froth-stabilizing additives it is possible to enhance the flotation performance.

*Key words*: Deinking – flotation – wettability – froth stability – cooperative adsorption

## Introduction

The recycling of waste paper is of growing importance, both to better utilize the natural resources of wood and to reduce the amount of solid waste which must otherwise be dumped or incinerated. The most important requirement in paper recycling is the effective separation of the valuable pulp fiber from substances added during production and utilization, especially of inks. A nearly quantitative removal of inks is necessary to obtain a high-quality paper with high brightness and a low number of unremoved particles, i.e., specks.

Traditionally, the deinking process is accomplished by combined washing and floating processes [1–4], the latter being preferred because of the higher specificity of the separation. A high degree of separation can be accomplished for common inks, e.g., newsprint ink, which consists of a pigment dispersed in an oil phase. Unfortunately, in the last decade a number of new inks have entered the market which have been shown to cause difficulties in the classical flotation process [5]. Among them are xerographic toners which are used in photocopiers and laser printers [5–8]. The amount of electrostatically printed waste paper from offices is steadily rising.

The difficulties encountered in the flotation of xerographic inks are partly due to their different chemical compositions compared to traditional oil-based inks. The main component of a toner is usually a polystyrene-polyacrylate copolymer to which 5–10 wt% carbon black is added as pigment. In some cases iron oxide as a magnetic carrier is added [9]. The toner particles are fused during the printing process, leading to large flat particles sticking to the paper fiber.

Because surface chemistry is one of the most important factors determining flotation efficiency, it is clearly important to know more about the specific phenomena taking place at the toner-solution interface. Particularly important is the effect of surfactants, which are frequently capable of changing and even reversing the surface properties.

Wide use is made of this possibility to "tailor-make" the surface of dispersed particles in mineral flotation [10–12]. In this field extensive studies concerning the adsorption of surfactants and the resulting changes in wettability were performed on "model particles" like highly pure oxides. This knowledge is seldom applied to the field of deinking flotation. Despite the extensive differences to the studies in mineral flotation, most notably the presence of an impure, technical grade material, we believe that a thorough investigation of the surface chemistry involved should allow one to better understand the flotation process in deinking.

In a previous study [13], we reported the investigation of electrostatic properties (zeta potential) and wettability (contact angles) for a selected xerographic toner in contact with surfactant solutions. The effects of cationic, nonionic, and anionic surfactants on the zeta potential were studied. We found strong adsorption, especially for long-chain surfactants, which increased markedly above the critical micelle concentration (CMC). From wettability experiments, we showed for *n*-hexadecyltrimethylammonium bromide (HTAB) that the adsorption occurs tail-down, i.e., with the hydrophobic hydrocarbon chain attached to the toner surface. Knowing that the toner is almost electrically neutral [9, 13], we surmised that all surfactants, regardless of their charge, adsorb in this way, because the driving force is the hydrophobic interaction between the toner surface and the hydrocarbon chains.

This kind of adsorption renders the toner particles more hydrophilic because the polar head groups are oriented towards the solution. As only hydrophobic particles can be effectively floated [10], excessive surfactant adsorption should decrease the floation performance. We predicted that, consequently, one should avoid high surfactant concentrations.

In this article, we report on flotation experiments on a xerographic toner carried out with a Hallimond tube. Our objective was to verify the above assumption with surfactants of different charge and to investigate the interplay between wettability and froth stability. Guidelines for choosing optimal surfactants and adjusting their concentrations are the practical goals for such studies.

## Experimental

We choose toner 1090 from Xerox Co. as a model toner because its composition is typical for many toners in common use (see [9] for an overview). Its ingredients are a styrene-acrylate copolymer ( $>$ 90 wt%, CAS-Nr. 25213-39-2), carbon black (5–10 wt%) and 1-*n*-hexadecylpyridinium chloride monohydrate ( $<$ 2 wt%). The toner was used in the pre-printed state, i.e., as a very fine powder, to take advantage of the narrow particle size distribution (10–15 $\mu$m), although it is recognized that such dispersions may differ from those occurring in repulped paper slurries. Flotation of printed toner would best be examined by repulping printed paper followed by flotation. However, in this case the toner exists in the presence of suspended fibers and in a wide variety of different sizes and shapes due to the printing process, all of which would complicate the evaluation of the experiments. The surface chemical properties we are interested in can be more easily studied with a homogeneous material, although it is acknowledged that some change in the surface properties during the printing (i.e., melting) process may occur.

