Cationic Surface-Active Agents

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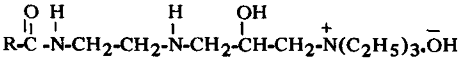
ABSTRACT

A group of cationic surfactants of 2-hydroxy-3-(2-heptadecyl, pentadecyl or undecyl amidoethylamino) propane-1-triethyl ammonium hydroxides was prepared. These derivatives were purified and characterized by microanalysis, molecular weight determination, infrared, nuclear magnetic resonance, and mass spectra studies. Their surface and interfacial tensions were determined.

INTRODUCTION

It has been reported by many investigators (1-3) that cationic surfactants, especially those having quaternary ammonium groups, display antimicrobial activities and emulsifying properties in addition to their anticorrosive effects. These facts encouraged investigation of a novel group of cationic surfactants having the general formula:



$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{H}{|}}{N}\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{H}{|}}{N}\text{-}CH_2\text{-}\overset{\overset{OH}{|}}{C}H\text{-}CH_2\text{-}\overset{+}{N}(C_2H_5)_3.\overset{-}{O}H$$

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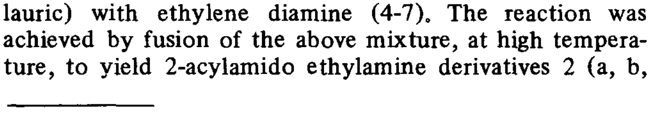
R = a, heptadecyl; b, pentadecyl; c, undecyl.

The design of these compounds was based on the presence of the essential long chain aliphatic hydrocarbon and the quaternary ammonium group, in addition to the chelating amido, amino, and hydroxyl groups. The preparation of compound 1 was achieved by condensation of N-acylamido-ethylamine derivatives 2 with N-(2,3-epoxypropyl) triethyl ammonium chloride 3 (Scheme I).

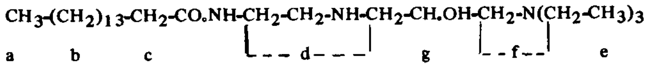


SCHEME I

Compound 2 was obtained by condensation of the chosen long chain fatty acid (a, stearic; b, palmitic; and c, lauric) with ethylene diamine (4-7). The reaction was achieved by fusion of the above mixture, at high temperature, to yield 2-acylamido ethylamine derivatives 2 (a, b, and c), as reported. The required quaternary ammonium group was prepared by stirring a mixture of epichlorohydrin with triethylamine (8-11) in aqueous medium at room temperature to yield N(2,3-epoxypropyl) triethyl ammonium chloride 3.

The optimum reaction conditions required to obtain compounds 1 (a, b, and c) at maximum yields were determined by variation of the relative equivalents of compounds 2 and 3 and the reaction solvents (Table I). It was observed that the maximum yields were performed by reacting equimolar amounts of 2 and 3 in isopropanol.

The structural formula of compound 1 (a, b, and c) was confirmed by elemental microanalysis, molecular weight determination,. infrared (IR, nuclear magnetic resonance (NMR), and mass spectra (Table II). Study of infrared spectra of compound 1 (a, b, and c) showed the characteristic bands at 4400-4500 cm^{-1} for γ (OH), 3300-3400 cm^{-1} for γ (NH), 1650, 1560 cm^{-1} amide I and amide II bands, respectively. NMR spectra for 1b in deuteropyridine, as a representative sample, exhibited the following:



$$\underset{a}{CH_3}\text{-}\underset{b}{(CH_2)_{13}}\text{-}\underset{c}{CH_2}\text{-}CO.NH\text{-}\underbrace{CH_2\text{-}CH_2\text{-}NH\text{-}CH_2}_{d}\text{-}\underset{g}{CH}.OH\text{-}\underbrace{CH_2\text{-}N(CH_2}_{f}\text{-}\underset{e}{CH_3})_3$$

at δ ppm, 0.5 (S, 3H, a-CH_3), 0.66 (S, 26H, b-CH_2), 1.05 (S,2H,c-CH_2), 1.45, 1.82 (brd, 6H, d-CH_2), 2.24 (S, 9H, e-CH_3), 3.9 (S, 8H, f-CH_2), and 4.3 (1H, g-CH).

