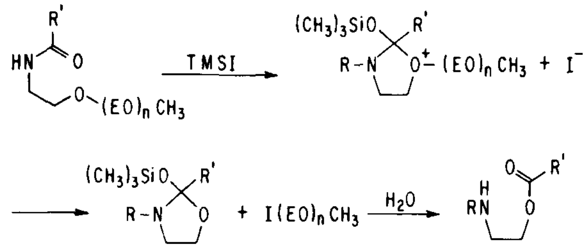

FIG. 4. Possible source of ester by-product from ether cleavage.

More detailed investigation of surfactant properties of monomeric N-hydroxyethylated amides will be performed in conjunction with studies of interactions of such compounds with soil.

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Synthesis and Properties of New Cationic Surfactants

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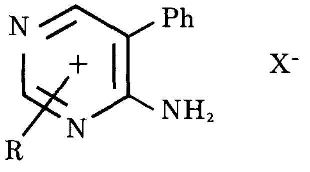
New pyrimidinium cationic surfactants containing a positively charged nitrogen atom of the pyrimidine ring and a long-chain alkyl group of 6,8,10,12,14 carbon atoms were prepared. The structural assignment of these compounds was made on the basis of the elemental analysis and spectroscopic data, infrared, nuclear magnetic resonance and mass spectroscopy. Surface tension and after-treatment of direct dyed cotton fabrics were determined for these surfactants. Antibacterial activities also were examined.

Cationic surfactants with a positively charged nitrogen atom and one or more hydrophobic long-chain alkyl substituents display antimicrobial activities (1). They are also used as auxiliaries in dyeing fabric (1,2). The little known chemistry and properties of pyrimidinium cationic surfactants (3) encouraged us to prepare and study the properties of such surfactants having the general formula:



$R=C_nH_{2n+1}$, n=6,8,10,12,14
X=I, Br

The above compounds were obtained in good yields (60-80%) by the reaction of 4-amino-5-phenyl-pyrimidine 1 with excess of alkylhalides 2 under reflux in methanol for 24 hr (Scheme 1).

The structural assignment of the prepared compounds 3 was made on the basis of elemental analysis and spectroscopic data (IR, NMR, MS) summarized in Table 1.

EXPERIMENTAL PROCEDURES

All melting points are uncorrected and were determined with a Koffler hot-stage apparatus. IR spectra were obtained with a Perkin-Elmer 281 B spectrophotometer, NMR spectra reported in δ units were recorded with a Varian A-60A spectrometer using D_2O as solvent and tetramethylsilane as an external standard. The mass spectra were measured with a Hittachi-Perkin-Elmer Model RMU-6L spectrometer with an ionization energy of 70 eV. Elemental analyses were performed with a Perkin-Elmer analyzer Model 240 B.

Preparation of starting materials. 4-Amino-5-phenyl-pyrimidin 1 was prepared according to the procedure described in the literature (4).

General procedure for the preparation of halide salts of 1(3)-alkyl-4-amino-5-phenyl-pyrimidines 3. A mixture of 0.01 mol (1.71 g) of 1 and 0.03 mol of 2 was carried out in absolute methanol and refluxed with stirring for 24 hr. The residue was evaporated and dissolved in hot water. The compounds 3 were precipitated after cooling and recrystallized from water.

Study of surface activity: Surface tension. Measure-

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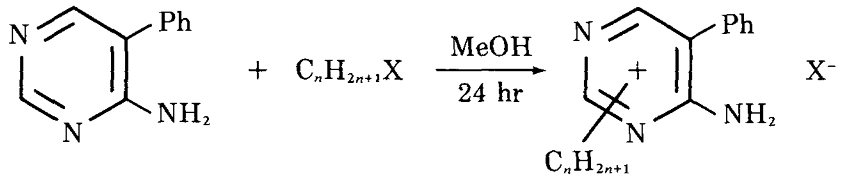

1 2 3

a: n=6, X=I; d: n=12, X=Br;
b: n=8, X=Br; e: n=14, X=Br.
c: n=10, X=Br;

SCHEME 1

TABLE 1

Physical, Analytical and Spectral Data of Cationic Surfactants 3 (a, b, c, d, e)

