

Amphoteric surface active agents

By A.M.F. Eissa

Chemistry Department, Faculty of Science, Zagazig University, Benha Branch, Benha - Egypt.

RESUMEN

Agentes tensioactivos anfotéricos

Se prepararon cuatro series de agentes tensioactivos del tipo 2-[trimetil amonio, trietil amonio, piridinio y 2-amino piridinio] alcanosatos, que contienen cadenas carbonadas con C₁₂, C₁₄, C₁₆ y C₁₈ átomos de carbono.

Se determinaron la tensión superficial e interfacial, el punto de Krafft, el tiempo humectante, el poder de emulsionamiento, la altura espumante y la concentración crítica de miscela (cmc) y se hizo un estudio comparativo entre la estructura química y sus propiedades tensioactivas. Se determinó también la actividad antimicrobiana de estos tensioactivos. Estas estructuras se caracterizaron por microanálisis, infrarrojo (IR) y resonancia magnética nuclear (RMN).

PALABRAS-CLAVE: *Actividad antimicrobiana — Agente tensioactivo anfotérico — Estructura química — Propiedades tensioactivas.*

SUMMARY

Amphoteric surface active agents

2-[trimethyl ammonium, triethyl ammonium, pyridinium and 2-amino pyridinium] alkanosates, four series of surface active agents containing carbon chain C₁₂, C₁₄, C₁₆ and C₁₈ carbon atoms, were prepared. Their structures were characterized by microanalysis, infrared (IR) and nuclear magnetic resonance (NMR). Surface and interfacial tension, Krafft point, wetting time, emulsification power, foaming height and critical micelle concentration (cmc) were determined and a comparative study was made between their chemical structure and surface active properties. Antimicrobial activity of these surfactants was also determined.

KEY-WORDS: *Amphoteric surface active agent — Antimicrobial activity — Chemical structure — Surface active properties.*

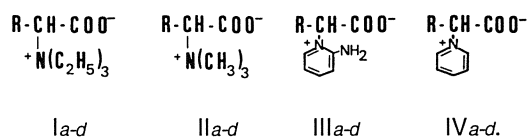
1. INTRODUCTION

Recent investigations have been concerned with the surface properties of well-purified, carefully characterized zwitterionic (amphoteric) surfactants (1)(2). A micellar properties of a series of 2-trimethyl ammonium alkanosate, N-alkyl-N,N-dimethyl glycines and 2-pyridinium alkanosate were studied (3).

Although this type of surfactant is used in a number of industrial products, there have been few studies of the surface properties of well-purified materials of this type.

The object of the present investigation is to prepare four series of amphoteric surfactants, which expected to have high biodegradation properties, from long chain fatty acids, lauric, myristic, palmitic and stearic acids via: a) direct

bromination of the appropriate fatty acids in presence of phosphorous trichloride, b) reaction of the obtained α -bromo acids with tertiary amines 9-triethyl amine, trimethyl amine, pyridine or 2-amino pyridine). The prepared surfactants having the general formula Ia-d, IIa-d, IIIa-d and IVa-d.



Where R = C₁₀H₂₁ = a , = C₁₂H₂₅ = b
 = C₁₄H₂₉ = c , = C₁₆H₃₃ = d

The surface active properties were determined and a comparative study was made between their chemical structure and their surface properties. The compounds were tested for their antimicrobial activity against different strains (bacteria and fungi).

2. EXPERIMENTAL

2.1. Bromo alkanic acids

These were prepared according to procedure described by El-Sawy et al. (4).

2.2. Conversion of obtained α -bromo acids to amphoteric surfactants

These were prepared according to (3).

2.3. Evaluation of the surface active properties of the prepared amphoteric surfactants

Surface active properties which include, surface and interfacial tension (5), Krafft point (6), wetting time, foaming height (7) and emulsification power (8) were determined.

2.4. Critical micelle concentration (cmc)

The critical micelle concentration values for the prepared surfactants were determined by the electrical conductivity method (9).

2.5. Biological activity

Antimicrobial activity of the prepared compound were tested via a modification of the cup-plate method (10).

2.6. Analysis

The structures of the proposed compounds were confirmed by microanalysis, infrared (IR) and nuclear magnetic resonance (NMR).

Elemental analysis: Analysis for C,H and N of the compounds agreed with theoretical values table (I).

Table I
Microanalysis of the prepared compounds.

