FULL LENGTH ARTICLE

Preparation and evaluation of some amide ether carboxylate surfactants

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Abstract A homologous series of new mild surfactants, namely: Alkyl amide ether carboxylates surfactants (AEC) RCO–NHCH2CH2O (CH2CH2O)nCH2COONa, were synthesized by esterification, amidation, ethoxylation and carboxymethylation reaction steps of fatty acids (Lauric, Myristic, palmitic, stearic, oleic or linoleic). The chemical structures of the prepared compounds were confirmed using different spectroscopic techniques, FTIR spectroscopy, mass spectra and HNMR. The surface properties including surface and interfacial tensions, foaming height, emulsification power, calcium ion stability, stability to hydrolysis and critical micelle concentration (cmc) were determined. The study of their surface properties showed their stability in hard water and in acidic and alkaline media. These compounds have high calcium ion stability. The low foaming power could have an application in the dyeing auxiliary industry. The lower values of the interfacial tension values indicate the ability of using these surfactants in several applications as corrosion inhibitors and biocides. The data revealed various advantages and potentials as a main surfactant as well as co-surfactants.

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1. Introduction

The synthesis of amide ether carboxylate surfactants has been reported more than twenty years ago in the patent literature. Fatty acid monoethanolamide [1] and coconut oil [2] have been used as starting raw materials. Today’s major reaction pathway in the formation of AEC starts up with the reaction of a fatty acid or its methylester with monoethanolamine (MEA) in the presence of an alkaline catalyst. The reaction product is ethoxylated by the addition of several moles of ethylene oxide to obtain the amide ether (AE), which is finally car-
boehmethylated through the reaction with sodium monochloroacetate (SMCA) and sodium hydroxide. To obtain (AEC) in a satisfactory high purity, this will qualify the products to be used in cosmetics as well as in all kinds of personal care products. It is very important to perform the amidation reaction at optimum condition in order to reduce by-products to the lowest possible level. By-products with reactive moieties like –OH or –NH groups will be multiplied in amount by the following ethoxylation and carboxymethylation reactions, resulting in higher levels of impurities which cause the finished product to behave different in foaming and the way the skin feels. The mildness of these products may partly be accounted for by the fact that the molecular structure of the AEC can be also looked upon as a modified amino acid [3,4].

The aim of this work is to prepare a series of amide ether carboxylates with different alkyl chain lengths from \((C_{12}–C_{18})\) and \((C_{18}–C_{18})\) and to evaluate the prepared compound as surfactants.

2. Experimental procedures

2.1. Synthesis of surfactants

2.1.1. Esterification of fatty acid

In 500 ml three-necked flask, connected with a condenser, equimolecular amounts of the acids (Lauric, Myristic, palmitic, stearic, oleic or linoleic) and methanol were mixed. Xylene was added as a solvent and the reactions were catalyzed with \(p\)-toluenesulfonic acid in an amount calculated as weight percent of alcohol (2%). The reaction mixture was refluxed with continuous stirring. The amount of water produced was collected in the dean stark trap and measured periodically. The product was obtained after drying over anhydrous sodium sulfate and removing xylene under vacuum [5].

2.1.2. Amidation of methylester of the fatty acid

This amidation was based upon the procedure for the preparation of high purity fatty acid alkanolamides [6,7]. The methyl ester of the fatty acids (0.318 mol) and (0.349 mol) monoethanolamine were heated to 100 °C. Freshly cut sodium 0.25 g was added and the reaction mixture stirred and heated at 115–125 °C for 40 min. The reaction flask was fitted with a condenser and a side arm for collection of the distillate. Heating was continued until methanol ceased to be collected. The reaction product was dissolved in hot absolute ethanol, clarified by hot filtration, and chilled at room temperature. The crystallized solids were collected in about 91% yield.

