Thermotropic phase transitions of catanionic dodecylsulfates with multi-charged and multi-tailed quaternary ammonium centers

Tea Mihelj[1]*, Jasminka Popović[2], Željko Skoko[3], Vlasta Tomašić[1]*

[1]*Division of Physical Chemistry, Ruđer Bošković Institute, POB 180, HR-10002 Zagreb, Croatia*

[2]*Division for Materials Physics, Ruđer Bošković Institute, POB 180, HR-10002 Zagreb, Croatia*

[3] *Department of Physics, Faculty of Science, University of Zagreb, Bijenička cesta 32, HR-10000 Zagreb, Croatia*

*To whom correspondence should be addressed:

Email: vlastom@irb.hr, tmihelj@irb.hr

Ruđer Bošković Institute, Department of Physical Chemistry

Laboratory for synthesis and processes of self-assembling of organic molecules

Bijenička c. 54, P.O. Box 180, HR-10002 Zagreb, Croatia

Fax: +38514680245

Tel: +38514571211

ABSTRACT

Five novel anhydrous catanionic dodecylsulfates containing multi-charged and multi-tailed quaternary ammonium centers were synthesized and examined with light microscopy, differential scanning calorimetry and X-ray powder diffraction. This study is an attempt to explain the relationship between chemical structure, molecular architecture, phase transition characteristics and thermodynamics, and the nature of intermolecular interactions of the individual amphiphiles that ultimately lead to different mesomorphic product. All examined compounds are of typical layered structure at room temperature. The long spacing decreases linearly with the increase of either ionic head or *n*-dodecyl chain number. The thermal analysis of the examined multi-charged catanionics indicates thermotropic mesomorphism, whereas multi-tailed dodecylsulfates show only properties of soft crystals. Maltese crosses, oily streaks textures, stepped drops and fan-shaped textures affirmed the existence of various smectic mesophases at room and higher temperatures. Thermodynamically the most ordered compound is dimeric didodecylsulfate, and the most disordered is three-tailed dodecylsulfate. The addition of the new quaternary ammonium center or alkyl chain causes the increment of the lattice energy first, and it decreases by further changes in the structure. The temperatures of crystallization decrease by any mentioned addition.

Keywords: catanionic dodecylsulfates, thermotropism, lamellar thickness, tilt angle,

multi-charged surfactant, multi-tailed surfactant

1. INTRODUCTION

Design of different surfactant complexes and tailored functionalized assemblies opens opportunities for a wide range of scientific research and potential applications in commercial products; from pharmaceuticals [1] and template materials [2], to sensors and semiconductors[3]. There has been a strong interest for these compounds due to their liquid crystalline properties that make them comparable with biological structures and functions. The interplay of softness and structure determines the functionality of cell membranes, and understanding the details of these processes is a potentially fundamental issue that underlies biological structure and function in life science. Surfactant molecules associate spontaneously into ordered aggregates as a result of noncovalent interactions and entropic factors. However, it is possible to form bilayer aggregate in a controlled manner and provide useful information to define the structure-activity relationship. Heterogeneous surfactant aqueous mixtures containing self-assembled aggregates represent an interesting alternative for the design of new materials due to their higher flexibility when compared with systems based on homogeneous molecules [4]. The effects of surfactants with more polar groups [5–10] or tails have been reported. While the equilibrium of micellar systems, aggregation number, morphology, counterion dissociation, fractional charge, vesicular, ion-transport properties and the thickness of these membrane organizations have been extensively studied, those of solid bilayer systems are rarely characterized [11,12].

The solid catanionics show complex thermal, polymorphic, mesomorphic and thermodynamic behavior during thermal treatment [13,14]. Compared to their parent anhydrous surfactants, they exhibit significantly different properties, as a result of specific thermal molecular motions and in correlation with their particular molecular structure, charge density and volume constraints [15], size, chemistry [15,16], number of the headgroups [15] or symmetry of alkyl chains [13]. Thermotropic behavior of various catanionic alkylsulfate salts has received huge attention. Symmetric alkylammonium decyl- to hexadecyl- dodecylsulfates have a bilayer structure [13]. The alkyl chains in trans form are packed parallel to each other, the long spacing points to tilting of the hydrocarbon chains with respect to the bilayer plane, all thermotropic liquid-crystalline (LC) phases are of the smectic (Sm) C type, and the thermodynamic parameters and phase transition temperatures change linearly with the total number of carbon atoms in a chain [13]. Asymmetric alkyltrimethylammonium alkylsulfates reveal the SmC phases, but the surfactant tails are more disordered in bilayers because of successive conformational changes, and consequently allow less dense molecular packing [13,17]. A large thermal stability of gemini dodecylsulfates, with the existence of disordered SmA phase is observed [18,19]. Both the transition temperatures and enthalpies of LC and isotropic liquid formation, as well as the sum of transition enthalpy among crystalline solids increase with the chain length of gemini moiety [18,19]. Despite a long standing interest on catanionics, several aspects deserve further investigation, in particular the effect of the varying number of headgroups in multi-charged, or varying number of alkyl chains in multi-tailed catanionics, considering their thermotropic, mesomorphic, and crystallographic properties. Little is known about the impact and consequence of such variations. The reported paper is a follow up of our work on thermotropic phase behavior of catanionic surfactants [13,14]. Five novel anhydrous catanionic dodecylsulfates containing multi-charged and multi-tailed quaternary ammonium centers were synthesized and examined with light microscopy, differential scanning calorimetry and X-ray diffraction. The crystal structure of sodium dodecylsulfate [20,21] and its thermal degradation [22] are well known. The cationic surfactants used were also previously well characterized; fully crystalline dodecyltrimethylammonium bromide with layered ordering of the interdigitaded chains and interlayer distance of 24.60 Ǻ [5,23], didodecyldimethylammonium bromide with the high temperature SmB phase [24]. Tridodecylmethylammonium chloride is enantiotropic, with Sm phase interplanar spacing of 23.50 Å [11]. A series of oligomeric bromides consisting of quaternary dodecyldimethylammonium ions connected by the same ethylene spacer at the headgroup level exhibit polymorphism and thermotropic mesomorphism of the Sm type [5].

This study is an attempt to explain the relationship between chemical structure, resulting molecular architecture, phase transition thermodynamics, and intermolecular interactions of the individual amphiphiles that ultimately lead to mesomorphic product. Moreover, our study is a contribution and encouragement for further potential chemical variations of molecular structure to add functionality to catanionics, useful as templates for nanostructure design [4], nanomaterials synthesis [25].

2. EXPERIMENTAL

2.1. Materials

Oligomeric cationic surfactants with bromide counter ions and the same spacer group separating the unimeric units, were synthesized in our laboratory as described earlier [5]: bis(*N*,*N*-dimethyl-*n*-dodecyl)ethylene-1,2-diammonium dibromide, M_w/g mol^{-1} = 614.68; *N*-bis[2-(*N'*,*N'*-dimethyl-*n*-dodecylammonio)ethylene]-*n*-dodecyl-*N*-methyl-1,2-diammonium tribromide, M_w/g mol^{-1} = 921.00. Cationic surfactants differing in the number of dodecyl chains on the same headgroup were used without further purification for the preparation of solid salts: dodecyltrimethylammonium bromide, M_w/g mol^{-1} = 308.35 (Fluka, > 99.0 % AT); didodecyldimethylammonium bromide, M_w/g mol^{-1} = 462.64 (Acros Organics, > 99.0 % AT); and tridodecylmethylammonium chloride, M_w/g mol^{-1} = 572.49 (Fluka, ≥ 97.0 % AT). Anionic surfactant, sodium dodecylsulfate, $NaC_{12}H_{25}SO_4$, M_w/g mol^{-1} = 288.38, obtained from BDH Chemical Ltd. was recrystallized several times from ethanol and dried in a vacuum oven at room temperature, RT.

2.2. Preparation of surfactant molecular complex

Synthesized and examined catanionic dodecylsulfates are shown in Scheme 1: dodecyltrimethylammonium dodecylsulfate (compound **1**), bis(*N*,*N*-dimethyl-*n*-dodecyl)ethylene-1,2-diammonium didodecylsulfate (**2**), *N*-bis[2-(*N'*,*N'*-dimethyl-*n*-dodecylammonio)ethylene]-*n*-dodecyl-*N*-methyl-1,2-diammonium tridodecylsulfate, (**3**), didodecyldimethylammonium dodecylsulfate (**4**), and tridodecylmethylammonium dodecylsulfate (**5**). Solid surfactant molecular complexes were prepared by mixing equivalent aqueous solutions of both cationic and anionic surfactants at *cca.* 325 K for 30 minutes. Exceptionally, sample **4** was prepared in ethanol under similar conditions, to avoid pure didodecyldimethylammonium bromide vesicles formation. The insoluble catanionic compound precipitates out, leaving the inorganic counterions dissolved in the water. Solid compounds were separated one week after synthesis; **1**, **2**, and **4** were filtered through Millipore filter type HA with 0.45 μm pore size, and compound **5** through Whatman 42, while **3** was centrifuged at 50 000 *G* and 277.15 K, for 2 hours (Sorval RC28S centrifuge, Kendro, USA) and then filtered as **1**. Samples were dried under the vacuum at room temperature till constant mass was obtained and stored in a desiccator, protected from light and moisture.