EXPERIMENTAL PROCEDURES

All melting points are uncorrected; microanalysis and molecular weight determination by the osmometric method, using chloroform as solvent, have been done at the microanalytical unit, Faculty of Science, Cairo University, Cairo, Egypt. The IR spectra as Nujul mul were measured

TABLE I

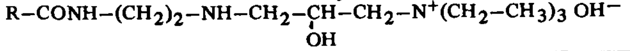
Effect of Molar Ratio of 2b and 3 and the Solvent on the Yield of Compound 1b[a]

Molar ratio 2b:	Solvent	% Yield
1:1	Isopropanol	25
1:2	Isopropanol	13.8
1:1	Benzene	23
1:1	Acetic acid	21

[a] The yield refers to 2b reacted.

TABLE II

Characterization of Compound 1 (a, b, and c)



$$R\text{-}CONH\text{-}(CH_2)_2\text{-}NH\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{C}H\text{-}CH_2\text{-}N^+(CH_2\text{-}CH_3)_3\ OH^-$$

R	Mol. formula	Mol. weight[a] Calcd.	Mol. weight[a] Obsvd.	c% Calcd.	c% Obsvd.	H% Calcd.	H% Obsvd.	N% Calcd.	N% Obsvd.
1a, Heptadecyl	$C_{29}H_{63}N_3O_3.2H_2O$	537	580	64.80	64.90	12.47	11.90	7.82	8.00
1b, Pentadecyl	$C_{27}H_{59}N_3O_3.2H_2O$	509	508	63.65	63.00	12.37	12.60	8.25	8.70
1c, Undecyl	$C_{23}H_{51}N_3O_3.2H_2O$	453	457	60.92	60.30	12.14	12.50	9.27	8.90

[a] Allowable error of the mol. weight determination by the osmometric method is 10%.

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[1] Author to whom all correspondence should be addressed.

TABLE III

Surface Tensions and Critical Micelle Concentrations (CMC) for Compound 1(a, b, and c)

Compound	Log conc.	Surface tension (dyne cm^{-1})	CMC	
			Log conc.	Surface tension (dyne cm^{-1})
1a	-1.72932	42.35	-2.03	42.3
	-2.03058	42.40		
	-2.33161	44.05		
	-2.82608	47.75		
	-3.12726	50.40		
	-3.42829	50.50		
	-3.72932	55.05		
1b	-1.20	42.00	-1.4	4.2
	-1.40483	42.00		
	-1.70586	43.70		
	-2.00689	45.10		
	-2.30793	45.00		
	-2.60896	47.10		
	-3.40483	50.90		
1c	-1.05789	31.20	-2.76	27.4
	-1.65995	31.20		
	-2.05799	30.70		
	-2.35951	30.45		
	-2.65995	27.10		
	-2.96098	28.10		
	-3.35892	31.40		
	-3.65995	33.30		
	-3.96098	37.30		
	-4.26201	48.70		
	-4.56383	64.20		

TABLE IV

Interfacial Tensions and Critical Micelle Concentrations (CMC) for Compound 1 (a and b)

Compound	Log conc.	Interfacial tension (dyne cm^{-1})	Log conc.	CMC Interfacial tension (dyne cm^{-1})
1a	-2.031	10.40	-2.57	10.4
	-2.222	10.44		
	-2.633	10.80		
	-2.827	11.80		
	-3.730	17.40		
1b	-1.706	11.00	-2.17	11
	-2.007	11.00		
	-2.308	12.10		
	-2.609	12.80		
	-3.104	15.00		
	-3.405	16.10		
	-3.706	17.50		

on a Pye-Unicam SR-1000 Infrared Spectrophotometer and NMR spectra on a Varian Spectrophotometer using d_5-pyridine as solvent and tetramethylsilane (TMS) as internal standard.

