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SYNTHESIS AND SURFACE PROPERTIES* OF SOME DYESTUFF ESTERS

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ABSTRACT

Some disperse dyestuffs, which include two sulphonate groups in their structures were esterified by different molar ratios of lauroyl chloride to produce some laureate esters. Surface properties before and after esterification were measured. Pc_{20}, Γ_{max}, A_{min}, π_{CMC} and $\Delta G°_m$ for the esterified compounds were also evaluated. The results obtained show promising applicability for these esterified compounds as surface active agents.

Key Words: Dye stuff, surface properties, CMC, Pc_{20}, surface tension.

INTRODUCTION

Heterocyclic amino compounds were used recently in the development of azodyes[1] and these dyes are of current interest as functional materials for electronic, optoelectronic and photonic devices[2]. The present work describes the esterification of some of these dyes to produce new surface active agents. Where the presence of two sulphonate groups in the structure of the azodye suggested that these compounds may have surface activity, where the attachment of the sulphonate group $S0_3M$ to an alkyl, aryl or alkylaryl hydrophobe make it highly effective solubilizing group. Also sulphonic acids are strong acids and their salts are relatively unaffected by pH and due to the strength of C-S bond, the sulphonate compounds are stable to hydrolysis and oxidation. All of these aspects make the sulphonate compounds take an important part in the production of anionic surfactants[3-5]. An important factor affecting the surface activity of the sulphonate type surfactants is the number of sulphonic acid groups found on the molecule, where the presence of two or more sulphonic acid groups make the molecule too hydrophiiic. Also the sulphonates of unsubstituted aromatic hydrocarbons have a little surface activity, so presence of a long aliphatic side chain which represents the hydrophobic part in the aromatic molecules confers surface activity to these sulphonates. In our study, the aliphatic side chain was introduced to the aromatic part by esterification with lauroyl chloride[6].

EXPERIMENTAL

Materials

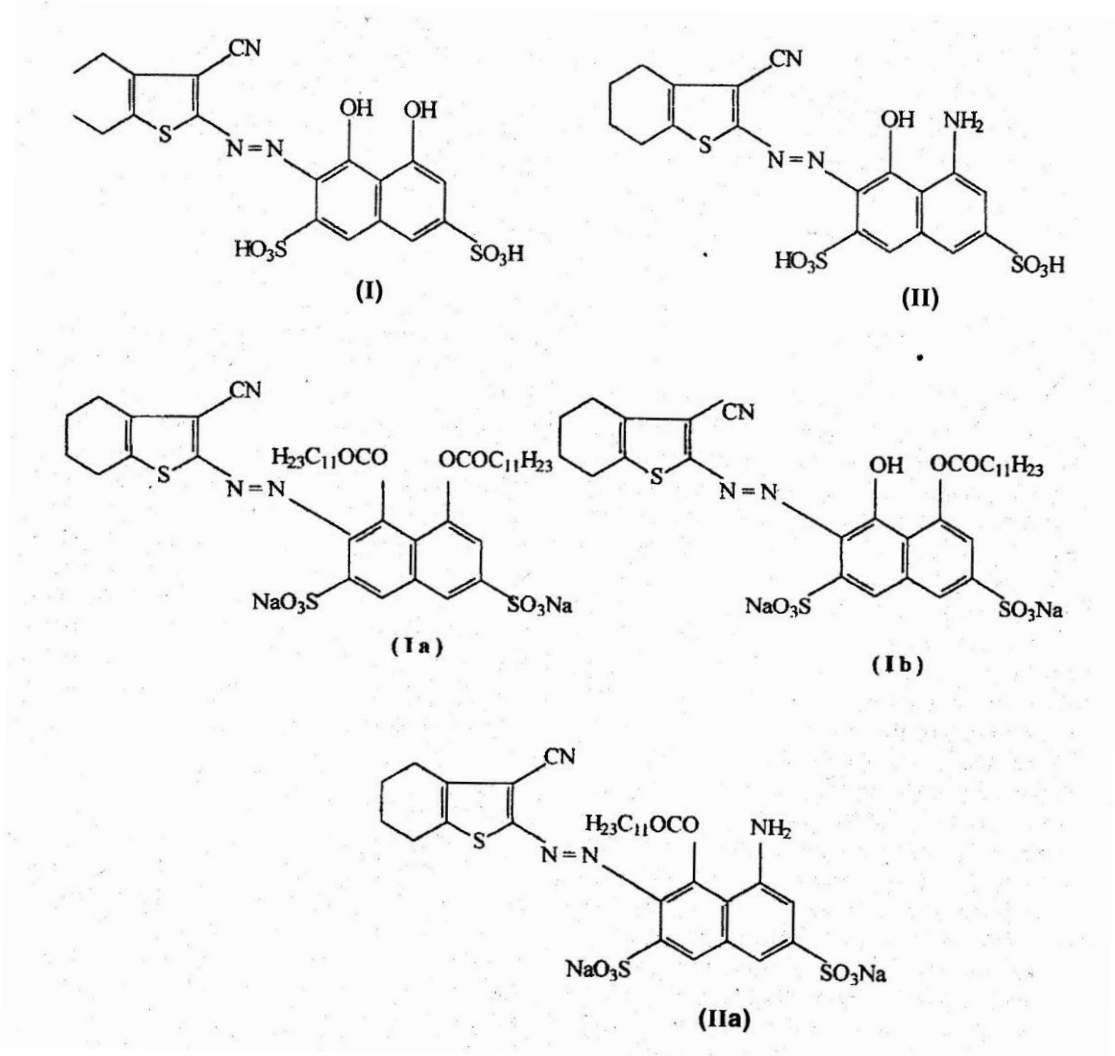
The dye stuff compounds namely: 2-Chromotropic acid amino-4,5,6,7-tetrahydrobenzo thiophene-3-carbonitriie (I) and 2H-acid amino-4,5,6,7-tetrahydrobenzothiophene-3-carbonitrile (II) which previously prepared' were esterified with lauroyl chloride where: (0.04mole,

