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# Higher Oligomeric Surfactants — From Fundamentals to Applications



# 1. Introduction

Surfactants (shorten for surface-active agents) are organic compounds containing in one molecule both lyophobic (hydrophobic) and lyophilic (hydrophilic) parts (Fig. 1.). Due to such amphiphilic structure surfactants exhibit specific properties in solutions, as well as in solid state. When present at low concentrations in solutions they adsorb at all available interfaces (liquid/gas, liquid /liquid, liquid /solid,) and as a consequence dramatically change their free energy. At higher concentrations, above so called critical micellization concentration (cmc), when all the interfaces are occupied, surfactants self-assemble in the bulk in various aggregates: micelles, vesicles and liquid crystals. The type of formed supramolecular structure depends upon the structure and concentration of the surfactant, presence of the electrolyte, temperature, etc. [1, 2].



Figure 1. Schematic representation of a) monomeric and b) dimeric surfactant molecule.

Surfactants versatile phase behavior and ability to form different structures, with sizes from nano to micro-scale, is a reason why they are widely used in various industrial processes,



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ranging from classical (paints, cosmetics, pharmaceuticals, foods) to modern technologies (synthesis of advanced materials, environmental protection). Moreover, surfactants have important roles in living organisms. Examples are pulmonary surfactants, proteins, biological membranes which can be considered to be self-assembled bilayers of surface active compounds (phospholipids), etc. [1, 2].

In constant search for more efficient and environmentally friendly surfactants, both academic and industrial interest has been focused on design and preparation of novel, complex, surfactant structures, with improved properties in comparison with conventional surfactants, i.e. those containing only one hydrophilic and one hydrophobic group.

Novel surfactants which have attracted considerable interest in last two decades are oligomeric surfactants. These compounds are made up of two (dimeric surfactants) or more (higher oligomeric surfactants) amphiphilic moieties covalently linked at the level of the head groups or very close to them by a spacer group [3]. This means that, in theory, it is possible to synthesize oligomeric surfactants using two or more molecules of identical and/ or different conventional surfactant and connecting them with a spacer group varying in chemical nature, length, hydrophobicity and rigidity. The number of possible architectures, and thus properties, is vast [3].

First to report about dimeric or gemini surfactant (Fig. 1. b) in scientific literature were Bunton and collaborators in 1971 [4] They have synthetized bisquaternary ammonium surfactants and studied rate of nucleofilic substitution in their micellar solutions. This work was followed by Devinsky and collaborators in 1985, who synthesized the great variety of bisquaternary ammonium surfactants and investigated their surface activity and micellization [5]. In 1990 Okahara and collaborators synthesized first anionic gemini surfactants, with two sulphate groups and two alkyl chains [6]. In 1990s work by Zana's, and latter Esumi's group, on bisquaternary ammonium surfactants in which they have shown that these surfactants posses unique properties and various self-assembly behaviors compared to the corresponding monomeric surfactants, motivated the investigation of different dimeric surfactants [7-17].

Constantly growing interest for the investigation and synthesis of novel gemini surfactants is a consequence of their superior properties in comparison to the conventional ones [3]:

- their cmcs are one or two order of magnitude lower than for the corresponding monomeric surfactants.
- they are more efficient in lowering surface tension.
- their aqueous solution can have a very high viscosity or even show viscoelastic properties at relatively low surfactant concentrations, whereas the solutions of corresponding monomers remain low viscous as water,
- also, they have better: solubilizing, wetting and foaming properties.

In addition, the Krafft temperatures of dimeric surfactants with hydrophilic spacers are generally very low giving to these surfactants the capacity to be used in cold water [3]. Some cationic dimeric surfactants even have interesting biological activity [5, 18].

The fact that the dimeric surfactants posses properties superior to the corresponding monomers, was motivation to extend the concept of gemini surfactants to higher oligomers (degree of oligomerization  $\geq$  3), expecting that their properties would be even better. This expectations were further supported by theoretical considerations predicting that the critical micellization concentration decreases continuously with increasing degree of oligomerization, while preferentially small spherical micelles form at low concentration and wormlike or threadlike micelles at high concentration [19,20]. In addition, since higher oligomeric surfactants represent transitional structures between conventional and polymeric surfactants, investigation of their properties can give insight in the behavior of the latter.

First synthesized and investigated higher oligomeric surfactants were trimeric [9, 11, 16, 17] and tetrameric [13] linear quaternary ammonium bromides with alkyl spacers. Up to now different cationic, anionic and nonionic oligomeric surfactants, with degree of oligomerization up to 7 [21] and linear, ring-typed or star-like topology [22] of the molecule have been investigated.

However, the efforts in investigation of higher oligomeric surfactants are hindered by the more complex synthesis and purification. Recently progress in this area has been reported. White and Warr have synthesized oligomeric alkylpyridinium surfactants by a simple elimination–addition reaction [23]. Also Feng and collaborators have reported a new method of synthesis for oligomeric surfactants by atom transfer radical polymerization (ATRP) [24, 25].

In this chapter the influence of the oligomerization degree, length of hydrophobic chains, nature of the spacer and topology of the molecule on the properties of higher oligomeric surfactants<sup>1</sup> in the solution and at the interfaces will be discussed. Comparison will be made with behavior of corresponding monomeric and dimeric surfactants. Possible applications of higher oligomeric surfactants will also be discussed.

# 2. Clasification of the oligomeric surfactants

Oligomeric surfactants, like conventional ones, are most commonly classified depending on the type of the hydrophylic headgroup surfactants in four major groups:

- anionic hydrophilic group is negatively charged,
- cationic hydrophilic group is positively charged,
- nonionic hydrophilic group bears no charge, but solubility in water is a consequence of its high polarity,
- zwitterionic molecule contain both positively and negatively charged hydrophylic groups.

So far cationic, anionic and nonionic higher oligomeric surfactants have been synthesized, but no synthesis of zwitterionic has been reported.

<sup>1</sup> The term oligomeric surfactants as used in this chapter does not include surfactants molecules in whose structure only part of the moiety, i.e. head group or tail, is repeated. Example of such amphiphilic molecules are nonionic oligomeric surfactants like Brij or polyetheramine surfactants.

Since oligomeric surfactants are made up of two or more amphiphilic moieties covalently linked at the level of head groups or very close to them (Fig. 1. b) by a hydrophylic or hydrophobic, flexible or rigid spacer group, they can also be classified based on:

- number of amphiphilic moieties present in the molecule dimeric (gemini), trimeric, tetrameric, etc.
- molecular structure (features of their spacer groups)-linear, ring-type, and star-shaped.

The structures of typical examples of the higher oligomeric surfacatants, reviewed in this chapter, are given in Fig. 2-4. They include:

- **cationic** different derivates of quaternary ammonium salts were prepared, like:
  - *quaternary ammonium surfactants with the alkyl spacers* [3, 7-17, 26, 27] (Fig. 2. 2A, 3A, 4A)
     they are usually denoted as *m-s-(m-s)<sub>x</sub>-m*, where *m* represents number of carbon atom in hydrophobic chain, *s* number of the carbon atoms in the spacer and *x=j-2*, where *j* is the degree of oligomerization. Up to now, these surfactants have been the most investigated oligomeric surfactants, due to the relative ease of their synthesis and possibility to tailor surfactant properties by changing spacer and chain length. Majority of these surfactants are bromide salts, chlorides were synthesized in lesser extent.
  - oligomeric quaternary ammonium surfactants prepared by epichlorohydrin [28, 29] (Fig. 2. 2B, 3B) these surfactants have short polar spacers containing –OH groups.
  - oligomeric quaternary ammonium chlorides with trans-1,4-buten-2-ylene, m-xylylene and pxylylene spacers (Fig. 2. 2C, 3C, 4B) – the spacers groups differ in both nature and length, and are all rigid. Chloride was chosen as counterion to increase solubility in water and to provide lower Krafft temperatures [30, 31].
  - *polyoxyethylene ether trimeric quaternary ammonium surfactants* (Fig. 2. 3I) these surfactants contain chains consisting of both polyoxethylene and dodecyl alkyl groups [32].
  - *star-shaped* trimeric quaternary ammonium bromides with different chain length [33] (Fig. 2, 3D).
  - star-shaped trimeric, tetrameric and hexameric quaternatry ammonium salts with amide groups (Fig. 2. 3E, 3F, 4C, 6A) – amide groups were chosen to increase solubility of these surfactants. The spacers are rigid. Non symmetric and symmetric trimeric surfactants were prepared with a slight difference in the spacer [22, 34-36].
  - Tris[2-hydroxy-3-(alkyldimethyammonio)-propoxymethyl]ethane]-these surfactants were designed in order to obtain surfactants with enhanced antimicrobial properties [37] (Fig. 2. 3G, 3H).
- anionic
  - *ring-type trimeric* surfactants synthesized by introducing three hydrocarbon chains to cyanuric chloride (Fig. 3. 3J) –they can dissolve in water only at pH around 13, which renders their applicability [38].

- *triple chain* surfactants with three hydrocarbon chains and two or three carboxylate headgroups (Fig. 3. 3K, 3L)– they exhibit same problem with solubility as ring type trimeric surfactants [39].
- *tetrameric surfactants with multiple-ring spacers* based on dioxane rings with different flexibility (flexible, semi-flexible and rigid) of spacers [40] (Fig. 3. 4D-G).



Figure 2. Molecular structure of cationic oligomeric surfactants-quaternary alkyl ammonium salts.

#### • nonionic

- *tyloxapol* (Fig. 4. 7A) repeating unit is close to Triton X-100 and maximum degree of polymerization is about 7 [21]. This surfactant is commercially available.
- *n-alkylphenol polyoxyethylene trimeric surfactants* with different lengths of hydrophilic group oxyethylene chains and hydrophobic group methylene chains [41] (Fig. 4. 3M).
- trimeric surfactants derived from tris(2-aminoethy)amine (Fig. 4. 3N) these surfactants offer possibility to change hydrophilic/lipophilic balance while keeping molecular skeleton the same [42].



Figure 3. Molecular structure of anionic oligomeric surfactants.



Figure 4. Molecular structure of nonionic oligomeric surfactants.

# 3. Oligomeric surfactants in solution

Unique properties that surfactants exhibit in aqueous solution and in the solid state are consequence of their amphiphilic nature. When present in low concentrations in aqueous solution, surfactants tend to concentrate at the available interfaces and in that way reduce the free energy of the system. At higher concentration, when all the interfaces are saturated the reduction of the system energy can be achieved, depending on the experimental conditions, by crystallization of the surfactant from the solution or by the formation of supramolecular aggregates (micelles, vesicles, liquid crystals etc., Fig. 5). The concentration above which micelle are formed is called critical micellization concentration (cmc). Micelles are thermodynamically stable dispersed species in equilibrium with surfactant monomers [1, 2].



Figure 5. Modes of surfactant reduction of surface and interfacial energies. After ref [1].

#### 3.1. Solubility of surfactants

Overall solubility of many ionic compounds increases as temperature increases. This effect is the result of the physical characteristics of the solid phase, namely crystal lattice energy and heat of hydratation of the material being dissolved.

