Study of the Ditallowdimethylammonium Chloride Interaction with Cellulose[1]

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ABSTRACT: From a theoretical standpoint, the driving force for the deposition of ditallowdimethylammonium chloride ("DTDMAC" or "quat") onto cotton must be distinguished from the nature of its interaction with cellulose. We found that the driving force is purely hydrophobic. Due to its strong hydrophobicity, DTDMAC is expelled out of the aqueous rinse bath and deposits onto available surfaces. Besides its tendency not to leave the cotton surface and return to solution (hydrophobic effect), it binds to cellulose by weak London dispersion forces. A strong Coulombic interaction occurs only when a negative charge is present. Consequently, the strong affinity of DTDMAC for cellulose mainly results from the large specific surface area of the fiber; negative charges play a secondary role. Much experimental evidence supports the hydrophobic nature of DTDMAC adsorption onto cellulose. DTDMAC deposits onto charge-free surfaces; its deposition is mainly governed by the available surface area, not by the surface nature. The hydrophobic nature of the interaction of DTDMAC with cotton may be displayed and distinguished from electrostatic binding. Structural effects demonstrate the correlation between hydrophobicity, deposition and the softening power of quaternaries. This model proposes a single mechanism to account for the deposition of DTDMAC onto cotton and synthetics. It is consistent with experimental facts that remain unexplained by the electrostatic model.
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KEY WORDS: Cellulose, cotton, deposition, DTDMAC, fabric softeners, hydrophobicity, mechanisms, quats.

Until recently, fabric softeners were based on cationic surfactants such as quaternary ammonium or imidazoline derivatives. It is commonly believed that their deposition onto cellulose results from a Coulombic attraction between the positive head and the negative charges borne by cotton in water (1–19). The fatty chains of the adsorbed ditallowdimethylammonium chloride (DTDMAC) molecules are reported to point outwards, into solution (Fig. 1).

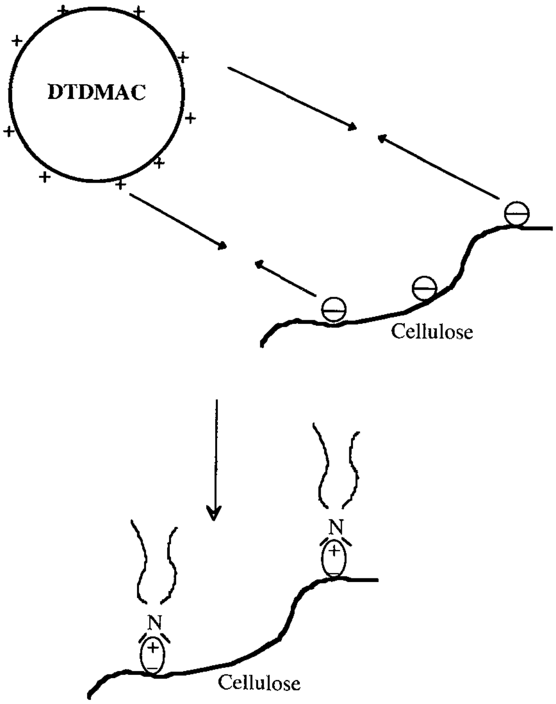

FIG. 1. Electrostatic model of ditallowdimethyl ammonium chloride (DTDMAC) deposition on cotton.

If the DTDMAC deposition resulted from an electrostatic interaction, it should be stoichiometrically related to the number of functional groups on cellulose. Actually, deposition does not level off until a large excess of DTDMAC is added to the medium. Likewise, that model cannot explain why DTDMAC deposits onto charge-free synthetics, or why nonionic species may deliver softness. It also fails to account for the effect of molecular structure on the softening performance.

How was the electrostatic model built? Most of the work on the deposition of quaternaries onto fabrics was carried out under conditions that do not adequately represent actual laundry conditions. Moreover, alternative explanations to some experimental observations may be proposed. This is discussed in the final section. Our hypothesis was that the driving force of DTDMAC deposition onto cellulose is not an electrostatic attraction by the fiber, but a hydrophobic ejection from water (Fig. 2). Due to their lack of affinity for water, DTDMAC molecules deposit onto available surfaces to leave