2.3. Measurements

Elemental analysis of synthesized complexes was performed by Perkin-Elmer Analyzer PE 2400 Series 2. Results confirmed high purity of samples. Compound **1**, $C_{12}H_{25}N(CH_3)_3SO_4H_{25}C_{12}$, M_w/g mol^{-1} = 493.84. Found: C, 65.67; H, 12.02; N, 2.82; requires C, 65.67; H, 12.04; N, 2.84 %. Compound **2**, $[(C_{12}H_{25})(CH_3)_2N\text{-}(CH_2)_2\text{-}N(C_{12}H_{25})(CH_3)_2]$ $(SO_4H_{25}C_{12})_2$, M_w/g mol^{-1} = 1003.68. Found: C, 64.66; H, 11.86; N, 2.80; requires C, 64.62; H, 11.85; N, 2.79 %. Compound **3**, $[(C_{12}H_{25})(CH_3)_2N\text{-}(CH_2)_2\text{-}(CH_3)N(C_{12}H_{25})\text{-}(CH_2)_2N(C_{12}H_{25})(CH_3)_2](SO_4H_{25}C_{12})_3$, M_w/g mol^{-1} = 1495.48. Found: C, 65.05; H, 11.81; N, 2.83; requires C, 65.06; H, 11.79; N, 2.81 %. Compound **4**, $(C_{12}H_{25})_2N(CH_3)_2SO_4H_{25}C_{12}$, M_w/g mol^{-1} = 648.12. Found: C, 70.44; H, 12.59; N, 2.13; requires C, 70.42; H, 12.60; N, 2.16 %. Compound **5**, $(C_{12}H_{25})_3N(CH_3)SO_4H_{25}C_{12}$, M_w/g mol^{-1} = 802.43. Found: C, 73.31; H, 12.91; N, 1.76; requires C, 73.34; H, 12.96; N, 1.74 %.

Loss of the weight due to heating (TG, thermogravimetry) was measured with the use of a Shimatzu DTG-60H. Samples were heated from room temperature to 530 K at the heating rate of 10 K min^{-1} in synthetic air flow of 50 mL min^{-1}. TG measurements confirmed thermal stability of all samples (**1**, **2**, **5** and **6**) under given experimental conditions, except compounds **3** and **4**, which start to decompose at about 503 K and 456 K, respectively. Regardless these findings, all samples except *n*-dodecyltrimethylammonium *n*-dodecylsulfate (**1**) were the subject of partial decomposition during X-ray powder diffraction (XPRD) measurements, when exposed to temperatures higher than ambient temperature.

Thermal transitions were monitored by differential scanning calorimetry, DSC, using Perkin Elmer Pyris Diamond DSC calorimeter in N_2 atmosphere, equipped with a model Perkin Elmer 2P intra-cooler. Samples were heated and cooled at the rate of 5 K min^{-1}. The temperature range for thermal analysis of each sample was determined by examination of TG and DTA curves. Temperature and enthalpy calibrations were performed using high purity standards (*n*-decane and indium). Transition temperatures, T/K, are the maximum and minimum of their endothermic and exothermic peaks. The resulted transition enthalpy change, ΔH/kJ mol^{-1}, was determined from the peak area of the DSC thermogram. The corresponding entropy change, ΔS/J mol^{-1} K^{-1}, was calculated using the equation $\Delta S = \Delta H/T$. All results were taken only from the first heating and cooling run as mean values of several independent measurements carried out on different samples of the same compound.

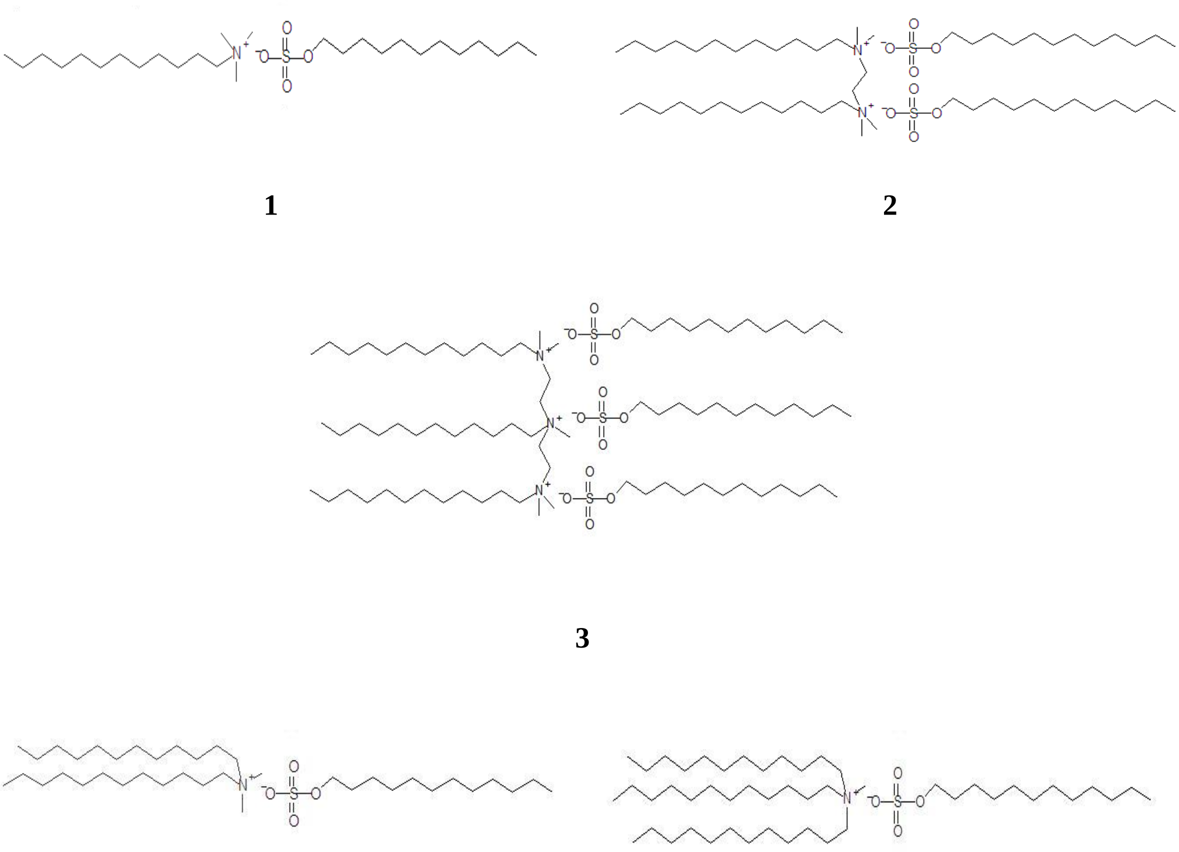
Monitoring of mesophases, morphology and textures of samples was performed with a Leica DMLS polarized optical light microscope, PLM, equipped with a Linkam LNP (model THMS 600) calibrated heating stage. The images were obtained with a Sony digital camera (SSC-DC58AP).

XPRD data was collected on a Philips diffractometer PW1830 equipped with Anton Paar attachment for non-ambient measurements. All attempts to produce solid crystals of examined catanionic dodecylsulfates suitable for single crystal X-ray analysis from water or ethanol solutions by slow evaporation were unsuccessful. The recording temperatures were chosen between points of phase transitions in accordance with the DSC curves. Heating and cooling rate was 30 °C min^{-1}. Room temperature data was collected between 5 and 40 ° 2θ in a step scan mode with steps of 0.02° and counting time of 4 s per step, while the high temperature *in-situ* measurements were recorded between 5 and 25 ° 2θ. For compounds **4** and **5** full pattern indexation was carried out via DICVOL algorithm [26] implemented in HighScore Xpert Plus program. Solutions were checked by N-TREOR09 routine inside EXPO2012 package [27–29]. Indexing was performed by trial-and-error search of the plausible cells by varying the Miller indices. Unit-cell can be chosen based on two figures of merit, M20 and FOMnew. Space group determination was performed by three step procedure: 1) extraction of structure factor amplitudes by the full pattern decomposition step assuming the largest Laue symmetry compatible with the crystal system and no extinction conditions; 2) normalization of structure factor moduli according to the Wilson plot method; 3) statistical analysis of the normalized structure factor moduli at order to detect systematically absent reflections and to calculate, for each extinction symbol (ES) compatible with the crystal system, a corresponding probability function, p(ES). Space group is chosen based on the probability function.

3. RESULTS AND DISCUSSION

In order to establish the effect of various cationic surfactant components on the thermal and structural behavior of the catanionic *n*-dodecylsulfates, a series of ion pair amphiphiles was synthesized. As seen in Scheme 1, chemical structures of examined compounds **1** – **5** are divided into two groups. The first group includes compounds **1** – **3** defined with increasing number of cationic headgroups (n_1 = 1 – 3), and consequently the number of anionic headgroups; and the second one includes **1**, **4** and **5** making the series of compounds with increasing number of *n*-dodecyl chains on the same ammonium headgroup (n_2 = 1 – 3).

