Antistatic and Wetting Properties of Chemodegradable Cationic Surfactants Containing 1,3-Dioxolane Moiety

Kazimiera A. Wilk*, Ryszard Poźniak, and Adam Sokołowski

Institute of Organic and Polymer Technology, Wrocław University of Technology, 50-370 Wrocław, Poland

ABSTRACT: In this paper we report some performance properties of [(2-alkyl-1,3-dioxolane-4-yl)methyl]trimethylammonium bromides (C_n-D-TAB, where C_n= n-C_9H_{19}, n-$C_{11}H_{23}$, n-$C_{13}H_{27}$), [(2,2-dialkyl-1,3-dioxolane-4-yl)methyl]dimethylammonium bromides (C_nC_m-D-TAB, where C_n= n-C_8H_{17}, n-$C_{10}H_{21}$ and C_m = CH_3 or C_n = C_m = n-C_6H_{13}), in relation to classical alkyltrimethylammonium bromides (C_n-TAB, where C_n= n-$C_{12}H_{25}$, n-$C_{14}H_{29}$ or $C_{16}H_{33}$) and dialkyldimethylammonium bromides (C_nC_m-DAB, where C_n = C_m = n-$C_{10}H_{21}$ and $C_{12}H_{25}$). Antistatic properties were measured by means of surface resistance (R_s), half charge decay time ($\tau_{1/2}$), and maximal voltage induced (U_{ind}) on polyethylene (PE) film and polypropylene (PP) nonwoven fabric. Wetting ability is reported as the concentration of surfactant necessary for immersion of a cotton-fabric ring in 100 s, according to the Polish Standard PN-74/C-04800. All acetal-type surfactants showed the antistatic effect. The best results were given by C_9-D-TAB [$R_s = 8.5 \cdot 10^7$ (PE), $1.1 \cdot 10^8$ Ω (PP); $\tau_{1/2}$ = 0.25 (PE), 0.30 s (PP); U_{ind} = 205 (PE), 220 V (PP)] and C_{11}-D-TAB [$R_s = 8.7 \cdot 10^7$ (PE), $1.3 \cdot 10^8$ Ω (PP); $\tau_{1/2}$ = 0.25 (PE), 0.30 s (PP); U_{ind} = 190 (PE), 340 V (PP)] in relation to pure PE foils and PP fabric: $R_s = 3.0 \cdot 10^{14}$ (PE), $9.8 \cdot 10^{14}$ Ω (PP); $\tau_{1/2}$ = >600 (PE), >600 s (PP); U_{ind} = 985 (PE), 940 V (PP). Both C_9-D-TAB and C_{11}-D-TAB indicate similar degrees of antistatic ability compared to $C_{10}C_{10}$-DAB. All C_n-TAB compounds do not show any antistatic effects. It was concluded that addition of the 1,3-dioxolane moiety to the hydrophobic tail of quaternary ammonium salts promotes both antistatic and wetting properties. Additionally, methyl or n-hexyl group incorporation at the C-2 carbon atom in the 1,3-dioxolane ring significantly decreases the surface conductivity.

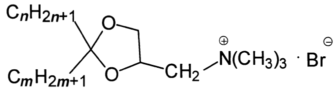
Paper no. S1149 in *JSD 3*, 207–211 (April 2000).

KEY WORDS: Antistatic effect, cyclic acetal-type surfactants, 1,3-dioxolane ammonium salts, quaternary ammonium salt, wetting ability.

Cationic chemodegradable surfactants have recently generated increased interest (1,2). Cyclic acetal-type cationic surfactants can be considered as potential antistatic, environmentally acceptable compounds providing substituents to generally applied alkyltrimethylammonium or dialkyldimethylammonium halides.