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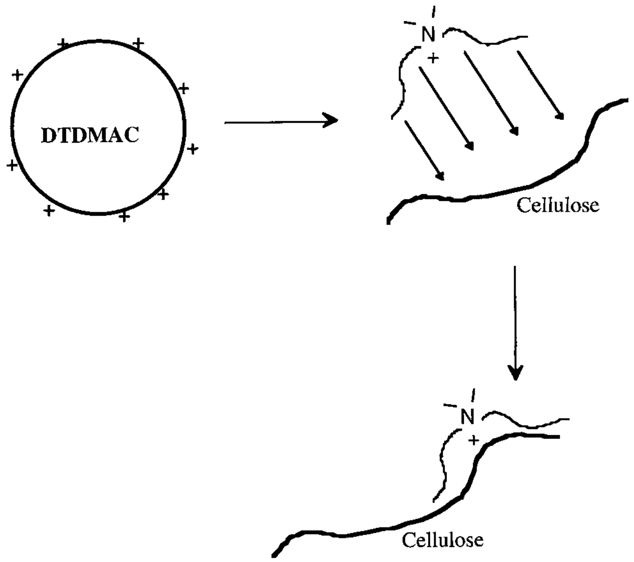


FIG. 2. Hydrophobic model of DTDMAC deposition on cotton. Abbreviation as in Figure 1.

the aqueous environment. Hence, DTDMAC must be considered as a highly hydrophobic material, whose charge mainly serves as a dispersing agent rather than as anchorage. In the neat product, DTDMAC exists as strongly charged vesicles, where fatty chains are completely out of the aqueous environment. During dilution, the vesicle structure is modified, so that the fatty chains come into contact with water, and DTDMAC is hydrophobically ejected out of the aqueous phase. So far, we do not know the exact structure of the ejected units, which are represented in Figure 2 as individual molecules. Once on the fiber, DTDMAC molecules interact with cotton through van der Waals interactions (besides their little tendency to go back into solution) and by electrostatic attraction if there are negative charges on the surface. This hydrophobic mechanism is consistent with experimental observations, because electric charges on the substrate and on the softening molecule are no longer a prerequisite.

The hydrophobic interaction that accounts for the deposition of DTDMAC onto cellulose must be clearly distinguished from hydrophobic binding. Hydrophobic interaction is an entropically driven process. When hydrocarbons are dispersed in an aqueous phase, water molecules get organized in their vicinity into a quasi-crystalline structure, which improves their hydrogen-bonding but strongly reduces their entropy (20–23). That phenomenon is known as "hydrophobic hydration." The huge loss of entropy resulting from the formation of a rigid structure near the hydrophobic moieties is not compensated by the small loss of enthalpy resulting from the improvement of hydrogen bonding. Conversely, when hydrocarbon chains are removed from the aqueous environment by associating or depositing onto surfaces, these water molecules go back into the bulk. Moreover, a number of solvent molecules must be desorbed from the surface to adsorb DTDMAC molecules. The entropy so gained by the system provides the driving force of the adsorption process. Hydrophobic binding is based on affinity of hydrocarbon chains for each other, which arises from like-to-like attractions. That effect plays a minor role in hydrophobic deposition and micelle formation.

EXPERIMENTAL PROCEDURES

Microcrystalline cellulose (Art. 2330; Merck, Darmstadt, Germany) was of chromatographic grade; quaternaries and sodium hypochlorite were of industrial grade and used without further purification. All other chemicals were of analytical grade.

DTDMAC (Praepagen WK ex Hoechst AG, Frankfurt, Germany) exhibited a typical composition of 74% cationic material (94% pure DTDMAC, 3% monotallow and 3% tritallow derivatives); the chainlength distribution was 30% C-16 and 65% C-18 saturated chains. The chainlength distribution of DCDMAC (dicocodimethyl ammonium chloride; Radiaquat 6462 ex Oleofina, Brussels, Belgium) was 12% C8-10, 56% C-12 and 18% C-14 chains while TtMAC (monotallowtrimethyl ammonium chloride; Radiaquat 6471 ex Oleofina) contained 30% C-16, 20% C-18 and 45% unsaturated C-18 chains.

Tap water was from the Liège (Belgium) area and exhibited a hardness corresponding to 300 ppm of Ca^{2+} with a Ca/Mg ratio of 3:1. Ultradeionized water was obtained by treating water on an Aqualab 8 ultrapurification system; it exhibited a conductivity of 0.05 S/cm.

Determination of zeta (electrokinetic) potentials. Samples were prepared by dispersing 0.10 g microcrystalline cellulose in water and adding increasing amounts of quaternary dispersed in ultradeionized water. After 5 min gentle stirring, the samples were injected in a Zetasiser IIc (Malvern Instruments Ltd., Malvern, Worcestershire, England); an alternative current of 160 mV–1 Hz was applied to the microelectrophoresis cell. Each data accumulation lasted one minute, and each measurement was replicated five times. Zeta potential was calculated by averaging the five individual results; standard deviations were usually below 1 mV.