N-Acyl-1,2-Diamino Ethane 2 (a, b, and c)

The N-heptadecyl, pentadecyl, and undecyl amide derivatives were prepared by condensation of equimolar amounts of the corresponding pure fatty acid (Unilever-Emery Gouda Co.) and ethylene diamine (Fisher Scientific Co.). The reaction mixture was heated at 140-180 C for 10 hr. The liberated theoretical amount of water was collected to ensure the reaction completion, using Dean and Stark apparatus and benzene as solvent. The organic solvent was removed under reduced pressure, and the residue was recrystallized from isopropanol; where R, yield %, and mp°C are: 2a, heptadecyl, 51, 151-52; 2b, pentadecyl, 67, 147-8; 2c, undecyl, 60, 150-1.

2,3-Epoxypropyl-Triethyl Ammonium Chloride 3

A mixture of epichlorohydrin (9.25 g, 0.1 mol) and of triethylamine (10.19 g, 0.1 mol) in 10 ml of distilled water was stirred at room temperature for 5½ hr. The resulting clear solution which consists mainly of compound 3 was used directly in the next step without further purification.

2-Hydroxy-3 (2-Heptadecyl, Pentadecyl, or Undecyl Amido Ethylamino) Propane-1-Triethyl Ammonium Hydroxide 1 (a, b, and c)

A mixture (0.1 mol) of the required fatty acid amidoamine 2 and an adequate amount of 2,3-epoxy-propyl triethyl ammonium chloride 3 in 100 ml of the appropriate solvent, was stirred under reflux for 24 hr. The solvent was evaporated, and the remaining waxy residue was thoroughly extracted with hot distilled water till no froth persisted. The aqueous extract was subjected to high speed centrifugation (10^4 rpm) for 15 min to remove the suspended particles of the unreacted matter. The supernatant clear aqueous layer was decanted, shaken with petroleum ether (40-60 C) to remove the residual unreacted matter, and rendered alkaline with 10% sodium hydroxide solution. The product was extracted three times each with 50-ml portions of isoamyl alcohol (12). The solvent was evaporated on a boiling water bath under vacuum to leave a pale yellow waxy residue. Several experiments were done to increase the yield of compound 1b as a representative product using different solvents and molar ratios of 2b and 3 (Table I). R,

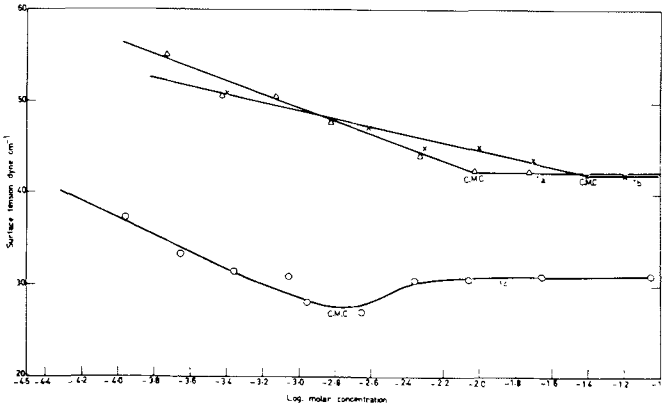

FIG. 1. Log. Molar concentration – surface tension for compounds 1a, 1b, and 1c.

elemental microanalysis data, and molecular weights are recorded in Table II.

The mass spectra data, m/e (relative abundance %) follow: 1a, $C_{29}H_{63}N_3O_3$, 499 (M^+, 1); 1b, $C_{27}H_{59}N_3O_3$, 471 (M^+, 2); 1c, $C_{23}H_{51}N_3O_3$, 417 (M^+, 1).

