Synthesis and Properties of New Cationic Surfactants. II. Odd Homologous Members

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In connection with our previous work on the synthesis and study of new pyrimidinium cationic surfactants, some new members of the N-alkyl-pyrimidinium salts homologous series were prepared. The above compounds contain long-chain alkyl groups of 7, 9, 11, 13, 15, 16, 17 and 18 carbon atoms.

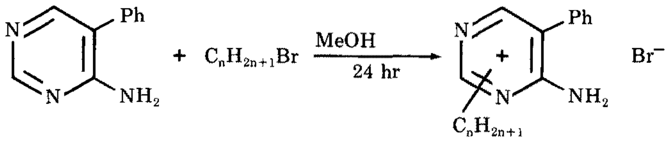
The series of these compounds having an alkyl chain of C_7-C_{18} has been completed, and a correlation between their constitution and some properties has been made.

The structural assignment of these compounds was made on the basis of the elemental analysis and IR, NMR, MS spectroscopic data. Surface tension, water solubility and antimicrobial activities were determined for these surfactants. The wet fastness of direct dyed cotton fabrics after-treated with these cationics also was studied.

Cationic surfactants with a positively charged nitrogen atom and one or more hydrophobic long chain alkyl substituents display antimicrobial activities (1). They also are used as auxiliaries in dyeing fabrics (1-4).

Reactive quaternary pyrimidinium compounds are known as pre-treatment agents in cellulosic fibers (5-7). On the other hand, cationic pyrimidinium surfactants have not been studied as fixing agents or antimicrobials.

In an extension of our interest in the synthesis and study of properties of cationic surfactants derived from 4-amino-5-phenyl-pyrimidine **I** and alkyl halides **II**, some new compounds having the general formula **III** were prepared.



I II III

a:n=7, b:n=9, c:n=11,
d:n=13, e:n=15, f:n=16,
g:n=17, h:n=18

The compounds **III(a-e)** and **IIIg** are odd members of the homologous series of N-alkyl-pyrimidinium salts, a relatively new class of cationic surfactants.

We have completed a series of these cationics and attempted to correlate their constitution (even and odd members) with their properties according to similar data given in the literature (8-12).

The above compounds **III** were obtained in good yields (60-90%) according to the method described earlier (13).

The structural assignment of the prepared compounds was made on the basis of the elemental analysis of infrared, nuclear magnetic resonance and mass spectroscopic data, which are summarized in Table 1.

EXPERIMENTAL PROCEDURE

All melting points are uncorrected and determined with a Koffler hot-stage apparatus. IR spectra were obtained with a Perkin-Elmer 281B spectrophotometer. NMR spectra reported in δ units were recorded with a Varian A-60A spectrometer using $CDCl_3$ or D_2O as solvent and tetramethylsilane as an internal or external standard, respectively. The mass spectra were measured with a Hitachi-Perkin-Elmer Model RMU-6L single focusing spectrometer using a direct insertion probe with an ionization energy of 70 eV. Elemental analyses were performed with a Karlo Erba MOD 1106 Elemental Analyzer.

All the alkylbromides **II** used were commercially available. 4-Amino-5-phenyl-pyrimidine **I** was prepared according to a known method (14).

General procedure for the preparation of halide salts of 1(3)-alkyl-4-amino-5-phenyl-pyrimidines I. A mixture of 0.01 mol (1.71 g) of **I** and a little excess (0.015 mol) of **II(a-h)** was carried out in methanol and refluxed with stirring for 24 hr. In the reaction mixture ether was added, the pyrimidine salt precipitated, then filtered off, and the residue was washed with ether and dissolved in cold water. Undissolved material was lyophilized.

The compounds **III** are decomposed on heating. The relatively broad range in mp's and the differences observed between calculated and found values in the elemental analysis are due to that decomposition.

Study of surface activity. Measurements of surface tension were made using a Du Nouy Model Cambridge Tensiometer at 25±0.2C.