Scheme 1. The examined *n*-dodecylsulfates: dodecyltrimethylammonium dodecylsulfate (**1**), bis(*N*,*N*-dimethyl-*n*-dodecyl)ethylene-1,2-diammonium didodecylsulfate (**2**), *N*-bis[2-(*N'*,*N'*-dimethyl-*n*-dodecylammonio)ethylene]-*n*-dodecyl-*N*-methyl-1,2-diammonium tridodecylsulfate (**3**), didodecyldimethylammonium dodecylsulfate (**4**), and tridodecylmethylammonium dodecylsulfate (**5**),



1

2

3

4

5

Preparation of catanionic molecular complexes with sodium *n*-dodecylsulfate anion is a result of electrostatic interactions between ammonium and sulfate headgroups, according to equations (1) and (2) for the first and second group, respectively:

$$\mathbf{A}^{m+} + \text{m X}^- + \text{m Na}^+ + \text{m C}_{12}\text{H}_{25}\text{SO}_4^- \leftrightarrow \mathbf{A}(\text{C}_{12}\text{H}_{25}\text{SO}_4)_{\mathbf{m}} + \text{m X}^- + \text{m Na}^+ \qquad (1),$$

$$\mathbf{B}^+ + \text{X}^- + \text{Na}^+ + \text{C}_{12}\text{H}_{25}\text{SO}_4^- \leftrightarrow \mathbf{B}\text{C}_{12}\text{H}_{25}\text{SO}_4 + \text{Na}^+ + \text{X}^- \qquad (2),$$

where **A** and **B** denote cationic multi-charged and single- or multi-tailed quaternary ammonium surfactant, X^- respective halide counterion, m stoichiometric coefficients, while $\mathbf{A}(C_{12}H_{25}SO_4)_{\mathbf{m}}$ and $\mathbf{B}C_{12}H_{25}SO_4$ represent catanionic salts, containing amphiphilic cation and anion in a 1:1 molar ratio. Besides electrostatic forces, inferior van der Waals interactions between *n*-dodecyl chains, and respective hydrogen bonds that determine the packing in lamellar layers and segregation of hydrophilic from hydrophobic regions, contribute the lattice energy of molecular packing.

3.1. Room temperature X-ray powder diffraction measurements

For as-prepared compound **1** (RT phase in Figure 1), ten diffraction lines were identified as multiple orders of diffraction from the 00*l* crystal planes, indicating layered ordering, or so called the crystal smectic (Sm) phase. By using the interplanar spacing corresponding to the 001 diffraction line, the lamellar thickness at room temperature amounts to 41.8(1) Å.

Figure 1. XPRD patterns of compound **1** at different temperatures during the heating process: 293 K, 375 K, 420 K, 441 K and the cooling process: 433 K, 410 K, 363K and 293 K.

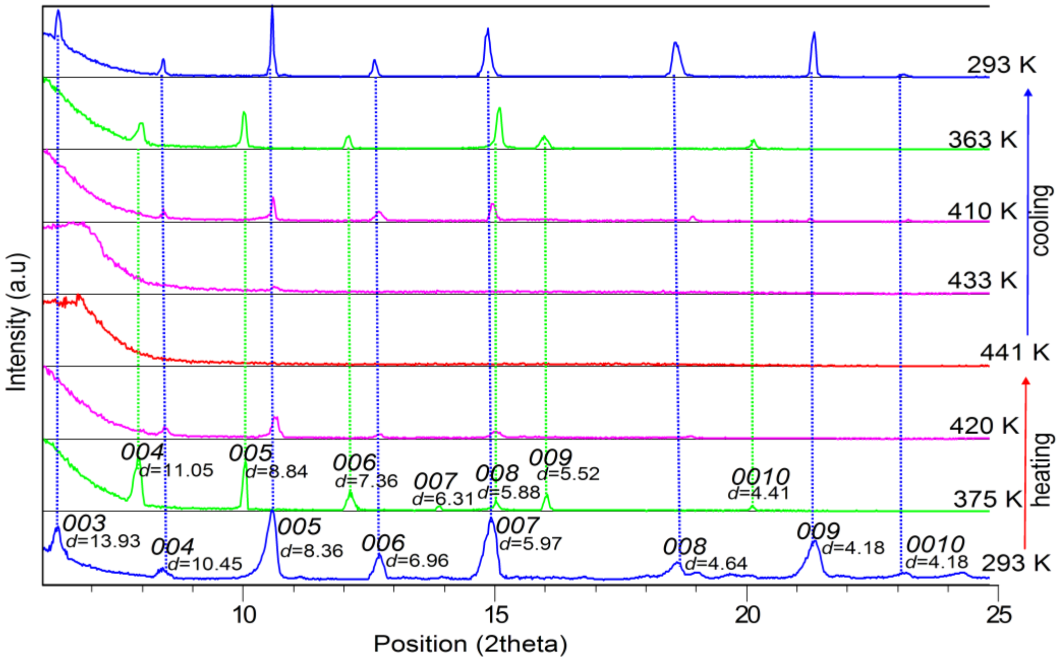
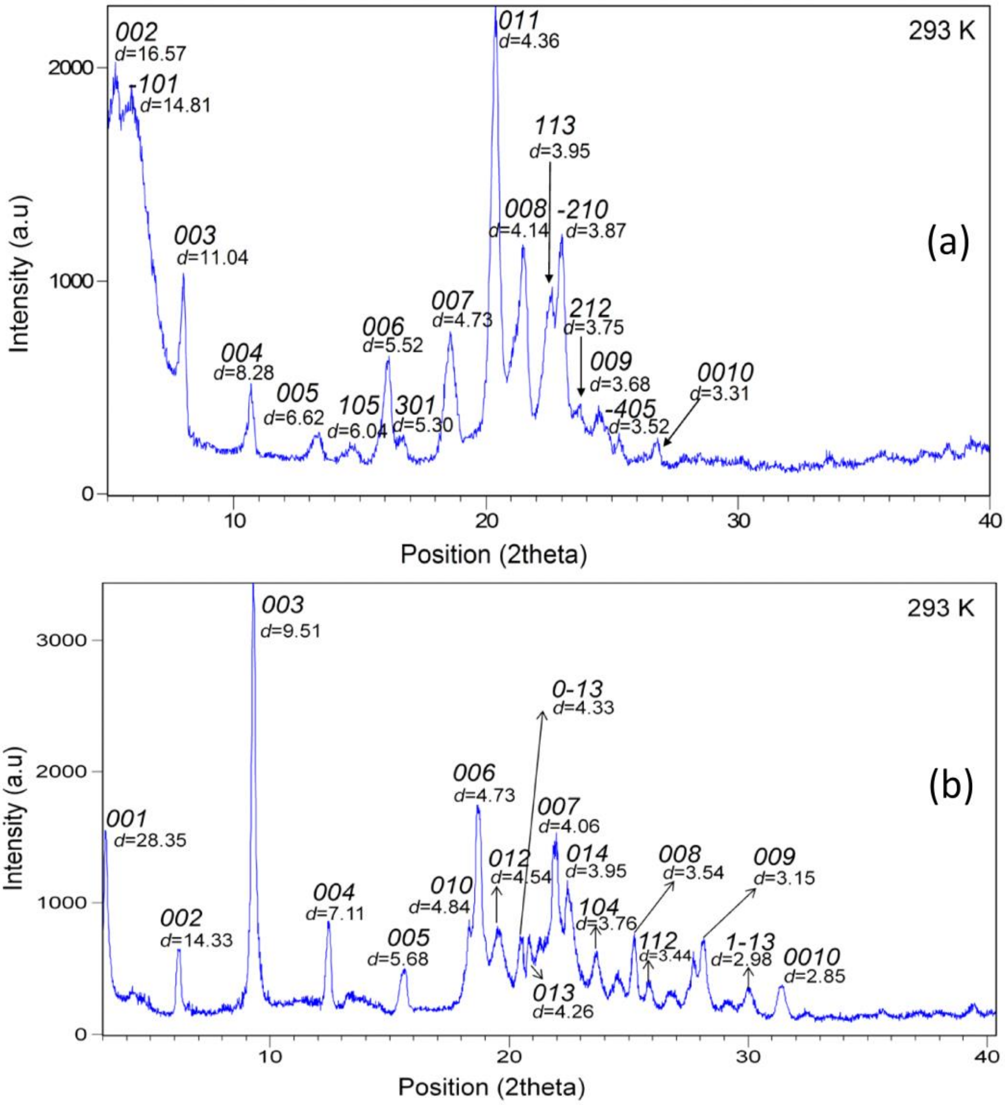


Figure 2 shows diffraction patterns for **2** and **3** taken at room temperature. Compound **2** has been indexed by using first 17 diffraction reflections. It crystallizes in monoclinic space group P 2_1/m, with unit-cell parameters: a = 16.25(1) Å, b = 4.41(1) Å, c = 33.17(1) Å, and β=92.319(8)°. Solution was characterized by highest figure of merit, M20 = 7.8 without any unindexed reflections. Compound **3** crystallizes in triclinic space group P 1, with unit-cell parameters: a = 4.71(1) Å, b = 4.91(2) Å, c = 28.22(1) Å, α=93,66(4), β=91.58(4), and γ=82.7(4)°. The solution was chosen between four suggested by N-TREOR09 routine based on highest figure of merit: M20= 11.1 Miller indices of first 17 reflections for both **2** and **3** are given on Figure 2a and 2b, respectively, together with corresponding *d* spacing values. Miller indices for low intensity diffraction lines are omitted from the figures for clarity. Major repeating distance for **2** corresponding to *c* axis of monoclinic lattice (33.17(1) Å) amounts to 33.14(4) Å. In the case of triclinic unit cell of **3**, the major repeating distance, repeated up to the tenth-order reflection, equals 28.35(7) Å. The XPRD patterns for compounds **4** and **5** at room temperature are shown at Figure 3. Both patterns exhibit sharp intensities identified as multiple order of diffractions from the crystal plane 00*l* indicating characteristic layer arrangement. Interlayer distances were calculated from interplanar spacing corresponding to the 001 diffraction lines and amounted to 38.04 Å for **4** and 33.76 Å for **5**.