For measurement of the deposition of DTDMAC onto polyethylene, the same procedure was used, while replacing 0.10 g microcrystalline cellulose by 0.10 g low-density polyethylene.

Quantitation of the adsorption of quaternaries. The quaternary uptake/unit of surface area as a function of the starting concentration in the bath was determined by mixing 0.20 g microcrystalline cellulose with increasing levels of quaternary for 30 min. After centrifugation of the samples, the supernatants were treated with bromophenol blue and extracted with chloroform [modified Auerbach's method (24,25)]. The color intensity developed in the organic phase is proportional to the amount of free quaternary in the sample. Standard curves were drawn by plotting the absorbances at 607 nm as a function of the amounts of quaternary introduced (PU8740 UV-Vis Scanning Spectrophotometer; Philips, Eindhoven, The Netherlands). The amount of quaternary adsorbed was calculated from the difference in absorbance between the samples of the same initial concentration with and without cellulose.

Determination of the hydrophobicity of quaternaries. The hydrophobicity was quantitated by determining the amount of isopropanol necessary to clarify aqueous emulsions of quaternaries. An example of the calculation would be: if 5.00 g of a 3% DTDMAC dispersion can be clarified with 0.98 g isopropanol (IPA):

$$\begin{aligned} &5.00\text{ g (97\% water)} = 4.85\text{ g water} = 269\text{ mmoles} \\ &0.98\text{ g isopropanol} = 16.31\text{ mmoles} \qquad [1] \\ &\therefore \%\text{ IPA (mole)} = \frac{16.31 \times 100}{16.31 + 269} = 5.72\% \end{aligned}$$

Effect of the specific surface area. Samples were prepared by adding 6.0 g of a commercial softening composition (5.8% DTDMAC) into 1000 g water that contained 20.0 g of finely divided cotton or microcrystalline cellulose. The samples were mixed with a magnetic stirrer for increasing periods of time. The cellulose/cotton was removed by centrifugation, and the DTDMAC excess in the supernatant was assayed as discussed previously. Each reported result is the average of three replicates.

Effect of IPA on DTDMAC–cellulose adduct stability. The samples of cellulose were treated with DTDMAC (as described previously), and the cellulose was removed by centrifugation. Half of the treated cellulose was suspended twice in 40.0 g IPA; the rest was suspended twice in 40.0 g water. The zeta potential of both cellulose fractions was determined in water.

Effect of isopropanol on DTDMAC–cotton adduct stability. DTDMAC deposition onto terry towels was carried out according to our standard softening procedure: 4.4 g softening composition and 120.0 g cotton/L tap water, 5 min rinse in a lab minisoftening machine (device simulating the rinse cycle of a washing machine), line-drying overnight in a conditioned room (22°C, 50% relative humidity). Swatches were cut into two parts, one of which was treated by 300 mL IPA. After drying, their softness was evaluated by 18 experienced judges. IPA was reconcentrated to 25 mL and added to 75 mL water; the DTDMAC content was assayed by bromophenol blue.

Oxidation of microcrystalline cellulose. Sodium hypochlorite (2.0 g, 11% active chlorine) was added to 1.0 g microcrystalline cellulose dispersed in 8.0 g deionized water. After 1 h stirring, the medium was diluted with 10.0 g deionized water, and the hypochlorite excess was destroyed by hydrogen peroxide (added drop by drop up to the end of bubbling). The oxidized cellulose was removed by centrifugation and redispersed in 100 g tap water.

RESULTS AND DISCUSSION

Identification of the DTDMAC–cellulose interaction. If the DTDMAC binding to cellulose depends on hydrophobic effects and London dispersion forces, DTDMAC should deposit onto a charge-free cellulose. Microcrystalline cellulose was selected as substrate because: (i) Its extreme purity guarantees its electric inertness and ensures result reproducibility. The lack of a characteristic peak in infrared spectra confirms the absence of carboxyl groups on microcrystalline cellulose (Fig. 3). (ii) It is insoluble but easily dispersed in water, therefore giving rise to light scattering, a necessary condition to determine the zeta potential with a Zetasizer IIC. (iii) The small particle size of its powder allows sedimentation slow enough for the measurements to be carried out.

