Foaming capacity of new superficial active cationic polyethers in food hygienization

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Abstract

Colloidal features [foaming capacity (FC); foam stability (FS) and foam density (FD)] of conditioning auxiliaries (additives) of plant protection active principles constitute, together with toxicity, a decisive technical index in forming administering receipts in modern ecological agriculture and foodstuff processing all during the agroalimentary processing and consumption chain.

In this paper we show the results of a study on a new class of superficial active compounds N, N – dimethyl – N – alkyl (R1) (CH$_3$÷C$_{16}$H$_{33}$) – N – β – alkylaryl (C$_9$H$_{19}$ – C$_6$H$_4$-) polyethylenoxy ($n$ = 3–20) ethylammonium chlorides. As diderived glimes, they have a guided regulation capacity of the HLB balance through the change of the medium degree of oligomerisation ($n$) of the polyoxyethylene chain (PEO). Can thus obtain a wide range of structures such as mycelium solute, dispersion, emulsion, and foaming agents, etc., through the cyanoethylation of polyethoxylated nonylphenols with a medium degree of oligomerisation ($n$) between 3 and 20 structural oxyethylene units (EO) in alkaline catalysis with monomer acrylonitrile, followed by a classical hydrogenation in heterogeneous catalysis of intermediary nitrile thus obtained, and finally alkyl quaternarisation of the polyetheramine obtained with methyl or alkyl (CH$_3$ ÷ C$_{16}$H$_{33}$) chlorides to obtain.

These are biodegradable in water plants, which ensure special ecologlcal features and high compatibility within the restrictive legal ensemble of a foodstuff processing integrated in an extremely polluted environment. Structures have real bacteriostatical abilities compared to a wide spectrum of microrganisms (tested in studies related to this paper). Low toxicity of polyoxyethylene chains (PEO) together with that of other structural units in this polyether cationic surfactants provide the studied glymes with a high compatibility in relation to environment and to plant and animal organisms of the food chain.

Keywords: foaming, foam density, foaming capacity, glime, polyether cationic surfactants

1. Introduction

Literature studies report a wide range of superficialactive cationic compounds [1-6] but limited and sporadic superficialactive cationic polyethers [7-14].

Studied cationic polyethers, (I) [1-6; 12-14] have been proposed, with optimum results in cleaning recipes in food processing with other nonionic – anionic components (soaps) based on bacteriostatic powers recognized of the class.

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Foam, as a colloid feature (disperse system gas in liquid) supposes the presence together with disperse phase (air) and dispersion medium (water), a foaming component, soluble in dispersion medium, with stabilising foam role. If between the two phases of the system there is no balance during the process of formation-destruction of foam, the third component of the system cannot be considered a foaming agent.

The main characteristics of a foaming agent in an aqueous flow (solution) are its foaming strength (capacity) \( FC \); its foam stability \( FS \); foam density \( FD \).

Colloid structures mentioned have been obtained and characterised in order to diversify the range of industrial technological additivation products that cumulate simultaneously adjusting foaming competence.

2. Materials and methods

2.1 Determination of foaming competences (similar RS EN 12728:2002)

Foaming power \( FC \) is the height of foam, (expressed in cm), formed under determination conditions.

Foam stability \( FS \) is the ratio of foam volume after a long rest and the initial foam volume. It is the ratio of foam height after 5 minutes and its initial height, or by indicating the initial height and after 5 minutes, in determination condition.

Foam density \( FD \) is the rapport between solution volume transformed in foam and the volume of formed foam. It is the rapport between corresponding height of foam volume formed by free-fall in determining conditions.

Equipment (figure 1)

- **200 mL pipette**, for superficialactive cationic polyether solution;
- beaker for foam, in mm, equipped with external jacket heating and drain tap. Outer cylinder is marked with three parts: at 50 mL; 250 mL and 900 ± 0.5 mL above the marker from 50 mL.

When the pipette is mounted above cylinder, the solution from pipette must move a vertical trajectory parallel to the axis cylinder, and the pipette tip to break up the uppermost.

Investigational product is dissolved in distilled water or soft water prescribed in quality standards (10° water hardness or harder than in special cases) to a double concentration than concentration prescribed in the quality standards, heated to boiling for dissolve if is necessary.
It is get to the required concentration (generally 2 g active product/L), by dilution with water having double hardness than that prescribed in quality standards.

For optimum colloidal characterization of the product, determination can be made for a wide concentration, generally between 0.5...5 g active product/L.

Actual determination is done to the temperature recommended in quality standards (generally 25 ± 2°C, 40 ± 2°C or 70 ± 2°C).