2.1.3. Ethoxylation

Polyoxyethylene fatty acid monoethanolamides were prepared by the ethoxylation of fatty acid monoethanolamides (1mole) inside the reaction reactor with 0.3 gm sodium metal as a catalyst and heated at 150–180 °C with continuous stirring while passing a stream of nitrogen gas through the system for 10 min to flush out air [8]. The mole numbers of ethylene oxide were calculated by the weight difference [9–12]. The number of moles of ethylene oxide units was adjusted to be about 6 units. The obtained product was weighed, neutralized with HCl, dissolved in isopropanol, and then salted out with super saturated NaCl solution. The organic layer was then separated and the isopropanol was distilled off. The obtained ethoxylated product has a brown viscous liquid appearance. The products were purified by recrystallization three times in ethanol, and then were washed with diethyl ether.

2.1.4. Carboxymethylation

The following procedure was used for the preparation of amide ether carboxylate. Sodium monochloroacetate (1.17 g, 0.01 mol) was added to (2.24 g, 0.01 mol) of the ethoxylated fatty acid monoethanol amide in 100 ml aqueous acetone in a 250 ml Erlenmeyer flask fitted with a condenser, the mixture was heated under reflux for about 5 h, left to stand for 2 hours and the solvent was removed by distillation under reduced pressure where a solid product was obtained which was purified by repeated crystallization from chloroform [13].

3. Structural confirmation of the prepared surfactants

The chemical structures of the prepared surfactants were confirmed by:

1. FT-IR spectra using ATI Mattson Infinity series TM, Bench top 961 controlled by Win First TM V2.01 software. (Egyptian Petroleum Research Institute).
2. The \(^1\)H NMR spectra were measured on a Varian Genini 200 MHz spectrophotometer, Laser Unit, Physics Department, faculty of Science, Cairo University.
3. The mass spectra were measured on Mass spectrophotometer HP Model GC/MS-QPL000EX (Shimadeu) at 70ev (Micro – analytical Center, Cairo University).

4. Evaluation of the surface properties of the prepared AECs

Methods for the evaluation and testing of surface active properties are described in [14]:

4.1. Surface and interfacial tension

The surface and interfacial tension of the prepared compounds (sodium salts solutions) was measured using Du-Nouy tensiometer (KRUS Type 8451) for different concentrations at 25 °C. De ionized water with a surface tension of 72.8 mN/m at 25 °C was used to prepare all solutions. The apparent surface tension was measured 5 times for each sample within a 2 min interval between each reading [15].

Interfacial tension measurements were made for surfactant-oil system at 25 °C using surfactant solution of concentration 0.1%.

4.2. Critical micelle concentration (cmc)

The critical micelle concentration values of the prepared surfactants were determined using surface tension method [16].

4.3. Emulsion stability

The emulsifying property for the prepared amide ether carboxylate was determined as follows: A surfactant solution (10 ml, 0.1%) was mixed with light paraffin oil (10 ml). The mixture
was put in a (100 ml) graduated stopper tube and shook vigorously for 2 min, then the tube was placed up right and the separation of the two layers is observed. The time taken for the separation of (9 ml) of aqueous layer indicates the emulsifying power of the surfactant [17,18].

4.4. Calcium stability

The calcium stability of amide ether carboxylates was determined by a modified HART method [19]. The surfactant solution (10 ml) from 0.1% solution was titrated against calcium chloride solution 0.1 N. The end point was determined by visual observation of cloudiness of the surfactant solution. The calcium stability: i.e. stability toward hard water was then expressed as ppm calcium carbonate.

4.5. Foam height

The foam heights of 0.1% solutions of the prepared surfactants were measured in bi-distilled water using Ross-Miles pour test [20,21] at 25 °C. The foaming behavior of amid ether carboxylate mixed with sodium dodecyl benzenesulfonate (1:3) was also studied at 25 °C [22].

4.6. Resistance to hydrolysis

The resistance of the prepared surfactants toward acid and base hydrolysis was determined using surface tension [23] measurements before and after boiling their solutions (0.1%) in 5% sulfuric acid and 1% sodium hydroxide for 30 min and one hour respectively.

