

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Effect of Certain Ethylene Oxide Heterogeneous Heterobifunctional Acyclic Oligomers (HEHAO) on Wetting

Calin Jianu

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/60998>

Abstract

The effect of ethylene oxide (EO) heterogeneous heterobifunctional acyclic oligomers (HEHAO) on wetting represents a continuation of the review of the research partly published by the author on ethylene oxide (EO) homogeneous heterobifunctional acyclic oligomers (HOHAO). Heterogeneous polyoxyethylene chains obtained by the anionic polymerization of EO (“anionic ring-opening polymerization”) with a certain polydispersity degree are hydrophilic, flexible (specific spatial conformation), biocompatible “bridges,” without toxicity. After the purification of polyethoxylated higher alcohols (technical products), heteroderivatization performed by an adapted classical reaction scheme led to the colloiddally evaluated HEHAO series.

Keywords: Polyoxyalkylene ether acid with higher alkyl group, alkyl polyethoxy carboxylate surfactants, carboxy propylated nonionic alkyl surfactants, wetting, ethylene oxide heterobifunctional acyclic oligomers

1. Introduction

Ethylene oxide heterogeneous heterobifunctional acyclic oligomers (HEHAO) represent a class of relatively recent (ca. nine decades) “niche” surface-active compounds, if we refer only to molecular architectures considered in this chapter for colloidal study. The material is a continuation of the research partly published by the author and collaborators in the period

1968–2014 on ethylene oxide homogeneous heterobifunctional acyclic oligomers (HOHAO) (Figure 1a). The difference between the two types of acyclic oligomers lies in the fact that HOHAO [1] have in their structure “homogeneous” polyoxyethylene chains (with strictly determined oligomerization degrees (n)), built by the adapted Williamson method [2–4], while HEHAO (Figure 1b) have “heterogeneous” polyoxyethylene chains [1] and oligomerization degrees (n^*), respectively, in a statistical distribution dependent on the operating parameters accessed.

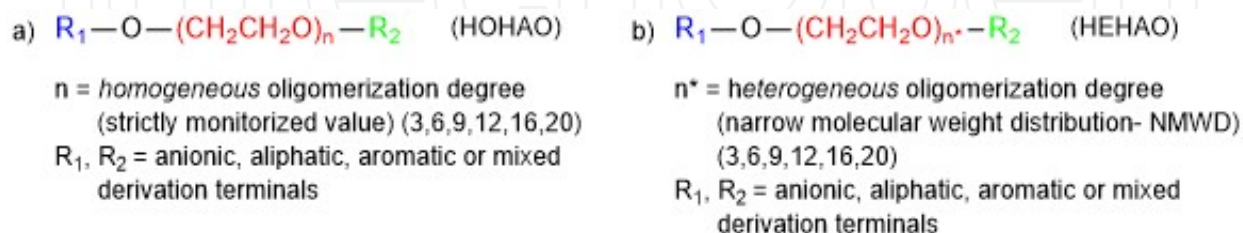


Figure 1. General structure of heterobifunctional acyclic oligomers of ethylene oxide

Interest in polyoxyethylene chains (PEO) was generated due to their conformational and colloidal properties. The reactivity of the three-atom ether heterocycle (oxirane), also founded on the “ring tension theory,” favors the nucleophilic attack of organic compounds with hydroxyl, thiol, primary and/or secondary amine, etc., function, with breaking of the C–O bond of the oxirane ring [1,5–7].

A narrow-range ethoxylated alcohol, also called “packed ethoxylated” alcohol, has a distribution curve that is narrower than the equivalent standard alcohol ethoxylate and a considerably lower content of unreacted alcohol. Reactions of ethylene oxide with fatty alcohols proceed in the presence of sodium metal, sodium hydroxide, and boron trifluoride and are used for the synthesis of surfactants (including HEHAO) [1,4,5,7].

To facilitate text comments on HEHAO compounds, their chemical names have been abbreviated. The main organic functions are symbolized by the initials of their chemical names (*e.g.*, PN–propionitrile, PD–propionamide [3], PC– β -substituted propionic acids [3], EP–primary ethylamine), the main hydrocarbon-chain homologues by the initials of their common names (*e.g.*, LM–lauryl/myristyl, CS–cetyl/stearyl), followed in parentheses by the ratio (7/3) signifying their relative distribution. The hydrocarbon chains attached later by synthesis are symbolized by the number of carbon atoms contained, for example, EC-1.1.16 [3] in the cationic structure, where we find two methyl groups indicated by 1.1 and a hexadecyl chain.

The actual distribution of PEO chain homologues, and hence of the oligomerization degrees (n_{average}), changes in the series $n_{\text{average}}=3-18$ from advanced symmetry for $n_{\text{average}}\leq 8-9$ to pronounced asymmetry for $n_{\text{average}}\leq 9-18$ [1,4,5,7].

Heterogeneous polyoxyethylene chains obtained by the anionic polymerization of ethylene oxide (“anionic ring-opening polymerization”) with a polydispersity degree $M_w/M_n < 1.1$ are hydrophilic, flexible (specific spatial conformation), biocompatible “bridges” [1].

For heterogeneous polyoxyethylene (PEO) chains, the statistical distribution quantitatively expressed through equations: Natta, Weibull/Nycander/Gold, Natta/Mantica, Poisson, etc., is accepted.

During our research, the results obtained contributed decisively to the confirmation of direct participation of PEO chains in nucleophilic addition reactions (cyanoethylation, amidoethylation) [1,3,4] of polyethoxylated higher alcohols purified of free higher alcohols, polyethylene glycols (PEG_n) and water, when processing yields under similar conditions increase proportionally with the oligomerization degree (n^*) of the PEO chain [1,3,4] (for further details, see section 4).

An overview of the theoretical and practical colloidal competences regarding several categories of classical ionic (anionic, cationic) and nonionic surface-active structures suggested the idea of making a new class of hybrid surface-active compounds of the nonionic-ionic HEHAO type with synergistic effects. For this purpose, a classical reaction scheme was followed adapted to the HEHAO series [3,4].

The literature reports similar structures of the mainly nonionic-ionic type with a length of the actual polyoxyethylene chain ($n^*=3$). In this chapter, the range of HEHAO surface-active structures is extended, using the reaction scheme not reported previously and higher polyoxyethylene chains ($n^*=3-20$) (Table 1) [8-20].

In the literature, 1939 is accepted as the year of the first reporting of β -alkyl (alkylaryl)-X (oxygen, sulfur, nitrogen) polyethyleneoxy ($n^*=3-50$) functional derivatives of saturated acids, through the patent granted to H. Haussmann at I.G. Farben Industrie.

Traditional soap was gradually replaced in sanitation recipes with similar polyethyleneoxy carboxylic surface-active structures, more soluble and unaffected by the hardness of washing waters. For their synthesis, new methods have been accessed, reported primarily in the patent literature [21-32,47,48].

2. Surface-active nonionic-ionic (anionic and cationic) colloids in the HEHAO category

The research conducted focused exclusively on nonionic-ionic (anionic and cationic) surface-active structures, where the "bridge" between the heterogeneous polyoxyethylene chain (PEO) and the polar (hydrophilic) anionic or cationic group is represented by the hydrophobic moiety R_2 = ethyl/propyl.

In these molecular architectures, the fragment R_1 (the determinant hydrophobic group) [33] is the lauryl/myristyl (7/3) (LM) and cetyl/stearyl (7/3) (CS) radical, respectively, and the fragment F_2 (R_2') as the hydrophilic ionic polar group includes functional groups [33].

In the reaction scheme accessed [5], heterogeneously polyethoxylated ($n^*=3, 6, 9, 12, 16, 20$) $C_{12}H_{25}/C_{14}H_{29}$ (7/3) (LM) higher alcohols and heterogeneously polyethoxylated ($n^*=3, 6, 9, 12,$

16, 20) $C_{16}H_{33}/C_{18}H_{37}$ (7/3) (CS) higher alcohols, respectively, were technical products obtained by the base-catalyzed reaction of the higher alcohols above with ethylene oxide [3,40].

They are mixtures of statistically distributed PEO chain homologues along with non-ethoxylated higher alcohols, polyethylene glycols as by-products, and accidental traces of water. These impurities possessing hydroxyl groups can unwantedly participate simultaneously in the cyanoethylation or amidoethylation processes of heterogeneously (n^*) polyethoxylated higher alcohols, generating impurities and serious purification difficulties [4]: additional consumption of acrylic monomer (AN), low useful nucleophilic addition yields, and finally limited purity of the HEHAO obtained.

