Synthesis and Properties of some N-acyl ethylenediamine triacetic acid Chelating Surfactants

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A new kind of surfactants with chelating properties named N-Acyl ethylenediamine triacetate (N-acyl ED3A) of different hydrocarbon chain lengths were synthesized from anhydrous ethylene diamine, fatty acid chlorides (Capryloyl, Lauroyl, myristoyl, palmitoyl, stearoyl or oleoyl chloride) and chloroacetic acid. The chemical structures of the prepared compounds were confirmed using different spectroscopic techniques, primarily Fourier transform infrared spectroscopy and nuclear magnetic resonance. The surface properties including surface and interfacial tension, foaming height, emulsification power, calcium ion stability, stability to hydrolysis and critical micelle concentration (CMC) were determined. The trisodium N-acyl ethylenediamine triacetates have been found to combine the properties of strong surfactancy, extreme mildness with a high tolerance to water hardness, and ability to chelate metal ions, which indicates a promising application prospect in many fields.

Key words: N-acyl ethylenediamine triacetic acid; multifunctional surfactant; chelating surfactants; chelactants

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1 Introduction

Calcium and magnesium ions in water can react with anionic surfactants and deteriorate their performance. The polyphosphates are often added to soften hard water when anionic surfactants are used. The use of phosphates has caused severe environmental problems. The synthesis of surfactants that are stable in hard water is a meaningful way to improve their effects and cut down consumption of phosphates [1-3].

Ethylenediamine tetraacetic acid (EDTA) is a commonly used chelator. Only three of its four acetic groups chelate with metal ions so substituting one of its acetic groups with oleophylic group can synthesize surfactants which are stable in hard water and they have an exceptionally low toxicity and are biodegradable than most conventional chelating agents [4-10].

The aim of our study was to apply a two step method to prepare a series of N- acyl ethylene diamine triacetic acid with different alkyl chain lengths (from C8 to C18) using the condensation reaction of ethylenediamine and fatty acid chlorides. The produced N-acyl ethylenediamines were reacted with chloroacetic acid to give rise to N-acyl ethylenediamine triacetic acid surfactants. The surface properties of resulting chelating surfactants were evaluated.

2 Results and Discussion

Synthesis Work:

$$RCOCl + H_2NCH_2CH_2NH_2 \longrightarrow RCONHCH_2CH_2NH_2 \quad (1)$$

$$\xrightarrow{ClCH_2COOH} RCO\text{-}N(CH_2COOH)CH_2CH_2N(CH_2COOH)_2 \xrightarrow{NaOH} RCO\text{-}N(CH_2COONa)CH_2CH_2N(CH_2COONa)_2$$

(N-acyl ED3A)(2) **(3NaN-acyl ED3A) (3)**

R= C_7, C_{11}, C_{13}, C_{15}, C_{17}, and (C_{17}=)

Scheme 1.

The synthesis of N-acyl ED3A (2) is outlined in **Scheme 1**. The fatty acid chlorides (capryloyl, lauroyl, myristoyl, palmitoyl, stearoyl, and oleoyl acid chloride) reacted with anhydrous ethylenediamine to yield the N-acyl ethylenediamine (1) with good yield. N-acyl ethylenediamine was reacted with chloroacetic acid at 50-60 ºC to give rise to N-acyl ED3A (2) with about 70% yield. When ethylenediamine was reacted with the acid chloride, by-products with more than one acyl substitution group were inclined to form. It was necessary to decide the reactant mole ratio to guarantee the product purity. Experiments were conducted at different mole ratios of ethylenediamine to the fatty acid chloride. When the mole ratio of ethylenediamine to the acid chloride was more than 40, the nitrogen content of the product was nearly closed to the theoretical value and did not change with the addition of ethylenediamine. The results of elemental analysis have deviations from calculated amounts and showed that its purity around 73%. This may be caused by a small amount of disubstituted material in the surfactants. It should be N,N'-diacyl ethylenediamine diacetic acid, which has structure and properties similar to those of the products. Consequently a small amount of impurity did little harm to the product performance.