Critical micelle concentrations (CMC) of the compounds **III** were also determined and are summarized in Table 2.

The Krafft points were measured by gradually heating a 1% dispersion of the test compounds until a clear solution was obtained (15,16) (Table 2). Table 2 also shows the Krafft points of the compounds n=6, 8, 10, 12, 14 (even number of carbon atoms) (13).

After-treatment of direct dyed cotton fabrics. All the above cationics **III(a-h)** were examined as fixing agents on direct dyed cotton fabrics (17) (Pegiadou-Koemtjopoulou, E. Tsatsaroni, J. Eleftheriadis and I. Iossifidis, unpublished data). We described here the procedure for the representative cationic surfactant **IIId**.

Dyeing process. Greek bleached cotton fabrics (commercially available) were dyed in a Model Rotadyer dyeing machine (John Jeffreys Ltd., Rochdale, Banbury) with the direct dye "Ciba Solophenyl Rouge 3BL" (3% dye, 20 g/l Glauber salt, liquor ratio 1:20). The dyeing process was made according to the exhaust method (13,17).

After-treatment of the dyed fabric. The after-treatment of the dyed fabric was made with 2%, 1% and 0.4% cationic surfactant **IIId** (on the weight of the

TABLE 1

Physical, Analytical and Spectral Data of Cationic Surfactants III(a-h)

Compound	M.P.C. °C (decomp.)	Yield	Molecular Formula	Analysis % Calcd/Found			Spectral Data
			MW	C	N	H	
IIIa	74-79	75	$C_{17}H_{24}N_3Br$ 350	58.28 56.13	12.00 12.33	6.85 6.92	IR(Nujol, cm^{-1}):3300(NH_2), 3140(NH_2), 1670(C=N); NMR($CDCl_3$, δ):9.40(s,1H), 8.25(s,1H), 7.50-7.76(m,5H), 4.64(t,2H), 0.68-1.75(m,13H); MS:m/z 269(8), 268(10), 242(8), 171(80), 170(100), 117(10), 102(10).
IIIb	67-73	87	$C_{19}H_{28}N_3Br$ 378	60.31 59.01	11.11 11.76	7.40 7.02	IR(Nujol, cm^{-1}):3320(NH_2), 3150(NH_2), 1650(C=N); NMR(D_2O,δ):9.10(s,1H), 8.55(s,1H), 7.75-8.00(m,5H), 1.38-1.73(m,17H)[a]; MS:m/z 283(5), 199(6), 171(90), 170(100), 127(10), 117(11), 102(10).
IIIc	45-50	82	$C_{21}H_{32}N_3Br$ 406	62.06 60.88	10.34 10.85	7.88 8.05	IR(Nujol, cm^{-1}):3290(NH_2), 3130(NH_2), 1665(C=N); NMR(D_2O,δ):9.00(s,1H), 8.50(s,1H), 7.86-8.00(m,5H), 0.88-1.66(m,21H)[a]; MS:m/z 252(10), 171(98), 170(100), 155(12), 117(8), 102(9).
IIId	52-56	70	$C_{23}H_{36}N_3Br$ 434	63.59 61.23	9.67 10.07	8.29 8.38	IR(Nujol, cm^{-1}):3305(NH_2), 3130(NH_2), 1650(C=N); NMR(CDC_3,δ):9.41(s,1H), 8.16(s,1H), 7.33-7.76(m,5H), 4.60(t,2H), 0.58-2.33(m,25H); MS:m/z 274(6), 193(5), 171(10), 170(10), 122(65), 105(100).
IIIe	53-59	70	$C_{25}H_{40}N_3Br$ 462	64.93 62.00	9.16 9.43	8.65 8.46	IR(Nujol, cm^{-1}):3290(NH_2), 3130(NH_2), 1680(C=N); NMR($CDCl_3$,δ):9.36(s,1H), 8.20(s,1H), 7.30-7.80(m,5H), 4.65(t,2H), 0.80-2.10(m,29H); MS:m/z 381(5), 269(8), 211(14), 171(90), 170(100), 117(12), 102(20).
IIIf	73-80	70	$C_{26}H_{43}N_3Br$ 476	65.54 64.12	8.82 9.37	8.82 8.60	IR(Nujol, cm^{-1}):3300(NH_2), 3130(NH_2), 1670(C=N); NMR(D_2O,δ)9.05(s,1H), 8.26(s,1H), 7.40-7.85(m,5H), 1.05-1.54(m,31H)[a]; MS:m/z 282(8), 225(10), 171(30), 170(32), 102(19).
IIIg	52-56	85	$C_{27}H_{44}N_3Br$ 490	66.12 64.78	8.57 8.61	8.97 9.04	IR(Nujol, cm^{-1}):3330(NH_2), 3160(NH_2), 1650(C=N); NMR($CDCl_3$,δ):9.31(s,1H), 8.05(s,1H), 7.25-7.50(m,5H), 3.50(t,2H), 0.75-2.16(m,33H); MS:m/z 395(8), 318(8), 274(9), 238(18), 171(15), 170(16), 135(16), 99(70).
IIIh	68-73	90	$C_{28}H_{46}N_3Br$ 504	66.66 65.10	8.33 7.95	9.12 9.35	IR(Nujol, cm^{-1}):3330(NH_2), 3160(NH_2), 1650(C=N); NMR($CDCl_3$,δ):9.28(s,1H), 8.16(s,1H), 7.36-7.78(m,5H), 3.53(t,2H), 0.85-2.25(m,35H); MS:m/z 334(10), 332(10), 288(10), 253(20), 172(40), 171(100), 170(99), 117(19), 102(22).