Three surfactants were used in the experiments: sodium n-dodecyl sulphate (SDS; technical grade, from Fisher Scientific Co.), *n*-hexadecyltrimethylammonium bromide (HTAB; reagent grade, from Fluka), and octylphenoxy polyethoxyethanol (Triton X-100; 9-10 ethoxy units; technical grade, from Sigma Corp.). *n*-Dodecanol was obtained in reagent grade from Matheson, Coleman & Bell (MCB). We used the technical grade of Triton X-100 and SDS because this grade is likely to be used in industrial processes. All solutions were prepared with double-distilled water.

To stay close to practical deinking flotation, we studied the adsorption of surfactants under alkaline conditions. The pH was adjusted with NaOH to 11.5–12.0, resulting in a constant ionic strength (conductivity 1.53–2.59 $\mathrm{mS\,cm^{-1}}$). All experiments were carried out at room temperature (20–25 °C).

Zeta potential determinations were performed with a Rank Brothers Mark II microelectrophoresis instrument. Contact angles were determined with a fiber balance as described by Berg [14]. The fibers were drawn from a toner melt and had a perimeter of 0.65–0.9 mm. The full experimental details can be found in [13].

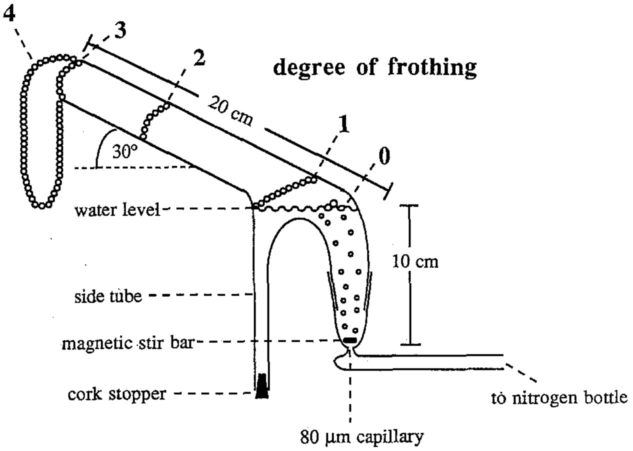

Fig.1 Schematic of the Hallimond tube employed in the flotation experiments. Numbers from 0 to 4 were assigned to the different degrees of frothing as shown

Flotation experiments were carried out in a modified Hallimond tube as described by Fuerstenau [15] and Larsson [16], shown schematically in Fig 1. To characterize the extent of frothing under these particular conditions, a scale from 0 to 4 was adopted. "0" means that no stable foam exists. Only isolated, unstable bubbles form on the water surface. "1" depicts a froth level, as shown, which extends to both parts of the tube, but does not leave the water surface. At a level of "2" the froth would reach a level inside the tube outlet, and at a level of "3" it would reach the opening but not overflow. Level "4" characterized an overflowing froth which was collected in a beaker placed below the tube outlet. This assignment, although arbitrary, proved to be helpful for froth characterization.

35–40 mg toner was dispersed in 10 ml solution and stirred for 20 min. The total area of the toner surface was sufficiently small that the fraction of the total surfactant adsorbed was negligibly small. Thus, initial surfactant concentrations, were essentially identical to those corresponding to adsorption equilibrium. The dispersion was then diluted to 100 ml, of which 65 ml were poured into the Hallimond tube. Flotation was performed for 10 min at 20 ml min$^{-1}$ nitrogen flow rate under constant stirring (same stirrer speed in all experiments). After the experiment the flotation accepts and rejects were collected.

Because of the low density of the toners (for this particular toner 1.14 g cm$^{-3}$ [17], it is very difficult to measure the amount of toner by gravimetric methods, as common in mineral flotation. Instead the toner content of the three fractions was determined by UV/VIS spectrometry at 580 nm with a Bausch & Lomb Spectronic 20 instrument. The absorbance was found to increase linearly with toner concentration; therefore, the distribution of the toner among the three fractions could be calculated.

## Results and discussion

Figure 2 displays the variation of the flotation response and froth stability with surfactant concentration for three different surfactants of different charge. Suitable sigmoidal curves were fitted to the froth stability data for clarity.