2.1 **Surface properties of the prepared surfactants**

Surface and interfacial tension: The synthesized anionic surfactants (sodium salts) showed lower values of surface tension and interfacial tension. The results are recorded in **Table (1)**. It was found that an increase in the length of the hydrophobic carbon chain will lead to an increase in the repulsion force due to the difference in their polarity, resulting in a decrease of surface tension values, this could be due to increasing the interaction forces between the chain and the polar medium (H_2O), which directs the surfactants molecules towards the air/water interface. [11]

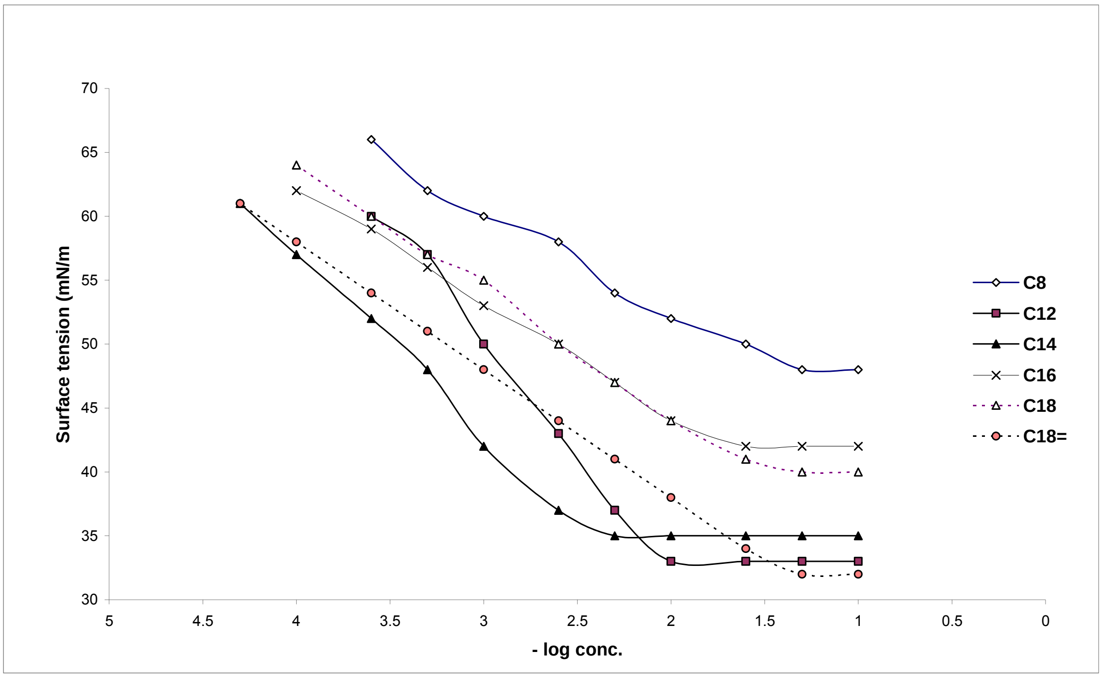
The interfacial tension of the prepared surfactants between their solutions and paraffin oil generally decrease by increasing the hydrophobic chain length, which may be due to the presence of surfactant molecules at the interfacial layer between the water and paraffin oil phases [12]. The presence of surfactants molecules at the interfaces may facilitate their amphipathic structure , the presence of polar groups (N ,COO^-) (hydrophile) and the non polar group (alkyl chain) .Hence ,the total energy of the system decreases as a result of solution of polar groups in the polar medium and the hydrophobes in the non polar phase.[13]

The critical micelles concentration (CMC): The critical micelle concentration (CMC) of prepared surfactants was taken as the concentration at the intersection points in the (γ) plotted against (- log c) curves showing in **Fig (1)**. (CMC) values were determined and stated at **Table (1)**. The increasing of the side chain length of the prepared surfactants decrease their critical micelle concentration (CMC) values till reaches to C14 and then it increases, perhaps this is because of the coiling of these long chains in water.

Table (1) the surface tension, interfacial tension and (CMC) of the prepared surfactants.