Taking into account extended *n*-dodecyl chain dimension in the trans configuration [30] (2 x 16.7 Å = 33.4 Å), the shortest distance of the ionic headgroup from the α-carbon atom (1.80 Å) [30], as well as thermochemical radii of the sulfate ion (2.6 Å) and ammonium ion (1.4 Å) [31], the length of the extended catanionic dodecylsulfate is 44.93 Å. The layer spacings of RT smectic phases obtained with the XPRD for all compounds are between 0.63 (**3**) and 0.93 (**1**) times of the calculated molecular length. The literature data for sodium *n*-dodecylsulfate and *n*-dodecylammonium *n*-dodecylsulfate are 19.43 Å [20,21] and 34.50 Å [13] with the related tilt angles of 55.14° [20,21] and 49.75° [13], respectively. The values vary upon changing the catanionic structure. Obviously, the layer spacing is related to different planar and spatial arrangements and molecular orientations, as well as the conformation of their *n*-dodecyl chains in aliphatic chains layers [32]. The existence of bilayer structures is also found for triazole-based adducts, where, unlike dimer and tetramer, the monomer bilayer-forming motifs seem to be tilted [7]. Cationic gemini surfactant arranges with sodium *n*-dodecyl sulfate perpendicularly to the lamellar plane [15], with alternation of the cationic and anionic layers, compactly arranged due to strong electrostatic interactions, and repeating distance equal to the sum of both dodecyl chain lengths.

Figure 2. The XPRD patterns of **2** (**a**) and **3** (**b**) at room temperature. Miller indices 00*l* and corresponding interplanar distances are shown for pronounced diffraction lines.



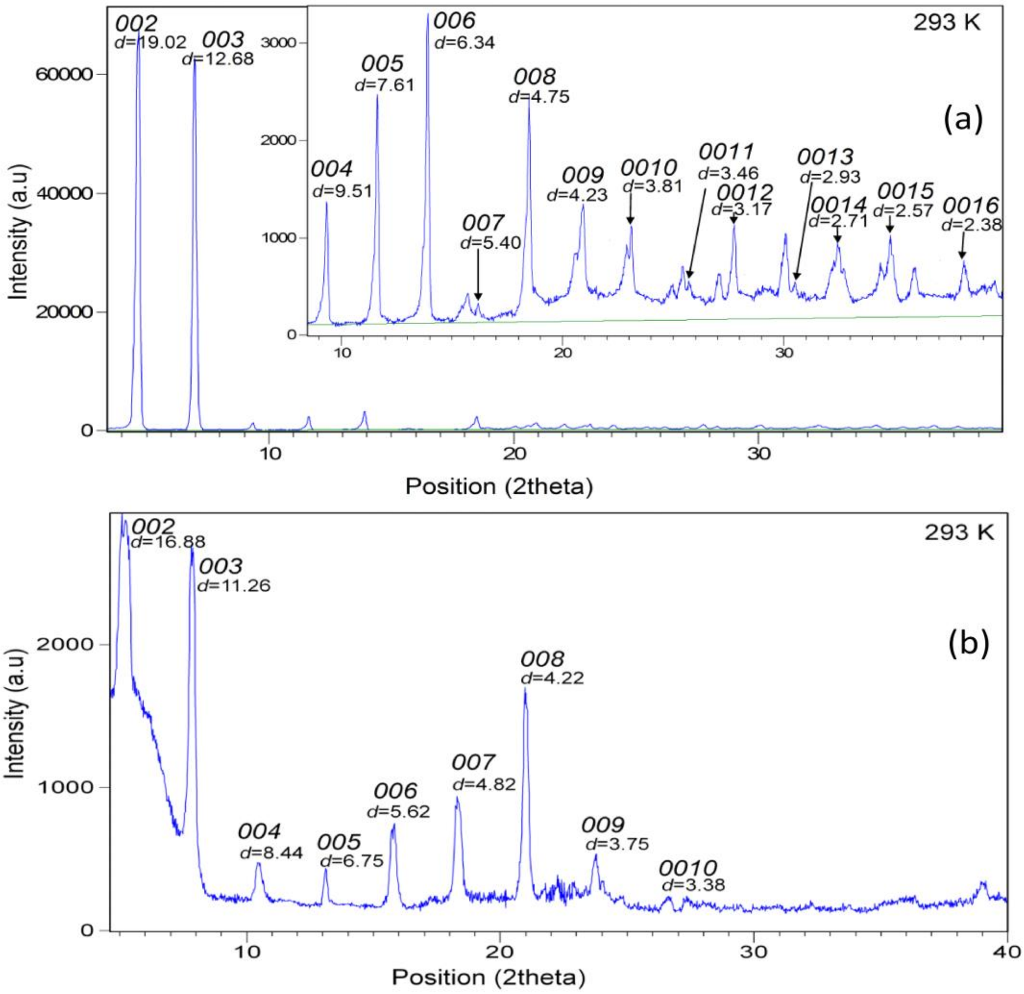
At RT the long spacing, d/Å, decreases linear by the increase of the number of ionic heads, n_1, unlike pure oligomeric surfactant bromides [5]; and also by the increase of n-dodecyl chains number, n_2 (Figure 4), from monomeric dodecylsulfate to trimeric tridodecylsulfate (d_1); and from single- to three-tailed dodecylsulfate (d_2), according to equations (3) and (4):

$$d_1/\text{Å} = -6.72\, n_1 + 47.87 \qquad (R = 0.987) \qquad (3) \text{ and}$$

$$d_2/\text{Å} = -4.01\, n_2 + 45.88 \qquad (R = 0.999) \qquad (4).$$

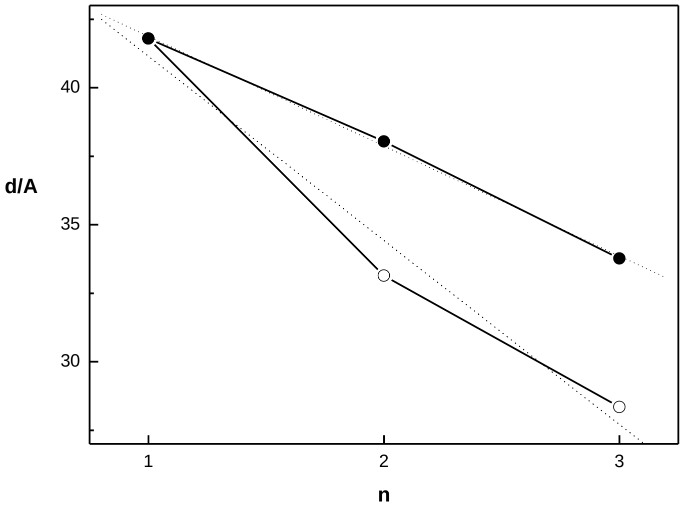
Differences experimentally evidenced in the decrease of lamellar thickness when comparing compounds with different degree of oligomerization, namely, monomer (**1**), dimer (**2**) and trimer (**3**) assemblies, are most likely caused by the decreasing tilt angle value of *n*-dodecyl chains within bilayer arrangements. The tilt is represented and calculated by an angle between dodecyl chain axis and bilayer normal, where the chain axis is defined by a vector connecting the head group and the twelfth carbon, according to its structure and thermodynamic state. According to the geometrical relations, an optimum packing can be obtained by placing the surfactant molecules within the interlamellar space. Knowing that the length of fully extended studied molecules is the same, the mentioned relations are different for multi-charged and multi-tailed dodecylsulfates, allowing more properly and more compactly adopting of *n*-dodecyl chains of the first one with the lower values of averaged tilt angle, and consequently slimmer bilayer thickness.

Figure 3. The XRPD patterns of **4** (**a**) and **5** (**b**) at room temperature. Miller indices 00*l* and corresponding interplanar distances are shown.



Unlike these results, the presence of Na^+ and Br^- [18] causes arrangement of cationic gemini surfactant with sodium *n*-dodecyl sulfate perpendicularly to the lamellar plane, with alternation of the cationic and anionic layers, compactly arranged due to strong electrostatic interactions, and repeating distance equal to the sum of both dodecyl chain lengths [18]. When comparing the interlayer distances of **4** and **5** with lamellar thickness of **1,** general trend can be observed: increasing number of *n*-dodecyl chains causes decrement of bilayer thickness motive most likely caused by significant inclination of dodecyl chains although the interpenetration of chains could also not be excluded.

