Synthesis and Properties of Amphoteric Surfactants

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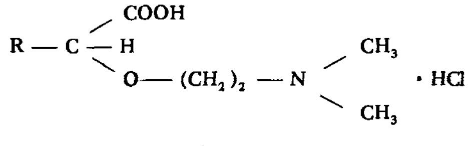
ABSTRACT

Carboxylic amphoteric surfactants containing ether tertiary amino and carboxylic groups were prepared. Specifically, 2-(2-dimethylaminoethoxy)octadecanoic, hexadecanoic and dodecanoic acid hydrochloride were synthesized. Surface and interfacial tension, emulsifying action, corrosion inhibition effect and after-treatment of direct dyed cotton fabrics were determined for these surfactants. Antibacterial activities were also examined.

INTRODUCTION

In an extension of our interest in the synthesis and study of the surface activity of nitrogenous surfactants derived from long chain fatty acids (1), a novel group of amphoteric surfactants possessing an ether linkage, a tertiary amine and a carboxyl group was prepared. Specifically, 2-(2-dimethylaminoethoxy)octadecanoic, hexadecanoic and dodecanoic acid hydrochloride [3(a, b and c)] were synthesized.

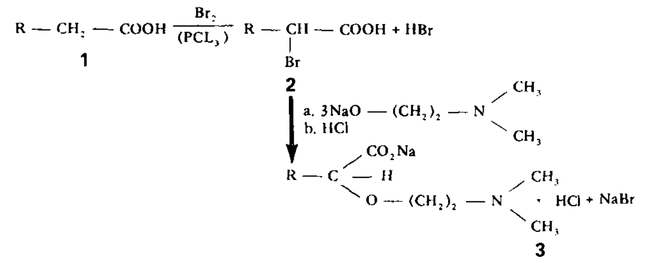


$$R-C(H)(COOH)-O-(CH_2)_2-N(CH_3)_2 \cdot HCl$$

R = a, n-$C_{16}H_{33}$; b, n-$C_{14}H_{29}$; c, n-$C_{10}H_{21}$

The reported activity of amphoteric surfactants (2-4) encouraged the investigation of the surface properties of these compounds. Furthermore, these ether derivatives have the advantage of better resisting the hydrolytic action of either acidic or alkaline working environments (5) than similar surfactants containing ester (6) or amide linkage (7).

The desired compounds were obtained according to the reaction pathway outlined in Scheme I.



SCHEME 1

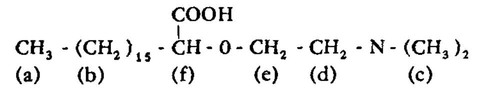
The synthesis of these surfactants comprises the preparation of α-bromo fatty acids by direct bromination of the appropriate fatty acids in the presence of phosphorous trichloride. A method similar to Williamson's synthesis was done (8). Three mol of sodium β-N,N-dimethylaminoethoxide was allowed to react with the α-bromo fatty acid in an aprotic solvent then acidified with aqueous hydrochloric acid to provide compound **3**.

The structural formulas of compounds [**3**(**a**, **b** and **c**)] were confirmed by nitrogen analysis (Table I), infrared (IR) spectra and nuclear magnetic resonance (^{1}HNMR) spectra.

The IR spectra of compounds [**3**(**a**, **b** and **c**)] showed the following bands (cm^{-1}):

3600 (ν OH, NH), 2925-2850 (ν CH_2), 2730-2300 (ν $\diagdown N^+ - H$), 1740 (ν $\overset{O}{\overset{\|}{C}}$), 1140 (ν C-O-C)

^{1}HNMR spectra for **3a**, as a representative sample, in deuterated chloroform exhibited the following signals (δ ppm):



$$\underset{(a)}{CH_3}-\underset{(b)}{(CH_2)_{15}}-\underset{(f)}{\overset{COOH}{CH}}-O-\underset{(e)}{CH_2}-\underset{(d)}{CH_2}-N-\underset{(c)}{(CH_3)_2}$$

0.95 (triplet, 3H, a-CH3, J=5 Hz); 1.25 (singlet, 30 H, b-CH_2); 2.94 (singlet 6 H, C - CH_3); 3.35 (multiplet, 2H, d-CH_2); 3.9 (triplet, 2H, e-CH_2, J=6 Hz) and 4.15 (triplet, H, f-CH, J=6 Hz).