0.02mole) of lauroyl chloride were used to esterify (0.02 mole) of dyestuff (I) to produce dilaurate ester of 2-Chromotropic acid amino-4,5,6,7-tetrahydrobenzothiophene-3-car bonitrile and monolaurate ester of amino-4,5,6,7-tetrahydrobenzo thiophene-3-carbonitrile, (I_a) and (I_b) respectively. (0.02 mole) of lauroyl chloride was used to esterify (0.02mole) of dyestuff (II) to produce monolaurate ester of 2H-acid amino-4,5,6,7-tetrahydrobenzo thiophene-3-carbonitrile (II_a).

Methods

Esterification of the dvestuffs (I, II) to produce (I_a, I_b, and II_a):

The appropriate molar ratio of lauroyl chloride was added dropwise to the dyestuff, I or II, dissolved in 10ml of pyridine[6]. After the addition was completed, the reaction mixture was refluxed for 25-30minutes.The cold reaction mixture was poured into (40ml 2N HCl). The supernatant aqueous liquid was decanted from the precipitated solid which was stirred vigorously with about



(10ml 1N Na_2C0_3) solution. The precipitate was filtered off, recrystallized from ethanol to obtain the corresponding sodium sulphonates.

Analysis

FTIR measurements were made using (Fourier Transform Infrared, ATI Matson Gensis FTIR™)

Microelemental analysis were carried in the central Lab., Cairo University using (VARIOELEMENTAR).

Evaluation and Techniques

The surface and interfacial tension measurements were made with Du Nouy Interfacial Tensiometer using a solution of 0.1% by weight concentration[7]. The surface tension of the used distilled water was 73.1 dyne/cm and the interfacial tension between medicinal paraffin oil and distilled water was 56.2 dyne/cm. Surfactant solutions were aged for two hours before any measurements were made. Three readings were made on each sample to determine any changes with time and to obtain an average value[8]. Values of the surface tension obtained for various concentrations of aqueous solutions of the prepared surfactants were plotted vs. the logarithm of the corresponding concentrations, from which the critical micelle concentration (CMC), and γ_{CMC} were obtained as the point of intersection of the two straight lines obtained, γ_{10}[5] also can be obtained.