5. Results and discussion

5.1. Synthesis of surfactants

New amide ether carboxylates (AEC) were obtained in high purity by amidation, ethoxylation and carboxymethylation reaction steps of a fatty acid or its methylester and subsequent neutralization and dilution steps. The chemical structure of the prepared compounds was confirmed by FTIR, 1HNMR and Mass spectra spectroscopic analyses Tables 1 and 2. The results are in good accordance with the expected structure of each compound.

These new surface active materials revealed interesting properties such as high foaming power combined with very good hard water compatibility.

AECs are characterized by their combined hydrophilic moiety, i.e. carboxylic anionic and ethoxylated nonionic parts, which dissociate weakly, exhibiting nonionic behavior at low pH.

The preparation steps of these surfactants are shown in scheme 1.

5.2. Structure confirmation

5.2.1. FTIR Spectroscopy

Basically, the synthesized anionic surfactants AECs have common function groups according to their preparation method. As the reaction proceeds through the formation of the characterized ester, amide and ether linkage, the FTIR spectra would show the general characteristics of these compounds.

The FTIR data in Table 1 show the peaks for the products as follows: a very strong absorption band arises mainly from asymmetric and symmetric stretching of methylene group, at ν sym (CH2) 2852 cm⁻¹, ν asym (CH2) around 2923 cm⁻¹ and C–H deformed band that appeared at 1464 cm⁻¹, ν (C═O) amide arranged between 1670–1640 cm⁻¹, ν (NH) stretching bands of AEC at 3283 cm⁻¹, ν (C–N) 1690 cm⁻¹, (C–O–C) at 1115 cm⁻¹. While the appearances of ν (C═O) at 1721–1730 cm⁻¹ for carboxylic acid. ν (C═C) at 1626 and 1618 cm⁻¹ represent unsaturated carbon for AECc18− and AECc18−− compounds respectively. The shift of intensity of the peaks depends on the difference in the alkyl chain length.

5.2.2. Proton nuclear magnetic resonance (1HNMR)

The 1HNMR spectra of the synthesized AECs in Table 2 show the appearance of the first peak at 0.83 which represent the triplet three protons of the terminal CH3 group. A singlet of 20 protons attached in the long hydrophobic part at 1.237 ppm, the –NH signal at 7.9 ppm, which confirmed the formation and distribution of hydrogen protons in the prepared surfactants.

5.2.3. Mass spectroscopy

Mass spectra of AECc12, the molecular ion peak m/e at 540 and also show the base peak at m/e 226 for the fraction: (C11H23C═ONHCH2CH3).

<table>
<thead>
<tr>
<th>Cpd.</th>
<th>I.R. Bands (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lauric AEC (c12)</td>
</tr>
<tr>
<td>V,C–Hst</td>
<td>2852.99</td>
</tr>
<tr>
<td>V₀C–Hst</td>
<td>2920.45</td>
</tr>
<tr>
<td>C–Hdef</td>
<td>1368.90</td>
</tr>
<tr>
<td>C═O</td>
<td>1652.54</td>
</tr>
<tr>
<td>C–N</td>
<td>1245.70</td>
</tr>
<tr>
<td>NH₂end</td>
<td>1538.86</td>
</tr>
<tr>
<td>NHst</td>
<td>3450.00</td>
</tr>
<tr>
<td>C–O–C</td>
<td>1109.35</td>
</tr>
<tr>
<td>C═C</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 1 FTIR spectral data for the prepared surfactants.
5.3. Surface properties of the prepared surfactant

5.3.1. Surface and interfacial tension

The surface tension values were measured for aqueous solution of the prepared surfactants (AECs) with different concentrations at 25 °C. As shown in Figs. 1 and 2 the surface tension of the samples solution decreases by increasing the concentration of surfactants, up-to defined concentration then there is no further decrease in the surface tension. This concentration is the critical micelle concentration (cmc).