EXPERIMENTAL PROCEDURES

All melting points are uncorrected. Microanalyses were performed at Bayer Co. Analytical Centre, Leverkusen, West Germany. The IR spectra, as KBr disks, were recorded on a Shimadzu 400 IR spectrophotometer. ^{1}HNMR spectra were recorded on a Varian spectrophotometer using d-chloroform as solvent and tetramethylsilane (TMS) as internal standard.

2-Bromooctadecanoic (Hexadecanoic and Dodecanoic) Acids [2(a, b and c)]

These α-bromoacids were prepared according to known procedures (9,10). They had the following characteristics: 2-bromooctadecanoic acid—mp 57-9 C, reported 60 C (11); 2-bromohexadecanoic acid—mp 52-4 C, reported 53 C (12,13); 2-bromododecanoic acid, oily product—reported mp 32 C and bp 157-9 C at 2 mm Hg (14,15).

2-(2-Dimethylaminoethoxy) Octadecanoic, Hexadecanoic and Dodecanoic Acid Hydrochloride [3(a, b and c, Table I)]

Sodium metal (2.07 g, 0.09 mol) was added to β-dimethylaminoethanol (10.68 g, 0.12 mol). The mixture was allowed to react at room temperature. When the reaction subsided, 20 ml of benzene was added. The mixture was then stirred and heated under reflux until complete dissolution of the sodium metal. The reaction mixture was cooled in an ice-salt bath and gradually treated with a solution of 0.03 mol of the appropriate 2-bromocarboxylic acid in 100 mo of benzene. The reaction mixture was continuously stirred and heated under reflux for 16 hr. The solvent was removed in vacuo. The remaining oily residue was dissolved in 40 ml water and acidified with 5 N HCl to pH 1. The aqueous layer was extracted twice with butanol in 25-mL portions. The extracts were collected, washed with water, and the solvent evaporated in vacuo on a boiling water bath. The resulting amber, waxy residue was dissolved in 100 ml of benzene, filtered and concentrated to a quarter of its volume. Then 70 ml of petroleum ether

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TABLE I

Characteristics of 2-(2-Dimethylaminoethoxy)octadecanoic, Hexadecanoic and Dodecanoic Acid Hydrochloride

Compound no.	Molecular formula	mpC	Yield (%)	N (%) (found)	(theory)	Surface tension CMC	Interfacial tensions CMC
						(mol l^{-1}) × 10^{-5}	
3a	$C_{22}H_{46}O_3NCl$	86-8	52.6	3.01	3.4	1.55	1.47
3b	$C_{20}H_{42}O_3NCl$	77-9	53	3.39	3.89	3.02	8.91
3c	$C_{16}H_{34}O_3NCl$	60-3	65	4.30	4.33	12.88	28.18

(40-60 C) was added and the product allowed to crystallize. The product was filtered and then recrystallized from petroleum ether. The produced white waxy crystals were collected by suction and dried in a vacuum dessicator over phosphorous pentoxide.

2-(2-Dimethylaminoethoxy) dodecanoic acid hydrochloride required further purification by column chromatography (silica gel, 100-200 mesh, packed with chloroform). The product was eluted with a mixture of chloroform and absolute ethyl alcohol (4:1).

