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Mesophase formation and thermal behavior of catanionic mixtures of gemini surfactants with sodium alkylsulfates

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Abstract The thermal behavior for three homologous series of cationic geminis surfactants of the type n-2-n, alkanediyl-α,ω-bis(alkyldimethylammonium bromide), with $n = 12$, 14, 16, and 18, and sodium alkyl sulfates, SC$_m$S, with $m = 12$, 14, and 16, is reported here. The cationic/anionic molar ratio is kept at 1:2 (equicharged mixtures), and salt is also present. Polarizing light microscopy and differential scanning calorimetry show a stepwise fusion for the mixtures with appearance of several mesophases between the crystalline structures and the isotropic liquid. A main endothermic transition is observed, associated with partial chain melting and consequent loss of crystalline order, followed by a transition to a smectic liquid crystal. The phase transition thermodynamics is interpreted in terms of an interplay between van der Waals chain–chain interactions and ionic head group interactions.

Keywords Catanionic mixture · Mesophase · Soft crystal · Smectic liquid crystal · Van der Waals interactions · Electrostatic interactions · Birefringence

Introduction

It is well-known that certain classes of amphiphilic molecules with long alkyl chains show a complex melting behavior, forming thermotropic liquid crystals (TLCs) prior to isotropization to the liquid phase [1–11]. TLCs are intermediate structures between the crystalline solid and the isotropic liquid, with varying degrees of positional and orientational ordering of the molecules. Both head group chemistry and nature of hydrophobic moiety (e.g., alkyl chain length, saturation, and branching) strongly influence the sequence and structure of these mesophases.

The stabilization of TLCs of ionic surfactants and their mixtures (including cationic/anionic mixtures) is largely dictated by the ionic interactions of the head groups (including counterions when present). Mesogenic surfactants include metallic soaps with mono-, di- and tri-valent counterions [1–4], alkylpyridines [5, 6], phosphorous catanionic amphiphiles [7], and carbohydrate derivatives [8–11]. For surfactants with the same hydrophobic moiety, thermotropic mesophases may appear at very different temperatures, for example, at ca. 100 °C for cationic alkylpyridines [5], at ca. 180 °C for cationic geminis [12], and above 180 °C for phosphorous catanionic amphiphiles [7], demonstrating the pivotal role of head group chemistry. Hydrogen bonding at the head group level, in some cases, is also considered as an important factor for mesophase formation, as seen for carbohydrate surfactants [9] and guanidinium alkylbenzensulfonates [4].

The effect of the hydrophobic moiety on the thermotropic phase behavior is associated with the van der Waals interactions involved in the hydrocarbon chain–chain packing [2]. The magnitude of these interactions is much smaller than the ionic ones, but its importance is demonstrated by the fact that the clearing points increase with increasing alkyl chain length [9, 10]. All the mesophases composed by surfactant molecules involve some degree of disorder of the long alkyl chains. Experimental data [4, 9, 10, 13–18], as well as Monte Carlo, molecular dynamics calculations, and theoretical thermodynamic considerations [19–23] have dealt with the type of chain disorder present

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in mesophases. Two types of disorder, comprising clusters of chains with a kink defect or conformational distortions, have been proposed [4, 13].

Considerable studies on mesogenic amphiphiles have suggested that the chain length strongly affects the temperature range and energy of formation of the mesophases [4, 6, 9, 10, 18]. The thermal stability and transition enthalpy usually increase with increasing chain length. However, chain length not only impacts rearrangement and disorder degree of the chains but also the packing of the head groups [4]. Further, the number of alkyl chains has strong influence on the type of formed mesophases; for instance, single-chained carbohydrate derivatives form smectic mesophases, while double-chained ones form columnar hexagonal mesophases [11, 24, 25].

At low temperature, crystal-to-crystal transitions, implying a rearrangement of the packing of alkyl chains, often appear before crystal-to-mesophase transitions [9]. However, for most surfactants, the enthalpies and temperatures for transitions between crystalline forms are difficult to be consistently determined due to a complex polymorphism in the solid state and the existence of metastable forms [3, 9, 26–29]. The presence of trace water or hydration water also has a large influence on the thermotropic behavior of amphiphiles [3, 9, 29, 52].

Catanionic surfactants are a class of net neutral amphiphiles obtained by equicharged mixing of cationic and anionic surfactants with removal of the inorganic counterions. Due to the strong head group electrostatic interactions, both the charged amphiphiles act as counterions to each other and the catanionic surfactant (ionic pair) behaves as a single surfactant in some cases. The thermal behavior of these amphiphiles is directly connected to head group chemistry (charge density and volume) and overall geometry (packing parameter) [4, 30–32]. These amphiphiles represent a simple way to design new mesogenic molecules, with the number and thermal stability of TLC phases (typically smectic) depending strongly on the degree of symmetry of the chain lengths [33, 34].

Investigations on the liquid crystal formation by cationic gemini surfactants of the alkanediyl-α,ω-bis(alkyldimethylammonium bromide) type, designated here as *n*-s-*n*, have focused on lyotropic phases and their thermal behavior [35–37], which strongly depends on the chain length and spacer length. The crystalline structure and thermotropic properties of the anhydrous surfactant have been addressed only in a few reports[12, 38–42]. Geminis of the type *n*-2-*n* (with $n = 12,14,16,18$) have been studied and show a main phase transition at about 100 °C and TLC formation in a narrow temperature range, changing weakly with chain length [12]. Catanionic mixtures of *n*-2-*n* and sodium dodecylsulfate (SDS) exhibit mesophases formation for a more expanded temperature range than neat *n*-2-*n* geminis [12].