It is open the tap water in heating outer sheath of foam cylinder, to prescribed working temperature. It is wash with water the cylinder walls and is allow draining for 10 minutes, and then the cylinder is closed.

Solution examined is maintained for 10 minutes before determination in a thermostat or in a constant temperature bath, at the prescribed working temperature.

It is introduced with the help of a pipette, 50 mL solution examined in cylinder for foam, along the walls by circular motion.

Is pipette 200 mL solution examined, pipette is placed above the cylinder and opens the valve to drain solution.

Is note the solution and the foam level, in the foam cylinder, immediately after leakage of the solution from pipette and after standing for five minutes.

To implement a new determination it opens the cylinder valve for foam and allow to drain content, walls are washed with distilled water, it allow to drain for 10 minutes and then continue as described above.

Evaluation of foaming competences is done with relations below:

\[
\text{Foaming capacity (FC)} = h_1 - h_2
\]

\[
\text{Foam stability (FS)} = \frac{h_3 - h_2}{h_1 - h_2}
\]

\[
\text{Foam density (FD)} = \frac{h_4 - h_2}{h_1 - h_2}
\]

where:

- \( h_1 \) - initial level of foam, [cm];
- \( h_2 \) - initial level of solution, [cm];
- \( h_3 \) - foam level, after 5 minutes, [cm];
- \( h_4 \) - solution level, after 5 minutes, [cm];
- \( h_5 \) - level corresponding of 250 mL mark, [cm];

If are interested only the foaming capacity and foam stability, is note exclusively the initial height of the foam \((h_1 - h_2)\) and foam height after 5 minutes rest \((h_3 - h_2)\). In the analysis bulletin of the beneficiary it’s specify temperature, solution concentration and water hardness which has made the determination.

3. Results and Discussion

Long chain cationic surfactants containing polyether linkage (1) were synthesized and also their antibacterial activities in terms of growth inhibition of *Staphylococcus aureus* and *Escherichia coli* were preliminary examined.

Some of them also preliminary tested against *Trichophyton asteroidis*, *T. interdigitale*, *T. granulosus*, *Epidermophyton floccosum* and *Microsporum canis*. The octyl radical (R₁) was more potent than the decyl radical (R₁). Also no definite correlation between positional isomers and chain length and antibacterial activities was observed.

**Foaming capacity (FC)**, \( \text{N, N-dimethyl-N-alkyl (CH}_3^\beta\text{C}_9\text{H}_{19}\text{-N-β-alkylaryl (C}_8\text{H}_{16}\text{-polyethyleneoxy } (\text{CH}_2\text{O})_n\text{) ethylammonium chlorides have a lower solubility, therefore their foaming capacity is practically between foam moderator domain and strong foam domain. The capacity of N,N-dimethyl-N-alkyl (R}_1\text{) (CH}_3^\beta\text{C}_9\text{H}_{19}\text{-N-β-alkylaryl (C}_8\text{H}_{16}\text{-polyethyleneoxy } (\text{CH}_2\text{O})_n\text{) ethylammonium chlorides to reduce the superficial tension at the separation interface air-aqueous flow diminishes with the increase of hydrocarbonate chain length R}_1\text{ because of the removal of the hydrophilic polar group towards the centre of the chain and of diminution of "packing" degree at the interface. This diminishes the foaming capacity by diminishing foam film elasticity. In the series of N,N-dimethyl-N-alkyl (R}_1\text{) (CH}_3^\beta\text{C}_9\text{H}_{19}\text{-N-β-alkylaryl (C}_8\text{H}_{16}\text{-polyethyleneoxy } (\text{CH}_2\text{O})_n\text{) ethylammonium chlorides, foaming capacity decreases less than in the series of N,N-dimethyl-N-alkyl (R}_1\text{) (CH}_3^\beta\text{C}_9\text{H}_{19}\text{-N-β-alkylaryl (C}_8\text{H}_{16}\text{-polyethyleneoxy } (\text{CH}_2\text{O})_n\text{) ethylammonium chlorides.}
The increase of flow temperature favours the foaming capacity (FC) as it strongly affects the solvation degree, viscosity, film elasticity in the elementary foam cell and mobility of cation micelle in the flow (table 1).

**Foam stability (FS)** of N,N-dimethyl-N-alkyl (Rᵢ) (CH₃₂C₈H₁₇)-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethylenoxy (n = 3–20) ethylammonium chlorides is determined by the adjustment speed of superficial tension at the level of foam film, among its different areas.