In the case of ionic surfactants, it is often observed that the solubility undergoes a sharp, discontinuous increase at some characteristic temperature, named the Krafft temperature ( $T_{\rm K}$ ) (Fig. 6). Below the Krafft temperature solubility of the surfactant is determined by the solid state properties, while above it the surfactant solubility increases due to formation of micelles, which are thermodynamically favored form [1, 2, 43].

The Kraft temperature varies with alkyl chain length and structure, as well as with counterion. Lowering of the Krafft temperature can be achieved by introducing chain branching, multiple



**Figure 6.** Schematical representation of the solubility curve for the ionic surfactants. The Krafft temperature ( $T_{\kappa}$ ) is the temperature at which surfactant solubility equals the cmc. Above  $T_{\kappa}$  surfactant molecules form a dispersed phase; below  $T_{\kappa}$  hydrated crystals are formed. After ref. [43].

bonds in the alkyl chain or bulkier hydrophilic groups in the surfactant molecules. In this way intermolecular reactions that promote crystallization are reduced [1, 2, 43].

The Krafft temperature is usually determined either by measuring the change of electrical conductivity with temperature or visually observing the change of turbidity of supersaturated surfactant solution (usually 1 wt %).

Knowledge of the Krafft temperature is crucial in many applications since below  $T_{\rm K}$  the surfactant will clearly not perform efficiently; hence typical characteristics such as maximum surface tension lowering and micelle formation cannot be achieved.

Ionic dimeric *m*-*s*-*m* surfactants with  $m \le 12$  are generally highly soluble in water. The Krafft temperatures below 0 °C have been reported for many series of anionic dimeric surfactants with hydrophobic or hydrophilic spacers [3].

Only the Krafft temperatures of cationic higher oligomeric surfactants were reported, to the best of our knowledge. Majority of the reported values are below 0 °C, which is important for their possible applications in cold water. Besides relative ease of their synthesis, low Krafft temperature is one of the main reasons why oligomeric quaternary ammonium surfactants have received much of the attention.

While trimeric 12-2-12-2-12 surfactant has Krafft temperature in the vicinity of 0 °C,  $T_{\rm K}$  for corresponding tetramer12-2-12-2-12 is 32 °C [27]. It is interesting to note that the Krafft temperature does not regularly change with the degree of oligomerization in this series of oligomeric dodecyl quaternary ammonium surfactants since the Krafft temperature of monomeric DTAB (1A) is below 0 °C and that of dimeric 12-2-12 is 15 °C [3].

Trimeric quaternary ammonium surfactants with polar spacers (3B) have also shown good water solubility and their Krafft temperatures are all below 0 °C [28].

In the series of quaternary ammonium surfactants with *trans*-1,4-butenylene, *m*-and *p*-xylylene spacers (2C, 3C, 4B) it was shown that the Krafft temperatures are reduced by a higher degree of oligomerization [30]. Interestingly,  $T_{\rm K}$  of the trimeric and tetrameric surfactants with the *p*-xylylene spacer (3Cpx and 4Bpx) are below 0 °C, whereas the analogous dimer 2Cpx surfactant has a Krafft temperature of 23 °C [30].

The Krafft temperature of trimeric surfactants 3E and 3F [34], and polyoxyethylene ether trimeric quaternary ammonium surfactant 3I is also found to be below 0 °C [32]. The  $T_{\rm K}$  of starshaped trimeric surfactants 3D were found to be lower than 5 °C [33].

Despite the large number of hydrophobic alkyl chains, the Krafft temperature of hexameric surfactant 6A is also found to be below 0 °C [22].

#### 3.2. Adsorption at the air/water interface

Many surfactant applications are based on their ability to absorb at various interfaces in an oriented fashion. The difference in the surface activity of different surfactants is a consequence of the difference in their packing density at the air/water interface. The packing density is reflected in the values of surfactant surface excess concentration ( $\Gamma_{max}$ ) and surface area occupied by a surfactant molecule ( $a_{min}$ ). The higher the value of surface excess concentration, consequently the lower the value of surface area, the more efficient surfactant is.  $a_{min}$  is not only measure of efficacy of adsorption, but it is also the first information about the orientation and packing of the surfactant at the interface [1, 2, 43].

Maximum surface excess concentration of a surfactant ( $\Gamma_{max}$ ), can be calculated from the surface tension ( $\gamma$ ) measurements, i.e. from the maximal slope ( $d\gamma/dlogc$ ) in the  $\gamma$  *vs.* log *c* before cmc (Fig. 7):

$$\Gamma_{\rm max} = -\frac{1}{2.303 nRT} \left( \frac{\partial \gamma}{\partial \log c} \right)_T \tag{1}$$

where *c* denotes concentration, *R* is the gas constant (8.314 Jmol<sup>-1</sup> K<sup>-1</sup>), *T* is absolute temperature and *n* is the number of solute species whose concentration at the interface changes with change in the value of surfactant bulk concentration (*c*) [2].

From the surface excess concentration, the area per molecule at the interface,  $a_{\min}$ , in square nms is calculated from the relation:

$$a_{\min} = \frac{10^{14}}{N_A \Gamma_{\max}} \tag{2}$$

where  $N_A$  is Avogardo's number and  $\Gamma_{max}$  is expressed in mol/m<sup>2</sup> [2].

In addition to  $\Gamma_{\text{max}}$  and  $a_{\text{min}}$  following quantities can be used to assess surfactant performance in lowering surface tension and its preference for adsorption in comparison to micellization [1, 2, 43]:

- the maximum reduction of surface tension (γ<sub>cmc</sub>) which can be attained in the solution of certain surfactant regardless of its concentration. Lower γ<sub>cmc</sub> means more surface active surfactant.
- the concentration required to produce a surface tension reduction of 20 mN m<sup>-1</sup> ( $C_{20}$ ), usually expressed as negative logarithm of such concentration,  $pC_{20}$ . The larger  $pC_{20}$  the more efficiently the surfactant is adsorbed at the interface and the more efficiently it reduces surface tension.
- the cmc/C<sub>20</sub>, ratio is a convenient measure of the relative effects of structural factors on the micellization and adsorption processes; the larger the values of the cmc/C<sub>20</sub> ratio, the greater the tendency of the surfactant to adsorb at the interface, relative to its tendency to form micelles.

Surface activity of higher oligometric surfactants was assessed based on  $\Gamma_{\text{max}}$ ,  $a_{\text{min}}$ ,  $\gamma_{\text{cmc}}$  and  $pC_{20}$  values. Data reported in available literature are summarized in Table 1.



**Figure 7.** Plot of surface tension versus log of the bulk phase concentration for an aqueous solution of a surfactant. Three distinctive parts of the curve represent [45]:

- i. At low surfactant concentrations surfactant monomers are forming monolayer at the air/water interface. Surface tension is decreasing with the surfactant bulk concentration due to the increasing surfactant surface concentration at the air/water interface.
- ii. At concentrations below, but close to cmc slope of the curve is constant because surface concentration reached its maximum value.
- iii. At concentrations above cmc, surface tension remains almost constant, due to constant monomer concentration.

	106	$\cdot \Gamma_{\max}$	a <sub>min</sub> a			Yeme	~	Т	<b>D</b> 4	
Surfactant	[mol molecule/ m <sup>2</sup> ]	[mol alkyl chain / m <sup>2</sup> ]	[nm <sup>2</sup> /molecule]	[nm <sup>2</sup> / alkyl chain]	п	$[mN/m^{-1}]$	pC <sub>20</sub>	[°C]	Ref.	
<i>Cationic</i> DeTAB*						40		25	[26]	
1A	3.5	3.5	0.62	0.59	2	38.6 38.9	2.3	25 30	[15, 16] [27]	
10-2-10						31.8		25	[44]	
12-2-12	2.7	5.4	0.72		3		31.4	25	[15,16]	
	1.7		1.04			30.3	3.8	30	[27]	
12-3-12	2.3	4.6		0.48	3			25	[15]	
12-6-12	1.35	2.7		0.72	3			25	[7,15]	
8-2-8-2-8	1.07		1.55		4	35.1		25	[26]	
10-2-10-2-10	1.38		1.21		4	25.8		25	[26]	
12-2-12-2-12	1.11		1.49		4	36.4		25	[26]	
	1.3		1.27			36.0	3.7	30	[27]	
12-3-12-3-12	1.75	5.25		0.49	4			25	[15]	
12-6-12-6-12	0.7	2.1		0.83	4			25	[15]	
12-2-12-2-12-2-12	0.9		1.84		5	29.7	4.0	40	[27]	
12-3-12-4-12-3-12	1.3	5.2						25	[15]	
1B						40.5		23	[30]	
BQADC**						37		20	[28]	
2B-12 Cl						35		20	[28]	
3B -12 Cl						32		20	[28]	
1C						39		23	[30]	
2Ctb						41.5		23	[30]	
2C mx						43		23	[30]	
2Cpx						45.0		23	[30]	
3Ctb						41		23	[30]	
3Cmx						40		23	[30]	
3Cpx						40		23	[30]	
4Btb						41		23	[30]	
4Bmx						38.5		23	[30]	
4Bpx						35		23	[30]	
31						38.9		25	[32]	
3H - 8	2.8		0.593			34.78	4.21	20	[37]	
3H - 10	2.88		0.575			34.03	4.70	20	[37]	
3H - 12	2.94		0.565			33.02	5.39	20	[37]	
*decyltrimethylammor	nium bromide, ** bisquaterr	nary ammonium dichloride	with dodecyl chain (R	CH3)2N+CH2CH-(OH)CH	12 <sup>+</sup> N(CH3)2I	R·2Cl-				
					. ,				<u> </u>	

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**Table 1.** The surface excess concentration  $(_{max})$ , the minimum area per molecule at the air/solution interface  $(a_{min})$ , the number of solute species whose concentration at the interface changes with change in the value of surfactant bulk concentration (n), the maximum reduction of surface tension  $(_{cmc})$  and the negative logarithm of concentration required to produce a surface tension reduction of 20 mN m<sup>-1</sup> (pC<sub>20</sub>) obtained at given temperature (T) for higher oligomeric and corresponding monomeric and dimeric surfactants. Abbreviated names of listed surfactants are given according to the figures 2-4.

The comparison of the experimentally obtained  $\Gamma_{\text{max}}$  and  $a_{\min}$  values for single chain surfactants is straight forward. However, this is far from being so for the oligomeric surfactants. The problem lies in the *n* in the expression for the surface excess concentration (eq. 1). The prefactor *n* represents the number of species at the interface, the concentration of which changes with the bulk surfactant concentration. This value depends on the degree of dissociation of ionic surfactants, which is not known exactly for all surfactants. There are two extreme cases, one assuming no dissociation, thus treating the surfactants as one particle, or the other assuming complete dissociation. In the case of single-chained surfactants situation is simple, this value is 1 for the nonionic, which are not ionized, and 2 for the ionic surfactants, which are considered to be fully ionized, when both ions are univalent. However introducing additional structural elements to the surfactant molecule complicates the situation. Not only that for many oligomeric surfactants degree of dissociation is unknown, but it can vary in the same series of surfactants either with changing the degree of oligomerization or the spacer length.