This study is a follow-up of the initial investigation of thermotropic phase behavior of mixtures of *n*-2-*n* geminis and SDS [12]. By expanding this study to other alkylsulfates, SC_mS, we gain deeper understanding on the mesomorphic behavior of the mixtures and focus on effect of chain length sum of the surfactants on phase structure and transition thermodynamics.

Experimental

Materials

Gemini surfactants, *n*-2-*n*, were synthesized and purified according to established methods [12, 43]. Sodium dodecylsulfate (SDS, Sigma, >99%), Sodium tetradecylsulfate (STS, Research Chemical Ltd, 99%), and sodium hexadecylsulfate (SHS, Merck, 99%) were used without further purification. The structures of *n*-2-*n* geminis and SC_mS anionic surfactants are shown in Fig. 1. The other organic solvents were regular *pro analysis* grade products for chemistry research work.

Preparation of *n*-2-$n\mathrm{Br}_2\cdot 2\mathrm{SC}_m\mathrm{S}$ mixtures

The equicharged catanionic mixtures were prepared from a stock solution of gemini surfactant in a mixed chloroform/methanol solvent and a stock solution of each SC_mS in methanol. The molar ratio of gemini surfactant to SC_mS in

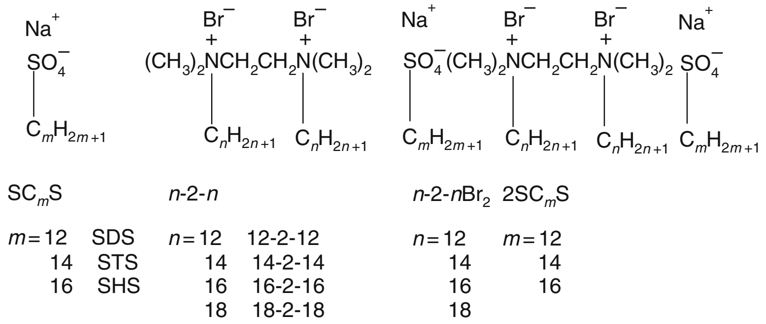

Fig. 1 Chemical structures of alkyl sulfates, SC_mS, gemini surfactants, *n*-2-*n*, and catanionic mixtures, *n*-2-$n\mathrm{Br}_2\cdot 2\mathrm{SC}_m\mathrm{S}$

the final solution was 1:2. If there was any precipitate, the ratio of chloroform and methanol was adjusted until the precipitate disappeared. The solvent was slowly evaporated at room temperature during about a week and at 50 °C for another week and then vacuum-dried for 24 h. Considering the presence of Na^+ and Br^- in the novel surfactant mixtures, we denote the formed compound as n-2-nBr$_2$·2SC$_m$S, with their structures shown in Fig. 1.

Differential scanning calorimetry

The curves were recorded with a differential scanning calorimeter (DSC) from Setaram, modelDSC141, properly calibrated, for a temperature range of 20–200 °C. The scanning rate was always 3K min^{-1}. Every sample was scanned at least three times, and all the enthalpy values shown in the text are mean values with an uncertainty of ±5%.

Polarizing light microscopy (PLM)

Observation of mesophases was performed with a Nikon polarizing microscope (Optiphot-Pol model), with a calibrated heating stage from Linkam (model TH600). The images were obtained with a Nikom Coolpix 995.

Results and discussion

Thermotropic phase behavior of n-2-nBr$_2$.2SC$_m$S

In a previous study, we have shown that both cationic gemini surfactants, n-2-n, per se, and their equicharged mixtures with SDS are mesogenic, exhibiting TLC phases at high temperature [12]. For neat n-2-n, the main endothermic peak occurs sharply at 97.3, 101.9, 106.5, and 108.4 °C, for $n = 12$, 14, 16, and 18, respectively, and is related to the disruption of crystalline structure and chain melting. This chain melting temperature increases weakly with chain length. For the equicharge mixtures with SDS, the thermotropic behavior is similar to that of corresponding neat n-2-n, showing the phase sequence solid crystal-soft crystal-LC-isotropic liquid [12].

SDS, STS, and SHS have the same head group, but increasing chain lengths. One can presume similar thermotropic behavior and investigate the effect of chain length sum on the thermal behavior. The curves of n-2-nBr$_2$·2SC$_m$S (combinations of $n = 12$, 14, 16, and 18 and $m = 12$, 14, and 16) are shown in Fig. 2, where the results for n-2-nBr$_2$·2SDS here obtained are consistent with those previously reported [12]. At about 100 °C, all the catanionic mixtures show a main endothermic peak and below that one or more peaks corresponding to phase transitions between crystalline states.