Generally, two forces affect the surfactant molecules in the aqueous medium. First, the repulsion forces between the hydrophobic part of surfactant and water molecules, and the attraction forces between water and the hydrophilic parts in the surfactant molecules. The competition between the opposite forces represents either the critical micelle concentration located at higher or lower values.

In the prepared surfactants we have found that the surface tension increases by increasing the alkyl chain length [24] and decreases with increasing unsaturations (double bond). The structure of the synthesized surfactants affects the surface properties to a large extent. The presence of the carbonyl group and ethylene oxides groups in the molecular structure makes the hydrophobicity of the molecules decrease and becomes more hydrophilic. That facilitates the molecules to be found in the bulk of their solutions and hence the surface tension stays at higher values.

Table 2

<table>
<thead>
<tr>
<th>Compound name</th>
<th>1HNMR(DMSO) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric AEC (c12)</td>
<td>0.83 (t, 3H, CH3), 1.237 (m, 20H), 2.67(q, 2H, CONHCH2), 7.9 (S, 1H, CONH), 3.20 (t, 2, CH2O), 3.5 (m, 24H, (CH2CH2O)nH), 2.5 (DMSO)</td>
</tr>
<tr>
<td>Oleic AEC (c18)</td>
<td>0.83 (t, 3H, CH3), 1.236 (m, 14H), 2.67(q, 2H, CONHCH2), 7.9 (S, 1H, CONH), 3.39 (t, 2H, CH2O), 3.5 (m, 24H, (CH2CH2O)nH), 5.33(m, 1H, C=CH–CH3) 2.5 (DMSO)</td>
</tr>
</tbody>
</table>

Scheme 1 The preparation of Amide ether carboxylate surfactants (AEC).

![Scheme 1](image)

Figure 1 Variation of the surface tension with logarithm of concentrations for synthesized AEC (c12–16) in water at 25 °C.

![Figure 1](image)

Figure 2 Variation of the surface tension with the logarithm of concentrations for synthesized AEC (c18,c18',c18'') in water at 25 °C.

![Figure 2](image)

5.3.2. Interfacial tension measurements

The interfacial tension of the prepared series of surfactants solutions was measured at interface with light paraffin oil at 25 °C. The interfacial tension values for the prepared surfactants are greatly affected by the hydrophobic part of surfactant and water molecules, and the attraction forces between water and the hydrophilic parts in the surfactant molecules. The competition between the opposite forces represents either the critical micelle concentration located at higher or lower values.

In the prepared surfactants we have found that the surface tension increases by increasing the alkyl chain length [24] and decreases with increasing unsaturations (double bond). The structure of the synthesized surfactants affects the surface properties to a large extent. The presence of the carbonyl group and ethylene oxides groups in the molecular structure makes the hydrophobicity of the molecules decrease and becomes more hydrophilic. That facilitates the molecules to be found in the bulk of their solutions and hence the surface tension stays at higher values.

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indicate the ability of using these surfactants in several applications as corrosion inhibitors and biocides.

5.3.3. Critical micelle concentration CMC

The cmc in aqueous media gives an indirect indication about the solubility of these surfactants in water. The surface tension decreases steadily as the surfactant concentration is increased; at some critical concentrations no further reduction in the surface tension is observed. This indicates the attainment of saturation in the surface adsorbed layer and the commencement of micelle formation in the bulk.

The cmc values for the prepared surfactants were determined by:

5.3.3.1. Surface tension method. The values of the surface tension obtained for various concentrations of aqueous solutions of the prepared surfactants in distilled water at 25 °C, are plotted against logarithm of the corresponding concentrations, Figs. 1 and 2. It is obvious for all surfactants that, very sharp decrease of the surface tension was observed as the concentration increases, then the curves break rather rapidly at relatively low concentration and continue to steep slowly as the concentration increases. From the intersection points in these figures the critical micelle concentrations (cmc) were determined for the prepared compounds and listed in Table 3.