Antistatic agents (antistats) are substances that, added to textiles or plastic materials, reduce their propensity to accumulate electrostatic charges. The main groups of antistats include ionic compounds such as quaternary ammonium salts and amines. Ammonium salts have proved to be very effective antistats and are the subject of many scientific dissertations (3,4). Among the quaternary ammonium salt derivatives the best antistatic properties have been shown with dialkyldimethylammonium chlorides and bromides (alkyl: C_{16}–C_{24}) (5), *N*-[3-alkyloxy-2-hydroxypropyl]-*N*,*N*-dihydroxyethyl-*N*-methylammonium methylsulfates (alkyl: C_8–C_{18}) (6), imidazolium salts (7,8) and derivatives of betaine (9). These antistats increase electrical conductivity of the material by increasing its surface conductivity. As in the case of textiles, antistats for plastic have to combine a low electrical resistivity with the ability to form a continuous film on low energy surfaces from a solution or dispersion in water or other inexpensive, volatile solvent. A comparison of antistatic and wetting abilities of these substances was necessary to determine the influence of their surface activity, i.e., effectiveness of surface tension reduction (π_{cmc}) and surface area per molecule (A), upon their antistatic effect.

The main purpose of this study was to investigate the antistatic properties and wetting ability of [(2-alkyl-1,3-dioxolane-4-yl)methyl]trimethylammonium bromides and [(2,2-dialkyl-1,3-dioxolane-4-yl)methyl]trimethylammonium bromides (hereafter called C_n-D-TAB and C_nC_m-D-TAB, where -D- is the 1,3-dioxolane ring, respectively; see Scheme 1).



C_9-D-TAB	$n = 9$	$m = 0$
C_{11}-D-TAB	$n = 11$	$m = 0$
C_{13}-D-TAB	$n = 13$	$m = 0$
C_8C_1-D-TAB	$n = 8$	$m = 1$
$C_{10}C_1$-D-TAB	$n = 10$	$m = 1$
C_6C_6-D-TAB	$n = 6$	$m = 6$

SCHEME 1

---

*To whom correspondence should be addressed at Institute of Organic and Polymer Technology, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.
E-mail: KAW@itots.ch.pwr.wroc.pl

In this work, the role of the 1,3-dioxolane grouping in cationic surfactants has been studied in terms of a comparison between chemodegradable surfactants and the "classical" alkyltrimethylammonium bromides C_n-TAB ($C_n = n$-$C_{12}H_{25}$, n-$C_{14}H_{29}$, and n-$C_{16}H_{33}$) and dialkyldimethylammonium bromides C_nC_m-DAB ($C_n = C_m = n$-$C_{10}H_{21}$, n-$C_{12}H_{25}$). Surface and micellization properties of C_n-D-TAB and C_nC_m-D-TAB were recently described in the literature (10). Accordingly, values of the standard free energy contribution of the 1,3-dioxolane ring [-D-] in the C_n-D-TAB derivatives to the micellization and adsorption processes ($\Delta G^o{}_{mic}$[-D-] = –5.7 kJ mol^{-1} and $\Delta G^o{}_{ads}$[-D-] = –21.5 kJ mol^{-1}, respectively) showed that the [-D-] moiety is approximately 1.7 times more hydrophobic than the methylene group of the alkyl chain in promoting micellization ($\Delta G^o{}_{mic}$[-CH_2-] = –3.5 kJ mol^{-1}) and 6.3 times more effective in promoting adsorption ($\Delta G^o{}_{ads}$[-CH_2-] = –3.35 kJ mol^{-1}). The difference $\Delta\Delta G^o$[-D-] (= $\Delta G^o{}_{ads}$[-D-] – ($\Delta G^o{}_{mic}$ [-D-] = –16 kJ mol^{-1}) indicates a higher tendency for adsorption of the five-membered 1,3-dioxolane ring at the infinite dilution surface film than a tendency for micellization.

EXPERIMENTAL PROCEDURES

Materials. C_n-D-TAB and [(2,2-dihexyl-1,3-dioxolane-4-yl)methyl]trimethylammonium bromides were available from previous studies (11). The preparation and purification of [(2-alkyl-2-methyl-1,3-dioxolane-4-yl)methyl]-trimethylammonium bromides were described in previous work (10). C_n-TAB ($C_n = n$-$C_{12}H_{25}$, n-$C_{14}H_{29}$, and n-$C_{16}H_{33}$) and C_nC_m-DAB ($C_n = C_m = n$-$C_{10}H_{21}$ and n-$C_{12}H_{25}$) were a commercial grade (Sigma-Aldrich, Milwaukee, WI). Polyethylene 0.18 mm thick film, POLITEN II 003/GO (Blachownia, Poland), and polypropylene 0.50 mm thick unwoven fabric, WIGOFIL (Wigolen, Poland), were used as polymer samples.