This problem was first encountered with dimeric *m-s-m* surfactants. The reported values were obtained using n=2 assuming that one of the headgroup is neutralized by a counterion [46, 47], or n=3 assuming that surfactant is fully ionized [7]. In order to be able to compare different series of the surfactants some studies reported values obtained using both values. Not even studies in which surface was determined directly by small angle neutron scattering manage to solve the problem, because it was shown that degree of dissociation depends on the nature of the spacer [48]. Nowadays it is commonly assumed that for series of linear quaternary ammonium surfactants with dodecyl chains and short ethylen space, n=3 for dimer, 4 for trimer and 5 for tetramer [15, 27].

In addition, when comparing  $\Gamma_{\text{max}}$  and  $a_{\min}$  obtained in different studies, one should be aware that they can be expressed either per molecule or per alkyl chain. The later is more convenient to determine spacer influence in the series of surfactants with the same degree of oligomerization.

Based only on the structure of the surfactant molecule it could be expected that  $a_{\min}$  will increase with the degree of oligomerization due to the increased number of headgroups in the molecule. However, since higher oligomers are more surface active, in some cases, their molecules are more closely packed at the air/water interface. As a result, sometimes  $a_{\min}$  doesn't vary with the degree of oligomerization and therefore it may be the same or even lesser than for corresponding monomer.

Most of the pioneering work in investigating oligomeric surfactant adsorption at the air/water interface has been done by Zana and collaborators [3,7], who have laid the basis for the understanding of oligomeric surfactant behavior at air/water interface.

The influence of the oligomerization degree, spacer and alkyl chain length of *m*-*s*-(*m*-*s*)*x*-*m* (1A-4A) surfactants on surface activity was investigated by different groups [15-17, 26, 27]. The dependence of surface area occupied by a surfactant molecule (expressed per alkyl chain) on oligomerization degree depends on spacer length for the surfactants with dodecyl chains. For spacer length *s*=2 and 3 surface area  $a_{\min}$  remains nearly constant going from

monomer to trimer [15, 26, 27], while for *s*=6 a slight increase going from dimer to trimer has been observed [15].

For *s*=2 values of both maximum surface excess concentration and the minimum area per molecule adsorbed at the air/solution indicate vertical orientation of hydrophobic tails towards the air of monomeric and oligomeric surfactants with the spacer of the latter located at the interface [27].

The  $\gamma_{cmc}$  value for dimeric (2A; *m*=12, *s*=2) and tetrameric (4A; *m*=12, *s*=2) surfactants are much lower than those for their monomeric counterpart, 1A. However, the  $\gamma_{cmc}$  value of the trimer (3A; *m*=12, *s*=2) is higher than those of the dimer and tetramer, but still lower compared to that of monomer 1A. Both surface efficiency and effectiveness of adsorption at the air/solution interface are lower for the trimer than these parameters for the dimer and tetramer. The differences found between surface activity within the oligomeric series may be attributed to different packing densities at the air/solution interface. The pC<sub>20</sub> values of these oligomeric surfactants are much higher than for monomer 1A. Within the oligomeric series, however, the degree of oligomerization does not significantly affect the pC<sub>20</sub> value [27].

In the series of trimeric 12-*s*-12-*s*-12 surfactants  $a_{\min}$  increases as *s* is increased, as is the case for the same series of surfactant dimers [15]. Among trimeric surfactants of quaternary ammonium bromide *m*-2-*m*-2-*m* type, where *m*=8, 10, or 12, 10-2-10-2-10 surfactant has highest efficiency, it occupies lowest surface at the air/water interface and has the lowest  $\gamma_{cmc}$  [26].

The reliable values of surface tension could not be obtained for 12-3-12-4-12-3-12 tetramer [15].

It can be concluded that in the series m-s-(m-s)x-m (1A-4A) higher oligometric surfactants exhibits somewhat better adsorption properties in comparison with monometric and dimetric surfactants. However, the difference in the surface activity is highest between monomer and dimet than between dimet and higher oligometric.

Kim [28] and Chelebicki [29] synthesized oligomeric quaternary ammonium salts using epichlorohydrin and epibromohydrine. In that way alkyl spacer containing hydroxy group was introduced (2B, 3B). The  $\gamma_{cmc}$  of compounds without central alkyl chain (gemini surfactant; 2B, *m*=1) were higher than that of coresponding lower analogs; bisquaternary ammonium dichloride with dodecyl chain (R(CH3)<sub>2</sub>N<sup>+</sup>CH<sub>2</sub>CH-(OH)CH<sub>2</sub><sup>+</sup>N(CH<sub>3</sub>)<sub>2</sub>R 2Cl<sup>-</sup>) and monomeric 1B. Contrary to that, compounds having three dodecyl chains (timeric surfactant, 3B) show lower  $\gamma_{cmc}$  than both monomer and dimer. In addition, positive charge in the center of the molecule contributes to the lowering of  $\gamma_{cmc}$  [28]. Chelebicki et al. [29] varied counterions (Cl<sup>-</sup>, Br<sup>-</sup>) and alkyl chain length at central nitrogen atom (2B; *m*=2 – 8). Obtained  $\Gamma_{max}$  and  $a_{min}$  values indicated that 2B surfactants with longer alkyl chain length are packed more tightly at the airwater interface. pC<sub>20</sub> values of all 2B (X=Br<sup>-</sup>) surfactants were higher than monomer 1B and analogous dichloride bis-ammonium salts 2B (X=Cl<sup>-</sup>). According to obtained  $\gamma_{cmc}$  values, investigated bromide salts reduce surface tension of water more than gemini surfactants and analogous dichloride bis-ammonium salts [29].

In conclusion, introducing additional hydrophobic chain results in the better surface activity of 2B and 3B surfactants. Surface activity is also influenced by counterion, bromides are more surface active than chlorides.

Laschewsky et al. [30] prepared large number of oligomeric quaternary ammonium surfactants with different degree of oligomerisation and various spacers. In the three investigated series (2C, 3C, 4B) the spacer length was chosen to be in the range between C4 and C6, because the most pronounced changes in the properties of dimeric surfactants were reported for rather short spacer groups. The spacer groups employed, namely trans-1,4-buten-2-ylene, m-xylylene, and p-xylylene, can be considered as rigid, thus fixing chemically the distance between the cationic groups within the same molecule.  $\Gamma_{\text{max}}$  i  $a_{\text{min}}$ values were not reported in order to avoid controversy which n value should be used (see section 3.2). Therefore surface activity was assessed based only on  $\gamma_{\rm cmc}$ . The surface tension at cmc decreases with the degree of oligomerization, the effect being more pronounced for the longer spacers. The nature of the spacer has important influence on packing of the molecules in monolayer. Based on the  $\gamma_{\rm cmc}$  obtained for the three series with different spacers suggest that the packing density of the dodecyl chains in the adsorbed monolayer stays approximately the same for the series with the trans-butenylene spacer, increases somewhat for the series with *m*-xylylene spacer, and improves much for the series with *p*xylylene spacer with increasing degree of oligomerization [30].

Greater possibility of adjusting surfactant physico-chemical properties through changing molecular structure and conformation has motivated synthesis and characterization of several star-shaped surfactants.

Yoshimura et al. [33] investigated star-shaped trimeric surfactants consisting of three quaternary ammonium surfactants linked to a tris(2-aminoethyl)amine core (3D). Each ammonium group had two methyls and a straight alkyl chain of 8, 10, 12, or 14 carbons. In comparison with corresponding monomeric and gemini surfactants with dodecyl chains,  $\Gamma_{max}$  and  $a_{min}$  of 3D are smaller and much larger, respectively. However,  $a_{min}$  calculated per hydrocarbon chain are close to that of a monomeric surfactant and  $a_{min}$  per molecule slightly larger than that of the linear-type trimeric surfactants. This indicates that 3D adsorbed to the air/water interface in an orientation which cause high surface activity, by interactions of the multiple hydrocarbon chains despite the strong electrostatic repulsion between multiple quaternary ammonium headgroups. These results were also supported by p $C_{20}$  and the cmc/ $C_{20}$  ratio [33].

Trimeric surfactant 3D exhibited  $\gamma_{cmc}$  values smaller than those of the corresponding monomeric surfactants, and almost the same  $\gamma_{cmc}$  values as those of the dimeric surfactants. Their  $\gamma_{cmc}$  were also lower in comparison with afore mentioned linear-type cationic trimeric surfactants with three dodecyl chains and two spacers such as ethylene (3A; *m*=12, *s*=2), *trans*-1,4-buten-2-ylene (3Ctb), *m*-xylylene (3Cmx), or *p*-xylylene (3Cpx). Although the adsorption kinetics of trimeric strar–shape surfactants to the air/water interface was slow, they have strongly adsorbed and oriented themselves at the interface, indicating that they efficiently lower the surface tension of water [33].

Wang et al. [22, 34-36] synthesized diversity of oligomeric star-shape surfactants: trimeric (3E, 3F), tetrameric (4C) and hexameric (6A). However, because of their unusual aggregation behavior and properties surface activity was investigated only for tetrameric molecule (4C). The obtained  $\gamma_{cmc}$  was higher than the most of the reported cationic gemini and higher oligomeric surfactants. In addition, the surface tension continues to decrease significantly after

cmc in large concentration range. This was attributed to the formation of premicellar aggregates before cmc through hydrophobic interaction among hydrophobic chains of different molecules [36].

Neutral and cationic series of trimeric  $\beta$ -hydroxy amino ammonium surfactants with different alkyl chain length (3G, 3H; *m*=8, 12, 18) was synthesized by Grau et al. [37]. Poor solubility of neutral trimers (3G) prevented a reliable determination of their surface active properties. On the other hand cationic compounds (3H) displayed a sharp break in the surface tension *vs.* concentration (on log scale) curves and a final plateau indicating a well-defined cmc. The variation of  $\Gamma_{\text{max}}$  and  $a_{\min}$  with alkyl chain length is almost negligible. The values of  $a_{\min}$  decrease somewhat with the increase in the alkyl chain length, which was attributed to the flexibility of the spacing group and stronger intermolecular van der Waals forces at increasing chain lengths [37].

All three cationic compounds (3H) have good surface activity as indicated by  $pC_{20}$  values. The cmc/ $C_{20}$  ratios indicate that compound with dodecyl alkyl chain has a slightly greater preference for adsorption than for micellization [37].

Contrary to the relatively large number of data for oligomeric cationic surfactants, data for anionic and nonionic surfactants are scarce.

Yoshimura and Esumi [38, 39] have synthesized diverse anionic surfactants. Physico-chemical properties of all surfactants were investigated in alkaline solution at pH 13 (3J-L).