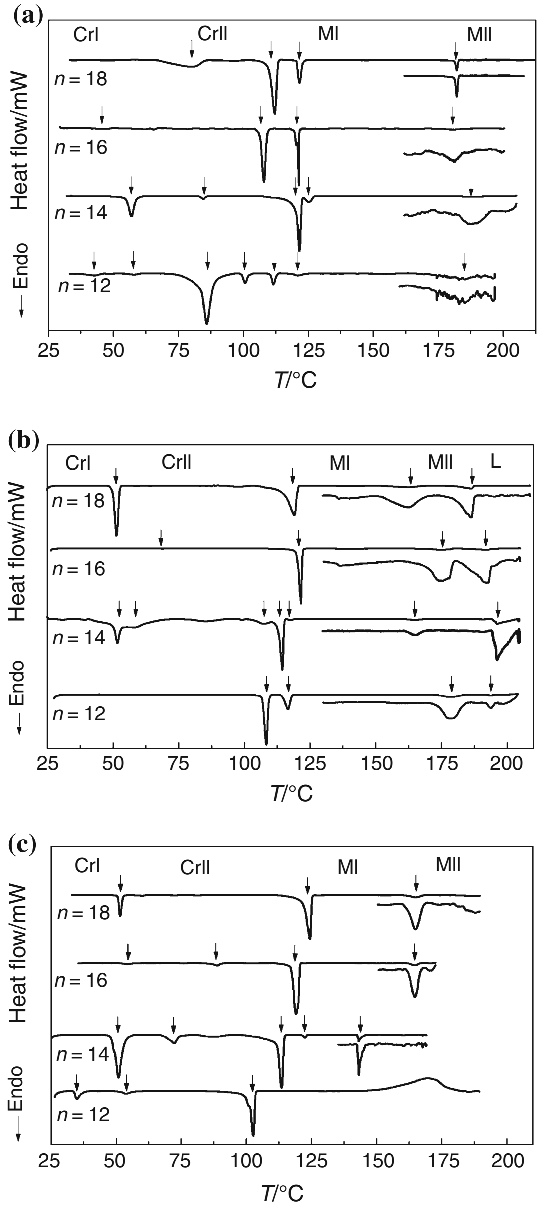

Fig. 2 DSC curves for: (**a**) n-2-nBr$_2$·2SDS; (**b**) n-2-nBr$_2$·2STS; (**c**) n-2-nBr$_2$·2SHS

Here, it is difficult to discern the details of solid–solid transitions due to polymorphism [9, 32, 34]. Polymorphism depends on the history of the sample, such as temperature history. It is well-known that after fusion less crystal-to-crystal transitions appear for the sample. However, even processing heating below the main temperature peak may cause changes in phase behavior. Figure 3a shows a curve with a heating–cooling–reheating cycle between 25 and 135 °C for 12-2-12Br$_2$·2SDS, for the same sample. For the first heating, the curve shows five peaks at 54.7, 83.8, 98, 110.4, and 119 °C, respectively. On cooling, an exothermic broad peak appears between 98 and 104 °C, corresponding to the last two peaks of the heating, and suggesting that the two phase transitions are reversible. Upon reheating, the peaks at 54.7 °C and at 98 °C disappear. The peak area at 83.8 °C decreases, while the one at 104 °C increases. Therefore, one can say that the first three solid–solid transitions are irreversible, whereas the last peaks, with ~1 °C shift to higher temperature, are reversible; the peak at 105 °C is the main peak.

For other catanionic mixtures, similar effects are observed. For comparison, all the samples are stored at 40 °C. If the sample is reheated after melting, the curve does not show any Cr–Cr transition, but only one broad peak, as shown in Fig. 3b, seemingly indicating a uniform crystalline structure. Concomitantly with the melting, the crystal composition changes (incongruent melting), as will be discussed below. We also note that the *n*-2-*n* component decomposes at high temperature, above 200 °C, so that all the curves have been recorded below this temperature.

Let us now turn to what happens around the main peak. Below the transition temperature, the sample is a crystal, as exemplified in Fig. 4a. When the temperature goes over the main peak, the sample initially loses birefringence (Fig. 4b). If one presses the cover slip, a weak and diffuse birefringence different from that of the solid crystals appears and the sample shows a paste-like consistency. These results imply that around this temperature the crystalline structure collapses, giving rise to a "soft" mesophase. This mesophase, designated here as MI differs both from the solid due to its high viscosity (rather than elasticity) under applied shear on the cover slip, and from the following mesophase (MII), due to its ill-defined, weakly birefringent texture, and lack of fluidity.