Antistatic properties. Antistatic effects of the salts were measured on polyethylene (PE) film and polypropylene (PP) unwoven fabric. Thin films of cationic surfactants were deposited on disks of PE film and PP fabric. PE and PP disks of 125 mm diameter were washed in acetone, then dried by placing them in an air-conditioned room. The disks were then immersed in a 0.5 wt% chloroform solution of quaternary salt for 30 s. They were then hung up so that the solvent could evaporate spontaneously. For each salt two disks were prepared. The disks were stored for 24 h in an air-conditioned room at 22 ± 1°C and relative humidity 50 ± 5%. Finally, the surface resistance, half charge decay time and maximal voltage induced on the surface of polymers were evaluated. The measuring apparatus and the method of measurement were described in Reference 7.

Wetting properties. Wetting properties were determined as the concentration (g·dm^{-3}) of surfactant solution necessary for immersion of a cotton-fabric ring (3.5 cm diameter) in 100 s (Polish Standard No. PN-74/C-04800 Perinorm). The results were averages of five determinations.

RESULTS AND DISCUSSION

Antistatic activity. Antistatic properties, expressed by surface resistance, half-charge decay time, and maximum voltage induced for the cationic surfactants used in our experiments, were determined by comparative methods. Surface resistance (R_s) was calculated from the formula

$$R_s = \frac{U \cdot l}{i \cdot s}, \text{ in } \Omega \qquad [1]$$

where U is the applied voltage (U = 100 V), l the length of electrodes (l = 100 mm), i the measured current intensity, and s the distance between electrodes (s = 10 mm). The half charge decay time ($\tau_{1/2}$) was found from relation:

$$\tau_{1/2} = \sqrt{\frac{\tau^2_{1/2(+)} + \tau^2_{1/2(-)}}{2}}, (s) \qquad [2]$$

where $\tau_{1/2(+)}$ and $\tau_{1/2(-)}$ are the mean half decay times of positive and negative charges, respectively. The maximum voltage induced (U_{ind}) on the surface of the air-conditioned disks is

$$U_{\text{ind}} = \sqrt{\frac{U^2_{ind.(+)} + U^2_{ind.(-)}}{2}}, (\text{V}) \qquad [3]$$

where $U_{\text{ind.(+)}}$ and $U_{\text{ind.(–)}}$ are the voltages induced by positive and negative charges, respectively.

The antistatic effect was determined following the criteria given by Biedermann (12) and Finck (13) (Table 1).

Antistatic properties are shown in Table 2. Nearly all the C_n-D-TAB and [(2,2-dihexyl-1,3-dioxolane-4-yl)methyl]-trimethylammonium bromides possess antistatic properties as they diminish the surface resistance at least by three orders of magnitude, and the half charge decay time reaches values below 100 s. Also smaller values of induced voltage on the PE and PP surfaces, which comprises a measure of its electrification susceptibility, were obtained compared to polymers without bromides.

The best results were obtained from C_n-D-TAB containing n-nonyl (C_9-D-TAB) and n-undecyl (C_{11}-D-TAB) hydrophobic chains. A good antistatic effect was obtained

TABLE 1
Criteria for Estimating the Antistatic Effect Based on Surface Resistance and Half Decay Time[a]

Biedermann (ref. 12)		Finck (ref. 13)		Antistatic
$\tau_{1/2}$ (s)	R_s (Ω)	$\tau_{1/2}$ (s)	R_s (Ω)	effect
<0.5	$<10^{10}$	0	$<10^9$	Excellent
0.5–2	10^{12}	1	10^9–10^{10}	Very good
2–10	10^{14}	2–10	10^{10}–10^{11}	Good
10–100	10^{15}	10–60	10^{11}–10^{12}	Sufficient
		>60	$>10^{12}$	Insufficient
>100	10^{16}		$>10^{13}$	Lack

[a] $\tau_{1/2}$, half charge decay time; R_s, surface resistance.