Surface activity of two trimeric surfactants (3K, 3L) was compared to the activity of corresponding single-chain sodium 2-aminododecanoate surfactant. All parameters,  $\Gamma_{max}$ ,  $a_{min}$  and  $\gamma_{cmc}$  show that investigated trimeric surfactants provide greater efficiency in lowering the surface tension than the single-chain surfactant. Surface area occupied by 3L molecule is somewhat larger than that of single-chained surfactant. On the other hand,  $a_{min}$  for 3K is very small. This can be attributed to the smaller electrostatic repulsion between the chains in the molecule of 3K because central chain bears no charged groups unlike the 3L. This enables closer packing of the chains. Among two triple-chain surfactants, 3K shows lower surface tension than 3L. It is considered that the orientation of the latter derived from tris(2-aminoethyl)amine is less effective at the air/water interface, due to the bulky structure compared to the former from 3-aza-1,5-pentanediamine [39].

The obtained  $\text{cmc}/C_{20}$  values for both trimeric surfactants 3K and 3L indicates their preference to adsorb at air/water interface due to the difficulty of packing three hydrocarbon chains into the micelles. The  $\text{cmc}/C_{20}$  of 3L is also much larger than that of 3K, suggesting that it is easier for the former to adsorb at the interface than for the latter [39].

Although it is expected that the areas occupied per molecule of the ring-type trimeric surfactants are large (3J), because they possess three hydrocarbon chains and a bulky triazine ring, they turned out to be small. The  $a_{\min}$  of the surfactant with shorter chain was comparable to the ones of single-chained surfactants. Increase in hydrocarbon chain length resulted in even smaller  $a_{\min}$ . It is suggested that the ring-type trimeric surfactant molecules pack densely at the air/water interface and therefore are highly surface active, probably due to the hydrophobic interactions between multi-hydrocarbon chains [38]. Ring-typed trimeric surfactants showed higher efficiency at reducing the surface tension in the alkali solution in comparison with single-chain sodium dodecanoate and sodium dodecyl sulfate (SDS). Increasing the length of the side chains results in lowering  $\gamma_{cmc}$ . The obtained values are similar to those obtained for 3K and 3L anionic trimeric surfactants [38].

The  $pC_{20}$  values of the ring-type trimeric surfactants were larger than those of the monomeric anionic surfactants (sodium dodecanoate and SDS) and increased when the hydrophobic chain length increased, indicating that a long hydrophobic chain in the molecule facilitates a more close packed arrangement at the air/water interface and a more efficient adsorption [38]. In comparison with 3K and 3L, based on cmc/ $C_{20}$  values, ring like surfactants are more likely to form micelles in the bulk solutions.

Grau et al. [40] synthesized tetrameric anionic surfactants with multiple ring spacers which are flexible (4E), semi-flexible (4D, 4F) or rigid (4G). To the best of our knowledge this is the only study of the influence of spacer nature on surface activity of anionic oligomeric surfactants. Dioxane groups in the spacer confer wet-ability of synthesized surfactants. It was shown that surfactant 4G with the most rigid spacer displayed a minor surface activity at 20 °C, but all four surfactants are surface active at 40 °C.

Obtained  $a_{\min}$  values are less than four times the value for the single-chain surfactant sodium 1-decanesulfonate (C<sub>10</sub>H<sub>21</sub>SO<sub>3</sub>Na) indicating that these tetrameric surfactants are somewhat more closely packed at the air–solution interface than the single chain reference compound [40].

The  $\gamma_{cmc}$  values are smaller than those of single-chain surfactants, but similar to those of doubleand triple-decyl chain surfactants with two sulfonate groups. The  $\gamma_{cmc}$  values of the investigated surfactants are not meaningfully different [40]. The pC<sub>20</sub> value of the surfactant 4D is larger than those of the corresponding 4 E-G surfactants, which are quite similar. This reveals that the pC<sub>20</sub> values decrease with an increase in the number of dioxane rings, in accordance with the fact that the shortest spacing group provides the maximum efficiency [40].

Although nonionic surfactants are widely applied, especially in the emulsion formulations and in drug delivery, there are only few papers dealing with higher oligomeric surfactants. One of the reasons can be that different polymeric nonionic surfactants are commercially available.

Surface activity of nonionic oligomeric 3M surfactants was compared with oligomeric trimeric nonylphenol polyoxyethylene surfactants (TNP) and monomeric nonylphenol polyoxyethylene ether surfactants (NP) [41].  $\gamma_{cmc}$  and the  $\Gamma_{max}$  values of the TNP surfactants are lower than those of corresponding monomer NP surfactants. For both TNP and NP surfactants  $a_{min}$  decreases greatly as the length of oxyethylene chain number is increased. In general, low  $a_{min}$  values suggest close packing of the surfactants at the air/water interface with almost perpendicular orientation of the surfactant molecule. The area per surfactant molecule of TNP is three times smaller than that of NP, which indicates that the trimeric surfactant molecules of TNP are not arranged side by side at the air–water interface, but staggered three-dimensional arrangement. This could be explained with increased hydrophobic interactions due to the

increase in number and length of the chains. Hence, TNP surfactants exhibit much better surface activities, including strong adsorption at the surface and wetting ability [41].

Surface activity of 3M surfactants is not improved as much compared to monomeric surfactants.  $a_{\min}$  increases with increasing hydrophobic spacer length. This may be explained as follows: with the number of carbon atoms in the hydrophobic spacer of the 3M increasing, the hydrophobic property is stronger. Therefore, it decreases the amount of the saturation of adsorption for 3M at the air–water interface, resulting in the increase of the surface tension at cmc,  $\gamma_{cmc}$ .

Mohamed et al. [42] prepared a series of trimeric nonionic surfactants based on tris(2-aminoethyl)amine with varying alkyl and poly(ethylene glycol) chain length, 3N. It was found that  $a_{\min}$  for the prepared trimeric surfactants increases by increasing the alkyl chain length because the surfactant molecules adsorb at the air/water interface to orient themselves so that the hydrophobes are directed away from water. But it is obvious that  $a_{\min}$  decreases by increasing the hydrophilic chain length within the group. This behavior was previously mentioned for nonionic surfactants and is explained by the increase in polyethylene glycol chain leading to coiling the chains in order to minimize any probable interactions between them [42].

In terms of minimum surface tension octyl-3N surfactants proved to be the most efficient in lowering the surface tension of aqueous solutions. The increase in the hydrocarbon chains from octyl to decyl to dodecyl caused an increase of the  $\gamma_{cmc}$ , whereas the increase in the poly(ethylene glycol) chain length within the same group leads to a decrease in the  $\gamma_{cmc}$  [42].

In conclusion, described higher oligomeric surfactants do poses better surface activity compared with monomeric surfactants. However, the change is, in most cases, lesser than for going from monomer to dimer. It was found that the influence of the nature and length of the spacer, as well as alkyl chain length, on adsorption is not the same for different surfactants series.

#### 3.3. Micellization

One of the main characteristics of surfactants is that physico-chemical properties of surfactant solutions abruptly change over small concentration range (see for example Fig. 7). This is a consequence of a significant change in the nature of a solute species, i.e. formation of supra-molecular aggregates called micelles. The surfactant concentration at which the change occurs is called the critical micelle concentration (cmc). cmc can also be defined as a minimum surfactant concentration at which micelles are formed and remain in dynamical equilibrium with free monomers [1, 2, 43].

The main driving force for the micelle formation in aqueous solution is the effective interaction between the hydrophobic parts of the surfactant molecules. Interactions opposing micellization may include electrostatic repulsive interactions between charged head groups of ionic surfactants, repulsive osmotic interactions between chainlike polar head groups such as oligo(ethylene oxide) chains, or steric interactions between bulky head groups [49].

Cmc values are characteristic for given surfactant. Factors influencing cmc value are alkyl chain length, type of hydrophilic group and/or counterions, ionic strength, pH, pressure, temperature, etc.

Micelles size and shape is another property of crucial importance for the application of surfactants. Micelles can vary in size and shape (e.g. spherical, cylindrical, disklike, wormlike), depending on the structure of the molecule and experimental conditions (e.g. surfactant concentration, presence of the electrolytes, temperature, etc.). Aggregation number of the micelles, i.e. number of the surfactant molecules present, ranges between 50 and 200, and can be determined by static light scattering (SLS) or small angle neutron scattering (SANS).

The change of free energy of micellization ( $\Delta G_{mic}$ ) tells us whether it is a spontaneous process ( $\Delta G_{mic} < 0$ ) or not ( $\Delta G_{mic} > 0$ ) and the magnitude of its driving force. Expression for the free energy of micellization of oligometric surfactants has been derived by Zana [12]:

$$\Delta G_{\rm mic} = \left(\frac{1}{j} + \beta\right) RT \ln \rm cmc - \left(\frac{RT}{j}\right) \ln j \tag{3}$$

where  $\beta$  is the degree of counterion association to the micelle/solution interface and *j* is the number of alkyl chains connected by some spacer groups. Micelle ionization degree,  $\alpha$ , is defined as  $\alpha$ =1- $\beta$ .

The fact that dimeric and higher oligomeric surfactants have several degrees of the magnitude lower cmcs than corresponding monomeric surfactants was among main reason for the investigation of these surfactants. Lower cmcs means that less surfactant is needed, which has both financial and environmental benefit. Observed general trend is decrease of cmc with increasing oligomerization degree which is mainly attributed to thermodynamical reasons [3, 30] as basically the entropic loss resulting from micellization of the surfactants becomes smaller. However, the difference in cmcs in the series of the same surfactants with the different degree of oligomerization is largest going from monomer to dimer, and gets smaller in going from one to the other higher oligomeric molecule. Micellisation properties of higher oligomeric surfactants were assessed based on cmc and  $\Delta G_{mic}$  values. Available data are summarized in Table 2.

For the dimeric, trimeric and tetrameric dodecyl quaternary ammonium bromides (1A-4B) the general trend of decreasing cmc with degree of the oligomerization was observed [15, 16, 27]. The cmcs values increase with the spacer length for trimeric surfactants, as it is the case for corresponding dimeric surfactants. In addition, the values of  $\Delta G_{mic}$  (per mole of dodecyl chain) are all around-20 kJ/mol, irrespective of the values of degree of oligomerization and/or spacer length as reported by In et al. [15]. Recent study showed that on a per chain basis for 1A – 4A surfactants (*m*=12, *s*=2)  $\Delta G_{mic}$  is more negative for the monomer than for oligomers [27]. This may be attributed to steric hindrance of the short ethylene spacer from becoming part of the micelle core. The  $\Delta G_{mic}$  values within the oligomeric series become less negative with increasing the degree of oligomerization as a consequence of lower driving force for micellization. Both  $\Delta G_{ads}$  and  $\Delta G_{mic}$  are negative, showing spontaneous adsorption and micellization.

Differences in their magnitudes reveal that these surfactants have greater preference toward adsorption in comparison with micellization. In the series of trimeric *m*-2-*m*-2-*m* surfactants (3A; *m*=8, 10, 12) cmc linearly decreases with increasing alkyl chain length, like for monomeric surfactants [26]. However, the effect of hydrocarbon chain length on the cmc is smaller for trimeric than for monomeric surfactants.