To eliminate these impediments, the raw materials (technical products) were purified [4] by repeated liquid/liquid extractions in various solvent systems. In the synthesis of HEHAO were accessed purified technical products [heterogeneous polyethoxylated (n^*) higher alcohols].

Preliminary cyanoethylation attempts of higher alcohols ($C_{12}H_{25}$ – $C_{18}H_{37}$) and of polyethoxylated ($n^*=3$ –20) higher alcohols ($C_{12}H_{25}$ – $C_{18}H_{37}$) [3,4] revealed that the oligomerization processes of the acrylic monomer, especially at temperatures exceeding 40°C , have a significant share. Nucleophilic addition yields decrease considerably and the reaction tends to proceed vehemently, highly exothermically, with the formation of brown-reddish resins (PPN), soluble in polar solvents (water, acetone, etc.), or yellow solid products $R(\text{EO})_{n^*}\text{PPN}$ soluble in medium-, low-polarity solvents [4].

Initially we worked without an acrylic monomer oligomerization inhibitor, in order to follow the evolution of cyanoethylation and oligomerization yields. Afterward under the optimum parameters established was introduced as an oligomerization inhibitor FeSO_4 [3–5].

The content of oligomers increases with temperature and excess monomer. Compared with cetyl/stearyl alcohol it is noted that cyanoethylation yields are higher at the same temperature value, even below 45°C . This behavior suggests that the cyanoethylation reaction has a reversible character, the polyethoxylated chain favors the addition, and the hydrocarbon chain with its increase, reduces the cyanoethylation yields.

In the research, the formation of AN oligomers was avoided by introducing anhydrous ferrous sulfate (FeSO_4) as an inhibitor of the polymerization of the acrylic monomer. For 1% addition of oligomerization inhibitor, the cyanoethylation yield of lauryl/myristyl alcohol (7/3) increases by more than 10%, without the formation of oligomers. Similar results are obtained in the series of polyethoxylated ($n^*=3$ –20) higher alcohols ($C_{12}H_{25}$ – $C_{18}H_{37}$).

By gradually adding polyethyleneglycols (PEG_{n^*}) ($n^*=9$) in the cyanoethylation phase, it was found that:

- -the increase of the oligomer content, because alkaline polyethyleneglycolates ($n^*=9$), as bidentate nucleophiles, have higher basicity than alkaline higher alkoxides;
- -the increase of the content of β -alkyl-(LM)-propionitriles, proportional to the quantity of polyethyleneglycols added due to inter-phase catalysis [4].

The polyethoxylated $C_{12}H_{25}/C_{14}H_{29}$ (7/3) (LM) ($n^*=3, 6, 9, 12, 16, 20$) and $C_{16}H_{33}/C_{18}H_{37}$ (7/3) (CS) ($n^*=3, 6, 9, 12, 16, 20$) higher alcohols can be considered as monoderivatized polyethyleneglycols (primary PEGylation fragment). There are many possibilities for modifying the determinant hydrophobic fragment between the $C_{12}H_{25}/C_{14}H_{29}$ and $C_{16}H_{33}/C_{18}H_{37}$ [40].

The inclusion of β -alkyl ($C_{12}H_{25}/C_{14}H_{29}$) polyethyleneoxy (n^*) derivatives [3,4] in the category of surface-active agents (HEHAO) involves the nomination of the hydrophilic (lipophobic)/hydrophobic (lipophilic) polar/nonpolar (amphiphilic) domain, which next determines their colloidal character.

Due to their composition, specific primary and secondary (conformational) structures, HEHAO have a pronounced heterogeneous character. The idea of their basic colloidal characterization becomes indicative, being the resultant of the colloidal manifestation of 24 unitary homologous structures (4 hydrophobic R series, each with 6 hydrophilic PEO series) [1,3,4,40].

Synergistic cumulation in the same surface-active structural architecture of the ionic (anionic, cationic) functional group (hydrophilic) with one or more polyoxyethylene chains (hydrophilic) with different oligomerization degrees (n^*) led to the HEHAO [1,4].

3. Structure–hydrophilicity (wetting competences) correlations in the HEHAO homologous series studied

The main colloidal characteristics of the surface-active compounds (technical products) depend on their structure and heterogeneous composition [3,40]. Laboratory evaluations performed on the homologous series ($n^*=0-20$) of the two sets of HEHAO purified prior to the synthesis fall into this casuistry.

Numerous industrial applications of HEHAO, due primarily to their varied composition and structure, are based on several colloidal phenomena: wetting, colloidal (micellar) solubility, adsorption, chemical reactions at the interface (chemisorption) and actual penetration into the dirt or support. Determining the value of use of HEHAO is most often more important than the classical chemical analysis, if we consider that most marketed products are mixtures with a wide distribution of hydrocarbon-chain R and polyoxyethylene-chain PEO homologues.

Knowing the main surface-active properties [1], are suggested directions for the application of the HEHAO synthesized, dependent on the structural elements of the respective homologous series (the hydrophilic–hydrophobic index, HLB). The use of the most suitable surface-active evaluation methods can generate some justified comments, both by the reproducibility of recording the basic colloidal phenomenon, and by the lack of widely recognized, accepted working practices. Therefore, the values commented have an indicative character, even though they represent the result of the statistical processing of a large number of experimental measurements. Were preferred standardized protocols supplemented with ISO recommendations, where applicable. For the estimation of the wetting effect [49], the data obtained correctly characterize the physico-chemical aspect, but less so the mechanical aspect of the

phenomenon, which differs most of the times through the wide variety of equipment employed in the processing, but also by the nature of the supports or the difference between the artificial and the natural polluted support. Laboratory measurements allowed the establishment of structure–surface-activity correlations, following that the absolute, comprehensive assessment on the scope to involve the investigation under conditions of actual equipment, support, float, etc. The main surface-active properties previously considered [3,40] were: surface tension (σ) and critical micelle concentration (CMC), foaming with its three aspects [foamability (F), foam stability (FS), foam density (FD)], wetting effect (U), the softening–antistatic effect (LA) and the washing effect (WE), respectively [1,3,4,7,18,19,33].

The HLB index, the balance between the hydrophilic (lipophobic) and hydrophobic (lipophilic) properties of the HEHAO, and in particular its controlled modification by structural elements allowed to obtain a wide range of HEHAO with directed potential of use.

Surface tension is dependent on the structural characteristics of the studied heterogeneous HEHAO [1,40]. Increasing the oligomerization degree of the PEO chain ($n > 6$) induces an increased capacity of surface tension reduction, simultaneously with decreasing the effectiveness of adsorption at the water/air interface [1,40].

The evaluation of wetting competences in the homologous HEHAO series mentioned (Tables 1–3) enabled the formulation (by extrapolation) of structure–wetting competences correlations, knowing a priori the basic colloidal characteristics (surface tension, critical micelle concentration, conformational behavior) [1,3,4,36–38,41–46]. Based on these in this chapter could be proposed and subsequently argued mechanisms of action, suggestively presented schematically (section 4).

Wetting, as an interface phenomenon indicating the magnitude and rapidity of establishing contact between a support and the aqueous float, depends on the ability of the surface-active structure to reduce under dynamic conditions the surface tension at the support–float interface, the molecule's mobility in the float and its capacity for adsorption at the interface. Since the adsorption capacity is also a function of the nature of the support (dielectric constant), are distinguished hydrophilic interfaces (dielectric constant lower than that of water, *e.g.*, cellulose, cotton) easily wetted by water and hydrophobic interfaces (dielectric constant higher than water, *e.g.*, synthetic fibers) little wetted by water or polar fluids. Along with the nature of the substrate, in the adsorption process can be distinguished two more parallel, concurrent phenomena, dependent on superficial structure and the permittivity of the environment: desorption (water adsorption at the interface) and the adsorption proper. The desorption is accompanied by a decrease of the water concentration in the adsorption layer and the local concentration of the colloidal solution is the more advanced as the hydrophilicity of support is higher.