The cmc values of the synthesized surfactants show an increasing trend with increasing the chain length of alkyl group, and increasing double bonds. The increase in cmc value can be attributed to an increase in the solubility of the surfactant molecules i.e., the presence of polar atoms as oxygen or nitrogen in the hydrophobic chain (but not associated with the head group), results in an increase in the cmc [25–28].

Table 3  Surface and interfacial tensions of amide ether carboxylates series at 25 °C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sodium salts</th>
<th>Surface tension (mN/m)</th>
<th>Interfacial tension (mN/m)</th>
<th>CMC (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric AEC (c12)</td>
<td>31</td>
<td>9.5</td>
<td>0.018 × 10⁻²</td>
<td></td>
</tr>
<tr>
<td>Myristic AEC (c14)</td>
<td>32.5</td>
<td>9</td>
<td>0.047 × 10⁻²</td>
<td></td>
</tr>
<tr>
<td>Palmitic AEC (c16)</td>
<td>38</td>
<td>8.5</td>
<td>0.104 × 10⁻²</td>
<td></td>
</tr>
<tr>
<td>Stearic AEC (c18)</td>
<td>49</td>
<td>8.5</td>
<td>0.075 × 10⁻²</td>
<td></td>
</tr>
<tr>
<td>Oleic AEC (c18=)</td>
<td>33</td>
<td>8</td>
<td>0.103 × 10⁻²</td>
<td></td>
</tr>
<tr>
<td>Linoleic AEC (c18==)</td>
<td>32</td>
<td>10</td>
<td>0.133 × 10⁻²</td>
<td></td>
</tr>
</tbody>
</table>

Micelle formation, or micellization is an important phenomenon not only because of a number of important interfacial properties, such as detergency and solubilization, and on the existence of micelles in solution, but also it affects other interfacial phenomena, such as the reduction of surface or interfacial tension, that do not directly involve micelles.

Table 4  Foam height, Foam, Foam half time, and Foam stability of amide ether carboxylates series at 25 °C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Foam height (mm)</th>
<th>Foam height of mixed system with Sodium dodecyl benzene sulfonate (1:3) (mm)</th>
<th>Foam half time (min)</th>
<th>Foam stability (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric AEC (c12)</td>
<td>8</td>
<td>120</td>
<td>9</td>
<td>14</td>
</tr>
<tr>
<td>Myristic AEC (c14)</td>
<td>5</td>
<td>90</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>Palmitic AEC (c16)</td>
<td>3</td>
<td>80</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Stearic AEC (c18)</td>
<td>2</td>
<td>73</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Oleic AEC (c18=)</td>
<td>6</td>
<td>95</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>Linoleic AEC (c18==)</td>
<td>3</td>
<td>75</td>
<td>10</td>
<td>7</td>
</tr>
</tbody>
</table>
5.4. Foaming power

One of the most important properties is the foaming power. The prepared compounds AECs (C12–C18) and (C18’,C18’’) have considerable foaming properties which decrease with increasing the chain length. By comparison with the conventional anionic surfactants, AECs (C12–C18) and (C18’,C18’’) have considerable foaming power when used in combination (in 1:3 ratio) with sodium dodecylbenzenesulfonate as shown in Table 4. It will be possible to develop new formulation concepts based on the prepared anionic surfactant and sodium dodecyl benzenesulfonate.

Foaming behavior of the prepared surfactants increases on mixing with sodium dodecyl benzene sulfonate. They gave higher foam height than the individual surfactants; However, the same behavior is observed when the chain length increases the foam height decreases as shown in Figs. 4 and 5. Low foaming power could have an application in the dyeing auxiliary industry.