Kim et al. [28] observed that the cmc values of the quaternary ammonium compounds with two dodecyl chains (2B; *m*=1) are 2 orders of magnitude lower, and those of the compounds with three dodecyl chains (3B; *m*=12) are 4 orders of magnitude lower compared with the conventional dodecyltrimethylammonium chloride (1B), regardless of the number of hydrophilic ammonio groups in the molecule. The cmc values of compounds having a dimethylammonio group in the center of the molecule are of the same order as that of compounds in which it is not present. This means that the additional charge in the center of the molecule has only a small effect on the cmc of the quaternary ammonium salts. In addition, there is a linear relationship between the total carbon number in the hydrophobic group and the cmcs on the semilogarithmic scale for all investigated quaternary ammonium salts, interestingly irrespective of the number of hydrophilic ammonio groups in the molecule [28].

Increase in alkyl chain length from 2 to 8 resulted in linear decrease of the cmcs values of 2A surfactants with both bromide and chloride counterions [29]. However, the type of counterion influences the cmc values, the values for the chlorides were higher than for bromides. Obtained values were 2 orders of the magnitude lower than those of corresponding monomeric 1A and 1B. They were also lower than that of dimeric *m-s-m* surfactants with hydrophobic flexible spacers (2A; s=3, 4, 6). The authors explained this with the formation of H-bonds between two OH groups in the spacer and water molecules, which facilitate the bending of the spacer toward the aqueous phase forming the convex micellar surface [29].

In conclusion, Kim and Chlebicki showed that introducing additional hydrophobic chain results in lower cmc values. Type of counterion also influences micellization process, bromide salts aggregates at lower concentrations than chloride. Obtained results are in accordance with generally observed trend for oligomeric surfactants.

The cmc values of oligomeric quaternary ammonium surfactants with various rigid spacers 2C, 3C, 4B are much lower than those of the structurally closely related surfactant monomers, 1B and 1C [30]. The decrease in cmc is more pronounced going from monomers to dimers, than going from trimers to tetramers. It was shown that the chemical nature of the spacer has an influence on the cmc values among the surfactants of the same degree of oligomerization. Comparing the isomeric spacers *m*-xylylene and *p*-xylylene the cmc slightly increases with increasing spacer length, similar to the behavior of oligomeric surfactants with flexible alkyl spacers. The oligomers with *m*-xylylene spacer have lower cmcs than those with butenylen, despite their increased length, due to the higher hydrophobicity [30]. Exception to this behaviour was 4Bpx surfactant. The reason lies in the formation of premicellar aggregates at very low concentration, resulting in shifting cmc to values higher than expected. Premicellar aggregation can occur in solutions of conventional surfactants that are sufficiently hydrophobic (at least 14 carbon atoms) and in those of dimeric *m*-s-*m* surfactants (for 12-*s*-12 with  $m \ge 12$ , for *m*-8-*m* with  $m \ge 14$ , and for 16-*p*-xylylen-16 [11].

Surfactant	cmc <sub>y</sub> [mmol / dm <sup>3</sup> ]	cmc <sub>x</sub> [mmol / dm <sup>3</sup> ]	α	$-\Delta G_{\rm mic}$ [kJ / mol alkyl chain ]	$N_{\rm agg}$	<i>T</i> [°C]	Ref
Cationic							
DeTAB*	67					2:	5 [26]
1.4	14	15.1	0.25	18.3		-2:	5 [15, 16]
IA	14	15	0.29	18.1		-30	0 [27]
10-2-10	5.0					2:	5 [44]
12-2-12	0.9					2:	5 [16]
12-2-12	0.8	1	0.27	23.2		30	0 [27]
12-3-12	0.96		0.22	20.8		2:	5 [15, 50]
12-6-12	1.03		0.33	18.8		2:	5 [15, 50]
8-2-8-2-8	14					2:	5 [26]
10-2-10-2-10	0.95					2:	5 [26]
12-2-12-2-12	0.065					2:	5 [26]
	0.6	0.8	0.26	19.3		30	0 [27]
12-3-12-3-12	0.14		0.19	21.5		2:	5 [15]
12-6-12-6-12	0.28		0.30	19		2:	5 [15]
12-2-12-2-12-2-12	0.7	0.8	0.35	16.7		40	0 [27]
12-3-12-4-12-3-12	0.06		0.20	22.6		2:	5 [15]
1B	18.3	22	0.34	21.94	34.3	2	3 [29, 30, 51]
BQADC**	0.78					20	0 [28]
2B-12 Cl	0.0062					20	0 [28]
3B – 12 Cl	0.0096					20	0 [28]
1C	7.0				27.3	23	3 [30, 51]
2Ctb	2.0				15.5	23	3 [30, 31, 51]
2C mx	1.5				11.3	23	3 [30, 31, 51]
2Cpx	2.1				10.5	23	3 [30, 31, 51]
3Ctb	0.36				5.0	23	3 [30, 51]
3Cmx	0.28				5.4	2	3 [30, 51]
3Cpx	0.29				3.5	2:	3 [30, 51]
4Btb	0.12				3.8	23	3 [30, 51]
4Bmx	0.09					2.	3 [30]
4Bpx	1.3				3.5	23	3 [30, 51]
31	1.0	1.0				2:	5 [32]
3H - 8	0.622					20	0 [37]
3H - 10	0.223					20	0 [37]
3H- 12	0.049					20	0 [37]
*decyltrimethylammo	nium bromide, ** bisquate	ernary ammonium dichlorid	e with dodecyl chain (R	$(CH3)_2N^+CH_2CH-(OH)CH_2^+N(CH_3)_2R\cdot 2C$	ŀ		

Surfactant	cmc <sub>r</sub> [mmol / dm <sup>3</sup> ]	cmc <sub>x</sub> [mmol / dm <sup>3</sup> ]	α	$-\Delta G_{\rm mic}$ [kJ / mol alkyl chain ]	N <sub>agg</sub> T [°C]	Ref
Cationic						
3D-10	1.17	1.60		30.0	25	[33]
3D-12	0.139	0.177		36.3	25	[33]
3D-14	0.00647	0.384		33.7	25	[33]
3E	0.20 <sup>a</sup>	0.32ª	0.45		25	[34]
3F	0.33ª	0.39ª	0.50		25	[34]
łC	0.08	0.12	0.73		25	[36]
5A	1 31ª	0.11 <sup>a</sup> 1.13 <sup>a</sup>	0.29		25	[22]
(	1.51	1.15	0.24		$( \cap )$	
Anionic						
C <sub>11</sub> H <sub>23</sub> COONa	20				20	[38]
C <sub>12</sub> H <sub>25</sub> OSO <sub>3</sub> Na	8.2				25	[38]
3J-4	0.19				32 25	[38]
3J-10	0.011				580±20 25	[38]
$C_{10}H_{21}CH(NH)_2COONa$	1			34.2	25	[39]
3K	0.0063			10.7	25	[39]
L	0.0167			9.9	25	[39]
D	0.0468 "				20	[40]
1E	0.178 "				20	[40]
F	0.105 "				20	[40]
Nonionic						
3N 8-PEG400	8.23 .10-4				25	[42]
3N 8- PEG1000	$7.57 \cdot 10^{-4}$				25	[42]
3N 8- PEG2000	7.1 ·10 <sup>-4</sup>				25	[42]
3N 10- PEG400	7.92 .10-4				25	[42]
3N 10- PEG1000	$7.34 \cdot 10^{-4}$				25	[42]
3N 10- PEG2000	6.91 ·10 <sup>-4</sup>				25	[42]
3N 12- PEG400	7.50 .10-4				25	[42]
3N 12- PEG1000	$7.15 \cdot 10^{-4}$				25	[42]
3N 12- PEG2000	6.63 ·10 <sup>-4</sup>				25	[42]
<sup>a</sup> the critical aggregation co	oncentration is reported					

**Table 2.** The critical micellization concentration determined by surface tension (cmc) and electrical conductivity measurement (cmc), the degree of counterion dissociation (), aggregation number (N<sub>agg</sub>) and the free energy of micellization (G<sub>mic</sub>) obtained at given temperature (T) of higher oligomeric and corresponding monomeric and dimeric surfactants. Abbreviated names of listed surfactants are given according to the figures 2-4.

The cmc of the cationic trimeric surfactants 3H linearly decreases with the number of carbon atoms in the alkyl chain. In other words, cmcs values decreases with alkyl length even for very hydrophobic molecule with tree octadecyl chains. Calculated cmc/ $C_{20}$  values point that trimeric surfactant with 16 C atoms in alkyl chains has slightly greater tendency to adsorb at air/water interface in comparison with tendency to form micelles [37].

In the 3D series [33] the cmc values decrease with increasing chain length from 10 to 14. The cmc of 3D-8 was not possible to determine because micelles did not form in solution even at the highest concentration studied, due to the short chains, and the solution simply became turbid. The cmc value of 3D-12 surfactant is lower than that of corresponding monomeric and gemini surfactants. The cmc in that series of surfactants decreases for an order of magnitude for each additional surfactant moiety. Compared with linear 12-2-12 surfactant, cmc of 3D-12 was slightly higher, in line with authors assumption that tris(2-amionoethyl)amine would have greater hydrophobicity. 3D-12 also exhibited cmc lower than that of the linear cationic trimeric surfactants with spacers such as *trans*-1,4-buten-2-ylene (3Ctb), *m*-xylylene (3Cmx), and *p*-xylylene (3Cpx), respectively [33]. The relationship between the logarithm of cmc and hydrocarbon chain lengths (as for monomeric and gemini surfactants) or chain number was linear [33]. This means that the longer the chain length and the higher the chain number of surfactants, the lower the cmc will be.

The values of  $pC_{20}$  and cmc/ $C_{20}$  ratio in 3D series were much larger than those of most ionic monomeric surfactants. In addition, the absolute values of  $\Delta G_{ads}$  are significantly greater than those of  $\Delta G_{mic}$  for all the hydrocarbon chain lengths. Both these facts suggest that in comparison to micellization, the adsorption of star-type trimeric surfactants is preferred [33].

Trimeric surfactants 3E and 3F display unusual aggregation behavior in aqueous solution [34]. Both trimeric molecules form vesicles just above critical aggregation concentration (cac) and then vesicles gradually transform to the micelles with the increase of surfactant concentration. Normally, surfactants form small aggregates first, and then the aggregates may become large with an increase of the surfactant concentration. The reported cac value of 3E is lower than that of the 3F. Both values are slightly lower from cmc of cationic gemini surfactants. The enthalpy changes for aggregation have large negative value for both surfactants indicating that they have similar aggregation behavior and ability, and that their aggregation is dominated by hydrophobic interaction. This is expected because investigated trimeric surfactants have similar molecular structure. 3F is a completely symmetric molecule, whereas 3E is not symmetric with spacer slightly different from 3F [34].