TABLE 2
Antistatic Effect of Cationic Surfactants on Polyethylene (PE) Film and Polypropylene (PP) Fabric Surfaces[a]

	LDPE (film)			PP (unwoven fabric)			Antistatic
Compound	R_s (Ω)	$\tau_{1/2}$ (s)	$U_{\text{ind.}}$ (V)	R_s (Ω)	$\tau_{1/2}$ (s)	$U_{\text{ind.}}$ (V)	effect
None	$3.0 \cdot 10^{14}$	>600	985	$9.8 \cdot 10^{14}$	>600	940	
C_9-D-TAB	$8.5 \cdot 10^{7}$	0.25	205	$1.1 \cdot 10^{8}$	0.30	220	Excellent
C_{11}-D-TAB	$8.7 \cdot 10^{7}$	0.25	190	$1.3 \cdot 10^{8}$	0.30	340	Excellent
C_{13}-D-TAB	$6.7 \cdot 10^{8}$	0.35	465	$8.3 \cdot 10^{8}$	0.55	470	Very good
C_8C_1-D-TAB	$8.5 \cdot 10^{9}$	0.65	630	$9.3 \cdot 10^{9}$	0.75	685	Good
$C_{10}C_1$-D-TAB	$6.5 \cdot 10^{9}$	0.55	545	$5.0 \cdot 10^{9}$	0.60	560	Good
C_6C_6-D-TAB	$2.5 \cdot 10^{11}$	89.2	980	$1.3 \cdot 10^{11}$	20.3	685	Sufficient
C_{12}-TAB	$2.3 \cdot 10^{14}$	>600	995	$3.8 \cdot 10^{14}$	>600	935	None present
C_{14}-TAB	$2.8 \cdot 10^{14}$	>600	995	$4.2 \cdot 10^{14}$	>600	945	None present
C_{16}-TAB	$3.2 \cdot 10^{14}$	>600	1000	$5.7 \cdot 10^{14}$	>600	955	None present
$C_{10}C_{10}$-DAB	$1.7 \cdot 10^{8}$	0.30	265	$2.6 \cdot 10^{8}$	0.25	270	Excellent
$C_{12}C_{12}$-DAB	$1.5 \cdot 10^{10}$	1.65	860	$1.3 \cdot 10^{10}$	1.15	685	Good

[a] C_n-D-TAB, (2-alkyl-1,3-dioxolane-4-yl)methyl]trimethylammonium bromides, where C_n = n-C_9H_{19}, n-$C_{11}H_{23}$, n-$C_{13}H_{27}$; C_nC_m-D-TAB, (2-alkyl-1,3-dioxolane-4-yl)methyl]trimethylammonium bromides, where C_n = n-C_8H_{17}, n-$C_{10}H_{21}$, and C_m = CH_3 or C_m = n-C_6H_{13}; C_n-TAB, alkyltrimethylammonium bromides; C_nC_m-DAB, dialkyldimethylammonium bromides; LDPE, low density polyethylene.

from C_{13}-D-TAB. Commercial C_n-TAB (C_n = n-$C_{12}H_{25}$, n-$C_{14}H_{29}$, and n-$C_{16}H_{33}$) did not impart antistatic properties whereas commercial C_nC_m-DAB (C_n = C_m = n-$C_{10}H_{21}$ and n-$C_{12}H_{25}$) were excellent ($C_{10}C_{10}$-DAB) and very good ($C_{12}C_{12}$-DAB) antistatic agents, respectively. It is remarkable that the effectiveness of surface tension reduction (π_{cmc}) for C_n-TAB in a surfactant-air-water system and surface area per molecule (A) in the soluble monolayer were significantly lower compared to the experimental acetal surfactants. The surfactants containing two hydrophobic chains at the C-2 carbon atom of the 1,3-dioxolane ring (i.e., C_nC_m-D-TAB) show minimal antistatic properties. Furthermore, the methyl derivatives, i.e., C_8C_1-D-TAB and $C_{10}C_1$-D-TAB, show good antistatic effects at the PE and PP surfaces. Thus, by increasing the carbon chain length above C_{11}, and increasing the number of alkyl hydrophobic groups at the C-2 carbon atom of the 1,3-dioxolane ring, there was a decrease in antistatic properties.