Among other things, the zeta potential of a colloid depends on the charge borne by its surface. Its determination under various conditions allows assessment of the effects of experimental changes on the charge; a positive slope means that the positive charge on the surface increases.

Figure 4 demonstrates the interaction between DTDMAC and microcrystalline cellulose, the zeta potential of cellulose increases as its dispersion in tap water contains increasing levels of DTDMAC. Despite the lack of carboxyl groups, cellulose binds DTDMAC.

Before any DTDMAC introduction, microcrystalline cellulose exhibits a negative zeta potential, which may be assigned to the well-known adsorption of anions at the surface of neutral colloids (26). When increasing amounts of DTDMAC are introduced in the suspension of microcrystalline cellulose, its zeta potential rises according to a sigmoid curve. The cellulose potential levels off at a value close to that of DTDMAC alone (+45 mV). That potential is observed for a DTDMAC/cellulose ratio of 35 micromoles/m^2. In the absence of cellulose, DTDMAC is first detected from an amount corresponding to 48 micromoles of DTDMAC/m^2 cellulose; the sample does not scatter adequately for less than that. This demonstrates that it is really the cellulose–DTDMAC adduct that is observed, and that it results from a nonelectrostatic interaction. Electric charges on the fibers are consequently not required to observe DTDMAC deposition. Zeta potentials show that neutral cellulose binds DTDMAC, but they do not necessarily tell to what extent (some excess of DTDMAC may remain in water but is too low in concentration to be detected). To accurately quantitate the amount of DTDMAC fixed by cellulose, it is necessary to assay the amount of free DTDMAC remaining in solution after mixing microcrystalline cellulose with increasing levels of DTDMAC. When

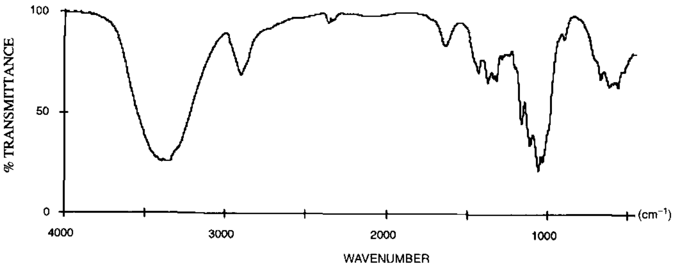


FIG. 3. Infrared spectrum of microcrystalline cellulose.

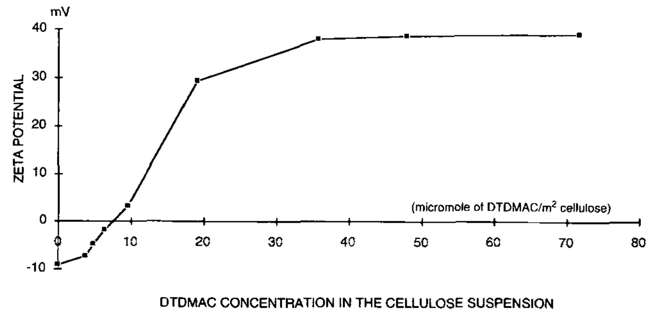


FIG. 4. Zeta potential of microcrystalline cellulose in presence of increasing amounts of DTDMAC (hard water). Abbreviation as in Figure 1.

the amount of adsorbed DTDMAC is plotted as a function of the DTDMAC level introduced in solution, four regions are observed. First, DTDMAC molecules deposit not only onto cellulose but probably also onto glassware. In a second step, DTDMAC is fully adsorbed onto cellulose (a in Fig. 5). Afterwards (third), only part of the DTDMAC available in solution is further fixed by cellulose (b in Fig. 5), probably because there is an electrostatic repulsion between adsorbed DTDMAC molecules and the oncoming ions, up to a plateau (fourth) corresponding to the end of adsorption. The cellulose saturation occurs at a level of 38 micromoles DTDMAC/m^2 cellulose.

Microcrystalline cellulose maintains a rigid structure that imparts a constant specific surface area (2.4 m^2/g). This is in contrast to regular cotton whose fibers swell in solution, so increasing the surface exposed to water.