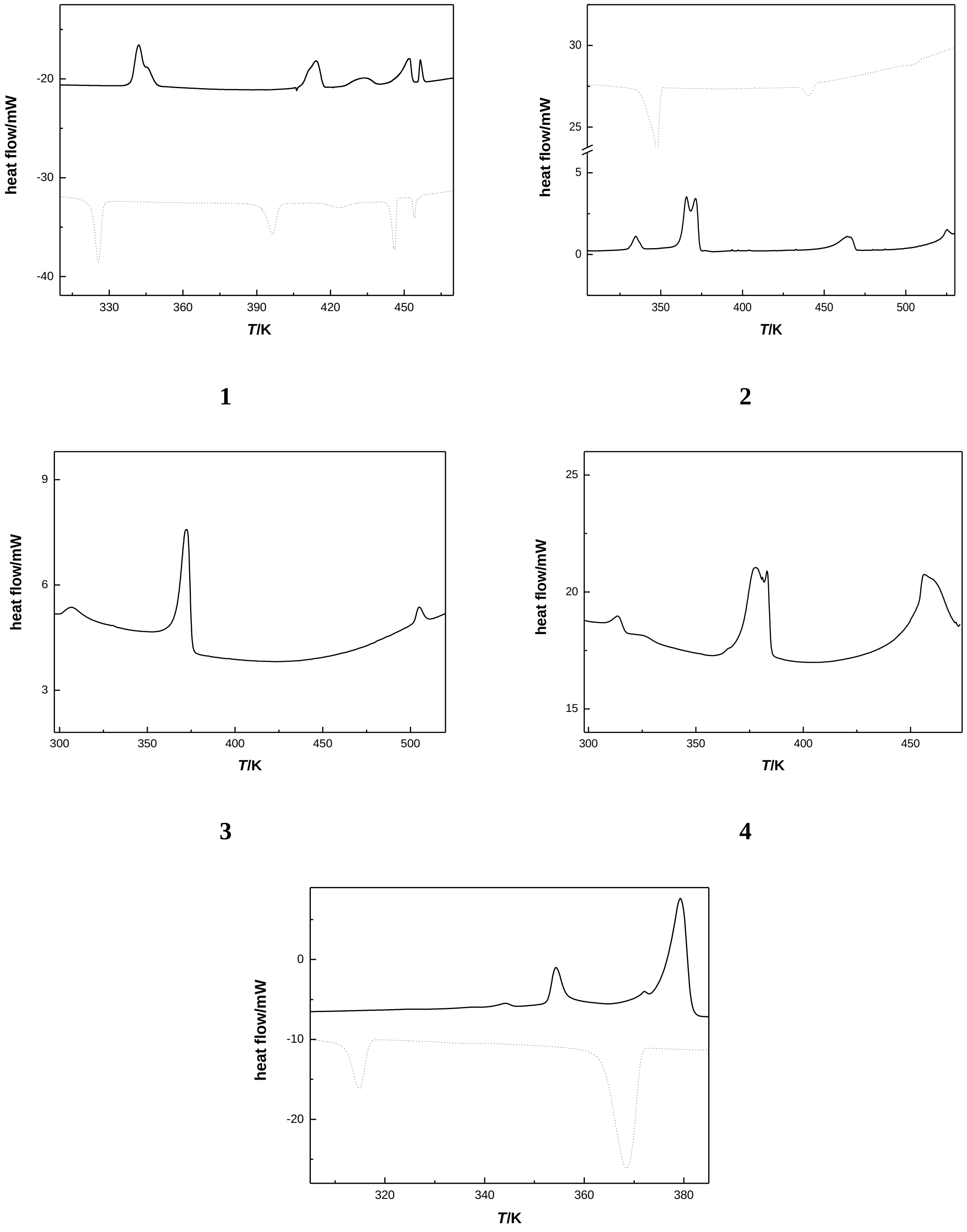
Figure 4. Changes of long spacing, *d*/Å, as found from XRPD patterns for multi-charged (open circle) and multi-tailed (solid circle) dodecylsulfates at ambient temperature, versus *n*; where *n* represents the number of cationic heads in multi-charged, n_1, or the number of dodecyl chains on the ammonium headgroup in multi-tailed, n_2, catanionics.



3.2. Temperature - dependent measurements

In order to compare the influence of various cationic surfactant components in compounds **1** – **5**, representative DSC measurements are presented in Figure 5 and Table 1. The DSC thermograms of all examined compounds reveal that all transitions are endothermic in the heating and, for samples that do not decompose (**1**, **2** and **5**), exothermic in the cooling cycle. These compounds exhibit temperature hysteresis; the crystallization temperatures are shifted down for 16.4 (**1**), 18.2 (**2**) and 13.4 K (**5**), indicating supercooled state. The number of thermal phase transitions during heating cycle varies from three to five (Table 1 and Figure 5), and all major peaks during heating show their corresponding peaks during cooling. The description of formed textures along with the detected phase transitions obtained with the DSC and microscopic observations are presented in Table 2.

Figure 5. Thermograms of examined catanionic dodecylsulfate compounds **1 – 5,** obtained by a differential scanning calorimeter during heating (endothermic transitions, solid line) and cooling (exothermic transitions, dotted line) scans.



1

2

3

4

5

Table 1. Transition temperatures, T/K; enthalpies, ΔH/kJ mol^{-1}; and entropies, ΔS/J mol^{-1} K^{-1}; for examined catanionic dodecylsulfate compounds **1** – **5** obtained from the DSC measurements.

		Heating			**Cooling**		
Compound	**n**	T/K	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}	T/K	$-\Delta H$/kJ mol^{-1}	$-\Delta S$/J mol^{-1} K^{-1}
	n_1						
1	1	$342.0^{\mathbf{dp}}$	10.2	29.7	325.6	9.6	29.3
		414.2	7.2	17.2	396.4	6.6	16.6
		433.6	2.8	6.6	423.4	1.9	4.6
		452.2	5.1	11.2	446.2	4.9	11.0
		456.6	1.3	2.9	454.1	1.5	3.2
2	2	334.2	2.9	8.8	347.3	25.4	73.1
		$365.5^{\mathbf{dp}}$	23.1	63.2	440.7	3.1	7.1
		464.5	5.4	11.6	505.3	1.2	2.3
		525.7	1.0	1.9			
3	3	307.1	2.3	7.5	Decomposition at T_i		
		372.5	6.4	17.2			
		505.0	1.3	2.6			
	n_2						
4	2	313.2	1.0	3.2	Decomposition at T_i		
		$377.9^{\mathbf{dp}}$	18.6	49.3			
		457.5	7.5	16.3			
5	3	345.0	0.7	2.0	314.6	12.0	38.1
		354.6	8.3	23.4	368.3	46.8	127.1
		372.5	0.4	1.1			
		379.6	32.2	84.8			

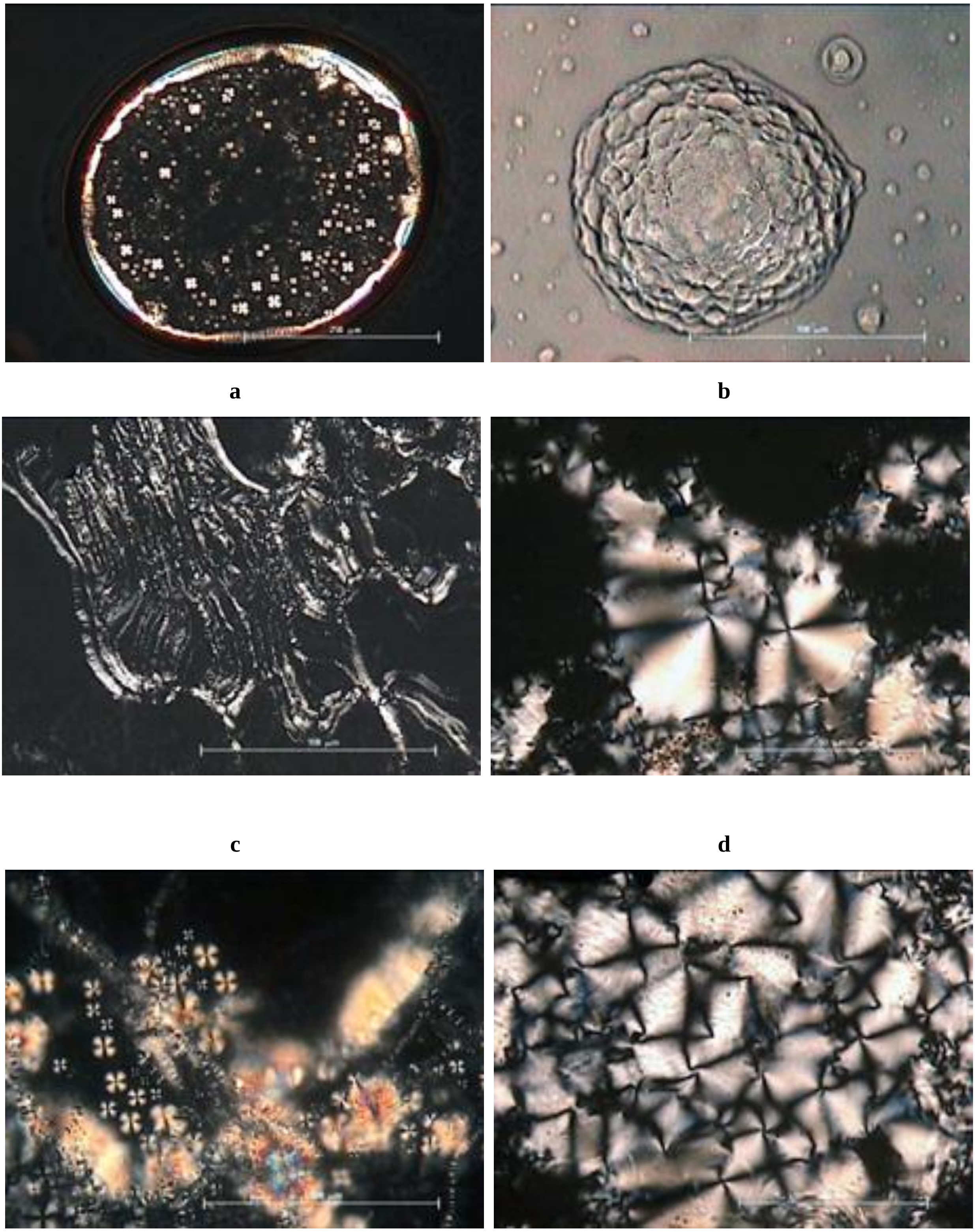
Abbreviation: **dp**, double peak.