[a] The triplet due to the two methylenic protons adjacent to the N of the pyrimidine ring was not visible, probably because it was mixed with the D_2O signal.

TABLE 2

CMC and Krafft points of Compounds III(a-h) and III(a′-e′)[a]

Compound	Krafft point °C	CMC	
		Conct(mol/lt)	γ (dynes/cm)
IIIa	18.0	$2.50 \bullet 10^{-3}$	53.83
IIIb	22.8	$8.31 \bullet 10^{-4}$	50.29
IIIc	27.0	$5.00 \bullet 10^{-4}$	46.56
IIId	29.0	$4.26 \bullet 10^{-4}$	41.61
IIIe	32.0	$3.31 \bullet 10^{-4}$	37.87
IIIf	31.5	$2.88 \bullet 10^{-4}$	34.64
IIIg	37.0	$2.37 \bullet 10^{-4}$	37.57
IIIh		$7.58 \bullet 10^{-5}$	34.39
IIIa′	6.0		
IIIb′	9.2		
IIIc′	13.5		
IIId′	17.0		
IIIe′	26.6		

[a] **III**(a′-e′): Compounds of the same structure with $R=C_nH_{2n+1}$, n=6,8,10,12,14 (13).

TABLE 3

Inhibition Zones (mm) Obtained with the Cationic Surfactants III

Compound	S. aureas	B. subtilis	Escherichia coli	C. Albicans
IIIa	–	–	–	–
IIIb	–	–	–	–
IIIc	13	12	12	13
IIId	10	10	5	13
IIIe	10	8	7	10
IIIf	–	–	–	–
IIIg	–	–	–	–
IIIh	–	–	–	–