Compound	M.P. °C	Yield	Molecular Formula MW	Analysis % Calcd/Found C	H	N	Spectral Data
3a[a]	67-70	60	$C_{16}H_{22}N_3I$ 383	50.13 50.31	5.74 5.81	10.96 11.43	Ir (Nujol, cm^{-1}):3330 (NH_2), 3140 (NH_2), 1670 (C=N); nmr (D_2O, δ):9.10 s(1H), 8.61 s(1H), 7.60-8.16 m (5H), 4.70 t (2H), 0.86-2.66 m (11H); ms:m/z 256(7), 212(4), 198(6), 182(15), 171(99), 170(100), 127(4).
3b	66-69	60	$C_{18}H_{26}N_3Br$ 364	59.34 59.71	7.14 7.29	11.53 11.81	Ir (Nujol, cm^{-1}):3310 (NH), 3170 (NH_2), 1640 (C=N); nmr (D_2O, δ):9.00 s(1H), 8.41 s(1H), 7.58-8.08 m(5H), 1.00-2.00 m(15H); ms:m/z 223(3), 171(3), 170(3), 83(5), 70(12), 56(18).
3c	61-64	70	$C_{20}H_{30}N_3Br$ 392	61.22 61.35	7.65 7.71	10.71 11.25	Ir (Nujol, cm^{-1}):3330 (NH_2), 3150 (NH_2), 1630 (C=N); nmr(D_2O, δ):9.33 s(1H), 8.76 s(1H), 7.91-8.16 m(5H), 1.60-1.91 m(19H); ms:m/z 313(4), 299(3), 198(5), 171(92), 170(100), 155(5), 141(5).
3d	78-81	76	$C_{22}H_{34}N_3Br$ 420	62.85 62.88	8.09 8.12	10.00 9.67	Ir (Nujol, cm^{-1}):3300 (NH_2), 3130 (NH_2), 1640 (C=N); nmr (D_2O, δ):9.40 s(1H), 8.75 s(1H), 7.73-8.16 m(5H), 0.90-2.06 m(23H); ms:m/z 340(2), 238(5), 223(12), 210(9), 198(4), 171(92), 170(100).
3e	53-56	80	$C_{24}H_{38}N_3Br$ 448	64.28 64.21	8.48 8.44	9.37 9.12	Ir (Nujol, cm^{-1}): 3320 (NH_2), 3170 (NH_2), 1630 (C=N); nmr (D_2O, δ):8.98 s(1H), 8.35 s(1H), 7.08-8.00 m(5H), 1.36-2.41 m(27H); ms:m/z 359(6), 279(10), 238(5), 224 (23), 198 (7), 182 (5), 171 (98), 170(100).

[a] Compound 3a showed a triplet at 4.7 δ(2 methylenic protons adjacent to the N atom). For compounds 3(b-e) this peak was not visible, probably because it was mixed with the D_2O signal.

ments of surface tension were made using a Du Noüy Model Cambridge Tensiometer at 22 C and are given in Table 2.

Critical micelle concentrations (CMC) of the compounds 3 also were determined and are summarized in Table 3.

After-treatment of direct dyed cotton fabrics. The cationic surfactant 3e was used as representative of the cationic surfactant series for the after-treatment of the cotton fabric dyed with direct dye.

Dyeing process: Greek bleached cotton fabrics (commercially available) were dyed in a dyeing machine Model Rotadyer John Jeffreys Ltd., Rochdale Bumbury with the direct dye "Ciba Solophenyl Orange TGL" (3% dye, 20 g/l glauber salt, liquor ratio 20:1, exhaust method) (5).

The temperature of the dyeing bath was gradually raised from 50 to 100 C for 1 hr. The glauber salt was added at boiling in two portions within an interval of 15 min. After dyeing, the fabric was thoroughly rinsed with cold water and dried. The after-treatment of the dyed fabric was made with the cationic surfactant 3e (in

TABLE 2

Surface Tensions for Compounds 3(a, b, c, d, e)