The curve shapes of the flotation response are similar: very little toner, then a continuous decrease to poor recovery again. The minimum at low concentration can be explained by poor froth formation. Actually, at these low surfactant concentrations, the bubbles tend to break almost instantaneously after reaching the surface, thereby not supporting any transport of the toner. The small percentage of toner recovery in this region is most likely due to a gradual mixing of the two Hallimond tube cells across the liquid bridge between the two cells. Consequently, the liquid bridge was kept to a minimum (see Fig 1).

After the surfactant concentration is sufficiently high to support a stable froth (level 1), the flotation response increases quickly. The best flotation response is reached immediately after the rise. The following decrease of the amount of floated toner at higher concentrations cannot be ascribed to frothing properties, as the froth stability is continuously rising.That only very little toner is sticking to the bubbles at high surfactant concentrations is also visible from the froth: instead of having a black, "dirty" look, it appears white and clean at high froth stability. It should be noted that from a practical point of view, extremely voluminous and stable froths are not desirable, as they cause overflow of the flotation cells.

The reason for this steady decline of recovery lies in the increasing hydrophilicity of the toner particles at higher surfactant concentrations. As

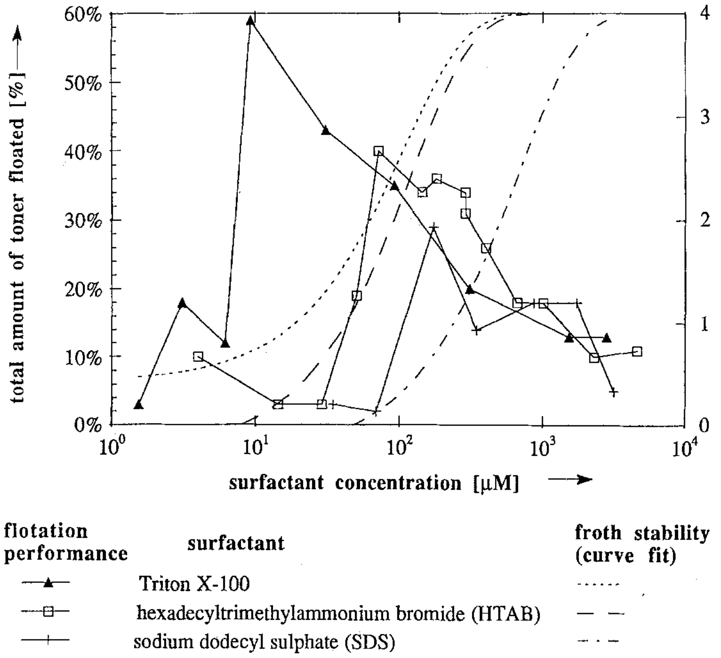

Fig.2 Flotation performance of the xerographic toner and froth stability for Triton X-100 (Nonionic), hexadecyltri methylammonium bromide (HTAB, cationic) an sodium dodecyl sulphate (SDS, anionic). For the froth stability only fitted curves are displayed for clarity

mentioned, surfactant molecules tend to attach with their hydrophobic tails to the toner surface. This leaves the hydrophilic head groups pointing towards the solution. Because only hydrophobic material can be floated, the floatability of the toner decreases with increasing adsorption density of surfactants.

In agreement with results obtained for oxide particles in mineral flotation [8–21], the adsorption of surfactants on toner particles was found to increase significantly at a surfactant concentration close to the critical micelle concentration (CMC) [13]. At this point, lateral interaction between the adsorbed surfactant molecules begins which, in turn, accelerates further adsorption, i.e., "cooperative adsorption". The CMC may therefore serve as a rough estimate of surfactant adsorption: at concentration below the CMC, we find weak adsorption, while at concentrations above the CMC, we find strong adsorption (close to a compact monolayer on the toner surface). The CMC for HTAB under these conditions (room temperature, pH 11.2–12.0) was 182 $\mu$M [13], in good accordance with literature values of 103 $\mu$M (0.01 M NaBr solution; 25 °C) and 490 $\mu$M (0.01 M NaCl solution; 25 °C) [22].

In Fig.3, five important parameters in the system toner-water-HTAB are displayed. The adsorption of surfactant on the toner surface, indicated by the zeta potential, shows only a small increase below the CMC, but rises steeply after surpassing it. Adsorption saturation seems to be reached at about 10 to 20 times the CMC.