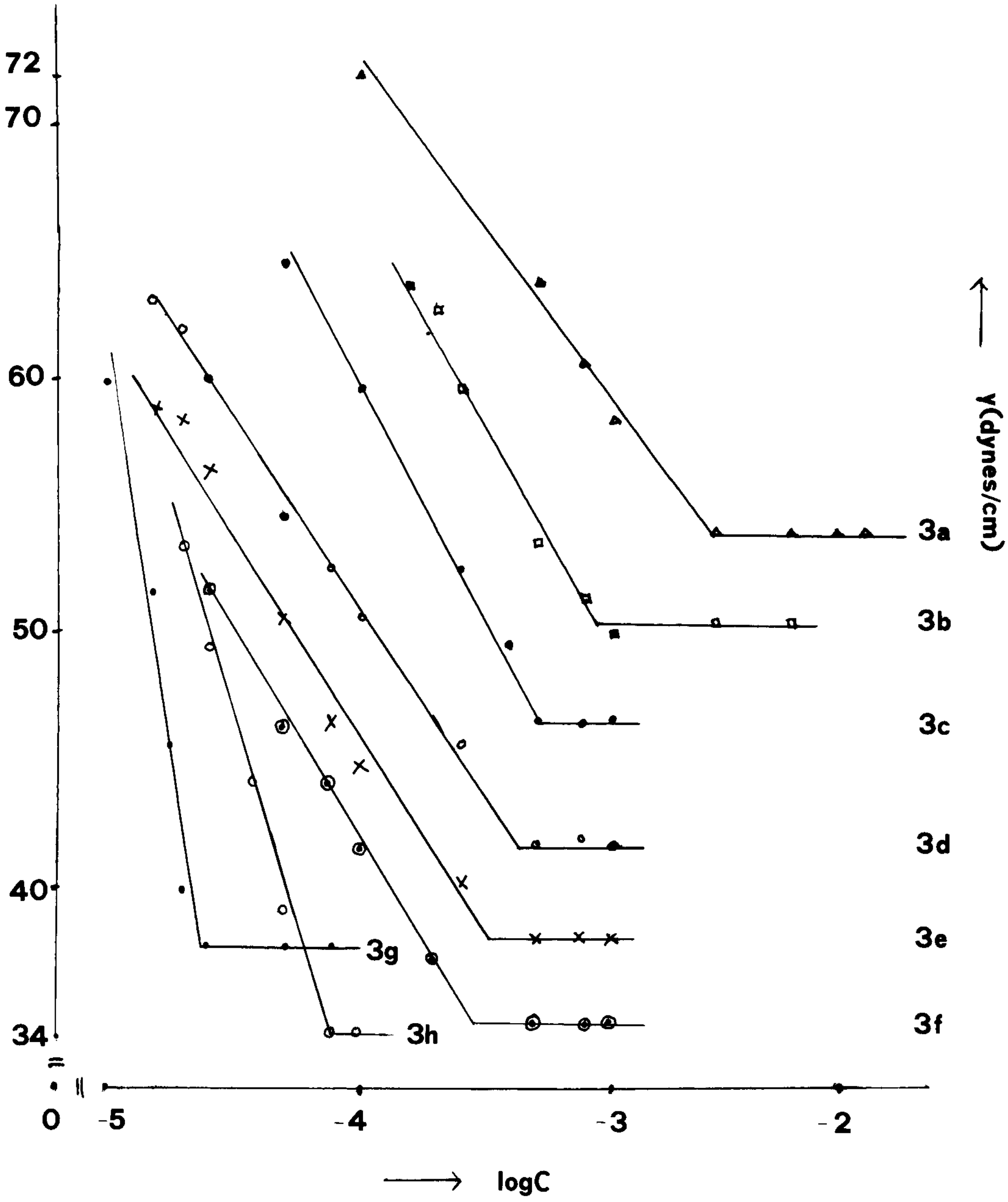


FIG. 1. Log molar concentration vs surface tension for compounds III(a-h).

fabric), liquor ratio 1:40, pH 6, washing temperature 45 C.

Strips of the direct dyed cotton measuring 4×10 cm and weighing 0.425 g were immersed in the previous recipe in a thermostated shaken water bath for 30 min. A comparison blank was similarly treated. Bleeding was measured spectrophotometrically using a Spectronic 20 Bausch & Lomb spectrophotometer at λ_{max} 520 nm.