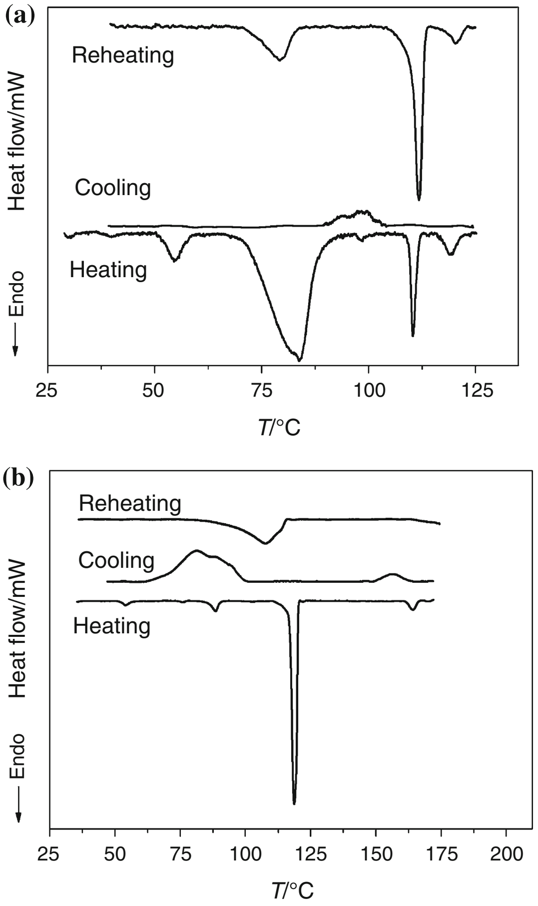

Fig. 3 DSC curves for (**a**) 12-2-12Br$_2$·2SDS and (**b**) 16-2-16Br$_2$·2SHS, for a heating–cooling–reheating cycle

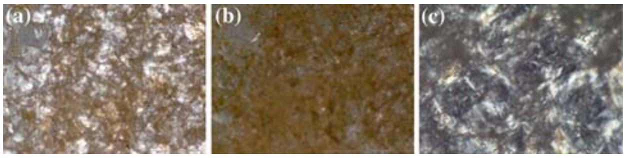

Fig. 4 PLM textures of the catanionic mixtures: (**a**) solid state from room temperature to the main peak temperature; (**b**) non-birefringent state of unperturbed mesophase MI, following the main peak; (**c**) birerfringent state of MI after applied shear

MI appears both on the heating and cooling traces. It is difficult to unambiguously assign it, but it is clear that this is a mesophase with still some high degree of order. We tentatively ascribe it to a soft crystal phase based on combined PLM and DSC evidence [44–48]. We cannot rule out an ordered (hexatic) smectic phase, but this is much less likely since no characteristic birefringent texture (either on heating or cooling) is observed [44–48]. The main peak is sometimes followed by small endothermic peak or peaks, or is accompanied with a "shoulder" for higher temperature. As the temperature is gradually raised, MI becomes more fluid-like state without incurring on a phase transition.

When the temperature rises nearly up to the onset of the second mesophase, MII, birefringent mosaic textures that gradually change to oily streaks [44] are seen for all the mixtures, as shown in Fig. 5a. Then, the sample fluidifies, and shows fan-shaped or focal conics textures, until an isotropic liquid phase appears. Mesophase II is thus

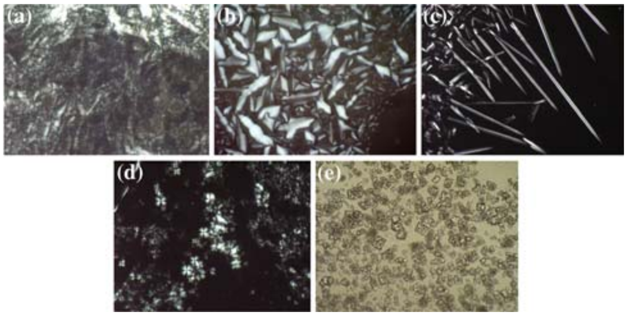

Fig. 5 PLM textures of mesophase MII (smectic liquid crystal): (**a**) mosaic, 12-2-12Br$_2$·2STS at 185 °C upon heating; (**b**) fan-shaped, 16-2-16Br$_2$·2SHS at 165 °C upon cooling; (**c**) lancets, 12-2-12Br$_2$·2SHS at 145 °C upon cooling; (**d**) focal conics, 12-2-12Br$_2$·2STS at 120 °C upon cooling trace; (**e**) NaBr crystallites at 200 °C in 14-2-14Br$_2$·2SHS under normal light

Table 1 PLM textures of smectic LC phases of n-2-nBr$_2$·2SC$_m$S on heating and cooling runs

Heating	Cooling			
Mosaic	Focal conics	Fan-shaped	Lancets	Mosaic
n-2-nBr$_2$		n-2-nBr$_2$		
n-2-nBr$_2$·2SC$_m$S	n-2-nBr$_2$·2SDS	n-2-nBr$_2$·2SC$_m$S	14-2-14Br$_2$·2STS	n-2-nBr$_2$·2SC$_m$S
	12-2-12Br$_2$·2STS		16-2-16Br$_2$·2STS	
	14-2-14Br$_2$·2STS		12-2-12Br$_2$·2SHS	

assigned to a disordered smectic LC phase (likely SmA) [44–48].

Figure 5 and Table 1 demonstrate some typical PLM textures in this study. It should be stated that both the heating and cooling traces give rise to LC textures, albeit of different type. The clearest way to observe the LC texture (giving rise to fan-shaped and focal conics textures) is by cooling the sample, either by rapidly heating to fully obtain the isotropic liquid and then rapidly cooling down to below 190 °C; or by focusing on the coexisting LC plus isotropic liquid and cooling it. Although fanlike shapes and mosaics are common to all the catanionics, those with shorter chain ($m = 12$ and 14) tend to form more focal conics.