3a		3b		3c		3d		3e	
Log conc.	Surface tension (dynes.cm^{-1})	Log conc.	Surface tension (dynes.cm^{-1})	Log conc.	Surface tension (dynes.cm^{-1})	Log conc.	Surface tension (dynes.cm^{-1})	Log conc.	Surface tension (dynes.cm^{-1})
−1.5	43.4	−1.8	42.4	−1.8	37.0	−2.0	36.7	−2.1	34.0
−1.6	50.9	−2.0	42.4	−2.0	37.0	−2.1	36.7	−2.3	34.0
−2.0	52.2	−2.1	46.1	−2.1	42.1	−2.3	32.9	−2.6	35.2
−2.1	53.4	−2.3	49.3	−2.3	46.4	−2.6	36.0	−3.0	36.4
−2.2	56.9	−2.6	54.9	−2.6	52.6	−3.0	41.3	−3.1	41.5
−2.4	62.8	−3.0	56.2	−3.0	55.0	−3.1	51.7	−3.3	43.1
−2.6	63.6	−3.1	60.6	−3.1	57.6	−3.3	57.7	−3.6	50.8
−3.3	71.4	−3.3	60.3	−3.3	61.8	−3.6	60.9	−4.0	54.4
−3.9	72.1	−3.6	65.7	−3.6	65.5	−4.0	65.7		
−4.6	72.1	−4.0	66.9	−4.0	67.4				
−6.2	72.1								

TABLE 3

CMC and Krafft Points of Compounds 3(a, b, c, d, e)

		CMC	
Compound	Krafft point °C	Log conct.	γ(dynes.cm^{-1})
3a	6.0	—	—
3b	9.2	−2.00	42.4
3c	13.5	−2.04	37.0
3d	17.0	−2.10	36.7
3e	26.6	−2.55	34.0

TABLE 4

Inhibition Zones (mm) Obtained with the Cationic Surfactants 3

Compound	*S. aureas*	*B. subtilis*	*Escherichia coli*			*C. albicans*
3a	—	—	—	—	—	—
3b	5	—	—	—	—	14
3c	7	—	—	—	—	25
3d	14	11	7	10	7	22
3e	7	6	—	—	—	11

concentrations 2%, 1% and 0.5% on the weight of the fabric), liquor ratio 40:1, pH 6, working temperature 45 C.

Strips of the direct dyed cotton fabric measuring 4 × 10 cm were immersed in the previous recipe in a thermostated, shaken water bath for 0.5 hr. The pieces were then squeezed and dried at 60 C. A comparison blank was similarly treated. Bleeding was measured spectrophotometrically using a Spectronic 20 Bausch & Lomb spectrophotometer at λmax 419 nm. The concentration of the bleeded dye in the absence of the cationic surfactant 3e was 0.0047%, whereas in the presence of 3e at concentrations 2%, 1% and 0.5% it was 0.0%, 0.0013% and 0.0020%, respectively.

Washing fastness was performed in 5 g/l commercially available soap, liquor ratio 50:1, during 45 min at 50 C in a shaken thermostated water bath. One piece of white cotton fabric and one of wool were sewn on each side of the dyed and after-treated fabric. The dyed and after-treated fabric were assessed for the color change the same score of 4, whereas for the cotton stain the scores of 1-2 and 2-3 respectively (ISO-test No. 2).

The Krafft points were measured by gradually heating a 1% dispersion of the test compounds until a clear solution was obtained (6,7). These are summarized in Table 3.

The antimicrobial activity of the cationic surfactants 3 was determined by the diffusion method (8). T.S.A. (Trypticase Soy Agar, Biolife) was inoculated with the test microorganisms *Staphylococcus aureas* (strain Oxford) NCTC 6571, *Bacillus subtilis, Candida albicans* and *Escherichia coli* 1,2 and 3 (locally isolated strain, Department of Microbiology, Faculty of Medicine, University of Thessaloniki). Each 100 ml of the medium received 1 ml of 24-hr broth culture. Then 0.01 ml of the tested compound solution in water (1 mg/ml) was placed separately in cups (4 mm diam) cut in the agar medium. The plates were incubated at 37 C for 24 hr. The resulting inhibition zones were measured and summarized in Table 4.

RESULTS AND DISCUSSION

The five prepared cationic surfactants lower the surface tension of water to an extent depending upon their concentration in the solution and the length of the alkyl chain. The higher the concentration of the compound in the solution, the lower is the surface tension until the critical micelle concentration (CMC) is reached, whereafter the surface tension is concentration-independent (9). Compound 3d, however, shows a minimum in surface tension values (Fig. 1). The compound 3a does not reach its critical micelle concentration (if it has any) in the concentration range investigated.