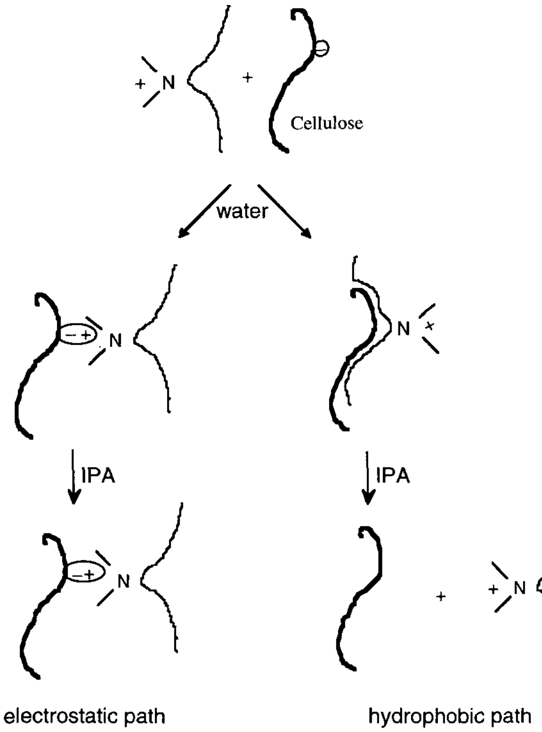


FIG. 6. Demonstration of the nature of ditallowdimethyl ammonium chloride–cellulose interaction. IPA, isopropanol.

Evidence of hydrophobic interaction. The hydrophobic nature of the DTDMAC–microcrystalline cellulose interaction may be unequivocally demonstrated by measuring DTDMAC–cellulose adduct stability in a water-soluble solvent of DTDMAC, such as IPA. This is illustrated in Figure 6. If the DTDMAC–cellulose interaction was exclusively electrostatic, i.e., if it relied on the sole Coulombic attraction between the positive heads and the negative charges on the surface, the coated cellulose would never release DTDMAC when dispersed in IPA. Electrostatic interactions are four times stronger in that solvent than in water (dielectric constants: $\varepsilon_{\text{water}} = 80$, $\varepsilon_{\text{IPA}} = 19.9$). Conversely, if the interaction is purely hydrophobic, i.e., if it hinges only upon the poor solubility of DTDMAC in water and on weak van der Waals interactions, the organic solvent will thoroughly solubilize the DTDMAC, destroying the DTDMAC–cellulose adduct.

Microcrystalline cellulose was mixed with a dilute dispersion of DTDMAC in water and centrifugéd; the supernatant was discarded. Half of the treated cellulose was twice suspended in IPA and the rest in water (for control purpose). The zeta potential of each cellulose fraction was finally determined in water. The DTDMAC withdrawal by the solvent was roughly estimated from the difference of cellulose potential before and after the IPA treatment.

The deposition of DTDMAC induces a rise of 60 mV. After the treatment with IPA, the zeta potential of the sample

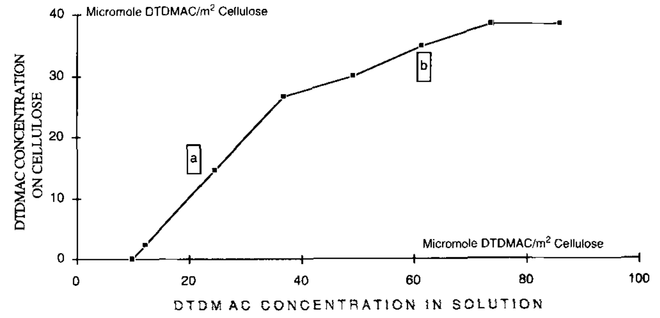
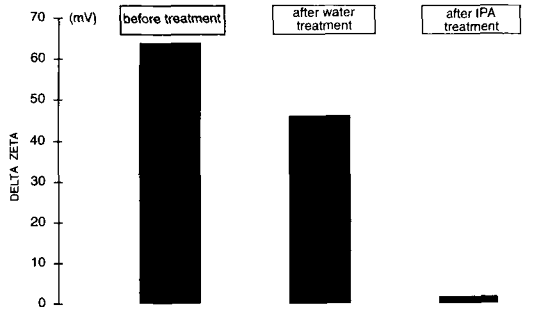


FIG. 5. Quantitation of DTDMAC deposition on microcrystalline cellulose. Abbreviation as in Figure 1.



Delta Zeta = Zeta (coated cellulose) – Zeta (uncoated cellulose)

FIG. 7. Solvent efficacy in removing ditallowdimethyl ammonium chloride from cellulose. Abbreviation as in Figure 6.

is close to that of microcrystalline cellulose before DTDMAC addition (Fig. 7). Conversely, the reduction of zeta potential due to water treatment remains small. So, the IPA treatment removes all DTDMAC from the cellulose surface. This clearly shows that neutral cellulose actually binds DTDMAC through hydrophobic interaction.