5.5. Emulsion stability

Emulsification is one of the most important properties of surfactants. In many textile processes such as scouring and dyeing, it is necessary to introduce surfactants into the bath to remove oily impurities from the fibers. The emulsifying power of the prepared anionic surfactants; AECs (C12–C18) and (C18’,C18’’) are listed in Table 5 as a function of time. It is clear that the emulsifying power depends on the variation of alkyl chain length.

Data in Table 5 show that AECc12 and AECc18’’ were more efficient in the stabilization of the emulsion, and they have been used in fields such as, shampoos, cosmetic, emulsion paints and the textile industry [3,4].

The, AECC14, AECC16, AEC c18 and AECc18’’ surfactants have in general low emulsion stability as a function of time, so that these surfactants cannot be used as long term emulsion stabilizers.

5.6. Calcium stability

The calcium stability of AECs (C12–C18) and (C18’,C18’’) is given in Table 5. The data revealed that the prepared compounds have excellent calcium stability. The results are dependent on the variation of alkyl chain length, they decrease as the chain length increases.

5.7. Resistance to hydrolysis

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

The prepared compounds AECs (C12–C18) and (C18’,C18’’) are classified as anionic surfactants, so they will be affected by the acidic environment rather than the alkaline one.

The prepared surfactants posses high extent of stabilization in their structure (depending on the values of their surface tension) when treated with acids in short periods of treatment, while prolonged heating with acids (up to 60 min) has an aggressive effect on their molecules; hence, the surface tension increased upon increasing the hydrophobic chain length, the

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Table 5 Calcium and emulsion stability of Amide ether carboxylates series at 25 °C.

<table>
<thead>
<tr>
<th>Compound sodium salts</th>
<th>Calcium stability (ppm)</th>
<th>Emulsion stability (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric AEC (c12)</td>
<td>&gt;2540</td>
<td>261</td>
</tr>
<tr>
<td>Myristic AEC (c14)</td>
<td>&gt;2772</td>
<td>77</td>
</tr>
<tr>
<td>Palmitic AEC (c16)</td>
<td>&gt;2772</td>
<td>20</td>
</tr>
<tr>
<td>Stearic AEC (c18)</td>
<td>&gt;2218</td>
<td>49</td>
</tr>
<tr>
<td>Oleic AEC (c18’)</td>
<td>&gt;2051</td>
<td>380</td>
</tr>
<tr>
<td>Linoleic AEC (c18’’)</td>
<td>&gt;2162</td>
<td>48</td>
</tr>
</tbody>
</table>

Table 6 Resistance to hydrolysis of Amide ether carboxylates.

<table>
<thead>
<tr>
<th>Compound sodium salts</th>
<th>Surface tension of 0.1% surfactant solution at 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>H2SO4 5%</td>
</tr>
<tr>
<td></td>
<td>30 min</td>
</tr>
<tr>
<td>Lauric AEC(c12)</td>
<td>31</td>
</tr>
<tr>
<td>Myristic AEC(c14)</td>
<td>32.5</td>
</tr>
<tr>
<td>Palmitic AEC(c16)</td>
<td>38</td>
</tr>
<tr>
<td>Stearic AEC(c18)</td>
<td>39</td>
</tr>
<tr>
<td>Oleic AEC(c18’)</td>
<td>33</td>
</tr>
<tr>
<td>Linoleic AEC(c18’’)</td>
<td>32</td>
</tr>
</tbody>
</table>
resistance toward acids decreases slightly as represented in Table 6.

6. Conclusions

A series of amide ether carboxylates with different alkyl chain lengths from C\textsubscript{12}–C\textsubscript{18}, and (C\textsubscript{18}′, C\textsubscript{18}′′) were synthesized. The study of their surface properties showed their stability in hard water and in acidic and alkaline media. These compounds have high calcium ion stability. The low foaming power could have an application in the dyeing auxiliary industry. The lower values of the interfacial tension values indicate the ability of using these surfactants in several applications as corrosion inhibitors and biocides. The data revealed various advantages and potentials as a main surfactant as well as a co surfactant.

References