Our studies of antistatic chemodegradable cationic surfactants indicated that the following conditions must be met in order to obtain excellent antistatic agents within in the group of cationic surfactants that were investigated:

- Only one alkyl substituent can reside at the C-2 position of the 1,3-dioxolane ring.
- The substituent in position C-2 of the 1,3-dioxolane ring should have an alkyl chain containing 9 or 11 carbon atoms.

Wetting power. We studied surfactant wetting ability (Table 3) by measuring the time that cotton-fabric rings floated on surfactant solutions. Relationships between wetting time and concentration are shown in Figure 1. Wetting ability was marginal when C_n was C_9 and C_{14} for C_n-D-TAB and C_n-TAB, respectively. C_6C_6-D-TAB was found to be the most effective wetting agent. Wetting ability results are summarized as follows:

- The presence of the 1,3-dioxolane moiety in C_n-D-TAB introduces hydrophobic character equivalent to three

TABLE 3
Surface Properties and Wetting Power of Cationic Surfactants[a]

Compound	π_{cmc} (mN·m^{-1})	A·10^{20} (m^2)	Wetting power[b] C_{100} (g·dm^{-3})	Wetting effect
C_9-D-TAB	40.4	97	> 1.0	None
C_{11}-D-TAB	41.2	98	0.300	Good
C_{13}-D-TAB	41.5	100	0.275	Good
C_8C_1-D-TAB	38.4	86	0.350	Good
$C_{10}C_1$-D-TAB	37.3	83	0.370	Good
C_6C_6-D-TAB	42.6	84	0.113	Very good
C_{12}-TAB	33.2	52	> 1.0	None
C_{14}-TAB	34.0	52	0.645	Sufficient
C_{16}-TAB	34.4	49	0.340	Good
$C_{10}C_{10}$-DAB	—	—	0.055	Excellent
$C_{12}C_{12}$-DAB	—	—	0.075	Excellent

[a] Surface tension reduction (π) at critical micelle concentration (cmc); A, surface area per molecule; from Reference 9. For other abbreviations see Table.

[b] Concentration of surfactant solution necessary for immersion of a cotton-fabric ring (3.5cm diameter) in 100 s (Polish Standard No. PN-74/C-04800).