When charged sites are created by oxidizing cellulose with sodium hypochlorite prior to mixing, DTDMAC is able to interact electrostatically with the cellulose. The zeta potential after DTDMAC deposition is the same as when cellulose was not charged, but a significant difference is observed after IPA treatment. As expected, some DTDMAC remains on oxidized cellulose (Fig. 8). The solvent removes the DTDMAC bound by hydrophobic interaction from both oxidized and nonoxidized cellulose surfaces equally well, but the electrostatic bonds cannot be released. Thus, we can conclude that when DTDMAC deposits onto cellulose, it is bound by hydrophobic interaction, and by electrostatic bonds when there are charges.

The universality of the DTDMAC hydrophobic deposition can be demonstrated by the deposition of DTDMAC onto polyethylene (which obviously does not bear electric charges). When a low-density polyethylene powder is sprinkled over a well-stirred aqueous dispersion of DTDMAC, it scatters into the medium and reassembles on top when stirring stops. Without DTDMAC, of course, no polyethylene dispersion into water occurs.

The DTDMAC-coated polyethylene exhibits a zeta potential of +58 ± 8 mV in tap water. The rather large standard deviation is due to difficult experimental conditions (during the measurement, the coated polymer slowly comes up to the top of the capillary, out of the zetasizer laser ray). The DTDMAC deposition is further confirmed by ESCA measurements. Nitrogen is detected at 402 eV on the DTDMAC-treated polyethylene sample, not on the reference (untreated sample).

Structural effects. As mentioned in the introduction, the electrostatic model of DTDMAC deposition on cellulose remained unable to account for the effects of the molecule structure on softening performance. According to our model, there must be a clear-cut correlation between the structure of quaternaries, their deposition and, hence, their softening performance. If the structure of the molecule is modified to make it less hydrophobic (fewer carbons in the fatty chains, fewer fatty chains, unsaturations, etc.), the quaternary will not be expelled from the aqueous phase with the same strength, and the amount of quaternary material deposited on cotton, hence the softening efficacy, will drop accordingly.

The effect of chainlength was measured by comparing DTDMAC to DCDMAC, and the effect of the chain number by evaluating TtMAC.

Effect of structure on hydrophobicity of quaternaries. The hydrophobicity of the quaternary may be easily quantitated from the amount of IPA necessary to clarify an emulsifier-free aqueous dispersion. Results are extremely reproducible (Table 1). The amount of IPA, expressed as mole percentage in the finally clear medium, depends on the structure of the quaternary only. It truly reflects the hydrophobicity of the quaternary; the ditallow derivative is more hydrophobic than the dicoco, while the monotallow derivative is much more water-soluble.

Effect of structure on deposition on cellulose. The curves of cellulose zeta potential as a function of DCDMAC and DTDMAC contents exhibit close patterns, different from the one of TtMAC (Fig. 9). This result suggests that the former deposits better than the latter onto charge-free cellulose. Quantitative evaluations of their depositions confirm that DTDMAC is more adsorbable than DCDMAC, and TtMAC much less (Fig. 10).

Effect of structure on softening performance. Replacing DTDMAC by DCDMAC at the same molar concentration significantly impairs softness. TtMAC is always outperformed by DTDMAC, irrespective of concentration. Hence, a correlation between hydrophobicity, deposition and softening performance may be drawn. The more hydrophobic the quaternary (increased number of alkyl chains and/or length), the greater the amount deposited onto the fabric, the better the fiber coating and, therefore, the better the softening performance at lower concentrations.

Effect of surface area. Because (according to our model) the DTDMAC–cellulose interaction is mainly nonspecific, deposition should mainly depend on the available surface area. When comparing the kinetics of DTDMAC adsorption onto constant amounts of cellulose, it was found that the

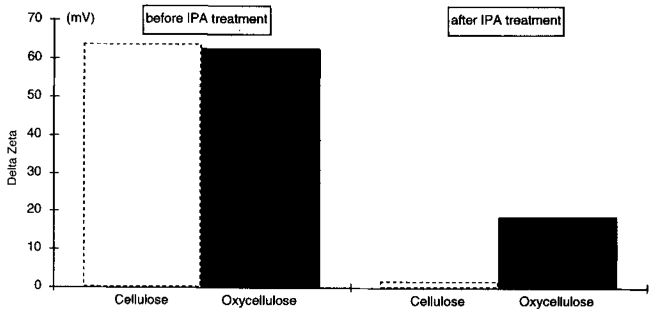


FIG. 8. Effect of electrostatic binding on the ditallowdimethyl ammonium chloride removal from cellulose by isopropanol (IPA).