The longer the alkyl chain of the compound, the lower are the concentration and the surface tension values of the CMC (10).

The solubility in water of the cationic surfactants 3 depends again on the length of the alkyl chain, that is the 3e (the most hydrophobic compound) is the most

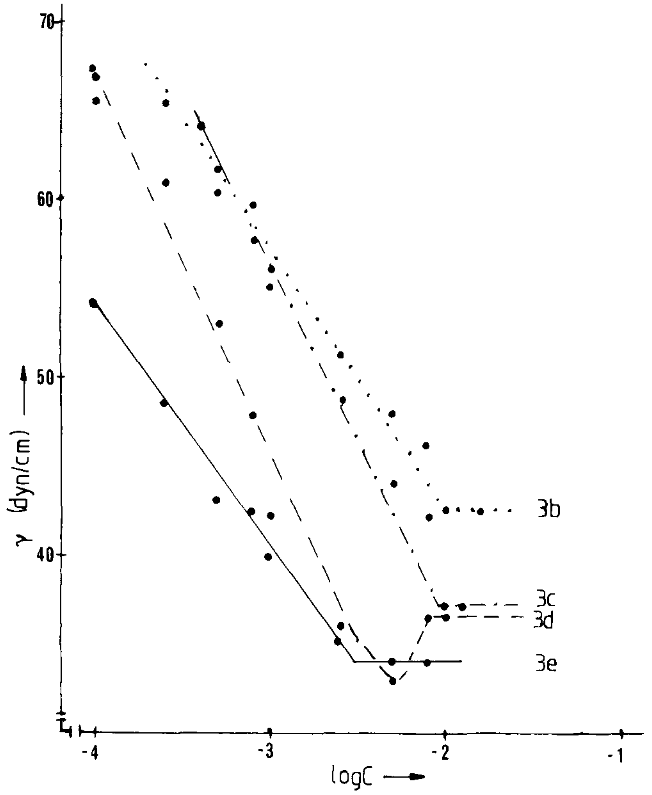

FIG. 1. Log. molar concentration-surface tension for compounds 3(b-e).

insoluble of all five (high Krafft point), whereas the 3a is the most soluble (low Krafft point).

The after-treated fabric with 3e gave a satisfactory result in the washing fastness test.

All the compounds 3 except 3a show strong antimicrobial activity.

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Counterion Effects on the Aqueous Solution Viscosity of Cationic Surfactants

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The effect of varying counterion structure on the aqueous solution viscosity of various cationic surfactants was systematically examined for compounds of the type: $CH_3(CH_2)_xN(CH_3)_3YAr$. Ar = functionally substituted aryl moieties and Y = carboxylate (CO_2^-), sulfinate (SO_2^-) or sulfonate (SO_3^-).

Aqueous solution viscosity, which is assumed to be a measure of ion pair stability, is clearly affected by anion and cation structure, temperature, concentration and stoichiometry. An ortho substituent to the anionic functionality, e.g. hydroxyl, substantially increases ion pair stabilization. Ion pair stability is also enhanced by increasing the solution concentration, decreasing temperature, increasing cation/anion ratio or by increasing the alkyl (x) chain length.

Unusual counterion effects have been reported for cationic surfactants of the quaternary ammonium and alkyl pyridinium type (1-5). For example, sodium salicylate exhibited unusually large viscosity effects with micellar solutions of cetyltrimethylammonium (CTA^+) which far exceeded those previously found for other CTA^+ salts (6). Substantial viscoelasticity and low critical micelle concentrations for the meta and para chlorobenzoate salts of CTA^+ also have been reported (2). However, most other substituted benzoic acids were found to have little or no unusual effect on surface or colloid properties when they were used as alternative counterions to bromide in CTAB.

Subsequent work by Gravsholt, Hyde and others has shown that the viscosity increases observed with salicylic acid/cationic surfactant complexes are actually due to concentration dependent anion/cation aggregate structures in solution (5,7). Work completed thus far suggests that there is a regular increase in solution order for ionic surfactants as follows: single ions, ion pairs, spherical micelles and rod shaped or lamellar micelles, leading finally to crystals. Such effects clearly have a direct bearing on the consistency and stability of formulated liquid cationic detergents.

A previous paper detailed the behavior of docosyltri-