The cosine of the receding contact angle reveals a trend from hydrophobic to hydrophilic, with no detectable further increase in hydrophilicity above the CMC. The froth stability increases with rising surfactant concentration, reaching the level of a very stable froth a little above the CMC. This is in good accord with standard knowledge about froth stability [23, 24]. The flotation response reaches a maximum at a concentration of 1/3 to 1/2 of the CMC.

The four parameters displayed exhibit discontinuities around the CMC, indicating that considerable changes in the surface properties are taking place. Very similar results were reported by Fuerstenau et al. for the flotation of quartz at variable dodecylammonium acetate concentration [18].

We now can conclude that two concurring effects influence floatability: the froth stability *increases* with increasing surfactant concentration, while the hydrophobicity *decreases*. It is clear that this must lead to a maximum in floatability for an intermediate concentration, and that is what was observed.

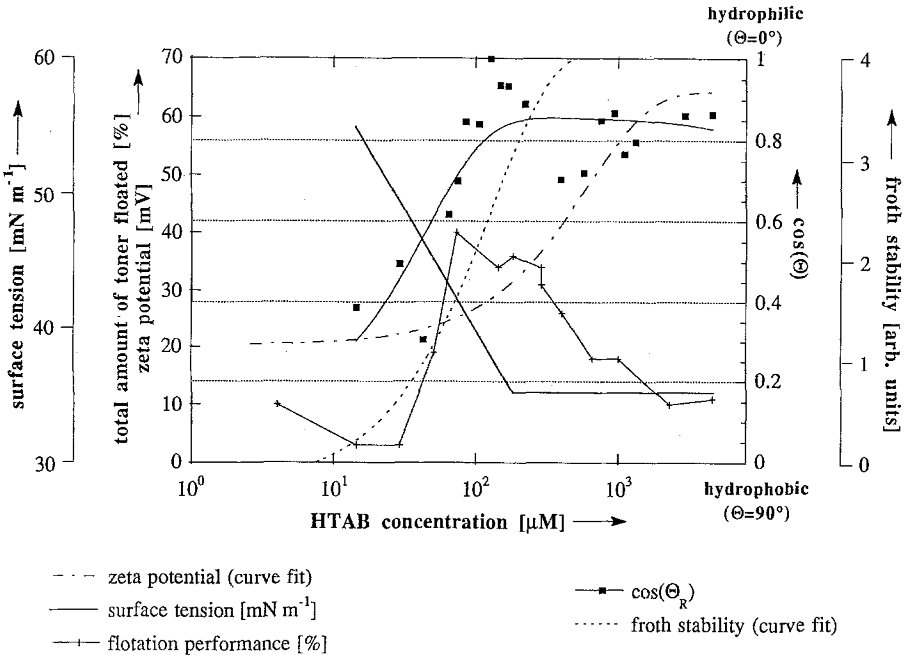

Fig.3 Comparison of four specific quantities related to the adsorption of HTAB on the xerographic toner. The receding contact angle and the zeta potential (data taken from ref. [13]), the flotation response and the froth stability all show the strongest change at concentrations close to the critical micelle concentration

The question remains of whether the floatability keeps decreasing above the CMC, although the wettability as measured by the contact angle has reached a constant level. Possibly an increasing electrostatic repulsion between positively charged toner particles and positively charged bubbles prevents the formation of stable aggregates, thus inhibiting effective flotation. For the uncharged surfactant Triton X-100, no such effect was observed (see below), which supports this assumption.

Wettability and flotation data for Triton X-100 are shown in Fig. 4. Triton X-100 is a better frother under these experimental conditions. Therefore, flotation occurs at lower concentrations as compared to HTAB (Fig. 2). The CMC in 0.01 M NaCl at 25 °C is reported at 330 $\mu$M [22], which corresponds well with our measured value. The contact angle decreases with rising surfactant concentration, changing the surface from hydrophobic to hydrophilic, leading to a decrease in floatability at higher concentration.

Figure 5 displays the results obtained for SDS. The CMC is reported with 4.9–6.8 mM in 0.01 M NaCl at 25 °C [22], in good agreement with our results. Due to the technical grade of SDS, a minimum in the surface tension curve was observed. This well-known effect stems from impurities from the manufacturing process (long-chain alcohols). The floatability shows a less pronounced maximum with a lower maximal yield than for HTAB and Triton. Obviously, the delicate interplay between froth stability and wettability is not very favorable for flotation in this case.