Interpreting the values obtained (Table 1), the following observations can be formulated: at room temperature, on hydrophilic surfaces as such or mixed (B, B–FR, B–PES), due to high desorption and adsorption at the interface, the wetting–lifting effect is pronounced (the wetting power values are of the order of seconds); under the same environmental conditions, on hydrophobic surfaces (PES, PNA, PES–Ac) the lower desorption and adsorption capacity

| No. | R | N* | Nature of solution | Float concentration (g/L) | Wetting time (sec.) | | | | Textile support |
|-----|-------|----|--------------------|---------------------------|---------------------|-----------------|------|------|-----------------|
| | | | | | Untreated support* | Treated support | | | |
| | | | | | | 20°C | 40°C | 60°C | |
| 1 | 12–14 | 3 | HCOOH | 2 | 148 | 5.8 | 5.6 | 3.5 | PES |
| 2 | 16–18 | 12 | HCOOH | 5* | 148 | 5.5 | 5.4 | 3.3 | |
| 3 | 12–14 | 6 | AcOH | 0.5 | 148 | 6.6 | 5.4 | 4.3 | |
| 4 | 12–14 | 9 | AcOH | 2 | 148 | 6.8 | 5.6 | 4.4 | |
| 5 | 16–18 | 3 | AcOH | 5 | 184 | 4.3 | 3.1 | 0.8 | PES-AC |
| 6 | 12–14 | 3 | HCOOH | 5* | 184 | 4.5 | 3.4 | 1.2 | |
| 7 | 12–14 | 6 | HCOOH | 2 | 184 | 4.6 | 2.4 | 1.3 | |
| 8 | 12–14 | 9 | AcOH | 0.5 | 184 | 4.9 | 2.7 | 1.5 | |
| 9 | 12–14 | 3 | HCOOH | 2 | 60 | 2.3 | 2.2 | 1.0 | B |
| 10 | 16–18 | 12 | AcOH | 5 | 60 | 1.4 | 1.1 | 0.8 | |
| 11 | 12–14 | 3 | HCOOH | 0.5 | 60 | 1.8 | 1.1 | 0.9 | |
| 12 | 12–14 | 6 | HCOOH | 5* | 60 | 1.4 | 1.2 | 1.0 | |
| 13 | 12–14 | 12 | HCOOH | 2* | 78 | 3.9 | 2.7 | 1.5 | B-PES |
| 14 | 16–18 | 3 | HCOOH | 5* | 78 | 4.2 | 3.0 | 2.9 | |
| 15 | 16–18 | 6 | HCOOH | 0.5 | 78 | 4.1 | 4.0 | 2.8 | |
| 16 | 16–18 | 9 | HCOOH | 0.5 | 78 | 4.9 | 3.8 | 2.7 | |
| 17 | 16–18 | 12 | HCOOH | 5* | 4200 | 11.2 | 11.0 | 10.8 | B-FR |
| 18 | 16–18 | 3 | AcOH | 2 | 4200 | 11.8 | 11.5 | 11.3 | |
| 19 | 16–18 | 6 | AcOH | 0.5 | 4200 | 20.6 | 18.4 | 11.4 | |
| 20 | 16–18 | 9 | AcOH | 5 | 4200 | 11.5 | 11.3 | 11.1 | |
| 21 | 16–18 | 12 | HCOOH | 5 | 116 | 12.3 | 12.1 | 10.7 | PNA |
| 22 | 16–18 | 9 | AcOH | 5* | 116 | 12.2 | 12.0 | 10.6 | |
| 23 | 16–18 | 3 | AcOH | 2 | 116 | 12.0 | 9.9 | 9.7 | |
| 24 | 12–14 | 9 | AcOH | 2 | 116 | 12.1 | 11.9 | 10.8 | |

*float hardness 5 dG (German degrees)

**not cleaned of softening/antistatic and/or mercerization products

***PES – polyester; PES-AC – polyester acetate; B – cotton; B-PES – cotton polyester; B-FR – cotton frotir; PNA – polyacrylonitrile.

Table 1. Wetting effect of β -alkyl polyethyleneoxy propionamides in formic and acetic solutions (Ac) [R-O-(CH₂CH₂O)_n-CH₂CH₂CONH₂]

determines the decrease of the wetting effect. Increasing the temperature of the float reduces both interface phenomena, but increases the mobility of HEHAO structures and their ability to reduce surface tension [3,4], so that overall the wetting effect is optimized; concentrations of HEHAO in the treatment floats below CMC provide a good wetting effect, especially at elevated temperatures, since at 20°C the mobility of β -substituted propionamides is greatly reduced.

β -Alkyl-polyethyleneoxy-propionamides in acetic solutions exhibit a greater wetting effect than in formic solutions, due to the difference in solubility in the two organic acids (solvation phenomena). Because β -substituted propionamides in acetic solutions have a better capacity of surface tension reduction [3,4], the wetting effect is more pronounced. Increasing the length of the polyoxyethylene chain increases the hydrophilicity, but lowers the wetting capacity by increasing the hydration degree and reducing the mobility in the float. Increasing the hydrocarbon chain provides a good wetting effect by the advanced reduction of surface tension [4]. The hardness of treatment floats in the case of polyoxyethylene chains larger than 12 oxyethylene units (EO) does not affect the wetting effect both in the case of the formic and acetic solution, due to the coordination phenomena of alkaline earth cations (Table 1).

The analysis of wetting characteristics (Table 2) in the category of nonionic soaps leads to observations similar to those made for β -substituted propionamides. Are noted the optimum wetting properties of the series of anionic-cationic structures of the β -lauryl/myristyl (7/3) polyethyleneoxy ($n^*=3$) ethylammonium β -alkyl ($C_{12}H_{25}$ – $C_{18}H_{37}$) polyethyleneoxy ($n^*=3$ –20) propionates [HLM-(EO)₃-EP⁺] type, probably due to the optimum capacity of surface tension reduction correlated with the high degree of “packing” at the interface (good entropic factor). Compared to the acetic or formic solutions of β -substituted propionamides, nonionic soaps are more efficient in the wetting operation in the same conditions of environment and structure, a fact that recommends them in washing (cleaning) operations.

The analysis of the wetting–lifting effect in these surface-active structures (Table 3) reveals structure–effect parallelisms similar to those observed previously, namely that shifting the polar hydrophilic group toward the center of the hydrocarbon chain R together with increasing the length of the latter, through the unfavorable entropic factor, determines the decrease of the wetting effect parallel with the surface tension reduction capacity.

Increasing the length of the polyoxyethylene chain increases the hydrophilicity, the hydration degree, and drastically reduces the mobility in the float. Along with the unfavorable entropic factor, it negatively affects the capacity under dynamic conditions of reducing the tension at the support–float separation interface. Overall, though the quaternary salts presented are better wetting agents than the nonionic-anionic structures analyzed, due to the affinity of the cationic polar group toward supports with anionic character, independent of their degree of hydrophobicity (cellulose, cotton, natural, or synthetic fibers), which secure the cationic structure at the support–float interface and facilitates the reduction of surface tensions.