Thus N,N- dimethyl-N-alkyl (Rᵢ) (CH₃₂C₈H₁₇)-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 3–20) ethylammonium chlorides strongly diminish superficial tension and form a very stable foam, while N,N-dimethyl-N-alkyl (Rᵢ) (C₁₀H₂₁+C₆H₄ᵢ)-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 3–20) ethylammonium chlorides diminish superficial tension and form foams less stable in time. Increasing ethylene oxide content for the same hydrocarbonate chain length increases the hydrophilia of the structure, foam stability (FS): it is the stronger the longer the hydrocarbonate chain (Table 1).

The increase of hydrocarbonate chain length Rᵢ attached to the quaternary nitrogen atom and the removal of the polar group towards the centre of the structure result, for the same ethylene oxide content, in a strong diminution of the reduction capacity of superficial tension, of foaming capacity (FC), but also of foam stability (FS) because of the decrease of "packing" degree of cation structure at the interface due, on one hand, to electrostatic repelling and, on the other hand, to steric effects (Table 1).

The flow temperature influences negatively the foaming stability (FS) by the removal to the right of foam formation-dissolution balance.

The phenomenon becomes significant in the case of N,N-dimethyl-N-alkyl (Rᵢ) (C₁₀H₂₁+C₁₂H₂₅)-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 3) ethylammonium chlorides, while in the case of N,N-dimethyl-N-alkyl (Rᵢ) (C₁₀H₂₁+C₁₂H₂₅)-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 3) ethylammonium chlorides we can talk about foam moderators.

**Foam density (FD)** increases with ethylene oxide content of the molecule (Table 2). In N, N, N-trimethyl-N,N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 3–20) ethyl-ammonium chlorides, foaming density (FD) increases less.

For the same ethylene oxide content, foam density in N,N-dimethyl-N-alkyl (Rᵢ) (CH₃₂C₈H₁₇)-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 3–20) ethyl-ammonium chlorides decreases with the increase of hydrocarbonate chain length due to the diminution of the reduction capacity of superficial tension at the film level, with the removal of the polar group towards the centre of the hydrocarbonate chain and with an increase of steric factor share in the process of "packing" of cation structures at the air-flow separation interface. Absolute decrease of foam density (FD) is lower in the series of N,N-dimethyl-N-alkyl (Rᵢ) (CH₃₂C₈H₁₇)-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 3–20) ethylammonium chlorides, where there is a moderate increase due to the higher content of ethylene oxide (high hydrophilia) than in the series of N,N-dimethyl-N-alkyl (Rᵢ) (CH₃₂-C₆H₄ᵢ)-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 3–20) ethylammonium chlorides, to reach higher values in the series of N,N-dimethyl-N-butyl-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 3) ethylammonium chlorides, to reach higher values in the series of N,N-dimethyl-N-butyl-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 3) ethylammonium chlorides, to reach higher values in the series of N,N-dimethyl-N-butyl-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 20) ethylammonium chlorides. In the series of N,N-dimethyl-N-butyl-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 3) ethylammonium chlorides, the increase of the carbohydrate chain length for the same ethylene oxide content does not change foam density (FD).

Foaming density of N,N-dimethyl-N-butyl-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 3) ethyl ammonium chlorides increases significantly compared to that of N,N-dimethyl-N-butyl-N-β-alkylaryl (C₆H₁₉-C₆H₄ᵢ) polyethyleneoxy (n = 20) ethylammonium chlorides, with an increase of polyethyleneoxy chain length. Evolution of the relative hydrophilic / hydrophobic balance (HLB) in the series N,N-dimethyl-N-alkyl (Rᵢ) (CH₃₂-C₆H₄ᵢ)-N-β-alkylaryl polyethyleneoxy (n = 3 –20) ethylammonium chlorides and its knowledge is decisive in directed choosing the optimal superficialactive structure of cleaning operation in food processing imposed by case law.
Besides this the conformation structure has a major role to ensure awareness and how to "wrapping" on separation interface of the metallic, ceramic, plastic, textile, food support/ Watering fleet – that display (wetting case) the metallic, ceramic, plastic, textile, food support/air (foaming case).

These are biodegradable in water plants, which ensure special ecological features and high compatibility within the restrictive legal ensemble of a foodstuff processing integrated in an extremely polluted environment. Structures have real bacteriostatical abilities compared to a wide spectrum of microorganisms (tested in studies related to this paper). Low toxicity of polyoxyethylene chains (PEO) together with that of other structural units in this polyether cationic surfactants provide the studied glymes with a high compatibility in relation to environment and to plant and animal organisms of the food chain. Increasing temperature diminishes viscosity, elasticity and size of the superficial film in the foam cell. The foaming capacity (strength) increases because of the change of superficial tension with temperature, while foaming density (FD) and stability (FS) decrease.