Compound Sodium salts	Surface tension (mN/m)	Interfacial tension (mN/m)	CMC (mol/L)
Capryloyl ED3A (C8)	48	11	$1.8x10^{-2}$
Lauryl ED3A (C12)	33	4.7	$8x10^{-3}$
Myristoyl ED3A (C14)	35	7	$3.3x10^{-3}$
Palmitoyl ED3A (C16)	42	5	$1.8x10^{-2}$
Stearoyl ED3A (C18)	40	6.5	$2.7x10^{-2}$
Oleoyl ED3A (C18=)	33	6	$3x10^{-2}$

Figure (1) Change of surface tension of the prepared compounds With concentration



Foam Height: The foaming height of the prepared surfactants was investigated. The measured data are given in **Table (2)**. It can be seen that the prepared surfactants have high foam height even in hard water (>300ppm). The foam height increases with increase in the length of hydrophobic part. The C18 derivative showed superior foam height.

Table (2) Foaming height of the 0.1% solution of the Prepared surfactants in hard water (300ppm)

Compound Sodium salts	**Foaming (ml)**
Capryloyl ED3A (C8)	**30**
Lauroyl ED3A(C12)	**200**
Myristoyl ED3A (C14)	**225**
Palmitoyl ED3A (C16)	**180**
Stearoyl ED3A (C18)	**300**
Oleoyl ED3A (C18=)	**85**

Emulsion Stability: In emulsion formation, one of the two immiscible liquids is broken up into droplets that are dispersed in the second liquid. Since the interfacial tension between two immiscible liquids is always greater than zero, this dispersion of the inner liquid, which produces at tremendous increase in the area of the interface between them, results in a large increase in the interfacial free energy of the system. The emulsion produced is consequently highly unstable thermodynamically, relative to the two bulk separated by a minimum area interface. The function of the emulsifying agent is to stabilize this basically unstable system to sufficient time so that it can perform some functions. The emulsifying agent does this by adsorption at the liquid/liquid interface as an oriented interfacial film. The emulsifying power of the prepared surfactants against light paraffin oil was listed in **Table (3)**. as function of time. In general the prepared surfactants pass good emulsion stability, the emulsion stability increase with increasing the hydrophobic chain length. Due to increasing the alkyl chain length, solubility of surfactant in oil phase will increase forming a high stable emulsion that can not be broken easily.

Table (3) the emulsifying power of the prepared
Surfactants against paraffin oil

Compound Sodium salts	**Emulsification power (seconds)**
Capryloyl ED3A (C8)	**37**
Lauroyl ED3A (C12)	**156**
Myristoyl ED3A (C14)	**186**
Palmitoyl ED3A (C16)	**210**
Stearoyl ED3A (C18)	**388**
Oleoyl ED3A (C18=)	**512**

Calcium Stability: High calcium stability values show that the prepared surfactants have good calcium ion stability (>3000 ppm), and can be used in hard water.

Stability to hydrolysis: In surfactants applications as detergents, acids or alkalis could be found in the environment, so that resistance of the detergents towards these media through their applications can be determined according to the hydrolysis test.

The results of acid and alkaline hydrolysis of the prepared surfactants are listed in **Table (4)**. The prepared surfactants are classified as anionic surfactants, so they will be affected by acidic environments rather than alkaline one. All prepared surfactants possess high extent of stabilization in their structure (depending on values of their surface tension), when treated with acids in start periods of treatment, while prolonged heating with acids (up to 60 min) has an aggressive effect, hence the surface tension increased.

Table (4) Resistance to hydrolysis of the prepared surfactants

Compound	Surface tension 0.1%surfactants solution at 25°C						
	Distilled water	H_2SO_4 5%	After boiling in H_2SO_4 5%		NaOH 1%	After boiling in NaOH 1%	
			30min	60min		30min	60min
Capryloyl ED3A (C8)	48	42	36	37	44	37	39
Lauroyl ED3A (C12)	33	34	32	34	31	31	33
Myristoyl ED3A (C14)	35	35	32	33	43	34	35
Palmitoyl ED3A (C16)	42	36	34	36	36	32	33
Stearoyl ED3A (C18)	40	40	34	36	38	36	36
Oleoyl ED3A (C18=)	33	35	31	35	33	31	32

3. **Conclusions**

A series of N-acyl ethylenediamine triacetic acid with alkyl chain length of 8, 12, 14, 16, 18, and (18=) were synthesized. Study of the surface properties of 3Na acyl-ED3A showed its stability in hard water and in acidic and alkaline mediums. These compounds have high calcium ion stability and the ED3A group in the molecule can chelate many kinds of metal ions, which indicates a promising application prospect not only in detergents but also in many other fields.

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