| No. | R | n* | Nature of cation | Float concentration (g/L) | Wetting time (sec.) | | | Textile support | |
|-----|-------|----|--|---------------------------------|------------------------|-----------------|------|--------------------|--------|
| | | | | | Untreated support** | Treated support | | | |
| | | | | | | 20°C | 40°C | | 60°C |
| 1 | 12–14 | 3 | Na | 5 | 148 | 3.2 | 2.6 | 1.5 | PES |
| 2 | 16–18 | 12 | | 2 ^x | 148 | 3.3 | 2.4 | 1.1 | |
| 3 | 12–14 | 6 | Na | 0.5 | 148 | 3.6 | 2.8 | 1.9 | |
| 4 | 12–14 | 3 | HLM-(EO) ₃ -EP ⁺ | 2 | 148 | 1 | 1 | 1 | |
| 5 | 12–14 | 0 | Na | 0.5 | 184 | 2.8 | 1.8 | 0.9 | PES-AC |
| 6 | 16–18 | 12 | Na | 2 | 184 | 2.3 | 1.7 | 0.8 | |
| 7 | 12–14 | 20 | Na | 2 | 184 | 3.8 | 2.2 | 1.3 | |
| 8 | 12–14 | 3 | HLM-(EO) ₃ -EP ⁺ | 2 | 184 | 1 | 1 | 1 | |
| 9 | 16–18 | 0 | Na | 2 | 60 | 1.1 | 1 | 1 | B |
| 10 | 16–18 | 9 | Na | 2 | 60 | 1.9 | 1.1 | 1 | |
| 11 | 12–14 | 9 | HLM-(EO) ₃ -EP ⁺ | 2 | 60 | 1 | 1 | 1 | |
| 12 | 12–14 | 20 | Na | 5 | 60 | 2.3 | 1.3 | 1 | |
| 13 | 12–14 | 20 | Na | 5 | 78 | 2.7 | 1.8 | 1.2 | B-PES |
| 14 | 16–18 | 0 | Na | 2 | 78 | 2.5 | 1.6 | 1.1 | |
| 15 | 16–18 | 0 | Na | 0.5 | 78 | 2.3 | 1.4 | 1 | |
| 16 | 12–14 | 12 | Na | 0.5 | 78 | 2.9 | 1.7 | 1.2 | |
| 17 | 16–18 | 9 | Na | 2 | 4200 | 9.3 | 5.3 | 3.3 | B-FR |
| 18 | 16–18 | 9 | Na | 2 | 4200 | 10.4 | 5.9 | 5.5 | |
| 19 | 16–18 | 0 | Na | 2 | 4200 | 7.5 | 6.0 | 4.8 | |
| 20 | 12–14 | 20 | HLM-(EO) ₃ -EP ⁺ | 2 | 4200 | 1.6 | 1 | 1 | |
| 21 | 12–14 | 3 | Na | 5 | 116 | 3.3 | 2.2 | 1.8 | PNA |
| 22 | 16–18 | 3 | Na | 2 | 116 | 10.5 | 7.5 | 5.8 | |
| 23 | 16–18 | 6 | Na | 2 | 116 | 12.3 | 7.8 | 6.2 | |
| 24 | 12–14 | 6 | Na | 0.5 | 116 | 4.5 | 2.3 | 1.4 | |

^xfloat hardness 5 dG (German degrees)

**not cleaned of softening/antistatic and/or mercerization products

***PES – polyester; PES-AC – polyester acetate; B – cotton; B-PES – cotton polyester; B-FR – cotton frofir; PNA – polyacrylonitrile

Table 2. Wetting effect of alkali and ammonium β-alkyl polyethyleneoxy propionates [R-O-(CH₂CH₂O)_n-CH₂CH₂COO⁺X⁻]

| No. | R | n* | R ₁ | Float concentration (g/L) | Wetting time (sec.) | | | | Textile support |
|-----|-------|----|----------------|------------------------------|------------------------|-----------------|------|------|-----------------|
| | | | | | Untreated support** | Treated support | | | |
| | | | | | | 20°C | 40°C | 60°C | |
| 1 | 12–14 | 3 | 1 | 2 | 148 | 2.5 | 2.1 | 1.5 | PES |
| 2 | 12–14 | 9 | 4 | 5 ^x | 148 | 3.0 | 2.5 | 1.2 | |
| 3 | 12–14 | 12 | 8 | 2 | 148 | 2.7 | 1.4 | 1.2 | |
| 4 | 16–18 | 20 | 10 | 0.5 ^x | 148 | 4.0 | 2.8 | 1.7 | |
| 5 | 12–14 | 3 | 4 | 0.5 ^x | 184 | 1.4 | 1.2 | 1 | PES-AC |
| 6 | 12–14 | 6 | 2 | 2 | 184 | 2.2 | 1.8 | 1.1 | |
| 7 | 12–14 | 12 | 2 | 5 | 184 | 1.8 | 1.1 | 1 | |
| 8 | 16–18 | 6 | 2 | 2 | 184 | 2.3 | 1.7 | 1 | |
| 9 | 12–14 | 12 | 10 | 5 ^x | 60 | 1.6 | 1.4 | 1.2 | B |
| 10 | 16–18 | 9 | 4 | 5 | 60 | 1.5 | 1.3 | 1.2 | |
| 11 | 16–18 | 12 | 16 | 0.5 ^x | 60 | 1.5 | 1.2 | 1.1 | |
| 12 | 16–18 | 12 | 20 | 1 | 60 | 1.7 | 1.5 | 1.2 | |
| 13 | 12–14 | 3 | 1 | 0.5 ^x | 78 | 1.5 | 1.0 | 1 | B-PES |
| 14 | 16–18 | 12 | 4 | 2 | 78 | 1.2 | 1 | 1 | |
| 15 | 16–18 | 20 | 2 | 5 _x | 78 | 1.0 | 1 | 1 | |
| 16 | 16–18 | 9 | 2 | 0.5 | 78 | 1.5 | 1.1 | 1 | |
| 17 | 12–14 | 3 | 8 | 0.5 | 4200 | 1.6 | 1.3 | 1.1 | B-FR |
| 18 | 12–14 | 9 | 2 | 5 ^x | 4200 | 1.2 | 1.0 | 1 | |
| 19 | 16–18 | 6 | 4 | 2 ^x | 4200 | 1.7 | 1.5 | 1.3 | |
| 20 | 16–18 | 9 | 1 | 0.5 | 4200 | 1.5 | 1.4 | 1.2 | |
| 21 | 12–14 | 3 | 1 | 2 | 116 | 1.9 | 1.6 | 1.2 | PNA |
| 22 | 12–14 | 9 | 8 | 5 ^x | 116 | 1.7 | 1.5 | 1.0 | |
| 23 | 16–18 | 9 | 12 | 2 | 116 | 1.9 | 1.7 | 1.3 | |
| 24 | 16–18 | 12 | 20 | 5 ^x | 116 | 1.8 | 1.6 | 1.4 | |

*float hardness 5 dG (German degrees)

**not cleaned of softening/antistatic and/or mercerization products

***PES – polyester; PES-AC – polyester acetate; B – cotton; B-PES – cotton polyester; B-FR – cotton frotir; PNA – polyacrylonitrile.

Table 3. Wetting effect of *N,N*-dimethyl-*N*-alkyl (R₁)-*N*-β-alkyl (R) polyethyleneoxyethylammonium chlorides

4. Structure–hydrophilicity correlations (wetting competences) in the homologous HEHAO series studied

To understand and coherently interpret the main experimental data (Tables 1–3), but also to argue the structure–colloidal (wetting) competences correlations previously formulated, it is necessary to consider several structural and colloidal features of the HEHAO evaluated.

4.1. The conformation of polyoxyethylene (PEO) chains and its consequences for the colloidal behavior of HEHAO [40]

The main features of these spatial architectures with consequences for the study of heterogeneous HEHAO are: dimensional flexibility; transfer mobility; the existence of "meander," "zig-zag," "helix" conformations with variable geometries; free C–C/C–O coaxial rotation, and absence of "ring tensions" specific to rigid structures [1,3,4,40].

Subsequent experimental facts [1,40] also confirmed for the first time the approximate dimensions of the coordination "helical cavity" (ca. 6 EO units/sodium cation and ca. 7 EO units/potassium cation, respectively).

4.2. Adsorption of HEHAO at the aqueous solution–air interface; formation of micelles

HEHAO are lyophilic association colloids which group instantly in aqueous floats as macromolecular associations (lyophilic micelles) at the value corresponding to the critical micelle concentration (expressed as mol/L 10^{-5}).

Surface tension as a form of free energy (expressed in N/m or dyne/cm) independent of the shape of the interface separating two phases in a system, is a function of temperature, time, and the structural characteristics of the HEHAO considered. Because the interface equilibrium is established within a short period, the existence of static and dynamic surface tension is accepted [1]. The latter manifests itself in aqueous floats of HEHAO and subsequently acquires great practical significance in the process of their actual use. Two aspects can be distinguished:

- The capacity of HEHAO to reduce the surface tension, expressed as the concentration required to achieve a certain effect of reducing the surface tension
- The effectiveness of HEHAO expressed by the minimum value which is capable of reducing the surface tension

In the case of heterogeneous HEHAO, the diversity of composition, structure, and conformations does not allow for such an approach, but only for the indicative evaluation of the following surface-active parameters: HLB balance, surface tension (σ_{cmc}), and critical micelle concentration (CMC).

In the homologous series of heterogeneous hydrophobic (R) and hydrophilic (PEO) chains of HEHAO, subsequently, structure–surface activity correlations can also be indicatively formulated.