The wettability measurements show that all three kinds of surfactants adsorb tail-on. Consequently, a maximum in floatability at high concentrations was found in each case. The charge of the surfactant apparently does not influence the nature of adsorption. This was predicted because of the hydrophobic toner surface and the electrically neutral character of the toner particles [13].

It should be mentioned that this maximum occurs because of the inverted situation in ink flotation as compared to mineral flotation. In mineral flotation, the material (e.g., an oxide) is usually initially hydrophilic or only weakly hydrophobic and is rendered more hydrophobic by head-on adsorption of a collector surfactant [10]. Here, the hydrophobicity increases with rising concentration, and so does the froth stability. As both effects take place simultaneously, it is not easy to separate them. Consequently, Fuerstenau et al. observed only a steady increase in

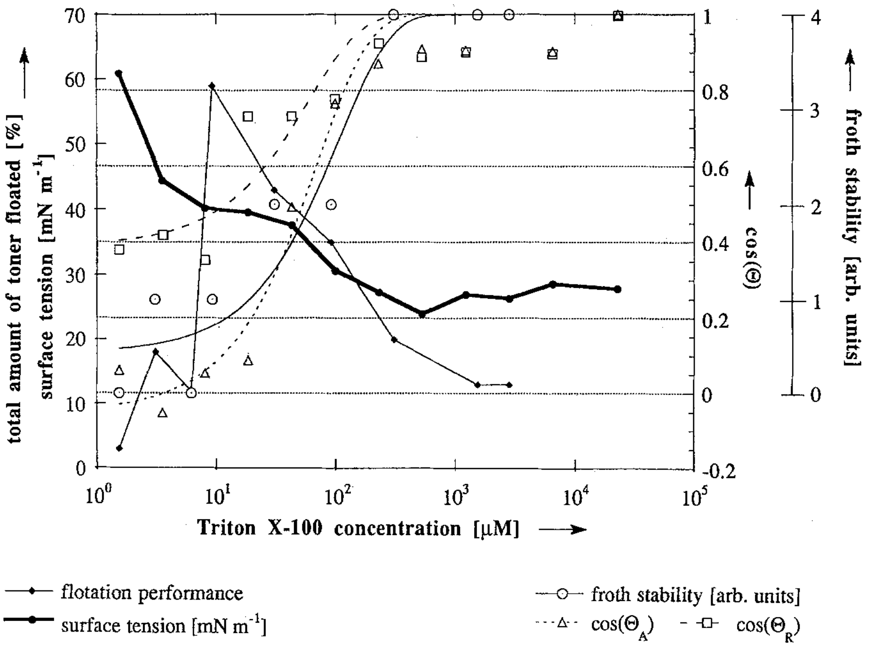

Fig.4 Flotation response, froth stability, and advancing and receding contact angles for the xerographic toner in Triton X-100 solutions. The reverse effects of decreasing hydrophobicity (lower contact angle) and increasing froth stability lead to a maximum in the flotation response

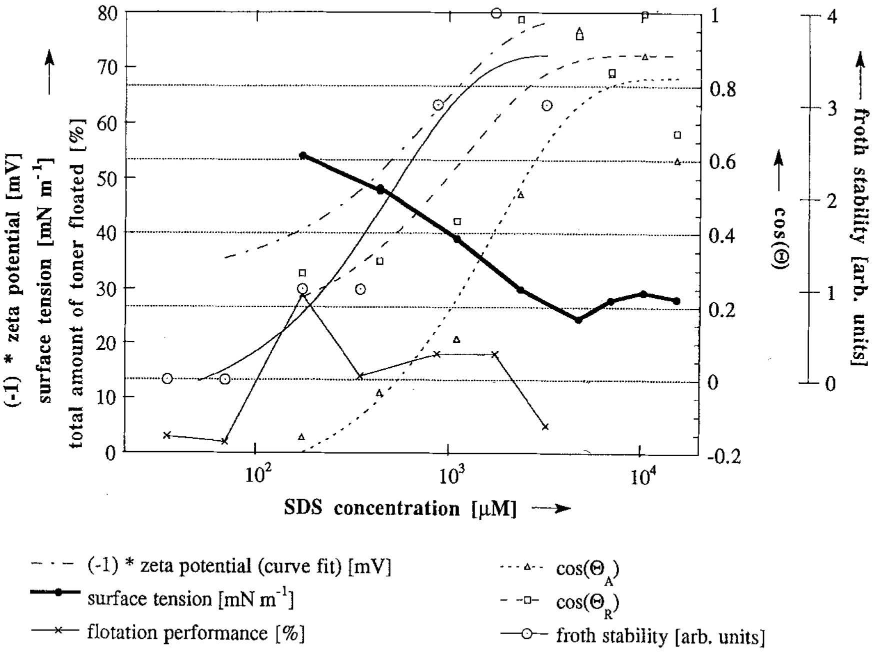

Fig.5 Zeta potential, flotation response, froth stability and receding contact angle for the toner immersed in sodium dodecyl sulphate (SDS) solutions. Zeta potential and contact angle data indicate strong tail-on adsorption near the CMC

floatability of oxide minerals with rising surfactant concentration [18].