The mesomorphic properties of compound **1** are characterized by means of X-ray powder diffraction (Figure 1). The XPRD measurements for compound **1** (Figure 1) are in accordance with the phase transitions detected with the DSC and microscopic observations. The room temperature phase is characterized as crystal smectic phase, as mentioned earlier. The sample undergoes through polymorphic phase transitions in the solid state as detected by DSC at 342 K and 414 K (Table 1). In accordance with these results, the XPRD detected at 375 K a significant shift of diffraction lines toward smaller Bragg angles, indicating an increase of the lamellar thickness which amounts from to

41.8(1) Å at RT to 44.2(2) Å at 375 K, and confirms the structural changes, such as changes in the angle of tilt of the chains [13]. Further increase of the temperature indicates premelting and formation of smectic (Sm) LC phases (433 K in DSC), seen in the XPRD (420 K) as the significant decrease of scattered intensities, however interestingly, in respect to lamellar thickness this pattern resembles the one taken at RT. The smectic phase was stable during melting (DSC at 452 K) until the izotropisation (DSC at 456 K), seen as the amorphisation of the sample by XPRD at 441 K. During the cooling process, starting from 454 K a number of continued processes took place, seen as Maltese crosses and focal conic forms of Sm LC, also confirmed by the low values of enthalpy and entropy changes in the DSC, as well as by XPRD results, until the crystallization temperature of 325 K, where again the crystal smectic phase of **1** appears, in form of polydisperse stepped drops (Figure 1b). As seen for previously examined dodecylammonium dodecylsulfate [13], sample **1** exhibited during the cooling cycle the phases that were structurally similar to the ones formed during heating cycle. Briefly, according to the XPRD at 433 K first indication of „room temperature like“ phase (long spacing ~41.8 Å) appeared while with further decrease in temperature the diffraction lines became more pronounced, indicating further crystallization. Existence of crystal phase characterized with larger lamellar thickness noted at 375 K during the heating (~44.2 Å) was confirmed also during the cooling process at 363 K. At the end of thermal treatment cycle diffraction lines became sharp indicating an advanced ordering in the direction of the long spacing in comparison to the state before heating. This fact enabled more precise determination of lamellar thickness which amounted 41.79(2) Å, measured at room temperature at the end of in-situ measurements. The calculated value of the interplanar spacing (44.93 Å) is a bit higher than experimentally determined (41.79(2) Å) leading to conclusion that monomer chains are, indeed, slightly tilted with respect to bilayer plane. It seems that the attachment of three methyl groups on the amino group, like in compound **1**, instead of hydrogens, like in previously studied dodecylammonium dodecylsulfate [13], causes differences in thermal behavior. These differences can be seen through higher transition temperatures, higher number of polymorphic phase transitions, and greater thermal stability of compound **1** than of dodecylammonium analogue [13]. The molecular packing differences are indicated by the greater bilayer thickness of **1**, *i.e.* 41.8 Å in juxtaposition with 34 Å for dodecylammonium analogue [13], making those chains more tilted than chains of compound **1**. Such behavior can be explained by the different molecular conformations and associated conformational disorder of the molecules, greater electron density of methyl groups compared to hydrogen, as well as geometric and steric factors, which are overall responsible for differences in the molecular packing [33], and consequently their thermal behavior.

Figure 6. Optical birefingent textures for catanionic dodecylsulfates at different temperatures, observed by the hot stage microscope under crossed polarizers (**a**, **b**, **d**–**f**) or phase contrast (**c**). Maltese crosses of the sample **1** at 454 K (**a**), oily streaks of the sample **2** at 473 K (**c**), Maltese crosses

of **3** at 380 K (**e**), fan-shaped mosaic with lancets of **4** at 395 K (**g**), and gradual softening of **5** at 360 K (**h**), all taken upon heating. The textures taken at ambient temperature after cooling the melt: stepped drops of sample **1** (**b**), and smooth fan-shaped texture of **2** (**d**) and **3** (**f**). The bar represents 250 µm (**a**), 100 µm (**b**, **c**, **e** and **h**) and 50 µm (**d**, **f** and **g**).



a **b**

c **d**

e **f**

g h

As compound **1**, studied catanionic compounds **2** and **3** undergo through continuous structural changes during heating and cooling cycle, characterized with polymorphic transitions and LC formation (Figure 6, Tables 1 and 2). Such thermotropic phases are formed and changed over a broader temperature range due to the ability of the compounds to accommodate chain disorder and strong ionic interactions. The increment of headgroup number to two causes higher temperatures of Sm LC phase appearance (464 K), while the introduction the third ammonium center in same molecule causes its pronounced decrement (372 K); also simultaneously this increment extends the temperature interval of LC phases appearance. The physico-chemical propeties of parent oligomeric surfactant bromides are also not necessarily linear function of the associated degree of oligomerization [5], and therefore, they promote such various behavior of their catanionics. The micrographs revealed characteristic textures such as Maltese crosses, oily streaks textures with stepped drops and fan-shaped textures in the cooling run that affirmed the existence of such mesophases (Figure 6, Table 2). This is in accordance with data published about Sm structures of dioctadecyldimethylammonium dodecylsulfate complex [34], a series of alkylammonium alkylsulfates [3,19,35], and disordered Sm phases in the mixtures of gemini surfactants with sodium alkylsulfates [18,19].

Because of the conformational flexibility of the greater number of long alkyl chains and weaker van der Waals forces between them, more than one type of molecular packing is possible in the solid state, thus allowing the formation of varieties and polymorphs. Thermal decomposition data of the oligomeric surfactant bromides and their monomer analogue dodecyltrimethylammonium bromide showed lowering of related decomposition temperatures with the increase of the headgroup number [5], and the tendency of trimeric tridodecylsulfate compound (**3**) to decompose. On the contrary, the increase of dodecyl chains number form one (compound **1**) to two and further to three (compounds **4** and **5**) completely hinders the phenomenon of LC phases appearing (Table 2). In the group of multi-tailed catanionic compounds (**4** and **5**) it seems that more disordered structure of **5**, obtained by the total entropy changes of transitions (Table 1) and probably as the result of steric hindrance factors and lower charge distribution compared to multi-charged compounds, causes less denser and less stable packing, which is seen through lower transition temperatures. However these catanionic dodecylsulfate crystalline structures are confirmed by XRPD measurements at room temperature as smectic layered structure (Figure 3), with successive polymorphic transitions (Table 1) and without any characteristic LC textures, as obtained by PLM; so one can characterize them as crystal Sm. These materials share an important common feature in predominant physical behaviors that occur at an energy scale comparable with room temperature thermal energy. Interestingly, the compound **4** with two dodecyl chains undergoes decomposition (Table 1), while compound **5** with three dodecyl chains on the same headgroup is thermally stable, with melting and izotropisation as last transition, as well as reversible (Figure 5.5 and Table 2). The explanation therefore exists in thermotropic properties of solid didodecyldimethylammonium bromide which exhibits highly ordered layered LC structures [24], and as well known, temperatures of pure surfactant transitions are remarkably depressed after complexation. The Figure 5.4 indicates the melting peak of the two hydrocarbon chains at 378 K, seen as a shoulder by DSC and this melting transition is facilitated by factors that reduce the polar headgroup network cohesion, after which a broad exothermic peak refers to decomposition of compound **4**.

Table 2. Thermal behavior of the catanionics **1 - 5** obtained by optical polarizing microscope.