In aqueous solutions, cationic structures form colloidal associations (normal micelles) and in organic solvents (reverse micelles), with a pronounced acidic character of the “cavity” of the micellar site [3,4] (Figure 2). The difference is due to the fact that in water, cationic colloidal electrolytes can dissociate as solvated ion pairs, while in non-aqueous solvents, with low dielectric constant, the solvation phenomena decrease in proportion to its value, and the cationic colloidal electrolytes exist as unsolvated ion pairs.

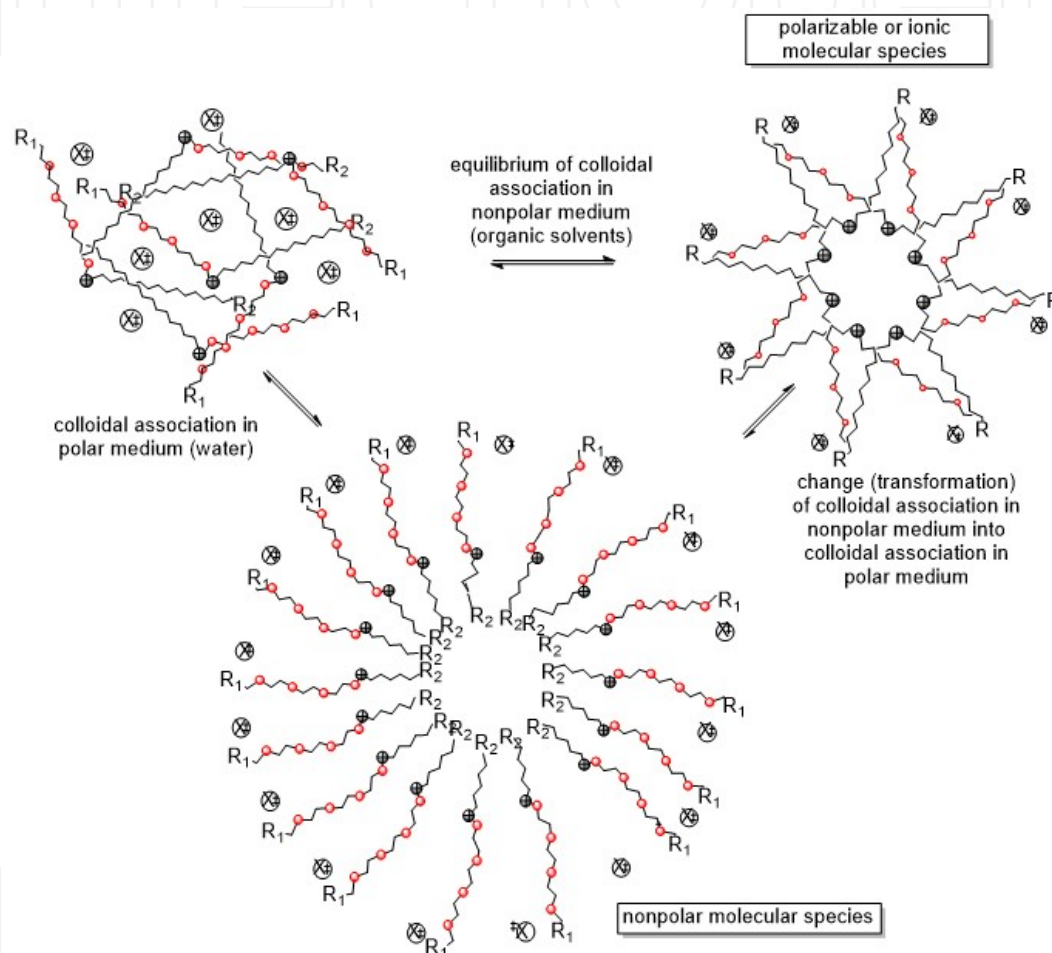


Figure 2. Scheme of the association mechanism of cationic surface-active agents and of micellar solubilization in polar (water) and nonpolar (organic solvents) medium

Modification of the hydrophobic chain influences the mutual steric or electrostatic repulsions through geometric coordinates and steric hindrance [1,4,40]. Corroborating the aforementioned conformational data of PEO chains in the literature with the structure of various HEHAO, in Figure 4 are presented several concrete instances of association at the hydrophobic or hydrophilic separation interface (polar and nonpolar media) of HEHAO. Micellar architectures with polar and nonpolar cavities are thus structured as “solubilization,” sequestration, and transfer spaces of potential entities in the sanitation practice (Figure 3).

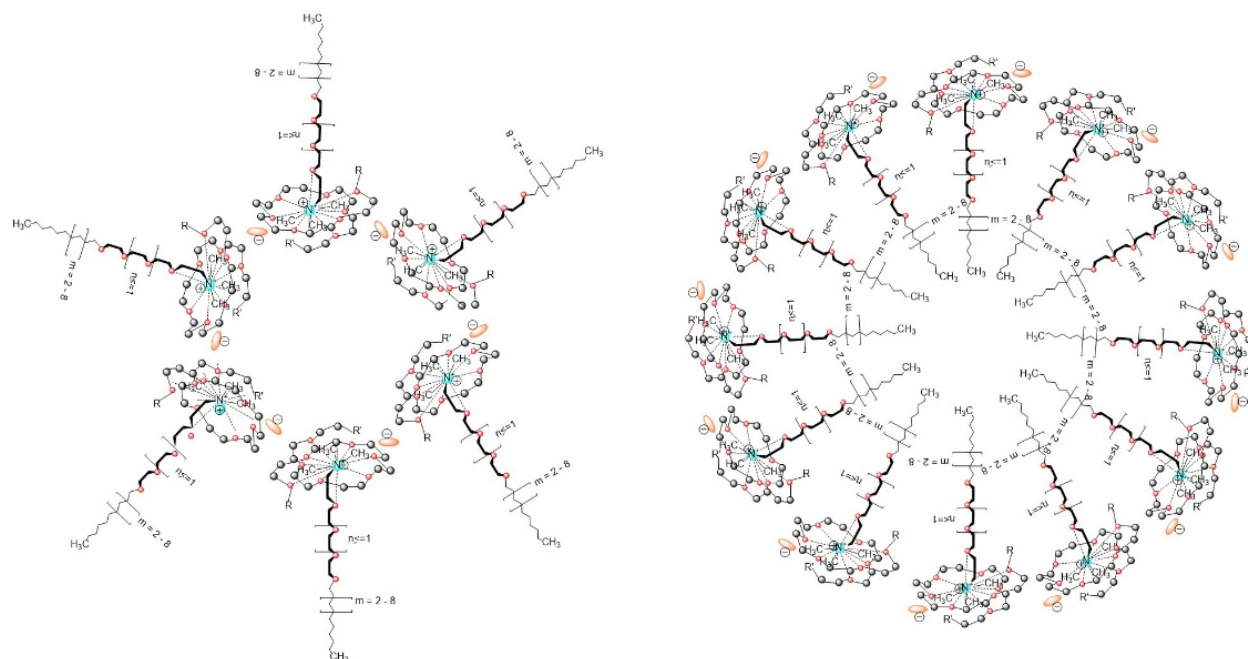


Figure 3. Mixed HEHAO "micellar architectures" with conformational (a), polar micellar (b), and nonpolar micellar (c) solubilization "cavities" (sites)

4.3. Adsorption of mixtures of heterogeneous HEHAO homologues at the aqueous solution–air interface; formation of mixed micelles

Mixtures of two or more different homologues in the HEHAO series show positive or negative "synergistic" interdependences [1,4,7,40]. The overall interfacial properties of the mixture of homologues can be more pronounced than those of a "homogeneous" (unitary) HEHAO structure.