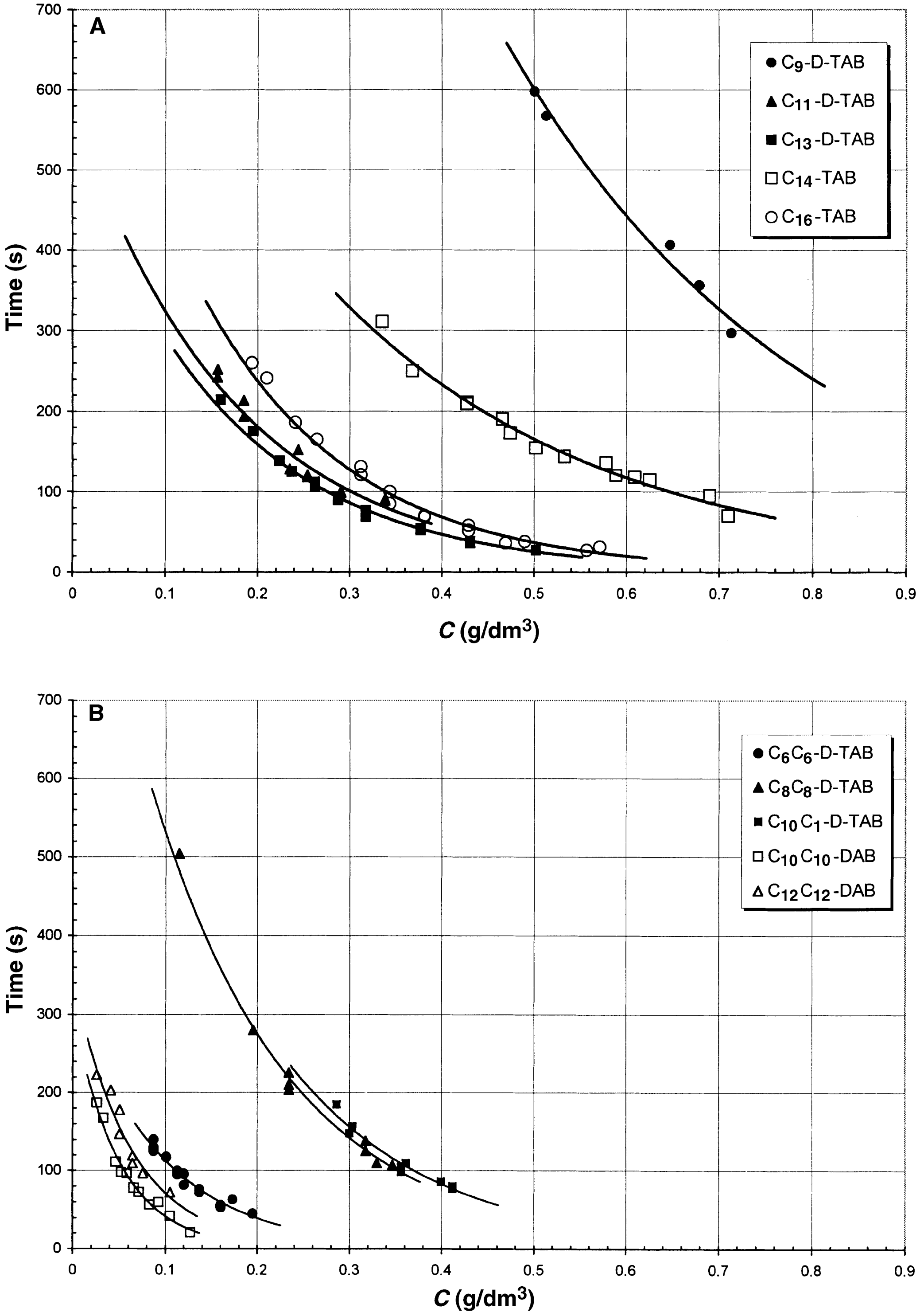


FIG. 1. Relationship between the concentration and wetting time of cationic surfactants. Abbreviations: C_n-D-TAB, (2-alkyl-1,3-dioxolane-4-yl)methyl]trimethylammonium bromides, where C_n = n-C_9H_{19}, n-$C_{11}H_{23}$, n-$C_{13}H_{27}$; C_nC_m-D-TAB, (2-alkyl-1,3-dioxolane-4-yl)methyl]trimethylammonium bromides, where C_n = n-C_8H_{17}, n = $C_{10}H_{21}$, and C_m = CH_3 or n-C_6H_{13}; C_n = TAB, alkyltrimethylammonium bromides.

methylene groups in the alkyl chain of C_n-TAB, with equal C_n value (see compounds C_{11}-D-TAB, C_{14}-TAB, Fig. 1A).

- Introduction of a methyl group in the C-2 position of the 1,3-dioxolane ring significantly increases the wetting ability of short chain length cationic surfactants (see C_9-D-TAB, Fig. 1A and $C_{10}C_1$-D-TAB, C_8C_1-D-TAB, Fig. 1B),

- Surfactants containing a short- or medium hydrophobic chain, i.e., $C_n \leq C_9$ for C_n-D-TAB and $C_n \leq C_{12}$ for C_n-TAB, had relatively poor wetting properties.

The incorporation of the 1,3-dioxolane ring into the surfactant hydrophobe significantly increases antistatic properties, wetting ability, surface area per molecule (9) and surface tension reduction (10) of chemodegradable cationic surfactants. The most profound differences appear in the case where an additional alkyl chain at the C-2 position was incorporated into the 1,3-dioxolane ring. This improves the cotton fiber wettability, however, it diminishes the antistatic performances at the polymer surface. The findings can probably arise from different position of the dioxolane ring plane in relation to the surface and various surfactant surface concentrations applied. Other methods are required to study and explain this problem more accurately.