Isoelectric Point

An emulsion (O/W) was prepared by vigorous stirring of paraffin oil in an aqueous solution of the emulsifier (5 × 10^{-5} mol l^{-1}; 10:100, v/v), using a suitable homogenizer (Virtis, Co., Gardiner NY). The emulsion was stirred for 4 min at successive 30-sec intervals. The zeta (ζ) potential of the emulsion was determined at various pH values for compound **3a**, as a representative of the amphoteric series. Results are presented graphically in Figure 1. The electrophoretic mobility was measured using a microelectrophoresis apparatus (Zeta-meter Inc., NY).

Study of Surface Activity

Surface and interfacial tension. Surface and interfacial tensions were measured using a Model 21 Fisher Tensiometer at 25 C with 10 min surface age (16,17). The surface tensions of the three amphoteric surfactants [3(a, b and c)] were plotted vs their log-molar concentrations. Critical micelle concentrations (CMC) were determined and are reported in Table I. The interfacial tensions of the amphoteric surfactants were measured against pure paraffin oil. These CMC are also given in Table I.

Emulsion properties. Compound **3a** was selected as representative of the amphoteric series to study its efficiency as an emulsifier compared to cetyl trimethyl ammonium bromide. The effect of electronic configuration of different aromatic oils on the stability of the adsorbed film covering the emulsion globules was studied. The emulsions were prepared as mentioned before. Emulsion lifetimes are given in Table II.

Corrosion inhibition effect. The anticorrosive effect of compounds[**3**(**a**, **b** and **c**)] was measured by the weight loss method (18) using low carbon steel coupons supplied by the Egyptian Copper Co. These coupounds measured 3.7 × 5 cm and had the following impurities: C, 0.1; S, 0.006; Mn, 0.34; P, 0.028; and Si, 0.005%. Samples were first polished using grade numbers 180, 280 and 500 waterproof silicon carbide papers until their surfaces were free from scratches. Degreasing of the specimens were done ultrasonically in 10% NaOH solution at room temperature for 10 min. The coupons were then washed thoroughly with running distilled water, dipped successively in chloroform and ethanol, then air-dried. Complete wetting of the surface was taken as an indication of the cleanliness of the surface. Steel coupons were hung on a glass hook support in 200 ml of 0.64 M HCl for 5 hr at 17 C. The percentage inhibition efficiency (IE%) was calculated as follows:

$$IE\% = \frac{W_o - W_i}{W_o} \times 100,$$

where W_o = weight loss/unit area/unit time in pure HCl solution; and W_i = weight loss in the presence of the inhibitor.

After-treatment of direct dyed cotton fabrics. The amphoteric surfactant **3a** was used as representative of the amphoteric surfactant series (2% concentration, on the weight of the fabric) for the after-treatment of cotton fabric dyed with direct dye.

Dyeing process (19). Egyptian bleached cotton fabrics were dyed with direct dye "Ciba Solophenyl Orange TGL." The recipe used was 3% dye, 20 g/ℓ glauber salt; liquor ratio 20:1. The temperature of the dyeing bath was gradually raised from 50 to 100 C in 0.5 hr, then held at 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.

After-treatment of the dyed fabric. Recipe composition: 2% amphoteric surfactant; liquor ratio, 40:1; pH 6; working temperature, 45 C.

Strips of the direct dyed cotton fabric measuring 4 × 12.5 cm and weighing 0.7 g were immersed in the previous recipe in a thermostated, shaken water bath for 0.5 hr. The pieces were then squeezed and dried at 80 C. A comparison blank was similarly treated. Bleeding was measured spectrophotometrically using a Unicam SP 1800 UV spectrophotometer at λ_{max} 419 nm. The concentration of the bleeded dye in the presence and absence of the amphoteric surfactant **3a** was 0.0004 and 0.0046%, respectively.

Fastness properties: light fastness. Light fastness was measured according to official standard methods in daylight for 8 days. The dyed fabric, as well as the after-treated fabric with the amphoteric surfactant, had an assessed score of 7 (19).