4.4. Cumulated consequences of structural and colloidal characteristics of HEHAO

The major consequences of colloidal and conformational behavior of HEHAO studied for the wetting operation can be summarized thus:

- The competence to sequester (coordinate) small molecular entities with mainly cationic character and variable dimensions depending on the "conformational flexibility" of the heterogeneous polyoxyethylene (PEO) chains
- The possibility of orientation and directed adsorption at the separation interface of two phases depending on their nature (specificity) and hydrophilic and/or hydrophobic character (micelle, support, etc.) (Figure 5)
- The possibility of penetration, displacement, micellar solubilization, and transfer of entities from the interface into its adjacent environment (Figure 6)

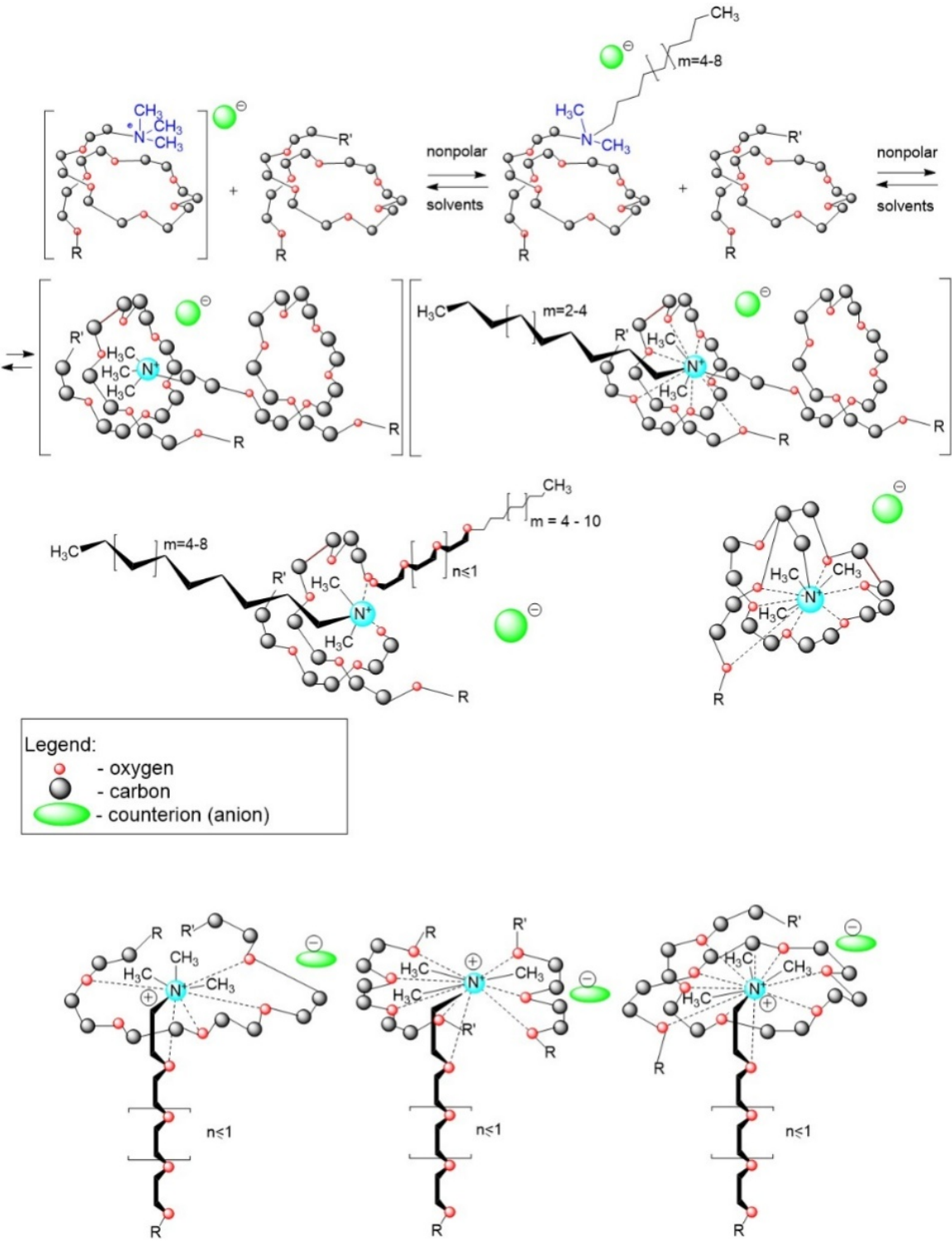


Figure 4. “Micellar architectures” of mixed HEHAO with conformational sequestration (solubilization) “cavities” (sites) [3,4]

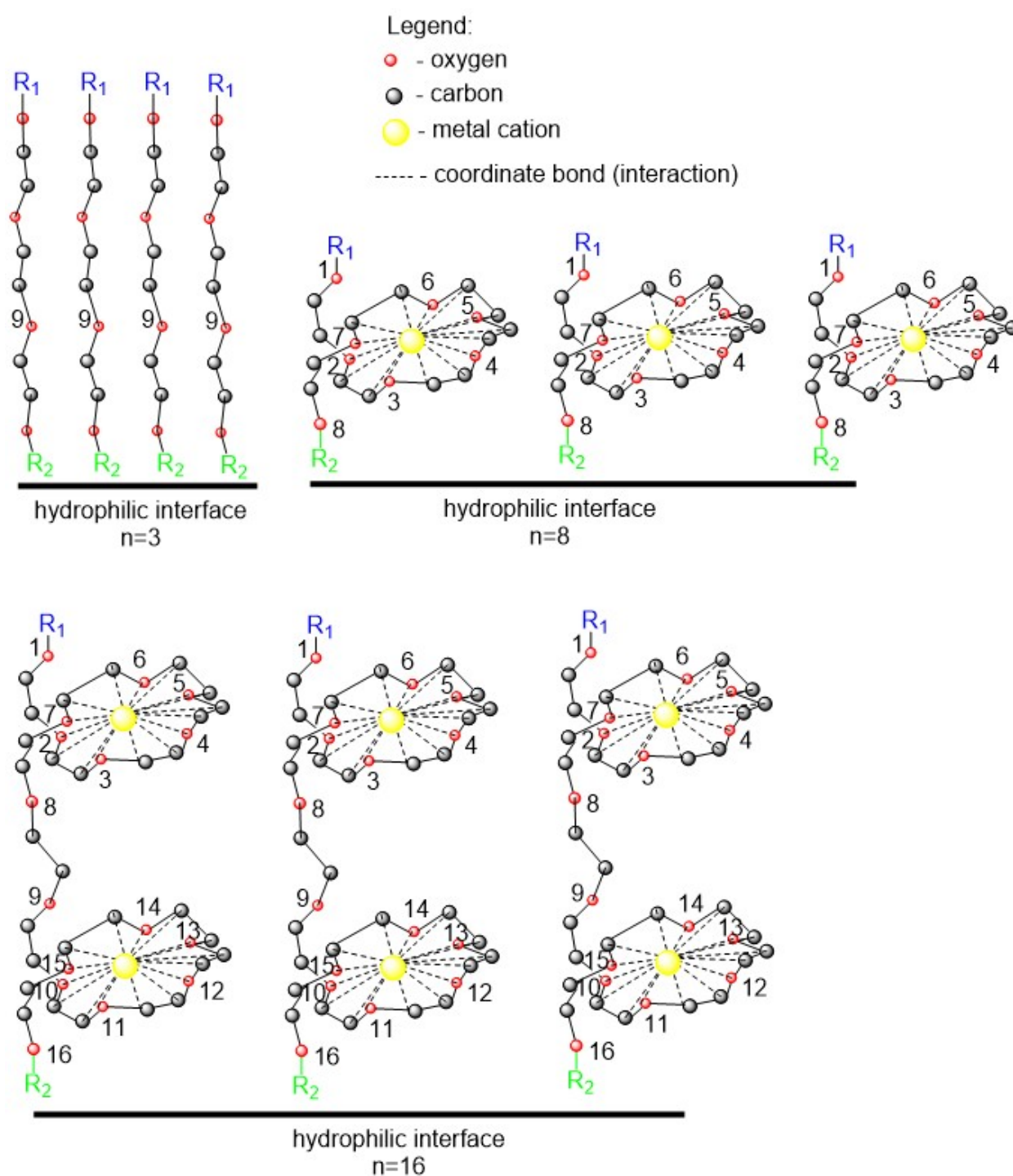


Figure 5. Schematic representation of the orientation and adsorption processes at the hydrophilic interface cumulated with the "encapsulation" of metal cations in the matrix of monoderivatized polyoxyethylene (PEO) ($n^*=3, 8, 16$) chains [4]