Foaming properties were determined by vigorously shaking 100ml of 0.1% concentration of the solution in a stoppered graduated cylinder of 250ml capacity[9]. Emulsifying power was determined by mixing five ml of 0.1 g/L surfactant solution with 5ml of paraffin oil in a test tube. After 20 vigorous shakes, the tube was allowed to stand undisturbed[10]. The emulsifying power was determined by the time required to separate the two phases. The surface excess (Γ_{max}), area / molecule adsorbed at the interface (A_{min}) and the standard free energy of micelle formation ($\Delta G°_{mic}$) were calculated by the method described by Rosen, *et a*/.,[11]. Pc_{20} and effectiveness (Π_{CMC}) were also measured. All measurements were made at room temperature, 25 ± 2°C.

RESULTS AND DISCUSSION

Analysis

The structure of the prepared compounds were confirmed by microanalysis given in Table 1, and Infrared absorption measurements. The IR spectra showed absorption bands at (2910-2920 cm^{-1}) due to aliphatic CH stretching, (1450cm^{-1}) due to CH_2 stretching,(2870 cm^{-1}) due to CH_3, (1740cm^{-1}) due to the presence of C=0 and at (3255-3393cm^{-1}) due to NH_2 group. The IR spectra for $S0_3H$ group revealed absorption bands at (1320- 1334cm^{-1}) due to antisymmetric stretching frequencies of $S0_3$ and at (1177- 1190cm^{-1}) for symmetric stretching frequencies of -$S0_3$.

Surface tension

Table- 1 **: Analytical data of the prepared surfactants**

Compound	Molecular weight	Crystalization Solvent	Yield, %	Elemental analysis, %					
				C		H		N	
				Calc	Found	Calc	Found	Calc	Found
I_a	873	Ethanol	75	59	59.3	6.8	6.6	4.8	4.7
I_b	691	Ethanol	70	53.8	53.7	5.3	5.4	6.0	6.2
II_a	690	Ethanol	76	53.9	54.1	5.5	5.2	6.0	6.1

Values Values of surface and interfacial tension which measured at 0.1% by-weight and recorded in Table 2 show a remarkable decrease in surface tension from the parent compounds (51 dyne/cm) to (32dyne/cm) for the esterified compounds. This is attributed to the hydrophobic part which introduced by esterfication and gives the compound its amphipathic structure.

CMC, $\gamma 10^5$, γ_{CMC}

It was observed *from Fig1 and Table 3 that adduct Ia had the best values for CMC, $\gamma 10^5$, γcMc and this is due to the presence of two hydrophobic groups which increase the concentration of surfactant at the interface.

Foaming properties

The foaming ability and foam stability for both parent compounds (I, II) and their esters (I_a , I_b ,II_a) were recorded in Table 2. It was observed that parent compounds showed unstable low foam height which disappeared after few seconds, while their esters showed high foaming ranging from (220-230) and also high stability indicated by the height of the foam after 3min. These high foaming effects probably are due to the introduced hydrophobic group which increases the surfactant concentration at the surface and hence produce a high cohesive forces.

Emulsifying power

Emulsification is one of the most important surface properties, since it measures the ability of the surfactant to emulsify the oily impurities in some purification processes.From the results obtained in Table 2 we observed that the emulsifying power was enhanced to a large degree after esterfication as was expected.

Effectiveness (π_{CMC})

π_{CMC} is the difference between the

Table- 2 : Surface active properties for the prepared compounds

Compound Compound	Surface tension (dyne/cm)	Interfacial tension (dyne/cm)	Foaming power (vol. ml)		Emulsification power (min)
			Initial	After 3 min	
I	51	25	-	'-	5
Ia	32	5.5	310	310	56
I_b	36	11.5	250	240	21
II	59	27	-	-	1.37
Ha	35	8.5	220	215	126

Table- 3 :The critical micelle concentration (CMC) of the prepared surfactants at 25°C

Surfactants	Critical micelle concentration $10"^3$ (Mole/L)	γ_{CMC}	γio^{-5}
Ia	1.00	26	57
Ib	2.43	35	56
Ha	2.57	27	51

surface tension of the pure water (γ_0) and the surface tension of the surfactant solution at the critical micelle concentration (γ_{CMC}). Values of π_{CMC} at room temperature were given in Table 4. The most efficient surfactant is that which gives the largest reduction of the surface tension at the critical micelle concentration. According to the results, I_a was found to be most effective compound.