Washing fastness was performed in 5 g/ℓ sodium oleate, liquor ratio 50:1, during 45 min at 40 C in a shaken, thermostated water bath. Two pieces of white cotton fabric were sewed on each side of the dyed and after-treated fabric. The dyed and after-treated fabric were assessed the same score of 4, whereas the stitched white cotton pieces was assessed a score of 1-2 (19).

Antimicrobial activity. The antimicrobial activity of the amphoteric surfactants was determined by the agar diffusion method (20). Sterile nutrient agar (oxide) was inoculated with the test organisms (*Staphylococcus aureus* NCTC 4163, *Escherichia coli* ABDRO1, *Candida albicans* 3501, *Bacillus subtilis*, locally isolated strain, Dept. of

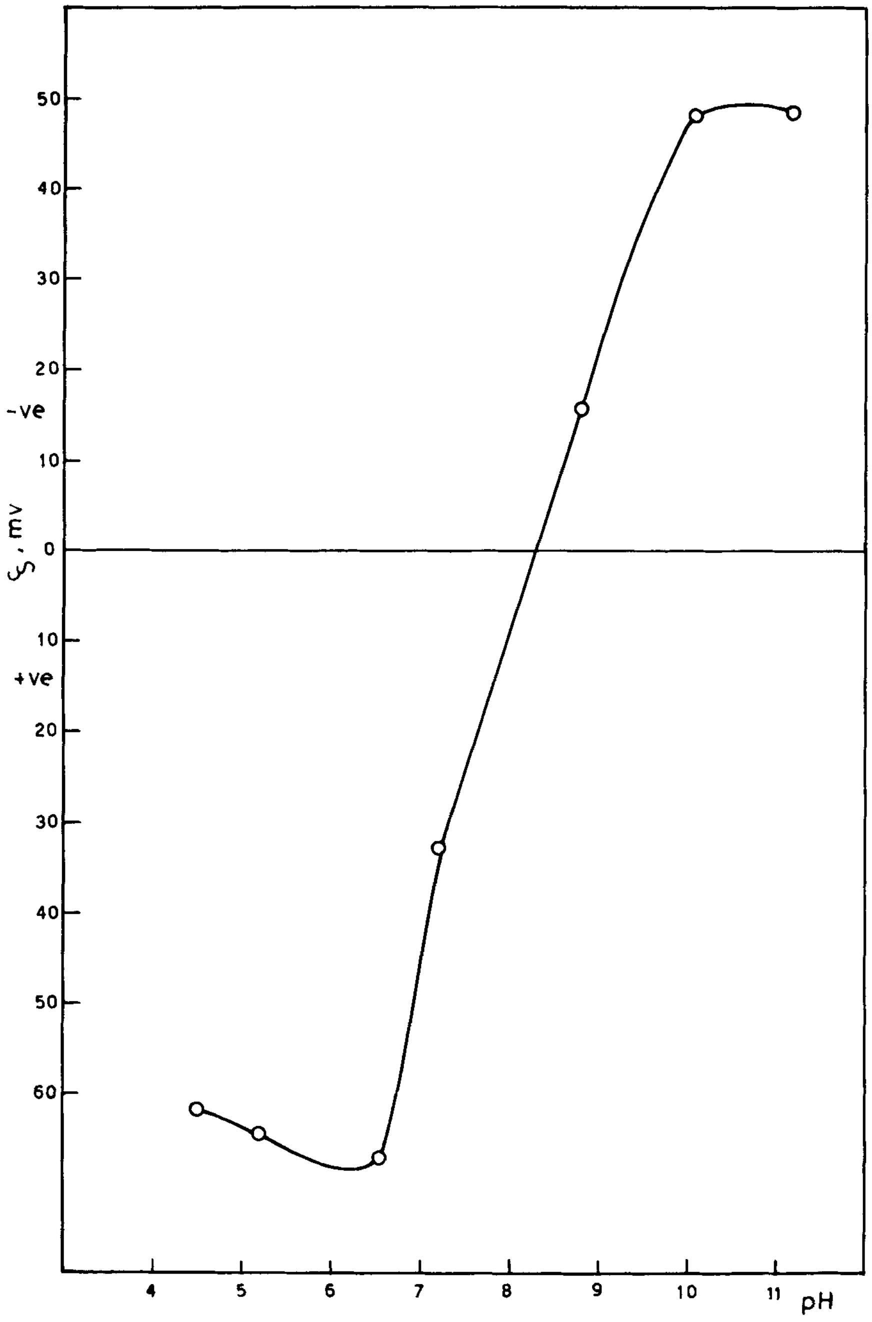

FIG. 1. Variation of ζ with pH for 25.

Microbiology, Faculty of Pharmacy, Alexandria University). 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) were placed separately in cups (8 mm diam) cut in the agar medium. The plates were incubated at 37 C for 24 hr. The resulting inhibition zones were measured and the results are presented in Table III.

DISCUSSION

Surface and Interfacial Tensions

The three amphoteric surfactants exhibited sharp breaks in their surface tension curves which corresponded to CMC of 1.54, 3 and 12.88 × 10^{-5} mol^{-1} for compounds **3a, b** and **c**, respectively. These values are inversely proportional to the chain length of the surfactants. Surface tension values were 37, 37.5 and 29.5 dyne cm^{-1}. The interfacial tensions at the CMC were well below 11 dyne cm^{-1}, predicting good surfactant performance was well as emulsifying properties (21). The interfacial tension values were 0.6, 1.6 and 2.4 dyne cm^{-1}, respectively.

Emulsifying Properties

The difference in stability among various O/W emulsions

TABLE II

Emulsion Lifetime Using Different Oils

	Life time (days)		
Type of oil	3a	Cetyltrimethyl-ammoniumbromide	Oil density (g/cm^3)
Chlorobenzene	1.8	0.5	1.105-1.108
Toluene	2.9	2.0	0.863-0.866
Xylene	5.0	2.5	0.850-0.865
Anisole	31.0	3.0	0.992-0.994

TABLE III

Inhibition Zones (mm) Obtained with the Amphoteric Surfactants