Table 1
Structure Effect on the Hydrophobicity of Quaternaries

Quat dispersion[a]	Amount of dispersion (g)	Isopropanol at the end point (%)
DCDMAC		
3%	5	3.11 ± 0.02
5%	5%	2.97 ± 0.03
DTDMAC		
3%	5	5.83 ± 0.06
5%	3	6.20 ± 0.05
TtMAC		
3%	5	0.00[b]

[a] DTDMAC, ditallowdimethyl ammonium chloride; DCDMAC, dicocodimethyl ammonium chloride; TtMAC, monotallowtrimethyl ammonium chloride.
[b] TtMAC gives a clear aqueous dispersion.

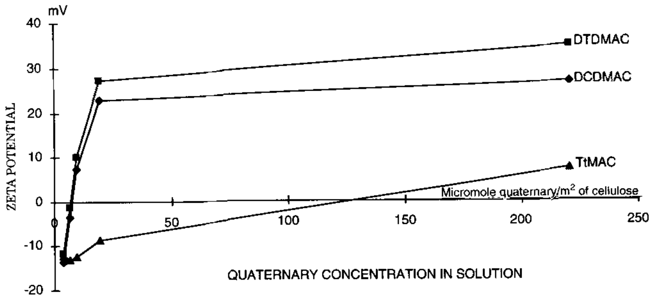


FIG. 9. Effect of the quaternary structure on its affinity for cellulose. Abbreviation as in Figure 1; DCDMAC, dicocodimethyl ammonium chloride; TtMAC, monotallowtrimethyl ammonium chloride.

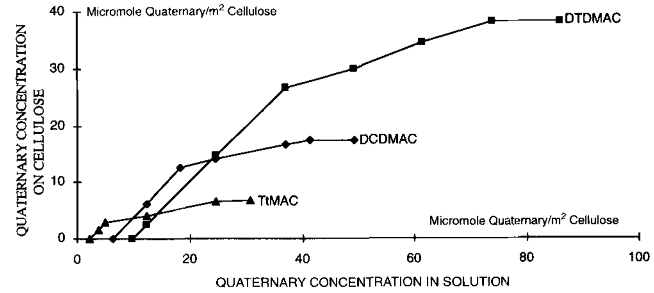


FIG. 11. Effect of the specific surface area of cellulose on the kinetics and extent of DTDMAC deposition. Abbreviation as in Figure 1.

larger the specific surface area, the faster and the more the DTDMAC deposition become (Fig. 11). Terry towels gather DTDMAC more quickly than short-napped cotton but much more slowly than microcrystalline cellulose. So, the deposition of DTDMAC onto an electrically neutral surface with a large specific surface area is larger and quicker than deposition onto the same amount of charged cotton with a smaller specific surface area.

Characterization of the DTDMAC–cotton interaction. So far, the DTDMAC–cellulose interaction has been studied under ideal conditions (microcrystalline cellulose, beakers, etc.). But what about real systems? Are the conclusions about the hydrophobic mechanism still valid under real-life conditions? To answer that question, we treated, according to realistic conditions, terry towels with a DTDMAC-based fabric softening composition. We chose Softlan, the Colgate Palmolive brand in Germany. After line-drying, half the towels were rinsed in IPA to extract the adsorbed DTDMAC, if any. DTDMAC fixed by electrostatic bonds should remain unaffected by that treatment, as demonstrated by zeta potential of oxidized microcrystalline cellulose. The DTDMAC amount released in IPA always exceeded 50% of the DTDMAC deposited onto the fabric and reached as high as 96%. Thus, most of the DTDMAC at the cotton surface is bound by hydrophobic interaction.

Softening efficacy of DTDMAC bound by hydrophobic interaction. Another question is the possible impact of the type of DTDMAC–cellulose interaction on its softening performance. In other words, is DTDMAC adsorbed by hydrophobic interaction still efficient from a softening standpoint? This question was answered by measuring the impact of IPA treatment on the softness of the Softlan-treated terry towels. Swatches treated with IPA were always much harsher than the untreated ones. In other words, towels are softer before IPA treatment than after. So, the removal of DTDMAC adsorbed by hydrophobic interaction induces a significant loss of softness. We can therefore conclude that under real life conditions, most of the DTDMAC is fixed on cotton by hydrophobic interaction and significantly contributes to its softening.