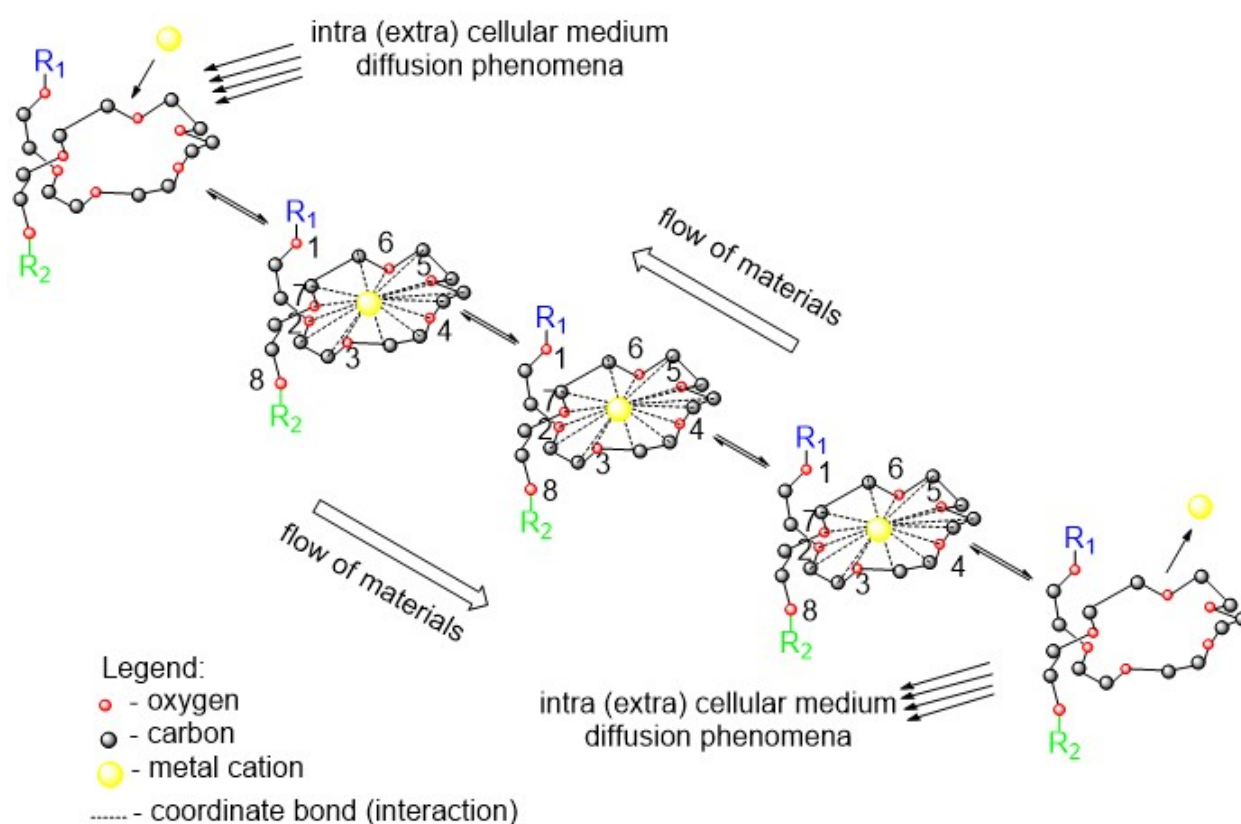


Figure 6. Schematic representation of the process of coordination and interphase transfer of some entities in the conformational "cavity" of HEHAO polyoxyethylene (PEO) ($n^*=8$) chains [4]

5. Conclusions

The present review of the more significant issues relating to the obtaining and characterization of HEHAO in the category of β -alkyl ($C_{12}H_{25}$ – $C_{18}H_{37}$) polyethyleneoxy ($n^*=3$ – 20) ethyl/propyl derivatives (Table 1) represents a novelty in the field of HEHAO. The material prepared allowed an outline of an overall picture of the colloidal (surface-active) potential with possibilities of further controlled directing of their value of use in an extended HLB range (lifting–antistatization, emulsification, micellar solubilization, coordination, interphase transfer, washing, etc.). The beneficial synergistic cumulation of heterogeneous polyoxyethylene (PEO) ($n^*=3$ – 20) (nonionic hydrophilic) chains with polar ionic groups (anionic and/or cationic) allowed the preliminary confirmation of this latent colloidal potential.

The binary and/or ternary directed (compatible) association in the perspective of various HEHAO structures (including β -alkyl ($C_{12}H_{25}$ – $C_{18}H_{37}$) polyethyleneoxy ($n^*=3$ – 20) propionitriles in acid and/or alkaline media) further extends the area of the application fields.

The biodegradability and advanced purity, along with the reduced toxicity of the raw materials and final molecular architectures (absence of by-products), further recommends the continuation and furthering of the research.

Acknowledgements

My entire gratitude to my mentor, Prof. Univ. Emeritus Ionel Jianu, Ph.D., the founder of Agrifood School of Timișoara, in whose team I started and trained as a researcher and discovered the hitherto unsuspected potential of homogeneous and heterogeneous polyoxyethylene chains.

Author details

Calin Jianu*

Address all correspondence to: calin.jianu@gmail.com

Department of Food Science, Faculty of Food Processing Technology, Banat's University of Agricultural Sciences and Veterinary Medicine, Timișoara, Romania

References

- [1] Jianu C. Ethylene oxide homogeneous heterobifunctional acyclic oligomers. In: Claire Lesieur (ed.), *Oligomerization of Chemical and Biological Compounds*. Intech, 2014, pp. 103-132.
- [2] Williamson, A. On Etherification. *J Chem Soc* 1852, 4: 229-239.
- [3] Jianu I. Aminoethers surfaceactive agents. Cationic surfaceactive agents. PhD Thesis. Polytechnic University; 1984 (in Romanian).
- [4] Jianu C. Research concerning the potential of some metal ion complexing additives to improve food value in horticultural raw matter. PhD Thesis. Banat's University of Agricultural Sciences and Veterinary Medicine; 2006 (in Romanian).
- [5] Edwards CL. Polyoxyethylene alcohols. In: van Os NM (ed.), *Nonionic Surfactants: Organic Chemistry; Surfactant Science Series*. Volume 72. Marcel Dekker, Inc: New York, USA; 1998, pp. 87-121.
- [6] Edwards CL. Chemistry and handling of ethylene oxide. In: van Os NM (ed.), *Non-ionic Surfactants: Organic Chemistry Science Series (Chapter 1)*. Marcel Dekker, Inc: New York, USA; 1998, pp. 2-4.
- [7] Schick, M. *Nonionic Surfactants* (ed.). Marcel Dekker, Inc: New York, USA; 1967, pp. 80-82; 230.
- [8] Sansebastiano G, Zoni R, Bigliardi L. Cleaning and disinfection procedures in the food industry general aspects and practical applications. In: McElhatton A, Marshall

- RJ (eds.) *Food Safety A Practical and Case Study Approach*. Springer New York; 2007, pp. 253-280.
- [9] Holah JT. Cleaning and disinfection. In: Lelieved HLM, Mostert MA, Holah J, White B. (eds.), *Hygiene in Food Processing*. Cambridge: Woodhead Publishing; 2003, pp. 235-278.
- [10] Jianu I. Process for obtaining polyethoxylate soaps, RO Patent 85437 (A2), International Classification: C11D1/02; C11D1/02; (IPC1-7): C11D1/02.
- [11] Drugarin C, Jianu I. Process for the preparation of surfaceactive agents, RO Patent 77367 (A2), International Classification: C07D233/08; C07D233/00; (IPC1-7): C07D233/08.
- [12] Drugarin C, Jianu I. Process for the preparation of new cationic agents, RO Patent 82439* (A3), International Classification: (IPC1-7): C07C87/30.
- [13] Jianu I. Beitrage zum kinetischen und thermodynamischen studium der cyano-ethyl-ierungs reaktionen höherer alkohole (C₁₀-C₁₈). Proceedings World Surfactants Congress. Surfactants in our World Today and Tomorrow; 1984, II: 188-196 (in German).
- [14] Drugarin C, Jianu I. Imidazoline derivatives and process for the preparation thereof, RO Patent 82335*(A2), C.A. 102, 26882p, 1985, International Classification: C07D233/20; C07D233/00; (IPC1-7): C07D233/20.
- [15] Weinheimer RM, Varineau PT. Polyoxyethylene alkylphenols. In: van Os NM. (ed.) *Nonionic Surfactants: Organic Chemistry*. Marcel Dekker Inc; 1998, pp. 120.
- [16] Drugarin C, Jianu I. The hydrolysis β - [(p) - Alkylphenyloxy polyethyleneoxy] - propionitrils under phase transfer catalysis - Part I: The synthesis of β - [(p) - Alkylphenyloxy polyethyleneoxy] - propionitrils. *Tenside Detergents* 1983; 20: 128-129.
- [17] Drugarin C, Jianu I. The hydrolysis β - [(p) - Alkylphenyloxy polyethyleneoxy] - propionitrils under phase transfer catalysis - Part II: The synthesis of β - [(p) - Alkylphenyloxy polyethyleneoxy] - propionitrils. *Tenside Detergents* 1983; 20: 130-131.
- [18] Drugarin C, Jianu I. Correlation between molecular structure and surface activity, Part I: The foaming power of the class of β -Alkyloxyethyl and β -Alkylpoly(ethyleneoxy) - ethyl-alkyl-dimethylammonium halides. *Tenside Detergents* 1983; 20: 76-77.
- [19] Drugarin C., Jianu I., Correlation between molecular structure and surface activity, Part II. The foaming power of the class of β -Alkyloxyethyl and β -Alkylpoly(ethyleneoxy)-ethyl-alkyl-dimethylammonium halides. *Tenside Detergents* 1983; 20: 78-79.
- [20] Drugarin C, Jianu I. Process for obtaining synthetic triglycerides, RO Patent 82041(A2), C.A. 103, 55720k, 1985, International Classification: C07D67/22; C07C69/003; C07C67/00; C07C69/00 (IPC1-7): C07D67/22; C07C69/003.
- [21] Haussmann H, Scheufer W, Kaupp J. Polyoxyalkylene ether acid compounds containing a higher aliphatic group, 1939. Patent Number US 2183853/1939.