Compound no.	*S. aureus*	*B. subtillus*	*E. coli*	*C. albicans*
3a	10	–	–	–
3b	13	16	–	–
3c	–	–	–	–

is a subject of great interest. An intensive review of the literature revealed no systematic studies of the dispersed phase effect upon the mechanical stability of O/W emulsions. The nature of the oil at the O/W interface exerts a considerable influence on various phenomena such as interfacial tension (17), micellization, solubilization (22), surfactant adsorption (23,24) and stability of the emulsion. An attempt to corrolate the stability of emulsions with either vapor pressure or viscosity failed to yield any correlation (25).

In this investigation, a study has been made to compare the stability of emulsions using compound **3a** as the emulsifier with that produced with cetyl trimethylammonium bromide. Also, the relationship between the molecular electronic configuration and/or the density of different aromatic oils and the stability of emulsions was examined. In this respect, it is clear that the lifetime of the emulsion depends greatly on the nature of the oil (Table II). The stability of the system was in the order: anisole > xylene > toluene > chlorobenzene.

This phenomena may be due to the difference in the force of attraction between the positively charged adsorbed emulsifier film and the oil globules. This observation is in agreement with the relative difference in the electron density covering the aromatic oil nuclei.

Corrosion Inhibitors

The amphoteric surfactants prepared proved to be good corrosion inhibitors for steel in acidic solution. Their corrosion inhibition efficiency amounted to 93.7-99.5%, indicating a similar adsorption process for each of the three compounds.

After-Treatment of Direct Dyed Cotton Fabrics

Compound **3a** proved to be effective in the after-treatment of direct dyed cotton fabric. It highly reduced the bleeding action of the direct dye in warm water. The after-treated fabrics showed outstanding daylight fastness. Fastness in soap solution was low, indicating dissolution of the adsorbed compound **3a** by soap similar to that cited for other compounds (26).

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