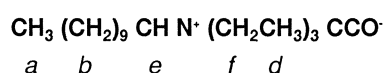
Compound	Mol. Wt.	C%		H%		N%	
		Calc-	Fd.	Calc-	Fd.	Calc-	Fd.
I _a	299	72.24	71.98	12.37	12.28	4.68	4.56
II _a	257	70.04	69.81	12.06	11.93	5.45	5.40
III _a	292	69.86	69.62	9.59	9.47	9.59	9.52
IV _a	277	73.65	73.61	9.75	9.70	5.05	5.00
I _b	327	73.39	73.18	12.53	12.47	4.28	4.20
II _b	285	71.58	71.32	12.28	12.21	4.91	4.87
III _b	320	71.25	71.06	10.00	9.88	8.75	8.66
IV _b	305	74.75	74.57	10.16	10.07	4.59	4.50
I _c	355	74.36	74.21	12.68	12.51	3.94	3.88
II _c	313	72.84	72.62	12.46	12.33	4.47	4.42
III _c	348	72.41	72.23	10.34	10.30	8.05	8.00
IV _c	333	75.68	75.56	10.51	10.49	4.20	4.13
I _d	383	75.20	75.01	12.79	12.68	3.66	3.57
II _d	341	73.90	73.72	12.61	12.58	4.11	3.89
III _d	376	73.40	73.26	10.64	10.61	7.44	7.32
IV _d	361	76.45	76.30	9.42	9.39	3.88	3.77

IR spectra: In KBr were recorded on a Unicam sp 1200 spectrophotometer. All the compounds showed COO-absorption at $\delta 1645 \text{ cm}^{-1}$ and the absence of the COOH absorption at $\delta = 1720 \text{ cm}^{-1}$.

¹H-NMR spectra: Were recorded on a Varian EM-390 spectrometer operating at 90 MHz. Deuteriochloroform was used for solvent and tetramethylsilane for internal standard. Chemical shifts are reported as δ (ppm) relative to tetramethyl silane.

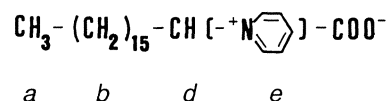
¹H-NMR spectra for I_a and IV_d as representative samples:

I_a exhibited the following signals (δ ppm)



0.93 (triplet, 3H, a-CH₃); 1.20 (singlet, 18H, b-CH₂); 2.26 (triplet, 9H, d-CH₃); 3.81 (triplet, 1H, e-CH) and 4.7 (quartet, 6H, f-CH₂).

IV_d exhibited the following signals (δ ppm)



0.87 (triplet, 3H, a-CH₃); 1.1 (singlet, 30H, b-CH₂); 3.4 (triplet 1H, d-CH) and 7.8 (multiplet 5H, e-)

3. RESULTS AND DISCUSSION

It is interesting to note that, although the decomposition points of the pure dry compounds >100°C in all cases, the

compounds can not be synthesized by heating the corresponding 2-bromo carboxylic acid with excess tertiary amine in dry ethanol, except in case of 2-amino pyridine a little dry ethanol was added and warming to about 50°C, due to decarboxylation of the product to the corresponding N-alkyl triethyl, trimethyl, 2-aminopyridinium or pyridinium bromide (3).

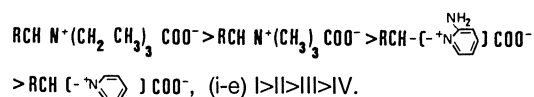
3.1. Surface properties

The results of surface tension determination (table II) show that the products obtained have a pronounced surface activity and reflect the following facts.

Table II
Surface properties of prepared compounds

Compound	Surface Tension 0.1% dyne/cm	Interfacial Tension 0.1% dyne/cm	Krafft Point 0.1% °C	Wetting Time 0.1% Sec	Foam Height 0.1% mm	Emulsification Power 0.5% %	Critical micelle Conc. m.mol
I _a	34	4.7	<0	15	63	84	8.7x10 ⁻²
II _a	36	4.3	<0	12	50	82	1x10 ⁻²
III _a	33	4.2	<0	10	82	80	7.3x10 ⁻³
IV _a	31	4.1	<0	9	68	84	5x10 ⁻³
I _b	38	5.3	18	22	82	91	4.1x10 ⁻²
II _b	37	8.1	13	33	70	85	1.1x10 ⁻³
III _b	34	5.7	28	25	116	83	9.1x10 ⁻⁴
IV _b	31	5.2	22	20	113	92	5.6x10 ⁻⁴
I _c	39	7.4	38	42	92	89	3.2x10 ⁻³
II _c	40	8.6	23	58	87	83	6.2x10 ⁻⁴
III _c	34	7.0	41	36	135	85	1.03x10 ⁻⁴
IV _c	35	6.7	39	27	136	90	6.4x10 ⁻⁵
I _d	42	8.7	57	37	102	77	2.3x10 ⁻⁴
II _d	41	10.0	49	49	112	73	1.1x10 ⁻⁴
III _d	39	11.3	68	47	165	71	6.7x10 ⁻⁵
IV _d	36	8.7	54	43	145	84	3.1x10 ⁻⁵

- Surface tension decreases with the decreasing in alkyl chain length.
- In general, Krafft points measurements proved that the higher the molecular weight the higher the Krafft point.
- Evident good emulsifying, foaming and wetting properties make the prepared surfactants of choice in pesticide and cosmetic formulations.
- Critical micelle concentrations (cmc's) of the prepared surfactants were taken as the concentration at the point of intersection of the two linear portions of the $\Omega^{-1} \log C$ plots (fig. 1). The values are inversely proportional to the alkyl chain length and decreased in the order C₁₂>C₁₄>C₁₆>C₁₈ also the value of cmc decreases in the following order



This may be due to the ease with which the planar positively charged pyridinium group can pack with the planar negatively charged carboxylate group. The bulky and the more bulky trimethyl ammonium and triethyl ammonium respectively in 2-position presumably can not pack as closely to the carboxylate group resulting in higher cmc values.