Figure 5e shows a normal light microscope image of 14-2-14Br$_2$·2SHS at 200 °C. If the microscope is switched to polarized light, no birefringent texture is observed, indicating that the observed crystallites (with very high thermal stability) are NaBr. In fact, the inorganic salt separates from the catanionic surfactant once this mixture melts [12]. This phenomenon is very similar to the incongruent melting observed for some solid mixtures that form stoichiometric compounds [49]. One consequence of this incongruent melting is that the DSC reheating traces should be very different from the first heating trace, as indeed seen in Fig. 3b.

Phase transition temperatures

As mentioned above, phase transitions between crystalline phases strongly depend on the sample history and polymorphism [9, 12, 32, 34], so that a thorough discussion of the results in this region is more difficult. Although, polymorphism also affects chain melting temperatures, the latter is essentially dependent on the length of the alkyl chain, as the transition should correlate with configuration and conformation of the chains and much less to the long-range crystalline order. On the basis of the results of DSC and Langmuir air–water monolayers (the head group area is equal to or smaller than the total area of four chains of n-2-nBr$_2$·2SDS) [50, 51], a smectic arrangement has been proposed [12], in which the cationic and anionic groups are alternatively arranged, and the repeating distance of hydrophobic moieties is composed of the sum of both the surfactant chain lengths (Fig. 6). Accordingly, the temperature of the main peak (Cr–MI), henceforth denoted by T_m, should depend on the total length. For dioctadecyldimethylammonium alkylsulfatecatanionics (without salt), similar results have been obtained by DSC measurements [52].

Figure 7 shows that T_m for n-2-nBr$_2$·2SC$_m$S mixtures increases roughly linearly with the $m + n$ sum. Furthermore, the largest deviation between systems with the same $m + n$, but different n and m is about 1.9 °C, and the largest deviation to the linear fit is about 5 °C. The results do not show any important effect of the difference $m - n$ (the "degree of asymmetry" of chain length) on T_m, so that we can deduce that sliding of layers at the chain ends (proposed in Fig. 6) is not likely to affect much this transition.

The MI–MII peak and the MII–Iso peaks are always weak, and sometimes very broad (Fig. 2). Therefore, there

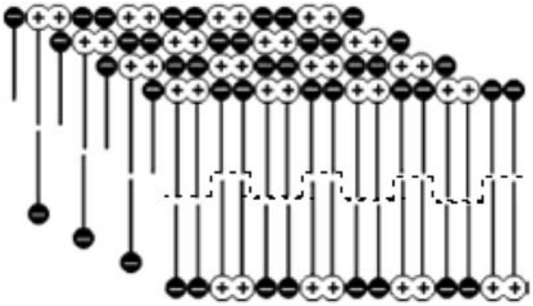

Fig. 6 Possible alkyl chain arrangement of the smectic layers for the n-2-nBr$_2$·2SC$_m$S mixtures

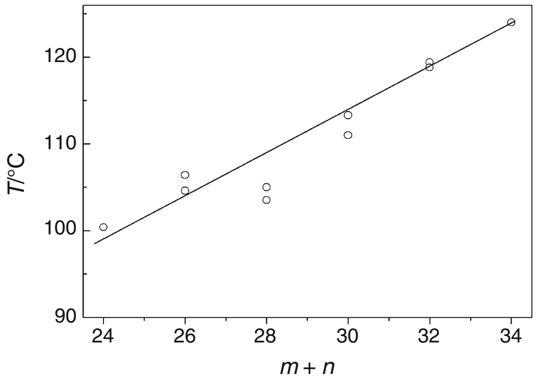

Fig. 7 Main peak temperature (Cr/MI transition) as a function of the chain length sum, $m + n$, for n-2-nBr$_2$·2SC$_m$S mixtures

is a somewhat higher uncertainty in the phase transition temperatures. However, the MII–Iso temperatures also increase gradually with $m + n$ increment.

Phase transition enthalpies

Figure 8a shows phase transition enthalpies versus gemini chain length for neat Gemini and for the n-2-$n\mathrm{Br_2}{\cdot}2\mathrm{SC}_m\mathrm{S}$ catanionic series. The main peak enthalpy (solid line), for the Cr–MI transition, increases linearly as the n increases. The solid lines have nearly identical slopes, yielding a value of 1.8 kJ (mol $\mathrm{CH_2})^{-1}$ for this transition. If the ΔH is plotted versus chain length sum (Fig. 8b), a linear dependency with the same slope is obtained. It can be concluded that this main peak characterizes initial disruption of crystalline order essentially by introduction of chain conformational disorder (melting). From the relation $\Delta S_{\mathrm{tr}} = \Delta H_{\mathrm{tr}}/T$, the obtained ΔS values also increase linearly with increasing chain length sum, $m + n$ (Fig. 8c), with a slope of 9.8 J $\mathrm{K}^{-1}(\mathrm{mol\ CH_2})^{-1}$. When compared to values of 3.8 kJ (mol $\mathrm{CH_2})^{-1}$ for the melting of n-alkanes [53] and even higher values, 7.5 kJ (mol $\mathrm{CH_2})^{-1}$for catanionic surfactants (without salt), we can also infer that the chain melting is only partial for n-2-$n\mathrm{Br_2}{\cdot}2\mathrm{SC}_m\mathrm{S}$ mixtures; this reinforces the assumption that MI is a soft crystal, a phase still with some degree of long and short range order [44]. The enthalpy plot of n-2-n shows a different slope than the catanionic mixtures, possibly due to a different crystalline structure and type of ionic interactions at the head group level.