Tetrameric (4C) and hexameric (6A) surfactants synthesized by the same group of authors [22, 36] also display interesting aggregation behavior which will be address in more detail in the next part of the chapter. Reported cmc value of tetrameric 4C (0.08 mmol dm<sup>-3</sup>) is at least an order of magnitude smaller than those of cationic gemini surfactants [36]. This is in accordance with the fact that increasing number of alkyl chains in the surfactant molecule results in decreasing cmc values.

Hexameric 6A (as 3E and 3F) above cac forms vesicles not micelles. It is reported that 6A displays two cac (C1 and C2) as a consequence of aggregate transformation caused by the

changes of the surfactant configuration through hydrophobic interaction among the hydrocarbon chains [22].

The enthalpy change for the aggregation of 6A exhibits a very large negative value, much larger than those of other surfactants with closely similar cationic ammonium amphiphilic moiety. This enthalpy change should concern the entire aggregation process including both the first and the second aggregation processes at C1 and C2 [22].

Enthalpy change of aggregation for 6A is much more negative than for 1A, 2A (m=12, s=6), 3F and 4C, due to the much stronger inter-and intramolecular hydrophobic interactions between the alkyl chains. That is to say, the cooperative hydrophobic interaction becomes stronger with the increase of the number of the hydrophobic chains in a surfactant molecule. Of course, hydrogen bonding between amide groups can also increase the enthalpy change per amphiphilic moiety for 3F, 4C, and 6A. However, each amphiphilic moiety of these molecules has one amide group, and the significantly enhanced enthalpy change per amphiphilic moiety for 6A confirms that the contribution of each hydrocarbon chain to inter-and intramolecular hydrophobic interaction in the 6A aggregation becomes much stronger than that for other surfactants [22].

The cmc values of ring type anionic trimeric surfactant 3J decrease with increasing the alkyl chain length from 4 to 10 [38]. Obtained  $\text{cmc}/C_{20}$  ratios are very small compared with the single chained surfactants suggesting that trimeric anionic ring type surfactants are more likely to form micelles in the bulk solution due to the interactions between multi-hydrocarbon chains.

Anionic triple chain surfactants [39] 3K and 3L have cmc values one-two order of magnitude lower than corresponding single chained sodium 2-aminododecanoate. This indicates that both surfactants have excellent micelle-forming ability at low concentration. The cmc of 3K is also lower than that of 3L, showing the effect in the number of hydrophilic groups on the cmc. On the contrary, absolute values of  $\Delta G_{mic}$  per hydrocarbon chain of 3K and 3L are much smaller than that of the single chain surfactant. It indicates that the steric hindrance of closely connected hydrocarbon chains makes it difficult for the triple-chain surfactants to form micelles. This result is supported by the large cmc/ $C_{20}$  ratio [39]. The opposite result for cmc/ $C_{20}$  ratio was obtained for ring type anionic trimeric surfactant 3J [38].

The cmc values of 4D-4G tetrameric surfactants depend on the architecture of the spacer [40]. Increasing the number of dioxane rings in the spacer increases the cmc value, surfactant 4D has the smallest cmc value among investigated surfactants. The dioxane rings appear to act as hydrophilic units, which contribute to increasing cmc values. Furthermore, a comparison between homologues compounds, as surfactants 4E and 4F, reveals that, as expected, the higher the flexibility of the spacer the higher the cmc. This behavior is more evident at higher temperature (40 °C) [40].

 $Cmc/C_{20}$  values indicate that 4D-4G surfactants have higher preference to aggregate than gemini surfactants. Authors proposed that this might be because the four hydrophobic groups are more suitably oriented to accommodate themselves in the internal part of the aggregates than the two hydrophobic groups of the gemini surfactants. The preference for

the aggregation, relative to the adsorption, increases with the number of dioxane rings and rigidity of the spacer [40].

As a rule cmc values of nonionic surfactants are lower in comparison with ionic surfactants due to the lesser electrostatic repulsion of the hydrophilic groups at the micelle/water interface. Although, the data for nonionic higher oligomeric surfactants are scarce, this trend has been observed in investigated higher oligomeric nonionic surfactants. The cmc value of Tyloxapol (7A) determined by time-resolved fluorescence quenching (TRFQ) is in the micromolar range, i.e., about a hundred times lower than for the "monomer" TX100 [21].

The cmc values of trimeric nonylphenol polyoxyethylene and monomeric nonylphenol polyoxyethylene ether surfactants 3M increase with the number of the oxyethylene groups in the spacer due to the greater hydrophilic characteristics. On the other hand, increasing the hydrophobic chain length results in lower cmc. Short hydrophobic chains are stretched and in contact with water. Therefore they need more free energy to form micelle and as a results the cmc of these surfactants are higher. Long hydrophobic chains, longer than the equilibrium distance of electrostatic repulsion of the head groups, pack inside the micelle hydrophobic core, which may decrease the free energy and consequently lower the cmc value [41].

The cmc values of trimeric nonionic 3N surfactants are small, which suggest that they easily form aggregates in solution. As expected, the cmc values decrease with increasing alkyl chain length. But they also decrease with increasing poly(ethylene glycol) chain length [42].

In conclusion, the cmc values of higher oligomeric surfactants are smaller in comparison with corresponding monomeric and dimeric surfactants. However, the changes are becoming less significant with increase of degree of oligomerization. Reported cmc/ $C_{20}$  ratios indicate that, as expected, structural factors have dominant role in determining higher oligomeric surfactants preference toward adsorption or micellization. This is collaborated with wide range of obtained  $\Delta G_{mic}$  values for different type of oligomeric surfactants (Table 2).

#### 3.4. Properties of higher oligomeric surfactants aggregates

The most striking feature of the dimeric surfactants with short spacers, in comparison with monomeric, is their tendency to form elongated micelles already at relatively low concentrations, without added electrolyte. Zana have pointed out that the origin of the different aggregation behavior of monomeric and dimeric surfactants lies in the different distribution of the head group distances at the micelle/water interface in these two classes of surfactants [3, 10]. For the monomeric surfactants, the head groups are randomly distributed on the surface separating the aqueous phase and the micelle hydrophobic core. The distribution of distances between head groups has a maximum at a thermodynamic equilibrium distance ( $d_T$ ) determined by the equilibrium of the opposite forces involved in micelle formation. In the case of dimeric surfactants, the distribution becomes bimodal. One maximum corresponds to the thermodynamic distance, the other one, narrower, at a distance  $d_S$  that corresponds to the length of the spacer. The length of the spacer is determined not only by the number of atoms in the spacer but also by its conformation. The distance  $d_S$  can be adjusted to be smaller, equal or larger than  $d_T$  by changing structure of the spacer opening a possibility to create variety of

structure [3]. The bimodal distribution of head group distances and the presence of the chemical link between head groups strongly affect the curvature of surfactant layers, and thus the micelle shape. Additional alkyl chains and hydrophilic or hydrophobic spacers in molecules of higher oligomeric surfactants complicate aggregation processes even more from this point of view. For higher oligomeric surfactants to date most data about aggregation behavior is given for linear and star-shaped dodecyl quaternary ammonium surfactants. Experimental techniques used for determining the aggregation number and structure of oligomeric surfactant micellar solutions are SANS, TRFQ, SLS, dynamic light scattering (DLS) and transmission electron microscopy at cryogenic temperatures (cryo-TEM).

In et al. [15] have shown, using cryo-TEM, that the sequence of the aggregates morphology of linear dodecyl quaternary ammonium surfactants 1A-4A, (*m*=12, *s*=3) with increasing degree of oligomerization from 1 to 4 is:

spherical micelles (monomer) → linear wormlike micelles (dimer) → branched wormlike micelles (trimer) → closedloop (ring) micelles (tetramer).

These results were confirmed with molecular modeling and molecular dynamic simulations [19, 20]. The changes of micelle shape can have a strong impact on rheology of the oligomeric surfactants solution, as will be discussed in following part.

In 12-*s*-(12-*s*)<sub>*x*</sub>-12 series with a long spacer, *s*=6, there is practically no change of micelle shape with the increasing degree of oligomerization. It was shown that aggregation numbers for these oligomeric surfactants are similar to the aggregation number of DTAB (1A) spherical micelles [15].

The size distributions for the micelles of the trimeric surfactants *m*-2-*m*-2-*m* (3A; *m*=8, 10, 12) were obtained by DLS at concentrations 2-to 16-fold cmc [26]. For all three surfactants bimodal size distribution was obtained. The smaller hydrodynamic diameter was determined to be 3.8–5.2, 3.8–5.4 and 4.8–6.6 nm for 8-2-8-2-8, 10-2-10-2-10, and 12-2-12-2-12, respectively. The hydrodynamic diameter of larger particles was 30–50 nm. The aggregation numbers at cmc, determined by SLS, increases with increasing alkyl chain length from 7±3 for 8-2-8-2-8, to 8±2 for 10-2-10-2-10 and 18±1 for 12-2-12-2-12. The aggregation number of 12-2-12-2-12 corresponds to 54 (3x18) alkyl chains in the micelle, which is almost identical to the aggregation number of DTAB (1A) and twofold for 12-2-12 [26]. The small aggregation numbers of 8-2-8-2-8 and 10-2-10-2-10 were attributed to shorter hydrocarbon chains [26].

The particle size measurements at a concentration 2-fold of the cmc revealed that the apparent hydrodynamic diameter of monomeric, dimeric trimeric and tetrameric dodecyl ammonium bromides with ethylene spacer is around 3.6 nm in all cases, indicating the formation of spherical micelles [27]. This is in accordance with the theoretical considerations [19] and experimentally obtained data for oligomeric surfactants, showing that their micelles are spherical at the cmc [15]. It is shown that both DTAB (1A) and 12-2-12 form spherical micelles, DTAB even at fairly high concentrations and the 12-2-12 up to 1.3 wt% [50, 51]. The larger particles observed in the Yoshimura's study [26] of trimer were not detected in this case.

Chlebicki et al. [29] reported the coexistence of small spherical micelles and large nearly spherical aggregates when the length of the alkyl chain at the central nitrogen is short (2B).

Furthermore, when this alkyl chain is longer, only larger aggregates are observed. In addition, it was also found that the aggregate size increased with an increase in the surfactant concentration. It can be concluded that the size distribution of investigated 2B surfactants depends on the alkyl chain length and concentration but not on the counterion, Br or Cl<sup>-</sup>.

DLS revealed the existence of only small aggregates (2 nm or smaller) in the solution of 2C, 3C and 4B (regardless of the spacer) surfactants up to 1% wt of surfactant [51]. TRFQ measurements were used to determine aggregation numbers ( $N_{agg}$ ). The relatively low  $N_{agg} < 40$  for solutions of ca. 3 wt %, was ascribed to the chloride counterion which are less bound to the cationic head groups (higher ionization degree) than bromide, resulting in a stronger electrostatic repulsion of the hydrophilic heads as well as a steric hindrance due to higher hydration of the latter. The nature of the spacer has a major influence on the aggregation number of the oligomeric surfactants. In general, the shorter the spacer the larger aggregation number is. For the trimers aggregation number decreases in series  $N_{agg}$  (tb) >  $N_{agg}$  (mx) >  $N_{agg}$  (px) in accordance with the behavior of dimeric surfactants. Contrary to *m-s-m* type of surfactants, the aggregation number of 2C, 3C and 4B surfactants decrease with the degree of oligomerization. In this case a decrease of  $N_{agg}$  with increasing degree of oligomerization, could be ascribed to the fact that further addition of long rigid spacers between the head groups reduces the overall flexibility of the structures and, hence, makes it difficult for the higher oligomers to pack tightly [51].