The greater the share of hidrocarbonate chain, the stronger the phenomenon is (Table 2). Absolute decrease of foam density (FD) is lower in the series of N,N-dimethyl-N-alkyl (Rᵢ) (CH₃-C₆H₄₅)-N-β-alkylaryl (C₃H₇-C₆H₄⁺) polyethyleneoxy (n=3–20) ethyl ammonium chlorides, where there is a moderate increase due to the higher content of ethylene oxide (high hydrophilicity) than in the series of N,N-dimethyl-N-alkyl (Rᵢ) (CH₃-C₆H₄₅)-N-β-alkylaryl (C₃H₇-C₆H₄⁺) polyethyleneoxy (n=3) ethylammonium chlorides, to reach higher values in the series of N,N-dimethyl-N-alkyl (Rᵢ) (CH₃-C₆H₄₅)-N-β-alkylaryl (C₃H₇-C₆H₄⁺) polyethyleneoxy (n=20) ethylammonium chlorides.

In the series of N,N-dimethyl-N-butyl-N-β-alkylaryl (C₃H₇-C₆H₄⁺) polyethyleneoxy (n=3) ethylammonium chlorides, the increase of the carbohydrate chain length for the same ethylene oxide content does not change foam density (FD).

Foaming density of N,N-dimethyl-N-butyl-N-β-alkylaryl (C₃H₇-C₆H₄⁺) polyethyleneoxy (n=3) ethyl ammonium chlorides increases significantly compared to that of N,N-dimethyl-N-butyl-N-β-alkylaryl (C₃H₇-C₆H₄⁺) polyethyleneoxy (n=20) ethylammonium chlorides, with an increase of polyethyleneoxy chain length.

Evolution of the relative hydrophilic / hydrophobic balance (HLB) in the series N,N-dimethyl-N-alkyl (Rᵢ) (CH₃-C₆H₄₅)-N-β-alkylaryl polyethyleneoxy (n = 3 – 20) ethylammonium chlorides and its knowledge is decisive in directed choosing the optimal superficialactive structure of cleaning operation in food processing imposed by case law.

Besides this the conformation structure has a major role to ensure awareness and how to "wrapping" on separation interface of the metallic, ceramic, plastic, textile, food support/ Watering fleet – that display (wetting case) the metallic, ceramic, plastic, textile, food support/air (foaming case).

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Table 1: Dependence of the structure of foaming features (FC/FS/FD) of N,N-dimethyl-N-alkyl (R<sub>1</sub>\((\text{CH}_3\div\text{C}_{16}\text{H}_{33})\))-N-β-alkylaryl (C<sub>9</sub>H<sub>19</sub>-C<sub>6</sub>H<sub>4</sub>-) polyethyleneoxy (n = 3 – 20) ethylenammonium chlorides (20°C, 2 g/L concentration)
Table 2. Dependence on temperature of foaming (FS; FD) characteristics in the series of N,N-dimethyl-N-alkyl \( R_1 \) (\( C_{10}H_{21} \))-N-\( \beta \)-alkylaryl (\( C_9H_{19}-C_6H_4- \)) polyethyleneoxy (\( n = 3-20 \)) ethylammonium chlorides, flow concentration 2 g/L

<table>
<thead>
<tr>
<th>No.</th>
<th>Hydrophilic polar group</th>
<th>( \bar{n} )</th>
<th>Foaming capacity</th>
<th>Foaming stability</th>
<th>Foaming density</th>
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<td>( 40 )</td>
<td>( 60 )</td>
<td>( 80 )</td>
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<td>6</td>
<td>7.9</td>
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Legend:
- \( \bar{8.4} \) – \( FC \)
- \( \bar{8.2} \) – \( FS \)

4. Conclusion

Experimental results reported confirm the colloid moistening displaying competences, of N,N-dimethyl-N-alkyl (\( R_1 \) (\( CH_3-C_{10}H_{21} \))-N-\( \beta \)-alkylaryl (\( C_9H_{19}-C_6H_4- \)) polyethyleneoxy (\( n = 3-20 \)) ethylammonium chlorides under study and recommend them as potential aditivization structures and in efficient hygiene receptures in agroalimentary processing (metal, ceramic, textile, plastic, etc. surfaces).

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References (selective list)
6. C. Jianu, Cercetări privind potențialul aditiv de complexare cu ioni metalici pentru îmbunătățirea valorii alimentare a unor materii prime horticole, Teză de doctorat, 2006
7. U.S. Patent, 5094770, 1992;
12. I., Jianu, ş.a., Contribuţii la studiul cinetic ş termodinamic al cianoetilării alcoolilor superioiri, *Lucrările Congresului Mondial de substanţe superficia active*, München, Germania, **1984**, 5-8 Mai, 125-127;