DISCUSSION

The three prepared compounds showed surface activity, which was manifested in a variety of ways. Thus, for example, they lowered the surface tension of water to extents depending upon their nature and concentration in solution. The measurements of the surface tension were carried out on a Model 21 Fischer Tensiometer at 17 C and 30 sec surface age. Table III and Figure 1 represent the variation of water surface tension γ as a function of the molar concentration logarithm of the additives in solution. As is seen from the curve of this figure, the surface tension decreases linearly with concentration, c, according to:

$$\gamma = a - b \log c$$

where a and b are constants. As the concentration of the additives is further increased, a break in the $\gamma - \log c$ curves is noted at a definite concentration, whereafter γ becomes concentration-independent. Apparently this occurs at the critical micelle concentration (CMC) of the respective compound. Compound 1c however, shows a minimum in γ before the curve levels up to give concentration-independent surface tension values. The minimum surface tensions measured in the case of compound 1 (a, b, and c) amount to 42.3, 42, and 27.4 dyne cm^{-1}, as compared to 73.2 dyne cm^{-1} for pure distilled water at 17 C (13). The new compounds of the present investigation thus lower the surface tension of water to extents similar to those of other cationic surfactants of analogous structure. Komkov et al. (14) reported that 1% aqueous solutions of the compounds of the formulae $C_{13}H_{27}CO_2CH_2\ CH_2\ N^+R_3\ CL-$ and $C_{13}H_{27}CO_2CH_2\ CH_2\ N^+Me_2R'\ Cl-$ have surface tensions varying between 33-41 dyne cm^{-1}. Similarly, Muzyczko et al. (1) found that the surface tension of water at the CMC of compound, $CH_3\ (CH_2)_{17}\ CO\ NH\ (CH_2)_3\ N^+\ (CH_3)_2$ acetate at 25 C, was 39.9 dyne cm^{-1}.

The same behavior noted with water solutions was similarly established with paraffin oil (Table IV and Fig. 2). In these measurements, only compound 1 (a and b) was used. The $\gamma - \log c$ curves also showed a region of linear decrease in γ at low concentrations of the additives, which was followed by concentration-independent values. The CMC in the case of paraffin oil were, however, considerably lower than those for aqueous solutions. The values for 1 (a and b) in case of paraffin oil amount to 2.69 and 6.76 x 10^{-3} mol l^{-1}, as compared to 9.33 and 39.81 x 10^{-3} mol l^{-1} for water solutions.

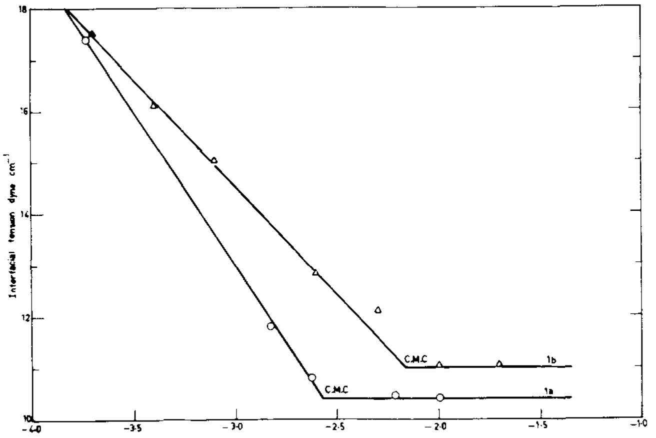

FIG. 2. Log. molar concentration – interfacial tension for compounds 1a and 1b.

The surface activity of the same compounds was further established from their lowering of the electrocapillary curve of Hg in 0.5N HCl. All compounds behaved in the same manner, namely by lowering the interfacial tension of Hg over the entire potential span (0 - 1.5 volt vs. SCE). This reveals that the additives are adsorbed both on the positive and negative branches of the ECM. This finding strongly recommends the application of the compound 1 series as corrosion inhibitors in pickling baths. In fact, our yet unpublished results show that as low as 1 x 10^{-4} M concentration of the three additives was enough to reduce the corrosion rate of low C steel plates in 0.5N NCl to more than 95% at 19 C. Corrosion inhibition increased further with the increase in the concentration of the additives. The bulk of the results, to be published elsewhere, indicate that the additives function by way of chemisorption.

ACKNOWLEDGMENTS

R.T. Holman, Hormel Institute, University of Minnesota, determined the mass spectra for this series of compounds.

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