The structure of the micelles formed in the solution of star-shaped trimeric surfactants 3D was significantly influenced by alkyl chain length, for m=10, ellipsoidal micelle formed, for m=12, the ellipsoidal micelle transformed to the threadlike micelles with increasing concentration, and for m=14, threadlike micelles were formed at low concentration and no transitions were observed as concentration increased [33].

Unusual aggregation behavior of star-shaped trimeric 3E and 3F, tetrameric 4C and hexameric 6A surfactants was explained by the dominant role of hydrophobic interactions which enables the configuration of the molecules to change [22, 34-36].

Due to the rigid spacer and the intramolecular electrostatic repulsion among the quaternary ammonium headgroups, the hydrophobic chains of 3E and 3F pack loosely, and the 4C molecule presents a stretched configuration at low concentrations [34-36].

Trimeric surfactants (3E and 3F) form vesicles just above the cac. With increasing concentration hydrophobic interaction becomes strong enough to pack the hydrophobic tails tightly and turn the molecular conformation into a pyramid-like shape, which results in the gradual transformation of vesicles in spherical micelles.

For tetrameric 4C these interactions are strong enough already below cac so 4C form large network-like premicellar aggregates that changes to small spherical micelles at high surfactant concentration due to the same reason as for trimeric surfactants [34-36].

Star-shaped hexameric (6A) surfactant also form network-like premicellar aggregates well below the cac and transfer to small spherical micelles at high concentration. Its aggregation behavior is more complex since two cacs are observed. Between two cacs the hydrophobic interaction becomes stronger so that the 6A may transfer to a claw-like configuration. Above second cac the hydrophobic interaction continues to strengthen, and to cause the molecular configuration to convert into a pyramid-like shape, which generates the transition of the large spherical aggregates to small spherical micelles as for 3E, 3F and 4C surfactants [22]. This research also proves that introducing more alkyl chains in molecules results with more complex aggregation process of oligomeric surfactants.

Yosimura and Esumi [38, 39] investigated size and aggregation number of anionic trimeric surfactants (3K, 3L, 3J) aggregates in solution by DLS and SLS.

The aggregation number of the ring-type trimeric surfactants 3J-4 and 3J-10 were 32 and 580±20, respectively as determined by SLS [38]. The  $N_{agg}$  of 3J-10 is very large, probably due to the strong cohesion derived from the interactions between longer three hydrocarbon chains in the ring-type trimeric surfactants. The size of the micelles was determined by DLS at the concentration 4-6-fold of the cmc of 3J. In the solution of both surfactants smaller and larger aggregates were detected. Both kinds of aggregates increased in size with increasing length of alkyl chains [38].

The large difference in aggregation numbers of 3K ( $N_{agg}$ =1304±8) and 3L ( $N_{agg}$ =39±2) was explained by the strong attractive interactions between hydrocarbon chains as well as the decrease of electrostatic repulsion due to less hydrophilic groups of 3K in comparison with 3L, which has usual micelle size [39]. DLS measurements revealed that in solution of 3K the aggregates 20–30 nm in size are formed, while in the solution of 3L aggregates of sizes 2–10 and 15–40 nm coexist. In the case of 3L, it is considered that the smaller ones correspond to the micelles and the larger ones correspond to the large aggregates similar to 3K [39].

The aggregation numbers of Tyloxapol (7A) and of TX100 micelles were determined by TRFQ. The Tyloxapol micelles were found to be smaller than the TX100 micelles. This behavior is opposite to that found for ionic surfactant oligomers (2A-4A) with respect to their corresponding monomers. Cryo-TEM showed that the Tyloxapol micelles remain spheroidal up to a concentration of about 10 wt%. At 15 wt%, some regions of ordered elongated micelles were also observed, which could be the precursors of the hexagonal phase known to occur at about 35 wt% [21].

#### 3.5. Viscosity

The peculiar aggregation behavior of oligomeric m-s-(m-s)<sub>x</sub>-m surfactants significantly influences the rheological behavior of their solutions. The change of the micelle shape, in the series of surfactants with short spacers, from spherical to wormlike or threadlike micelles with increasing degree of oligomerization affects viscosity of the surfactant solution. The phenomenon that attracts special attention, in this sense, is viscoelastic behavior that is observed in solution of long wormlike micelles. For example dimeric surfactants with a short spacer, such as 12-2-12, give rise to worm-like micelles at fairly low surfactant concentrations, even in the absence of added salt [3, 9-11, 14, 15, 52].

No such changes were observed in the solution of the surfactants with longer spacers, like in going from the monomeric [53] to the dimeric (12-6-12) [10] and trimeric surfactant (12-6-12) analogues [15]. This indicates that the large, rodlike aggregates were not formed

in the solution of these surfactants. The same absence of the effect was observed by Laschewsky et al. [30] who concluded that despite general theoretical predictions made for oligomeric surfactants [19, 20] the remarkable thickening power of certain oligomeric surfactants is apparently restricted to molecular structures with very short spacer groups (namely s=2 or 3).

Rheological behavior of star-shaped trimeric surfactants strongly depends on alkyl chain length [33]. The shear-rate dependence of viscosity of the star-shaped 3D-10 solutions was the same as that for water. On the basis of previous findings it was concluded that 3D-10 forms the spherical or ellipsoidal micelles [33].

At lower concentrations the viscosity of 3D-12 solution was also the same as that for the water. But at higher concentrations viscosity decreased with increasing shear rate the behavior known as shear thinning typical for the rod-or wormlike micelles and chainlike polymers. The results point out that with increasing concentration of 3D-12 surfactant a transition of the spherical micelle-to-rodlike micelle occurs, which was confirmed with SANS and cryo-TEM techniques. When concentration was further increased, growth of wormlike micelles was observed, accompanying the extrusion of the water from the micelles. In order to elucidate this behavior the surface charge per unit length and the end-cap energy of monomeric 1A, dimeric 12-2-12 and trimeric 3D-12 were obtained from the analysis of the volume fraction dependence of the zero-shear viscosity. Results have shown that molecular structure (linear or star-shaped) and degree of oligomerization (*j*=1, 2 or 3) have no influence on the surface charge per unit length. However, the end-cap energy of wormlike micelles decreased in order 3D-12 > 12-2-12 > 1A, indicating that wormlike micelles form more easily in the solutions of trimeric and dimerics surfactants even at lower concentrations. The crucial difference in the molecular structure between 3D-12 and 12-2-12 is the number of spacer chains. It seems that it is the spacer responsible for the increase of end-cap energy, one of the reasons being limitation of intramolecular motion by increasing the number of spacer groups in the molecule. The shape of the molecule also affects the end-cap energy. Trimeric star-shaped 3D surfactant is more round shaped than the linear one which results in lower end-cap energy of its wormlike micelles [54].

Viscosity of 3D-14 solutions was higher than that of water and it didn't change with increasing shear rate which was attributed to presence of threadlike micelles in solution [33].

Already in these several studies the complex rheological behavior of higher oligomeric surfactants was observed. Results have shown that number and length of spacer in surfactant molecule have key role in their aggregation and thus rheological behavior. It seems that the interplay of contribution of spacer and alkyl chains in resulting behavior is even more subtle than for dimeric surfactants. Considering the unusual aggregation behavior of tetrameric 4C and hexameric 6A it would be interesting to see how it reflects to their rheological behavior.

# 4. Applications

Synthetic surfactants are nowadays present in many everyday products and are utilized in many industrial processes. Although, dimeric and higher oligomeric surfactants have shown

better properties compared to conventional ones, the difficulties in their synthesis in sufficient quantities are rendering their commercial application. In addition, in order for new surfactant to be used in certain application, its toxicity and harmfulness should be assessed, which requires both time and money. Considering their improved physico-chemical properties it would be worthwhile to perform such tests. Possibility to use higher oligomeric surfactants for several different applications has been investigated.

#### 4.1. Solubilization

Solubilization of poorly water-soluble or insoluble compounds is among most frequent surfactant application.

Laschewsky at el. [30] investigated solubilization capacity of a 2C, 3C and 4B for *p*-xylene and 2,3-dimethylbut-2-ene. The results indicated that the solubilization depends on both the chemical nature of the spacer and the couple surfactant-solubilizate used. Degree of oligomerization, within a given series of oligomers, didn't have significant influence on the solubilization capacity.

#### 4.2. Foaming

Foams are encountered in many important technological areas.

It was shown that the trimeric surfactant 3B has almost the same foaming ability and the foam stability as corresponding bisquaternary ammonium dichlorides which indicates that balance of hydrophobicity and hydrophilicity strongly affects the foaming properties [28]. Simple test of bubbling the air through aqueous solution of a fixed concentration until a given height of foam was produced was used for determining foaming ability of 2C, 3C and 4B [30]. For both trimeric and tetrameric surfactants it was observed that the short spacer favor foam formation and stability. Trimeric surfactants stabilize foam significantly more than corresponding dimeric, but the difference between corresponding trimers and tetramers is marginal. This effect cannot be explained by the difference in viscosity.

#### 4.3. Emulsification

The oil/water emulsions are fine dispersions, encountered in many household and industrial products. The role of surfactants in emulsions is to stabilize them by adsorbing at the water/oil interface preventing phase separation into oil and water phases.

Ability of hexameric quaternary ammonium salt 6A to emulsify heptanes, dodecane, toluene, xylene was investigated. As described in section 3.4, hexameric 6A forms network-like premicellar aggregates at very low concentration, which have compeled the authors to study emulsion forming efficiency at the concentrations far below first cac. It was found that oil/ water emulsion form quickly after vigorous shaking. The surfactant 6A can emulsify heptanes and dodecane, emulsions being stable at the level of 60 - 70 %, but can't emulsify toluene and xylene. The reason was proposed to be the greater compatibility of 6A with linear fatty acids due to its long hydrophobic alkyl chains. Due to the hexameric structure, in comparison with

monomeric and dimeric surfactants, the emulsification ability and the strength of interfacial films are greatly enhanced [22].

Abdul-Raouf et al. have studied factors affecting stability of oil-in-water emulsions prepared by shearing together known amounts of Land Belayim crude oil and aqueous solutions of nonionic 3N surfactants. It was observed that equilibrium interfacial tension of nonionic 3N surfactants decreases with the length of ethylene oxide chain for the same alkyl chain length. After 24 h coalescence process has started only in a few emulsions, indicating that the emulsions were mostly stable. The stability of the emulsions depended on oil percentage and oil/ water ratio. The emulsions with higher oil percentage were found to be more stable. The effectiveness of the emulsifiers decreases with increasing alkyl chain length for 3N surfactants. The emulsions stability increased with increasing surfactants concentration from 300 to 400 ppm, but decreased by further increasing the surfactants concentration to 500 ppm. These findings led to the conclusion that there is an optimum concentration at which the emulsion droplets are fully encapsulated, preventing agglomeration and coalescence which occur at lower concentrations. At higher concentrations surfactant molecules interact with each other and cause the disorder of the arrangement at the interface which facilitates the coalescence [42].