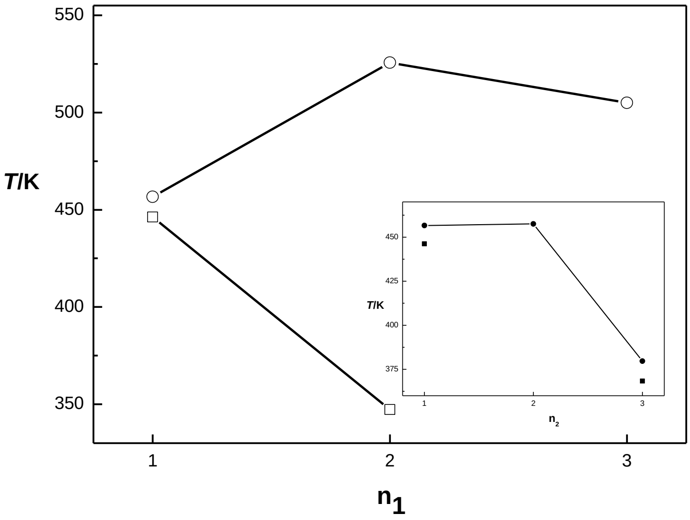
Compound	Temperature range/ K	PLM textures	Phase assignment
1	296 – 298	Crystalline; also upon cooling with stepped drops	Cr (Sm)
	299 – 434	Marble-like	Cr (Sm)
	435 – 453	Spherulites of lamellar phase; also upon cooling	Sm LC (SmA)
	455 –457	Isotropic liquid	I
2	296 – 334	Crystalline	Cr (Sm)
	335 – 365	Granitelike; smooth fan-shaped upon cooling	Cr (Sm)
	366 –463	Fan-shaped mosaic; also upon cooling	Cr (Sm)
	464 – 525	Oily streaks; also upon cooling	Sm LC
	526	Isotropic liquid	I
3	296 – 307	Crystalline	Cr (Sm)
	308 – 371	Focal-conic	Sm LC (SmA)
	372 – 505	Oily streaks and mosaic	Sm LC

		with homeotropic areas	
	506	Isotropic liquid, simultaneously decomp.	I, D
4	296	Crystalline	Cr (Sm)
	379–484	Fan-shaped mosaic and lancets	Cr (Sm)
	485	Izotropisation, simultaneously decomp.	I, D
5	296	Crystalline; also upon cooling	Cr (Sm)
	345–355	Granitelike; lancets upon cooling	Cr (Sm)
	356–379	Softening of crystal	
	380	Isotropic liquid	I

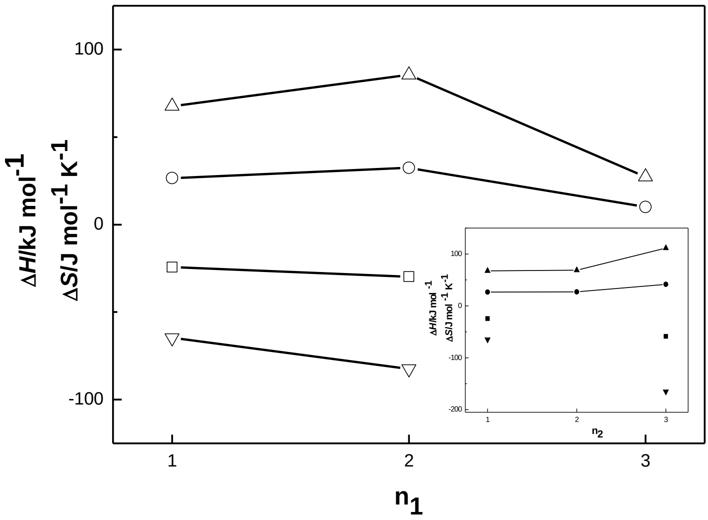
The catanionic bilayers are formed and stabilized by the short-range entropy governed repulsive forces that are of crucial importance for all biological systems, van-der Waals interactions between dodecyl chains, and hydrogen bonding between cations and anions. As concluded earlier, the repulsive force is generally dependent on the polar group size rather than on its chemical composition, and on the alkyl chain length [36], which is kept constant in our examinations. All these amphiphilic mesogenic molecules show microsegregation of incompatible units, aggregation of compatible units and the minimization of volume that lead at suitable temperature conditions to appearance of smectic ordered thermotropic mesophases [37]. The liquid crystalline phase advances between the melting and clearing point, reversibly between the deizotropisation and crystallization temperatures in the cooling cycle.

Figure 7. (**a**) The izotropisation (circle) and crystallization temperature (square), *T*/K, of examined catanionic dodecylsulfates; (**b**) total enthalpy, ΔH/kJ mol^{-1} (circle) and total entropy changes, ΔS/J mol^{-1} K^{-1} (up triangle) during heating, and cooling scans (square, down triangle, respectively); as a function of the ammonium headgroup number in multi-charged (open symbols) and the number of dodecyl chains on the same ammonium headgroup in multi-tailed catanionics (solid symbols, insert).

a



b



Besides crystal Sm appearance a RT, thermotropic mesomorphism and polymorphism of Sm type, specific for each compound in its appearance as a consequence of different structural and packing affinities, thermal stability also changed with the structural variations in examined catanionics. The temperature at which the izotropisation occurs varies within groups of multi charged and multi tailed compounds, and this process is also accompanied with decomposition for three-charged (**3**) and three-tailed (**4**) compounds. Knowing that the crystal lattice energy determines the melting and izotropisation temperatures of ionic surfactants, one can conclude that in the case of oligomeric dodecylsulfates (Figure 7a) the lattice energy increases by adding the new charged quaternary ammonium center, similar as noticed for related bromides [24]. The reason therefore could be found again in higher charge distribution and the fact that one ammonium group includes simultaneos incorporation of two chains, bringing more complex structures.Similar behavior is also noticed by the addition of the second alkyl chain, while on further ammonium center or alkyl chain addition, the mentioned temperatures decrease (Figure 7a). Furthermore, crystallization temperatures decrease (Figure 7a) with these structural changes. The temperature interval between melting and clearing point (temperature at which the transition between the mesophase of the highest temperature range and the isotropic phase occurs) becomes wider with the implementation of each new ammonium center, and as the consequence, with two associated chains, but surprisingly it becomes significantly narrower with addition of the new *n*-dodecyl chains (Table 2). The izotropisation temperatures of multi-charged are higher than those of multi-tailed catanionics, but the crystallization temperatures show the opposite trend (Figure 7a). The changes of corresponding total enthalpies and entropies, obtained from the heating cycle, (Figure 7b) point to the advanced organized phases with the increment of n_1 and less organized phases with the increment of n_2, where the most stable compound is dimeric didodecylsulfate, *i.e.* *N*-bis[2-(*N'*,*N'*-dimethyl-*n*-dodecylammonio)ethylene]-*n*-dodecyl-*N*-methyl-1,2-diammonium tridodecylsulfate (**3**), and the most disordered is found to be three-tailed dodecylsulfate, *i.e.* tridodecylmethylammonium dodecylsulfate (**5**). As expected, more complex molecular structures result with numerous conformations of *n*-dodecyl chains [5,38,39] with through-bond and through-space physical forces that favor less regular ordering. The comparison of crystal packing of similar compounds, *i.e.* dimeric dibromide [5], dimeric dipicrate [12], and tridodecylammonium picrate [11] and corresponding *n*-dodecylsulfates, points to most probably stable *trans* alkyl chains isomers, being able to pack more tightly, with higher melting points and higher thermochemical stability [40]. Thermal behavior of examined monomeric *n*-dodecylsulfate (compound **1**) points to higher number of reversible phase transitions, lower melting temperature, and lower enthalpy and entropy changes than of *n*-dodecylammonium *n*-dodecylsulfate [13]. The trimethylammonium group is tetrahedral ion that occupies a larger volume when compared to ammonium group, and consequently, the geometric factors, including packing of the heads and chains, appear to be mainly reflected on the enthalpy and entropy values.

Generally, discussing the relationship between the structures and liquid crystalline or thermodynamic properties of these materials and looking for general strategy which could be implement under various conditions and thermodynamic constraints, until today there is no theory that could predict, starting from a known structure, probability of mesophase formation, type and number of mesophases, or their temperature interval of stability. The data reported in this paper demonstrate how small changes in molecular design of catanionics lead to large changes in the physico-chemical properties. Our studies contribute the understanding of the composition effect on the phase behavior and molecular microstructure, and the ways of tailoring the properties of such microstructure for potential novel applications.

4. CONCLUSIONS

Novel catanionic *n*-dodecylsulfates were synthesized and examined with several complementary techniques. The compounds differ in the cationic part of the molecule making two different series; the first one is multi-charged, defined with increasing number of ammonium headgroups; and the second one is multi-tailed, characterized with increasing number of *n*-dodecyl chains on the same basic headgroup. The dimeric didodecylsulfate crystallizes in monoclinic space group P 2_1/m, while trimeric tridodecylsulfate crystallizes in triclinic space group P 1. The typical layered structure is found to dominate in all examined compounds at room temperature. The long spacing decreases linearly in both series, caused by the increment of the tilt angle values of *n*-dodecyl chains within bilayer arrangements for multi-charged dodecylsulfates; or by significant inclination of dodecyl chains in combination with simultaneous interpenetration of chains for multi-tailed catanionics. All examined catanionics show rich thermal behavior. Thermotropic phases formation is characteristic for the first series, while compounds of the second group are characterized as soft crystals. The changes of the corresponding thermodynamic parameters point to the more organized multi-charged catanionics, and to the less organized phases of multi-tailed dodecylsulfates. The addition of the new quaternary ammonium center or alkyl chain causes the increment of the lattice energy first, and it decreases by further changes in the structure. The temperatures of crystallization decrease by any mentioned addition.

This study provides information about relationship between molecular architecture and thermal properties, demonstrating the easy way to control the properties of new compounds, by changing one part of the molecule, and as the result making mesomorphic product or new, potentially applicable material.