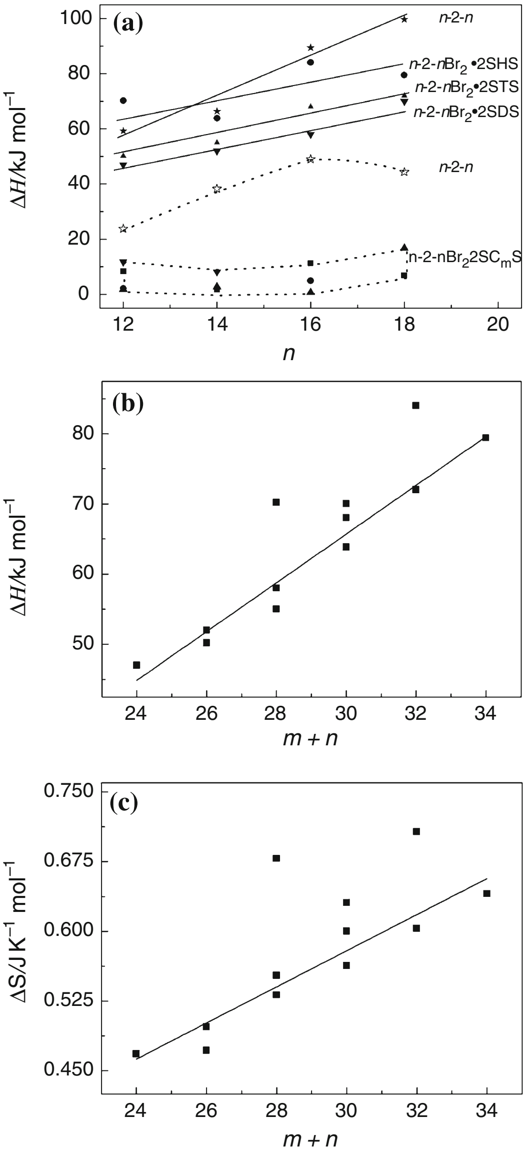

Fig. 8 Transition thermodynamic parameters versus chain length: (**a**) Cr/MI transition enthalpy for n-2-$n\mathrm{Br_2}$ and n-2-$n\mathrm{Br_2}{\cdot}2\mathrm{SC}_m\mathrm{S}$ (*points with solid lines*), and MI/MII transition enthalpy for n-2-$n\mathrm{Br_2}$ (*open stars and dashed line*) and for n-2-$n\mathrm{Br_2}{\cdot}2\mathrm{SC}_m\mathrm{S}$ (*lower points with dotted line*); (**b**) Cr/MI transition enthalpy versus chain length sum, $m + n$, for n-2-$n\mathrm{Br_2}{\cdot}2\mathrm{SC}_m\mathrm{S}$; (**c**) Cr/MI transition entropy versus $m + n$ for n-2-$n\mathrm{Br_2}{\cdot}2\mathrm{SC}_m\mathrm{S}$. In (**b**) and (**c**) lines are linear regression fits excluding upper two points

The ΔH values for the MI-to-MII and MII-to-Iso transitions are very small for the catanionic mixtures, typically less than 10 kJ mol^{-1} or even about 1 kJ mol^{-1} (Fig. 8a). We note that the corresponding enthalpies of neat gemini (open stars in Fig. 8a) are larger by a few to 20 times than for the mixtures. The cationic geminis are mesogenic molecules for a narrow temperature range, while the mixtures show thermotropic phases over a much broader temperature range due to the higher ability to accommodate chain disorder and to stronger ionic interactions. The possible existence of aggregates in the molten state of amphiphiles has been suggested for some divalent and trivalent metal soaps, where the carboxylate–metal interactions are strong [3, 54]. One can also infer here from the very low MII/Iso enthalpies that the isotropic liquid state of the catanionic mixtures may still retain some "structuring" due to ionic correlations between the oppositely charged chains.

Conclusions

Calorimetric and microscopy studies show that the catanionic mixtures formed by gemini and sodium alkylsulfate surfactants, n-2-$n\mathrm{Br_2}{\cdot}2\mathrm{SC}_m\mathrm{S}$, are mesogenic, giving rise to a complex polymorphism in the solid phase and two main types of mesophases, designated here as MI and MII. Both temperature and enthalpy for the transition between crystal and the first mesophase (presumably a soft crystal phase) have a linear dependence with the total chain length of the catanionic compound and suggest that a partial chain melting takes place. The second mesophase is a disordered smectic liquid crystal. Incongruent melting is found for these mixtures, with solid sodium bromide separating at the isotropization temperature of MII. For the mixtures, the mesophases appear for a more expanded temperature range and at lower temperature than for the neat gemini surfactants, due to the strong ionic interactions of the charged head groups in the former.