Differences in the surfactant antistatic activity of C_n-D-TAB and C_nC_1-D-TAB compared to C_n-TAB can be attributed to hemimicelle formation in the case of C_n-TAB, which causes uneven distribution of surfactant on the polymer surface.

REFERENCES

1. Bieniecki A., B. Matuszewska, and K.A. Wilk, Nucleophilic Aromatic Substitution in Microemulsions Stabilized by Chemodegradable Surfactants, *Polish J. Chem. 69*:1174 (1995).
2. Holmberg K., Cleavable Surfactants, in *Novel Surfactants*, edited by K. Holmberg, Marcel Dekker, Inc., New York 1998, pp. 334.
3. Holme I., J.E. McIntyre, and Z.J. Shen, Electrostatic Charging of Textiles, *Text. Progr. 28*:1 (1998).
4. Reck R.A., *Encyclopedia of Polymer Science Engineering*, edited by H.F. Mark *et al.*, J. Wiley–Interscience, New York, 1985, Vol. 2, p. 99.
5. Fisher, R.W., and K.E. McCaleb, Diisostearyldimethylammonium Chloride as Fabric Softener, U.S. Patent 3,395,100 (1968).
6. Poźniak R., A. Pasternak, and M. Dul, Antistatic Properties of Quaternary Ammonium Methylsulphates with Alkoxy-2-hydroxypropyl Radicals, *Przem. Chem. 68*:175 (1989).
7. Pernak J., R. Poźniak, Z. Krejpcio, and A. Skrzypczak, The Antielectrostatic Properties of Quaternary Imidazolium Chlorides, *Acta Polymer. 38*:299 (1987).
8. Pernak, J., A. Arndt, and R. Poźniak, The Antielectrostatic Effect of Benzimidazolium Salts, *Polymer 39*:603 (1998).
9. Sano, Y., T. Saegusa, and Y. Kimura, Antistatic Modification of Synthetic-Fibers by Blend-Spinning of Polymers Containing Zwitterionic Antistatic Modifiers and Their Copolymers, *Angew. Macromol. Chem. 224*:153 (1995).
10. Sokołowski, A., A. Bieniecki, K.A. Wilk, and B. Burczyk, Surface Activity and Micelle Formation of Chemodegradable Cationic Surfactants Containing the 1,3-Dioxolane Moiety, *Colloid Surface A 98*:73 (1995).
11. Wilk, K.A., A. Bieniecki, B. Burczyk, and A. Sokołowski, Synthesis and Hydrolysis of Chemodegradable Cationic Surfactants Containing the 1,3-Dioxolane Moiety, *J. Am. Oil Chem. Soc 71*:81 (1994).
12. Biedermann, W., Zur elektrostatischen Auflandung organischer Hochpolymer und zum Einsatz von Antistatika, *Plaste Kautschuk 16*:8 (1969).
13. Finck, H.W., Antistatika für Kunststoffe, *Kunststoffe 64*:64 (1974).

[Received May 13, 1999; accepted January 11, 2000]

Dr. Kazimiera A. Wilk studied chemistry at the Wrocław University of Technology, Poland, and received her Ph.D. (1979) and Habilitation (1991) degrees from the Wrocław University of Technology to become a professor of chemical sciences in 1997 at the same university. Her research interests are in the field of surfactant and dispersed systems chemistry, synthesis of environmentally acceptable surfactants, and aggregation phenomena in solution.

Dr. Ryszard Poźniak studied chemistry at the Wrocław University of Technology, Poland, and received his Ph.D. (1979). His research interests are in the field of additives for plastics: synthesis of antistatic and antifogging agents, relations between their chemical structure and activity; and selected problems of industrial organic chemistry.

Dr. Adam Sokołowski studied chemistry at the Wrocław University of Technology, Poland, and received his Ph.D. (1977) and Habilitation (1992) degrees from the Wrocław University of Technology. His research interests are in the field of surfactant sciences: synthesis of chemodegradable, acetal-type surfactants; chemical structure–surface activity relationships of amphiphilic substances; and selected problems of microemulsion systems.