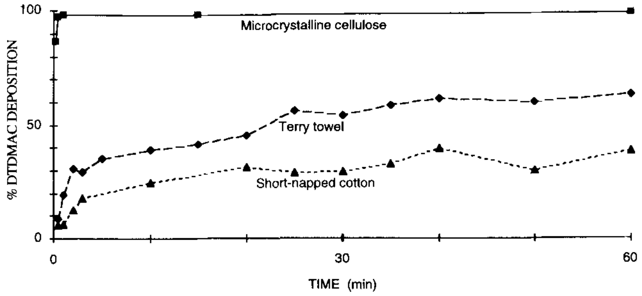


FIG. 10. Effect of the quaternary structure on its deposition on cellulose (quantitative evaluation). Abbreviations as in Figure 9.

These observations explain why most, but not all, DTDMAC is withdrawn from cotton fabrics during subsequent washes. DTDMAC bound to cellulose through hydrophobic interactions is removed by surfactants like any other fatty material, whereas electrostatically attached DTDMAC remains unaffected.

Discussion of the literature mechanism. Only recently has the physical process by which softeners deposit onto cotton been linked to a combination of molecular ion exchange and physical adsorption (27). Why is the Coulombic attraction so widely invoked to explain DTDMAC deposition onto cotton (1–17)?

Most of the work on the mechanism of deposition of quaternaries was done with monoalkyl quaternaries (12–17), and the conclusions were extended to the dialkyl cationics, the active ingredient of fabric softeners. Such an extension is incorrect because the monoalkyl derivatives are water-soluble, the dialkyl are not, and soluble monoalkyl derivatives exhibit little trend to be ejected out of the aqueous phase.

Few studies were carried out on DTDMAC. Beal *et al.* (18) conclude from their study of the effects of fabric finish on DTDMAC deposition that ionic interaction forces play an important role in the sorption process. Similarly, Ramsbotham (9) reports that the nature of the fabric is important; DTDMAC is strongly adsorbed onto the fabric, and the coverage does not extend beyond a monolayer and is probably less. Egan (19) invokes an ion exchange mechanism at the fabric surface to explain the enhancement of softener deposition due to the presence of polyphosphate residues.

Braüer *et al.* (3) justify the electrostatic model by the pattern of DTDMAC adsorption isotherms on textiles, which is of the high-affinity type. These patterns are mainly encountered with chemisorbed substances.

Alternative explanations, however, exist to account for these features. DTDMAC deposition onto cellulose levels off, due to electrostatic repulsion that occurs between the oncoming ions and those already adsorbed by hydrophobic interaction. That limits the deposition to less than a monolayer [as reported by Ramsbotham (9)]. When negative charges are present on the fiber (18,19), they neutralize the positive charge of DTDMAC, and a surfactant double-layer may be formed at that spot; the extent of softener deposition is consequently enhanced.

Moreover, as stated by Laughlin (27), if the softener is a commercial raw material containing TtMAC, the sign of the charge on cellulose will be quickly neutralized, or even inverted by this soluble, and therefore mobile, surfactant. On the other hand, because the driving force of DTDMAC deposition lies in its lack of affinity for water, it is not surprising that its adsorption is of the high-affinity type (3).

Many other experimental observations reported in the literature support the hydrophobic deposition. Some authors (13,14) mention that adsorption of cationic surfactants increases with increasing molecular weight of the hydrophobic part. White (28) even states that a long hydrophobic chain seems to impart an affinity above and beyond that rising from electrostatic interactions. It is also reported that an inversion of the fiber zeta potential results from the deposition of the softening molecule (15,29). But, how would such an inversion occur if the deposition solely relied on a Coulombic attraction between DTDMAC and cellulose? The potential of coated fibers should be zero. Moreover, most of DTDMAC is removed from cotton by organic solvents [although the removal is not complete, even after several cumulative treatments (30)]. We have shown that electrostatic bonds resist such a treatment, whereas DTDMAC fixed by hydrophobic interaction is released. This is in line with the observation that the washfastness increases when the number of anionic adsorption sites increases (31). So, most DTDMAC is bound by hydrophobic interaction.

Several authors (7,9,12,18,30,32,33) report that a temperature rise increases DTDMAC adsorption. Such an effect is typical of an entropy-driven phenomenon (second principle of thermodynamics). The liberation of water molecules involved in hydrophobic hydration much increases the system's entropy (see Introduction). So, ejection of hydrophobic molecules, such as DTDMAC, from the aqueous phase is entropy-driven and will consequently be favored by a temperature increase.

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