The froth stability can be improved by adding other compounds, e.g., long-chain alcohols [23, 24]. These slip between the surfactant molecules on the surface of the foam lamellae and enhance the stability of this film by van der Waals and ion-dipole interactions. They also lower the effective CMC by incorporation into the micelles. We performed flotation experiments using HTAB with 50 wt% *n*-dodecanol added, which significantly increased the froth stability. The results are shown in Fig. 6.

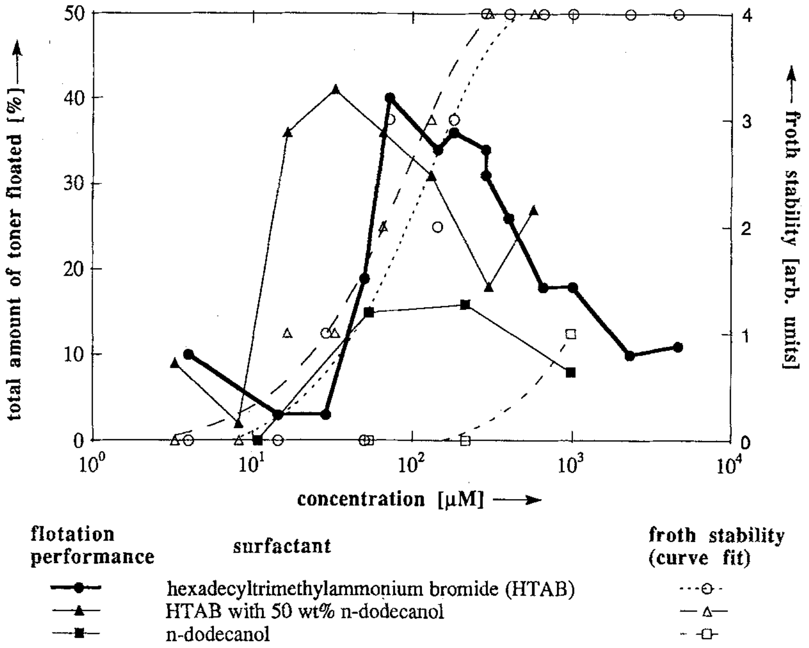

Fig.6 Flotation performance of toner in Hallimond tube experiments with pure HTAB and HTAB with 50 wt% *n*-dodecanol. The foam-stabilizing action of the dodecanol leads to a better flotation response at lower concentrations as compared to pure HTAB. This demonstrates that the low froth stability is responsible for the poor flotation response with pure HTAB at concentrations below $\approx 50\,\mu M$. For the mixture HTAB/*n*-dodecanol the concentration of HTAB was used for the x-axis data

The flotation response is higher at low concentration. The froth stability is now high enough to support flotation while the wettability is still low. Of course, at even lower concentrations the flotation response drops in this case, too, because of poor froth stability. This graph illustrates the interplay between froth stability and wettability in flotation. A variation in the type of additive and the added amount would probably lead to an even better froth stability at low concentrations. *n*-Dodecanol alone is a poor frother under these conditions, and consequently gives only a low flotation response.

It is known that the tendency to adsorb from an aqueous solution to a solid surface is higher for long-chain surfactants than for short-chain surfactants [20, 25]. This is true for hydrophilic as well as for hydrophobic surfaces. We have demonstrated this by zeta potential experiments for the case of *n*-alkyltrimethylammonium bromides ($C_{12}$–$C_{20}$) adsorbing on a xerographic toner [13], in good accordance with earlier results on polystyrene latices [26]. This behavior stems from the above-mentioned cooperative adsorption on the surface enhanced by chain-chain interactions. Consequently, in this case a short-chain surfactant will adsorb less on the surface and leave it more hydrophobic. Because there is an optimal chain length for froth stabilization by surfactants [23, 24], an optimal chain length for toner flotation should exist in a homologous series of surfactants. Optimization of the hydrophobic tail for a given surfactant head group type should allow one to reach a maximum flotation response for a weakly adsorbing but still froth-stabilizing surfactant. Although chain length was the only hydrophobe property investigated here, branching, aromaticity and other structural variations are possible.