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References

1. Collings PJ, Hird M. Introduction to liquid crystals. London: Taylor & Francis; 1997.
2. Tandon P, Neubert R, Wartewig S. Thermotropic phase behaviour of sodium oleate as studied by FT-Raman spectroscopy and X-ray diffraction. J Mol Struct. 2009;526:49–57.
3. Akanni MS, Okoh EK, Burrows HD, Ellis HA. The thermal behaviour of divalent and higher valent metal soaps: a review. Thermochim Acta. 1992;208:1–47.
4. Mathevet F, Masson P, Nicoud JF, Skoulios A. Smectic liquid crystals from supramolecular guanidinium alkylbenzenesulfonates. Chem Eur J. 2002;8:2248–54.
5. Knight GA, Shaw BD. Long-chain alkylpyridines and their derivatives. New examples of liquid crystals. J Chem Soc. 1938;1:682–3.
6. Stella I, Müller A. Mesomorphic behaviour of N-(n-alkyl) pyridinium hydrogensulfates. Colloids Surf A: Physicochem Eng Aspects. 1999;147:371–4.
7. Al-Ali F, Brun A, Rodrigues F, Etemad-Moghadam G, Rico-Lattes I. New catanionic amphiphiles derived from the associative systems (α-hydroxyalkyl)-phosphinic or (α-hydroxyalkyl)-phosphonic acid/cetyltrimethylammonium hydroxide. preparation, characterization, and self-organization properties. Langmuir. 2003;19:6678–84.
8. Fischer E, Helfrich B. Über neue synthetische glucoside. Ann Chem. 1911;383:68–91.
9. Galema SA, Engberts JBFN, van Doren HA. Synthesis, purification and liquid-crystalline behaviour of several alkyl 1-thio-D-glycopyranosides. Carbohydr Res. 1997;303:423–34.
10. Van Doren HA, van der Geest R, Kellogg RM, Wynberg H. Synthesis and liquid crystalline properties of the n-alkyl 1-thio-α-glucopyranosides, a new homologous series of carbohydrate mesogens. Carbohydr Res. 1989;194:71–7.
11. Borisch K, Diele S, Goèring P, Muèller H, Tschierske C. Amphiphilic N-benzoyl-1-amino-1-deoxy-D-glucitol derivatives forming thermotropic lamellar, columnar and different types of cubic mesophases. Liq Cryst. 1997;22:427–43.
12. Wang Y, Marques EF. Thermotropic phase behavior of cationic gemini surfactants and their equicharge mixtures with sodium dodecyl sulfate. J Phys Chem B. 2006;110:1151–7.
13. McClure DW. Nature of the rotational phase transition in paraffin crystals. J Chem Phys. 1968;49:1830–9.
14. Strobl G, Ewen B, Fisher EW, Piesczek W. Defect structure and molecular motion in the four modifications of n-tritriacontane. I. Study of defect structure in the lamellar interfaces using small angle X-ray scattering. J Chem Phys. 1974;61:5257–64.
15. Ewen B, Fisher EW, Piesczek W, Strobl GJ. Defect structure and molecular motion in the four modifications of n-tritriacontane. II. Study of molecular motion using infrared spectroscopy and wide-line nuclear magnetic resonance measurements. J Chem Phys. 1974;61:5265–72.
16. Zerbi G, Magni R, Gussoni M, Moritz KH, Bigotto A, Dirlikov S. Molecular mechanics for phase transition and melting of n-alkanes: a spectroscopic study of molecular mobility of solid n-nonadecane. J Chem Phys. 1981;75:3175–80.
17. Doucet J, Denicolo I, Craievich A. X-ray study of the ''rotator'' phase of the odd-numbered paraffins $C_{17}H_{36}$, $C_{19}H_{40}$, and $C_{21}H_{44}$. J Chem Phys. 1981;75:1523–9.
18. Jeffrey GA, Wingert LM. Carbohydrate liquid crystals. Liq Cryst. 1992;12:179–202.
19. Vacatello M, Avitabile G, Corradini P, Tuzi A. A computer model of molecular arrangement in a n-paraffinic liquid. J Chem Phys. 1980;73:548–52.
20. Vacatello M, Busico V, Corradini P. The conformation of hydrocarbon chains in disordered layer systems. J Chem Phys. 1983;78:590–1.
21. Van der Ploeg P, Berendsen HJC. Molecular dynamics simulation of a bilayer membrane. J Chem Phys. 1982;76:3271–6.
22. Nagle JF. Theory of the main lipid bilayer phase transition. Annu Rev Phys Chem. 1980;31:157–96.
23. Bell GM, Combs L, Dunne L. Theory of cooperative phenomena in lipid systems. J Chem Rev. 1981;81:15–48.
24. Prade H, Miethchen R, Vill V. Thermotrop flüssigkristalline Kohlenhydrat-Amphiphile. J Prakt Chem. 1995;337:427–40.
25. Vill V, Böcker T, Thiem J, Fischer F. Studies on liquid-crystalline glycosides. Liq Cryst. 1989;6:349–56.
26. Small DM (1986) Handbook of lipid research. vol. 4. New York and London: Plenum Press; Appendix VI Phospholipids, p. 627.
27. Pinazo A, Pérez L, Lozano M, Angelet M, Infante MR, Vinardell MP, et al. Aggregation properties of diacyl lysine surfactant compounds: hydrophobic chain length and counterion effect. J Phys Chem B. 2008;112:8578–85.
28. Brito RO, Marques EF, Gomes P, Araújo MJ, Pons R. Structure/property relationships for the thermotropic behavior of lysine-based amphiphiles: from hexagonal to smectic phases. J Phys Chem B. 2008;112:14877–87.
29. Morán MC, Pinazo A, Clapés P, Pérez L, Infante MR, Pons R. Investigation of the thermotropic behavior of isomer mixtures of diacyl arginine-based surfactants. Comparison of polarized light microscopy, DSC, and SAXS observations. J Phys Chem B. 2004;108:11080–8.
30. Drummond CJ, Wells D. Nonionic lactose and lactitol based surfactants: comparison of some physico-chemical properties. Colloids Surf A: Physicochem Eng Aspects. 1998;141:131–42.
31. Wunderlich B. A classification of molecules, phases, and transitions as recognized by thermal analysis. Thermochim Acta. 1999;340–341:37–52.
32. Silva BFB, Marques EF. Thermotropic behavior of asymmetric chain length catanionic surfactants: The influence of the polar head group. J Colloid Interface Sci. 2005;290:267–74.
33. Filipovic-Vincekovic N, Pucic I, Popovic S, Tomašic V, Tezak D. Solid-phase transitions of catanionic surfactants. J Colloid Interface Sci. 1997;188:396–403.
34. Tomasic V, Popovic S, Filipovic-Vincekovic N. Solid state transitions of asymmetric catanionic surfactants. J Colloid Interface Sci. 1999;215:280–9.
35. Menger FM, Mbadugha BNA. Gemini surfactants with a disaccharide spacer. J Am Chem Soc. 2001;123:875–85.
36. Ryhänen SJ, Pakkanen AL, Säily MJ, Bello C, Mancini G, Kinnunen PKJ. Impact of the stereochemical structure on the thermal phase behavior of a cationic gemini surfactant. J Phys Chem B. 2002;106:11694–8.
37. Oliviero C, Coppola L, Mesa CL, Ranieri GA, Terenzi M. Gemini surfactant–water mixtures: some physical–chemical properties. Colloids Surf A: Physicochem Eng Aspects. 2002; 201:247–60.