Pc_{20} values

The Pc_{20} value measures the efficiency of adsorption of the surfactant at the interface[12] and it is measured by negative log of the surfactant molar concentration required to reduce the surface tension of the solvent by 20 dyne/cm, values of Pc_{20} for the prepared surfactants which listed in Table 4 indicate that the adduct I_a adsorbed more efficiently at the interface than the other two adducts.

Surface Excess (Γ_{max})

The values of the surface excess Γ_{max} were calculated from the plot of surface tension vs.-log surfactant concentration which is given in Fig 1 according to Gibb's equation:

$$\Gamma_{max} = 1/2.393RT(-\partial\gamma/\partial \log C)_T$$

where, R = 8.314Jmol^{-1}K^{-1}, T is absolute temperature, $(-\partial\gamma/\partial \log C)_T$ is the

Figure -1 : Effectiveness, efficiency, maximum surface excess and minimum surface area of the prepared surfactants at 25°C.

Surfactants	π CMC (Dyne/cm)	PC_{20} (Mole/L)	Γ_{MAX} X10^{10} (Mol/ecm^{-2})	A_{min} (nm^2)	$\Delta G°_m$ Kj/mol
I_a	46	5.0	3.25	5.1	-17.117
I_b	44	4.0	3.05	5.4	-13.390
II_a	45	4.3	2.73	6.0	-14.846

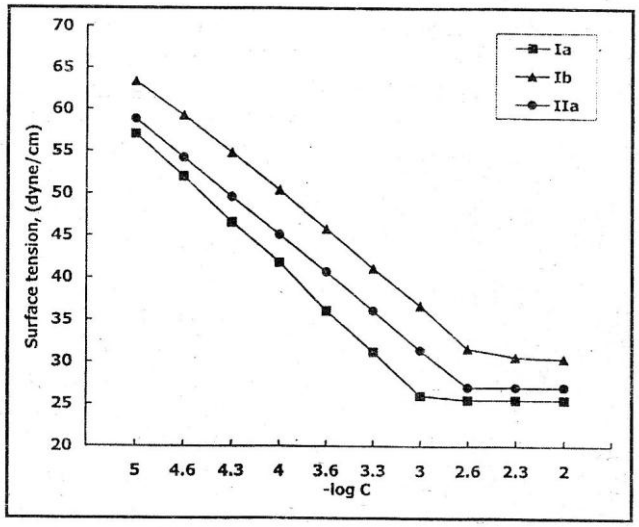


Figure -1 : Relation between surface tension and -log C for the prepared compounds I_a, I_b and II_a at 25°C.

slope of the γ vs. logC plot at room temperature and Γ_{max} is the surface excess in mol/cm^2.

By analyzing the data given in Table 4 for the values of Γ_{max}, it was observed that Γ_{max} increased by increasing the hydrophobic part where it was reached a maximum value for I_a which contain two hydrophobic parts, and this indicates that the molecules are more tightly packed in the surface for the higher hydrophobic content[12].

Minimum Surface Area *(A_{min})*

The area occupied by each molecule at the interface was calculated from the surface excess by the following equation:

$$A_{min} = io^{-16}/r_a . N$$
$$mm \qquad max$$

where, A_{min}. is the area per molecule (nm^2X10^2) and N is Avogadro's number.

Increasing the hydrophobic content and consequently increasing Γ_{max} values for surfactant molecules cause a decrease in A_{min} values as shown in Table 4[8,12].

Standard free energy of micelle formation ($\Delta G°_m$)

The standard free energy of micelle formation, $\Delta G°$, was calculated from the CMC by the following equation:

$$\Delta G°_m = -2.303RTlogCMC$$

The effect of the molecular structure on the $\Delta G°_m$ values which is given in Table 4 appeared clearly where the $\Delta G°_m$ values decrease as a result of increasing the hydrophobic content in I_a adduct[8].

CONCLUSIONS

From the above surface properties it was observed that I_a had the best surface activity and this is due to the presence of two hydrophilic and two hydrophobic groups, where compounds of this type can have much greater surface activity than comparable conventional surfactants with one hydrophilic group and one hydrophobic group in the molecule[13-15].

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