Acknowledgments

This work was supported by the Ministry of Education, Science and Sport of the Republic of Croatia (Projects Nos. 098-0982915-2949 and 119-0982886-1009).

References

[1] A.-T. Kuo, C.-H. Chang, W. Shinoda, Molecular dynamics study of catanionic bilayers composed of ion pair amphiphile with double-tailed cationic surfactant, Langmuir. 28 (2012) 8156–8164..

[2] A.D.W. Carswell, E.A. O'Rea, B.P. Grady, Adsorbed Surfactants as Templates for the Synthesis of Morphologically Controlled Polyaniline and Polypyrrole Nanostructures on Flat Surfaces: From Spheres to Wires to Flat Films, J. Am. Chem. Soc. 125 (2003) 14793–14800..

[3] C.N.R. Rao, A. Govindaraj, F.L. Deepak, N.A. Gunari, M. Nath, Surfactant-assisted synthesis of semiconductor nanotubes and nanowires, Appl. Phys. Lett. 78 (2001) 1853–1855.

[4] N. Hassan, J.M. Ruso, Á. Piñeiro, Hydrogenated/fluorinated catanionic surfactants as potential templates for nanostructure design, Langmuir. 27 (2011) 9719–9728.

[5] D. Jurašin, A. Pustak, I. Habuš, I. Šmit, N. Filipović-Vinceković, Polymorphism and Mesomorphism of Oligomeric Surfactants: Effect of the Degree of Oligomerization, Langmuir. 27 (2011) 14118–14130.

[6] S. Bhattacharya, S.K. Samanta, Surfactants Possessing Multiple Polar Heads. A Perspective on their Unique Aggregation Behavior and Applications, J. Phys. Chem. Lett. 2 (2011) 914–920.

[7] S. Bhattacharya, J. Biswas, Vesicle and stable monolayer formation from simple "click" chemistry adducts in water, Langmuir. 27 (2011) 1581–1591..

[8] S. Bhattacharya, J. Haldar, Thermodynamics of Micellization of Multiheaded Single-Chain Cationic Surfactants, Langmuir. 20 (2004) 7940–7947.

[9] J. Haldar, V.K. Aswal, P.S. Goyal, S. Bhattacharya, Role of Incorporation of Multiple Headgroups in Cationic Surfactants in Determining Micellar Properties. Small-Angle-Neutron-Scattering and Fluorescence Studies, J Phys Chem B. 105 (2001) 12803–12808.

[10] J. Haldar, V.K. Aswal, P.S. Goyal, S. Bhattacharya, Molecular Modulation of Surfactant Aggregation in Water: Effect of the Incorporation of Multiple Headgroups on Micellar Properties, Angew. Chem. Int. Ed. 40 (2001) 1228–1232.

[11] T. Mihelj, Z. Štefanić, V. Tomašić, Thermal and structural properties of surfactant–picrate compounds, J. Therm. Anal. Calorim. 108 (2012) 1261–1272.

[12] V. Tomašić, N. Biliškov, T. Mihelj, Z. Štefanić, Thermal behaviour and structural properties of surfactant—Picrate compounds: The effect of the ammonium headgroup number, Thermochim. Acta. 569 (2013) 25–35.

[13] N. Filipović-Vinceković, I. Pucić, S. Popović, V. Tomašić, Đ. Težak, Solid-Phase Transitions of Catanionic Surfactants, J Colloid Interface Sci. 188 (1997) 396–403.

[14] G. Ungar, V. Tomasić, F. Xie, X. -b. Zeng, Structure of Liquid Crystalline Aerosol-OT and Its Alkylammonium Salts, Langmuir. 25 (2009) 11067–72.

[15] E.F. Marques, R.O. Brito, Y. Wang, B.F.B. Silva, Thermotropic phase behavior of triple-chained catanionic surfactants with varying headgroup chemistry, J. Colloid Interface Sci. 294 (2006) 240–247.

[16] T. Mihelj, V. Tomašić, Thermal Behavior of Dodecylpyridinium Based Surfactant Salts with Varied Anionic Constituent, J. Dispers. Sci. Technol. 35 (2014), 581-592

[17] V. Tomašić, S. Popović, L. Tušek-Božić, I. Pucić, N. Filipović-Vinceković, A novel catanionic surfactant: Hexadecyltrimethylammonium dodecyl sulfate, Berichte Bunsenges. Für Phys. Chem. 101 (1997) 1942–1948.

[18] Y. Wang, E.F. Marques, Thermotropic Phase Behavior of Cationic Gemini Surfactants and Their Equicharge Mixtures with Sodium Dodecyl Sulfate, J. Phys. Chem. B. 110 (2006) 1151–1157.

[19] Y. Wang, E.F. Marques, Mesophase formation and thermal behavior of catanionic mixtures of gemini surfactants with sodium alkylsulfates, J. Therm. Anal. Calorim. 100 (2010) 501–508.

.

[20] L.A. Smith, R.B. Hammond, K.J. Roberts, D. Machin, G. McLeod, Determination of the crystal structure of anhydrous sodium dodecyl sulphate using a combination of synchrotron radiation powder diffraction and molecular modelling techniques, J. Mol. Struct. 554 (2000) 173–182.

[21] L.A. Smith, A. Duncan, G.B. Thomson, K.J. Roberts, D. Machin, G. McLeod, Crystallisation of sodium dodecyl sulphate from aqueous solution: phase identification, crystal morphology, surface chemistry and kinetic interface roughening, J. Cryst. Growth. 263 (2004) 480–490.

[22] J.M. Patterson, Z. Kortylewicz, W.T. Smith, Thermal degradation of sodium dodecyl sulfate, J. Agric. Food Chem. 32 (1984) 782–784.

[23] K. Iwamoto, Y. Ohnuki, K. Sawada, M. Senō, Solid-Solid Phase Transitions of Long-Chain n-Alkyltrimethylammonium Halides, Mol. Cryst. Liq. Cryst. 73 (1981) 95–103.

[24] M. Godlewska, S. Wróbel, B. Borzęcka-Prokop, M. Michalec, P. Dynarowicz, Phase Behavior of Didodecyldimethylammonium Bromide, Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. Mol. Cryst. Liq. Cryst. 300 (1997) 113–126.

[25] V.T. John, B. Simmons, G.L. McPherson, A. Bose, Recent developments in materials synthesis in surfactant systems, Curr. Opin. Colloid Interface Sci. 7 (2002) 288–295.

[26] A. Boultif, D. Louër, Indexing of powder diffraction patterns for low-symmetry lattices by the successive dichotomy method, J. Appl. Crystallogr. 24 (1991) 987–993.

[27] A. Altomare, G. Campi, C. Cuocci, L. Eriksson, C. Giacovazzo, A. Moliterni, et al., Advances in powder diffraction pattern indexing: *N-TREOR09*, J. Appl. Crystallogr. 42 (2009) 768–775.

[28] A. Altomare, M. Camalli, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, *EXPO2009*: structure solution by powder data in direct and reciprocal space, J. Appl. Crystallogr. 42 (2009) 1197–1202.

[29] A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, EXPO2011: A new package for powder crystallography, Powder Diffr. 26 (2011) S2–S12.

[30] M.J. Rosen, Surfactants and interfacial phenomena, Wiley & Sons Inc., New York, NY, USA, 1989.

[31] N.A. Lange, J.A. Dean, Lange's Handbook of chemistry, McGraw-Hill, 1979.

[32] N. Filipović-Vinceković, V. Tomasic, Solid-Phase Transitions of Ionic Surfactants, in: A.T. Hubbard (Ed.), Encycl. Surf. Colloid Sci. Por-Z, Marcel Dekker, 2002.

[33] D.F.R. Gilson, A.S. Kertes, R.S.J. Manley, J. Tsau, G. Donnay, Polymorphism in n-alkylammonium chlorides: X-ray powder diffraction studies, Can. J. Chem. 54 (1976) 765–8.

[34] J. Cocquyt, U. Olsson, G. Olofsson, P. Van der Meeren, Temperature quenched DODAB dispersions: fluid and solid state coexistence and complex formation with oppositely charged surfactant, Langmuir ACS J. Surf. Colloids. 20 (2004) 3906–3912.

[35] T. Lu, Z. Li, J. Huang, H. Fu, Aqueous surfactant two-phase systems in a mixture of cationic gemini and anionic surfactants, Langmuir. 24 (2008) 10723–10728.

[36] P. Jokela, B. Joensson, A. Khan, Phase equilibria of catanionic surfactant-water systems, J Phys Chem. 91 (1987) 3291–3298.

[37] K. Binnemans, Ionic Liquid Crystals, Chem Rev. 105 (2005) 4148–4204.

[38] D. Berthier, T. Buffeteau, J.-M. Léger, R. Oda, I. Huc, From Chiral Counterions to Twisted Membranes, J Am Chem Soc. 124 (2002) 13486–13494.

[39] G. Caracciolo, G. Mancini, C. Bombelli, P. Luciani, R. Caminiti, The Structure of Gemini Surfactant Self-Assemblies Investigated by Energy Dispersive X-ray Diffraction, J. Phys. Chem. B. 107 (2003) 12268–12274.

[40] M.B. Smith, J. March, March's advanced organic chemistry: reactions, mechanisms, and structure, Wiley-Interscience, 2007.