#### 4.4. Lubricants

Surfactants that can self-assemble in smooth bilayers are promising water-based lubricants. However, the cohesion of adsorbed layers is not always satisfactory. Lagleize et al. [55] have investigated the possibility of combining surface-adsorbing surfactants and coadsorbing polymer in order to obtain dense and cohesive lubricant films by self-assembly on mica surfaces. The three studied quarternary ammonium surfactants, monomeric cetyl triethylammonium chloride, dimeric 12-3-12 and trimeric 12-3-12 form flat bilayers at the negatively charged mica surface at the concentrations above cmc [3]. It was shown that the degree by which coadsorption of the anionic–neutral poly(acrylic acid)–polyacrylamide diblock copolymer reinforces the adsorbed layers, as well as the nature and the characteristic times of shear-induced dynamic transitions between states of low-and high-friction forces depend on the degree of oligomerization. Behaviour of systems containing dimeric and trimeric surfactants under shear and compression are qualitatively simillar, while systems with monomeric surfactant have shown different response indicating lower cohesion of the layers [55].

#### 4.5. Adsorption at mineral surfaces

Many practical applications of the surfactants are based on their ability to adsorb at different surfaces. Understanding the interactions between surfactants and mineral surfaces are of special interest for agriculture and oil recovery and consequently for the environment.

Esumi et al. [17] investigated adsorption of 2A and 3A (*m*=12, *s*=2) surfactants, on silica as well as adsolubilization of 2-naphtol. Adsorption of dimeric and trimeric surfactant differs from the monomeric as revealed by adsorption isotherms. Density of adsorbed surfactants decreases with oligomerization degree. The ratio of maximum amount of 2-naphtol adsolubilized to the adsorbed amount of surfactant on silica increases with the oligomerization degree. From a

two-step process of adsorption-adsolubilization it was concluded that oligomers are adsorbed at silica much more strongly than the monomeric surfactant keeping 2-naphtol in their adsorbed layers.

The same group investigated competitive adsorption of pesticide paraquat and 2A and 3A (m=12, s=2) surfactants, on clay [56]. The results indicate competitive adsorption between paraquat and the surfactants. Oligomerization degree didn't have a significant influence on replacement of paraquat.

In et al. [15] investigated adsorption of 12-3-12-3-12 and 12-6-12-6-12 trimers and 12-3-12-4-12-3-12 tetramer at silica and compared it with behavior of corresponding dimers. The values of surface surface excess concentration per mol of adsorbed chain indicate that 12-3-12-3-12 and 12-3-12-4-12-3-12 form bilayer on silica, while value for 12-6-12-6-12 indicates that it forms cylindrical micelles, similar to 12-6-12.

The efficiency of oil recovery process is affected by the wettability of oil reservoir rocks. It was shown that trimeric 12-2-12-2-12 surfactant can alter wettability of both water-wet and oil-wet mica surfaces more efficiently then monomeric or dimeric cationic surfactants. The change in wettability is a consequence of surfactant adsorption in the form of monolayer at the mica surface. The orientation of the surfactant molecules in the monolayer depends on the type of the surface (oil or water wet) [57].

Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and PC model calculation showed that trimeric 3F forms highly-ordered bilayers on the mica surface [35]. Such an ordered structure is induced by match of 3 charged surfactant head groups with negatively charged sites on mica surface. In addition, the formation of the bilayer is promoted by intermolecular bonding and hydrophobic interactions. It was concluded that structural features of an oligomeric surfactant can greatly affect its manner of adsorption, which can help in design of self-assembling molecules for the fabrication of surface patterns.

#### 4.6. Synthesis of advanced materials

So far higher oligomeric surfactants have been used in synthesis of two classes of materials – mesoporous silica materials and ZnO quantum dots.

Preparation of the materials with pores of controlled size, shape and connectivity is of great importance for the practical applications where the shape of the molecules should be recognized. Examples are catalysis, molecular sieves, selective adsorption, sensing, etc. Different applications put different demands for the material properties. Therefore the new routs of synthesis or modifications of existing ones are constantly thought. Surfactants, in general, are frequently used as templates in the synthesis of inorganic materials. Among different mesoand microporous materials, silica based materials take special place.

Although different gemini surfactants of bis-quarternay ammonium type has been used in preparation of different cubic, hexagonal, lamellar mesoporous silica materials [3], only 14-2-14-2-14 [58] and 10-2-10-2-10 [59] have been used as structure directing agent. By using 14-2-14-2-14 surfactant it was possible to synthesize, high quality, ordered two-dimensional hexagonal mesoporous silica under mild conditions. In the presence of 10-2-10-2-10 surfactant

highly ordered supermicroporous silica with the pore structure belonging to the two-dimensional hexagonal structure and pore size from 1.92 to 2.16 nm was obtained.

Quantum dots are inorganic nanoparticles with photoluminiscent properties. They can be prepared either in water or in organic solvents. Synthesis in organic solvents do offer better shape control and achieving higher crystallinity of the product, since organic ligands (most often alkyl amine) are used to control crystal growth. As a result particles coated with hydrophobic layer are obtained. This layer should be removed if nanoparticles are to be used in the water, without affecting their optical properties. Strategy based on encapsulation of nanoparticles in amphiphilic molecules aggregates is proving to be successful in this sense.

Dazzazi et al. [60] investigated the phase transfer of highly monodispers ZnO nanocrystals using monomer (DTAB, 1A), dimer (12-3-12 2Br), trimer (12-3-12-3-12 3Br) and polymer alkyl ammonium surfactants. It was shown that 60 % transfer yields could be obtained with the oligomers and polymer, but no measurable transfer was observed with monomeric surfactant. Trimer and polymer were more efficient than dimer. The results were explained by more quantitative molecular aggregation of surfactants at nanocrystals surface with increasing degree of oligomerization. In addition, the dynamics of molecular exchange between the bulk and double layer coating decreases with increasing degree of oligomerization. Obtained nanocrystals exhibited strong photoluminiscence in the water, as well as long term chemical and photo-chemical stability.

#### 4.7. Antistatic properties

It was shown that the antielectrostatic effect of oligomeric quaternary ammonium derived from epichlorohydrin 2B strongly depends on the counterion, i.e. bromide or chloride. However, both chlorides and bromides have shown very good antistatic properties, similar to commercially available antistatic agent Catanac. No influence of increasing the central chain length on the antielectrostatic properties was observed [29].

#### 4.8. Biomedical applications

Surfactants are frequently used in pharmacy in preparation of drug carriers or systems for targeted drug delivery. In addition, many drug molecules are amphiphilic and therefore surface active.

Motivated by the fact that some dimeric surfactants have antimicrobial activity, neutral and cationic trimeric surfactants 3G and 3H were tested against fungi, Gram positive and Gramnegative bacteria. Both types of trimeric surfactants were the most efficient against Gram positive bacteria. Cationic trimers were more efficient then neutral. Compounds with 12 C atoms in alkyl chain were found to be most active, while those with 8 and 18 C atoms were found to be almost inactive [37].

A proposed approach in the prevention or therapy of Alzheimer's disease is decreasing or eliminating the neuritic plaques composed of fibrillar  $\beta$ -amyloid (A $\beta$ ). The strong tendency of 4C to self-assemble even below cmc prompted authors to study disassembly of amyloide fibrils in its presence. It was shown that both 4C premicellar and micellar aggregates can effectively disassemble matutre A $\beta$ (1-40) fibrils in aqueous solution. Unlike 4C, 12-6-12 loses its efficiency

with decreasing the concentration, indicating that 4C significant self-aggregation ability below cmc could be the key factor in the fibril disassembly. Authors have proposed two key features of the fibril disassembly. First is binding of positively charged 4C surfactant with negatively charged fibriles through electrostatic interactions. Second is self-assembly of the bound 4C molecules which lead to fibrils disaggregation and formation of mixed surfactant/  $A\beta(1-40)$  molecules aggregates [61].

# 5. Conclusion

Current investigations in surfactant science are driven by the requirements to design surfactants that possess enhanced physico-chemical properties, new surfactant utilization in complex systems and specific applications in modern technologies. Hence, investigations of the structure–property relationship in surfactant systems are very important in order to be able to design new surfactants and their supramolecules for specific applications [62]. Although, in theory, higher oligomeric surfactants are text book example how the properties could be tailored by changing structural elements of the surfactants molecule, in the practice investigation of higher oligomeric surfactants are still more driven by the feasibility of the synthesis than the intended application. Additional reason is that the process of their aggregation is still largely unpredictable.

So far mostly cationic oligomeric quaternary ammonium surfactants have been synthesized and investigated, due to the relative ease of their synthesis, low Krafft temperatures and interesting rheological behavior. Oligomeric quaternary ammonium surfactants with different molecular architecture, linear [15-17, 26, 27], dissymmetric [62-65] and star-shaped molecules [22, 33, 34, 36], have been synthesized. Anionic and nonionic oligomeric surfactants have been studied to much lesser extent.

Common conclusions that can be drawn for these different classes of higher oligomeric surfactants are:

- most frequently the dodecyl chain was chosen as hydrophobic building block because it is long enough to confer good surfactant properties to amphiphiles, while it is still short enough that good water solubility for higher oligomeric or polymeric derivatives could be expected. Also, in the most cases, within certain series of surfactants the best properties have surfactants with dodecyl chains,
- the increase of the number of alkyl chains, i.e. degree of oligomerization, within oligomeric surfactant series:
  - enhances the surface activity,
  - shifts the critical micelle concentration (cmc) to lower concentrations, although the changes are becoming less significant with increase of degree of oligomerization above 2,

- linear relationship between the total carbon number in the hydrophobic group and the cmcs on the semilogarithmic scale has been shown for different oligomeric quaternary ammonium surfactants series, as for monomers and dimers
- quaternary ammonium oligomeric surfactants with short spacers (*m*=12, *s*=2 or 3) and starshaped topology exhibit peculiar aggregation behavior, which significantly influences the rheological behavior of their solutions. Such a behavior was not observed for the oligomeric surfactants with longer spacers.
- the length and nature of the spacer within the series of surfactants with the same alkyl chain length and hydrophilic group are most dominant factors in determining the overall surfactant behavior. However, influence of the nature and length of the spacer on adsorption and micellization is not the same for different surfactants series, i.e. it depends on entire molecular architecture.

Although solid state properties of surfactant, in general, attract considerable attention due to their polymorphism and mesomorphism, to the best of our knowledge only one study of higher oligomeric surfactants has been reported [67].

Despite the obstacles, the results of a number studies which have shown the potential of oligomeric surfactants for different applications give additional motivation for the future research.

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