38. Zana R. Alkanediyl-α, ω-bis(dimethylalkylammonium bromide) surfactants: II. Krafft temperature and melting temperature. J Colloid Interface Sci. 2002;252:259–61.
39. Alami E, Beinert G, Marie P, Zana R. Alkanediyl-.alpha, omega-bis(dimethylalkylammonium bromide) surfactants. 3. Behavior at the air–water interface. Langmuir. 1993;9:1465–7.
40. Alami E, Levy H, Zana R, Skoulios A. Alkanediyl-alpha, omega-bis(dimethylalkylammonium bromide) surfactants. 2. Structure of the lyotropic mesophases in the presence of water. Langmuir. 1993;9:940–4.
41. Fuller S, Shinde NN, Tiddy GJT, Attard GS, Howell O. Thermotropic and lyotropic mesophase behavior of amphitropic diammonium surfactants. Langmuir. 1996;12:1117–23.
42. Sikirić M, Šmit I, Tušek-Božić L, Tomaši V, Pucić I, Primožč I, et al. Effect of the spacer length on the solid phase transitions of dissymmetric gemini surfactants. Langmuir. 2003;19:10044–53.
43. Menger FM, Littau CA. Gemini-surfactants: synthesis and properties. J Am Chem Soc. 1991;113:1451–2.
44. Dierking I. Textures of liquid crystals. Weinheim: Wiley-VCH; 2003.
45. Demus D, Kölz KH, Sackmann HZ. Isomorphic relations between crystal-liquid phases. 17. Polymorphism of crystal-liquid states of dialkyl para terphenyl-4,4”-dicarboxylate – smectic E modifications. Z Phys Chem. 1973;252:93–112.
46. Demus D, Diele S, Klapperstück M, Link V, Zaschke H. Investigation of a smectic tetramorphous substance. Mol Cryst Liq Cryst. 1971;15:161–74.
47. Gray GW, Goodby JW. Smectic liquid crystals—textures and structures. Glasgow: Leonard Hill; 1984.
48. Sackmann H, Demus D. The problems of polymorphism in liquid crystals. Mol Cryst Liq Cryst. 1973;21:239–73.
49. Levine IN. Physical chemistry. 5th ed. New York: MC-Graw Hill; 2007.
50. Wang YJ, Pereira CM, Marques EF, Brito RO, Ferreira ES, Silva F. Catanionic surfactant films at the air–water interface. Thin Solid Films. 2006;515:2031–7.
51. Wang Y, Marques EF, Pereira CM. Monolayers of Gemini surfactants and their catanionic mixtures with sodium dodecyl sulfate at the air water interface: chain length and composition effects. Thin Solid Films. 2008;516:7458–66.
52. Marques EF, Brito RO, Wang Y, Silva BFB. Thermotropic phase behavior of triple-chained surfactants with varying headgroup chemistry. J Colloid Interface Sci. 2006;294:240–7.
53. Seurin P, Guillon D, Skoulios A. Smectogènes dissymétriques III. Syhthèse et propriétés mésomorphes des p, n-alkoxybenzydène-anilines parasubstituées. Mol Cryst Liq Cryst. 1981;65:85–110.
54. Marques EF, Burrows HD, Miguel MG. The structure and thermal behavior of some long chain cerium(III) carboxilates. J Chem Soc FaradayTrans. 1998;94:1729–1736