3.2. Biological activity

On the other hand, the compounds were tested for their antimicrobial activity against different strains *Bacillus subtilis*, *Escherichia coli*, *Aspergillus niger* and *Candida albicans*. The results obtained indicated that, compounds (I_d, II_d, III_c and IV_d) were relatively more active as bactericidal and fungicidal agents than the other compounds (table III).

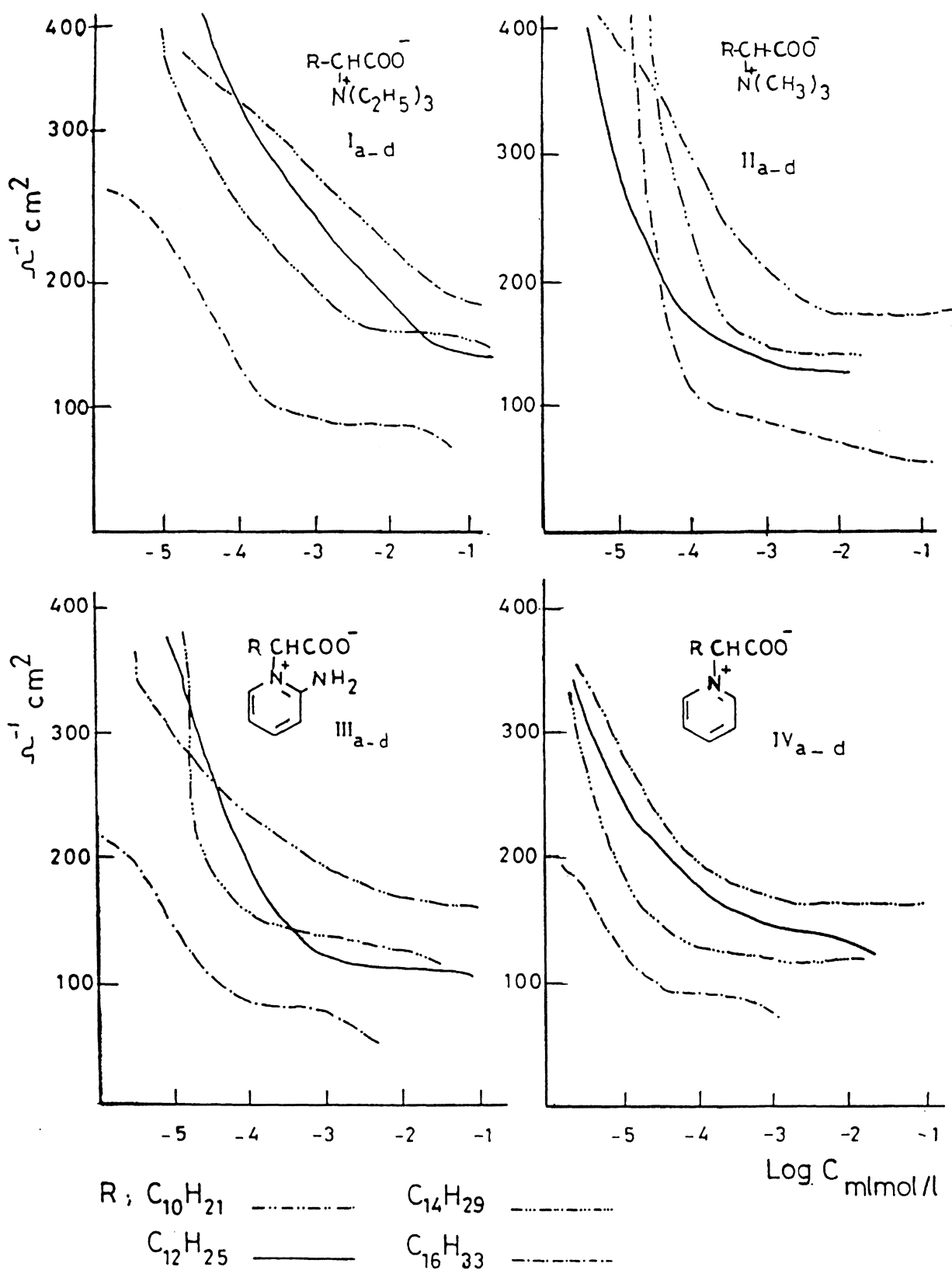


Fig. 1
CMC by electrical conductance

Table III
Biological activity

Compound	Bacillus subtilis	Escherichia coli	Aspergillus niger	Candida albicans
I _a	-	-	-	-
II _a	-	-	-	-
III _a	-	-	-	+
IV _a	+	-	+	+
I _b	-	-	-	-
II _b	-	-	-	-
III _b	+	-	+	+
IV _b	+	-	++	++
I _c	-	-	-	-
II _c	-	-	+	+
III _c	+	-	-	++
IV _c	+	+	++	+++
I _d	-	-	+	+
II _d	+	+	+	+
III _d	+	+	+	++
IV _d	++	++	+++	+++

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