The concentration of the bled dye in the absence of cationic surfactant **IIId** was 0.0104%, whereas in the presence of the **IIId** at concentrations 2%, 1% and 0.4%, it was 0%, 0% and 0.001%, respectively.

Washing fastness was performed in 5 g/l commercially available soap, liquor ratio 1:50, for 45 min at 50C in a shaken, thermostated water bath (ISO test No. 2).

The procedure was analogous to that described previously (13). The dyed and after-treated with 1% of **IIId** fabrics were assessed for the color change the same score of 4, whereas the scores of 1-2 and 3-4, respectively, were assessed for the cotton stains.

Antimicrobial activity. The antimicrobial activities of the cationic surfactants **III** were determined by the diffusion method (18). T.S.A. (Trypticase Soy Agar, Biolife) was inoculated with the test organisms *Staphylococcus aureas* (strain Oxford) NCTC 6571, *Bacillus subtilis*, *Escherichia coli* ATCC 10418 and *Candida albicans*. The process was analogous to that described previously (13). The concentration of the tested compounds solution was 1 mg/ml. The resulting inhibition zones were measured and are summarized in Table 3.

RESULTS AND DISCUSSION

The prepared cationic surfactants lower the surface tension of water to an extent depending upon their concentration in the solution, the length of the alkyl chain and the even or odd number of carbon atoms of the molecule. 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 (Fig. 1).

The alkyl pyrimidine salts with an odd number of carbon atoms in their molecule have greater surface activity when compared with the corresponding even carbon number molecules (13). Table 2 shows the critical micelle concentrations of the compounds **III(a-h)**.

The longer the alkyl chain of the compound (in each of the two series), the lower are the concentration and surface tension values of the CMC.

The solubility in water (Krafft point) of the cationic surfactants **III** depends again on the length of the alkyl chain and whether the alkyl group has an odd number of carbon atoms. It is obvious (Fig. 2) that the even carbon number members have a higher solubility (lower Krafft point) than the odd ones. That is in agreement with the Krafft point values of the sodium-n-alkyl sulphates given in the literature (8).

The alternating properties between the compounds with even and odd numbers of carbon atoms are in agreement with similar data in the literature for sodium-n-alkyl sulphates (8,9), saturated fatty acids (10) and n-dicarboxylic acids (11) and can be explained on the basis of the structural differences between even and odd members of homologous series (9,12).

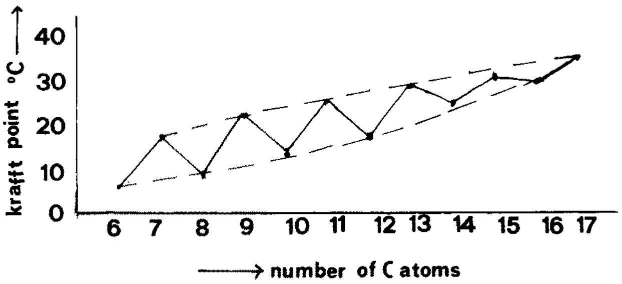


FIG 2. Krafft point °C vs number of carbon atoms for compounds III(a-g) and III(a′-e′). III(a′-e′): Compounds of the same structure with $R=C_nH_{2n+1}$, n=6, 8, 10, 12, 14 (13).

The **IIId** after-treated fabric gave a satisfactory result in the washing fastness test.

Only the compounds **III(c-e)** show antimicrobial activity against the tested microorganisms.

In conclusion, only the compounds with $R=C_nH_{2n+1}$, where n=11-15, show satisfactory antimicrobial activity. [Compare with the compounds in (13).]

This relation between biocidal efficiency and the length of the alkyl group is in agreement with similar data (19,20) for some non-aromatic quaternary ammonium salts and amine oxides. The above compounds show optimum antimicrobial efficiency in the area of 10-14 carbon atoms in the long chain.

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