Figure 7 shows the results of flotation experiments with *n*-dodecyltrimethylammonium bromide (DTAB), HTAB and *n*-eicosanyltrimethylammonium bromide (ETAB), the flotation maxima are shifted to lower concentrations for longer alkyl chains, because the tendency to adsorb increases. The same is true for the froth stability. The $C_{20}$ compound (ETAB) gives a less stable froth than the short-chain compounds. This may be explained by exceeding the optimal chain length for froth formation or by the fact that the CMC of ETAB is not reached (the Krafft point of ETAB is above room temperature). This concentration dependence of the flotation efficiency is analogous to the dependence of the zeta potential [13].

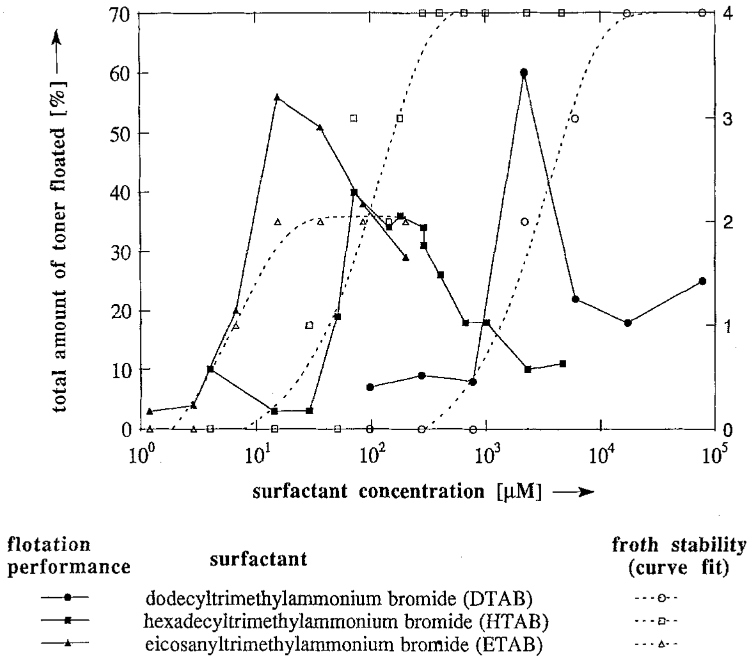

Fig.7 Dependence of the flotation response from the chain length for three *n*-alkyltrimethylammonium bromides ($C_{12}$ = DTAB, $C_{16}$ = HTAB, $C_{20}$ = ETAB). Due to cooperative adsorption, the flotation maxima are shifted to lower concentrations for longer hydrocarbon chains

## Conclusions

The interplay between froth stability and wettability in flotation of a xerographic toner was investigated. We found that both parameters are strongly affected by the surfactant concentration and chain length. While the froth stability increases with rising surfactant concentration (leading to a better flotability), the hydrophobicity decreases due to surfactant adsorption on the toner surface (lowering the floatability). This adsorption occurs tail-on, i.e., with hydrocarbon chains, the driving force being the hydrophobic interaction between toner surface and hydrocarbon chain. Thus the toner becomes hydrophilic and less suited for flotation. This is the case for anionic, nonionic, and cationic surfactants, as shown by wettability experiments.

Because these two parameters change the floatability in counteracting ways, a maximum in floatability occurs. The optimal surfactant concentration probably lies a little below the CMC. The dependence on the chain length was demonstrated for *n*-alkyltrimethylammonium bromides, as predicted by the concept of cooperative adsorption. The limited floatability at low surfactant concentrations can be improved by adding suitable long-chain organic molecules which enhance the froth stability. Experiments of HTAB with 50 wt% *n*-dodecanol demonstrated how a high flotation response can be achieved at lower concentrations.

Although the experiments were performed with a Hallimond tube, i.e., under highly idealized conditions, the surface chemical principles outlined here should also apply to technical flotation processes. Although one must keep in mind that the specific conditions can change significantly when scaling up from laboratory experiments to commercial plants [10], the same basic principles must apply.

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