- [22] Isa H, Inoniya T, Karube K, Takemoto T, Nagayama M. Verfahren zur Herstellung von carboxylaten: 1973. DE 2.303.829 (A1).
- [23] Rodney MW, Thomas AC. Light-duty liquid or gel dishwashing detergent composition containing an alkyl ethoxy carboxylate surfactant, 1993. Patent Number US 5230823/1993.
- [24] Kon-Chang L. Preparation of carboxypropylate non-ionic surfactants; 1987. Patent Number US 4692551/1987.
- [25] Abe Y. Long-chain fatty acids containing ether linkage. I. The antimicrobial and fungicidal activities of some new p-alkyloxypropionic acids and their methyl esters. *Lipids* 1966, 1(2):141-145.
- [26] Abe Y, Osanai S. Long-chain carboxylic acids containing ether linkage. III. The antibacterial and antifungal activities of the amine salts of some β -alkoxypropionic acids. *J Am Oil Chem Soc* 1969, 46(7):365-367.
- [27] Abe Y, Osanai S, Matsumura S. Long-chain carboxylic acids containing ether linkage. IV. The antibacterial activities of O-{2-Alkylaminoethyl}-3-oxypropionic and N-(2-Alkyloxyethyl)-3-aminopropionic Acids. *J Am Oil Chem Soc* 1972, 49(6):357-360.
- [28] Abe Y, Osanai S, Matsushita T. Long-chain carboxylic acids containing ether linkage. V. N-methyl substituted glycine-type amphoteric containing alkoxy radical. *J Am Oil Chem Soc* 1974, 51(9):385-388.
- [29] Schafer W, Schafer R, Schafer D, Aalbers JG, Smid JK. Novel polyether carboxylic acid derivatives, as well as their use, 1989. Patent Number US 4818440/1989.
- [30] Cripe TA, Ofosu-Asante K. Alkaline light duty dishwashing detergent composition containing an alkyl ethoxy carboxylate surfactant, magnesium ions, chelator and buffer, 1994. Patent Number US 5376310/1994.
- [31] Ofosu-Asante K. Liquid or gel dishwashing detergent containing alkyl ethoxy carboxylate divalent or ions and alkylpolyethoxy polycarboxylate. 1998. Patent Number US 5739092/1998.
- [32] Man VFP. Alkaline cleaners based on alcohol ethoxy carboxylates; 2001. Patent Number US 6274541 61/2001.
- [33] SR ISO/TR 896:1995 Surface active agents. Scientific classification (identical with the International ISO/TR 893:1977). Romanian Standards Association (ASRO); <http://magazin.asro.ro/>.
- [34] Jianu C. Synthesis of nonionic-anionic colloidal systems based on alkaline and ammonium beta-nonylphenol polyethyleneoxy (n=3-20) propionates/ dodecyl-benzene-sulfonates with prospects for food hygiene. *Chem Central J* 2012, 6:95, doi: 10.1186/1752-153X-6-95.
- [35] Jianu C, Nedelea G, Lazureanu A, Jianu I, Adamescu A. Diversifying and functional featuring of some PEG coacervates as ecological nanocomponents in the soil-plant-

- man (food consumer) circuit of some nutrients. *Bull Univ Agric Sci Vet Med* 2004, 60:507.
- [36] Jianu C, Butnariu M, Cocan I, Rinovetz A, Bujanca G, Jianu I. Hydrolysis of β -alkyl ($C_{12}H_{25}/C_{18}H_{37}$) polyethyleneoxy ($n = 3-20$) propionitriles in micellar catalysis conditions (I). *J Agroalim Proc Technol* 2009, 15(1):72-78
- [37] Jianu C, Trașcă T, Riviș A, Mișcă C, Chiș M, Jianu I. Hydrolysis of β -alkyl ($C_{12}H_{25}/C_{18}H_{37}$) polyethyleneoxy ($n = 3-20$) propionitriles in phase transfer catalysis conditions (II). *J Agroalim Proc Technol* 2009, 15(1):79-87.
- [38] Jianu C, Jianu I. Colloidal competences of new tailor-made lipids. *J Food Agric Environ* 2010, 8(3&4):148-155.
- [39] Jianu C. Colloidal competences of some food cleaning agents based on alkaline and ammonium nonionic soaps. *J Food Agric Environ* 2012, 10(1):10-15.
- [40] Riviș Adrian. Basic surfaceactive properties in the homologous series of beta-alkyl ($C_{12}H_{25}/C_{18}H_{37}$) polyethyleneoxy ($n=0-20$) propionamides. *Chem Central J* 2013, 7:31, doi:10.1186/1752-153X-7-31.
- [41] Jianu C, Riviș A, Trașcă T, Jianu Adelina, Bujanca G, Controlled of colloidal parameters through gradual ternary association of new "homogeneous" nonionic structured lipids, *J. Agroaliment. Proc. Technol.*, 2014, 20(4):354-362.
- [42] Jianu C, Trașcă T, Riviș A, Jianu Adelina, Costescu Corina, Cazacu Mihaela. Colloidal characteristics in gradual binary associated systems of new "homogeneous" polyoxyethylene structured lipids. *J Agroaliment Proc Technol* 2014, 20(4):383-390.
- [43] Yanagida S, Takahashi K, Okahara M. Metal-ion complexation of noncyclic poly(oxyethylene) derivatives I. Solvent extraction of alkali and alkaline earth metal thiocyanates and iodines. *Bull Chem Soc Jpn* 1977, 50(6):1386-1390.
- [44] Harvey RD, Barlow DJ, Drake AF, Kudsiova L, Lawrence MJ, Brain A, Heenan RK. The effect of electrolyte on the encapsulation efficiency of vesicles formed by the nonionic surfactants, 2C18E12. *J Colloid Interface Sci* 2007, 315:648-661.
- [45] Yokoyama Y, Hirajima R, Morigaki K, Yamaguchi Y, Ueda K. Alkali-cation affinities of polyoxyethylene dodecylethers and helical conformation of their cationized molecules studied by electrospray mass spectrometry. *J Am Soc Mass Spectrom* 2007, 18:1914-1920.
- [46] Jackson AT, Scrivens JH, Williams JP, Baker ES, Gidden J, Bowers MT. Microstructural and conformational studies of polyether copolymers. *Int J Mass Spectrom* 2004, 238:287-297.
- [47] Man VFP. Alkaline cleaners based on alcohol ethoxy carboxylates; 2002. Patent Number US 6479453 82/2002.

- [48] Leinweber D. Dahlmann U, Kupfer R. Process for the solvent-free preparation of ether carboxylic acids having a low residual salt content, 2007. Patent Number US 7208118 B2/2007.
- [49] SR EN 1772/2009, Surface active agents. Determination of wetting power by immersion (identical with the European Standard EN 1772:2000).

IntechOpen

IntechOpen

