A dual-structure liquid crystal sulfate-free shampoo based on taurine surfactants: suspension & delivery of functional actives to hair and scalp

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Introduction:

Liquid crystal structured shampoo is a new type of shampoo with excellent performance, including good help for silicon deposition, especially for the damaged hair[1]. There are not many liquid crystal structured shampoo products on the market due to the complicated formulation, difficult processing control, and other factors. Despite the fact that intensive research is ongoing, the liquid crystal shampoos that have been reported generally use sulfate surfactants as the primary surfactants[1]. On the other hand, considering the high irritation of sulfate surfactant[2], consumers nowadays tend to choose milder shampoos such as sulfate-free, amino-acid surfactant shampoo instead.

Among all amino-acid surfactants, the taurine-based surfactant is a highly trending main amino-acid surfactant in various high-end and baby products due to its rich and delicate foam, excellent stability under a wide pH range, and low skin irritation[2-4]. The stability and suspension performance relied on traditional rheology modifiers in taurine shampoo has significant limitations such as depression of foam and sometimes low active deposition efficacy. Therefore, formulating liquid crystal structured shampoo based on taurine surfactant is one of the enduring hot topics in rinse-off products, especially in Asia hair care. This allows the maximized combination of the good features of taurine surfactant and the structured shampoo technology to give excellent stability and conditioning benefits.

In this study, for the first time, we report an interesting dual-structure liquid crystal taurine shampoo system that processes easy formulation procedure, excellent formulation stability, suspension ability, largely enhanced deposition of active substances, and excellent conditioning performance.

Materials & Methods:

Formulation design and Liquid-crystal structure characterization:

A systematic design of formulations using a model taurine surfactant, sodium methyl cocoyl taurate as the primary surfactant, is prepared and characterized. The rest co-materials to construct the base including cocamidopropyl betaine, cocamide MEA, sodium chloride, cetyl alcohol and trihydroxystearin. The processing parameters such as melting temperature, emulsification temperature and mixing speed are also investigated. Besides the basic formula designed, other additional functional components can be added accordingly to study the shampoo performance such as suspension stability, sensorial and active delivery performance.

A combination of bright-filed light microscopes (BLMs) and polarized light microscopes (PLMs) with a long working distance 10X lens (OLYMPUS BX53M，Olympus Corporation) are used to identify the liquid crystal bulk structure. PLMs are utilized to visualize the crystal morphology, the number of crystals, and crystal size. Microscope sample preparation follows a simple procedure by applying a drop of the liquid sample onto a glass slide without a coverslip. Furthermore, synchrotron small/wide angle X-ray scattering measurements (SAXS/WAXS) are used to quantify the microstructure of the dual-structure liquid crystals. SAXS/WAXS measurements are performed on the laboratory-based equipment (Xeuss 3.0, Xenocs, France) using a Cu Kα radiation source (wavelength λ = 1.54 Å). Samples are loaded into a gel capsule holder and measured at room temperature.

Stability, foam & sensorial performance

Formulation stability are studied by placing the sample in varying temperature challenges including -5℃, 25℃ and 48℃ for at least one month. In addition, the freeze-thraw challenge is carried out with at least five cycles of -10℃ to 40℃, 48hrs per cycle. After storage at these various challenging conditions, samples are restored to room temperature and are observed by visual inspections for any appearance changes and by PLMs for any liquid crystal structure changes. The suspension ability of actives after storage are observed similary by visual appreance inspections. Clear phase separation occurs if stability and suspension are not good.

The foam ability is evaluated by the foam tester (SITA R-2000, SITA Messtechnik GmbH) and single spindle three speed drink mixer (Waring WDM120E, Fabrique TAIWAN). For the foaming property test by foam test(SITA), the test conditions are as follows: the temperature at 40 ℃, stirring speed at 900rpm, and shampoo concentration at 0.5 wt%. A three-speed drink mixer measures foaming capacity and half-life. The test conditions are concentration at 1wt%, speed 1.

Both panel expert evaluations and instrumental testing are carried out to compare the shampoo performances. The sensorial panel evaluation with a minimum of 10 experts is carried out: the hair is cleaned with a blank cleanser shampoo to remove residuals (without silicones or functional ingredients) and then washed with the tested sample as usual. Ratings are given during and after wash for both wet and dry conditions, where a score of 5 means the perfect performance for a specific aspect. Instrumental testing on the sample set as following: the hair swatches are cleaned with a Sodium Lauryl Ether Sulfate (SLES) to remove residuals (without any silicones or functional ingredients), and then is washed with the tested sample. Hair swatches are dried at controlled room temperature and humidity. Furthermore, the samples are performed by Universal Testing Machines tensile, static device (INSTRON 3343, Illinois Tool Works) to quantify the wet and dry combing forces.

Deposition and delivery of functional actives

Fluorescence Whiteness Meter (KANGGUANG WSD-3U, Beijing Kangguang) is used to quantify the surface deposition efficacy of the cationic conditioner on wool swatch via the red dye method.

Fourier transform infrared-Attenuated total reflectance spectroscopy (FTIR-ATR) (IS50, Thermo scientific) is used to determine whether silicon is deposited on wool swatch semi-quantitatively. Additionally, a scanning electron microscope energy dispersive spectrometer (SEM-EDS) (SU8010, Hitachi Japan) is used to quantify the silicone surface deposition and delivery quantitatively. Again, the wool swatches are prepared and washed following the washing method described previously.

Results & Discussion:

The liquid crystal structure is a self-assembled supramolecular structure, which can be observed under PLMs. This is because liquid crystas have refractive index anisotropy, and under specific orientation, they can show certain brightness and color under crossed polarizers to form patterns. For instance, Maltese cross is a typical sign for lamellar structure. By contrast, tranditional shampoo without liquid crystal structure will show only dark field under PLMs. At varying formulation conditions, the PLMs micrographs are obtained and are used to determine the optimal formulation conditions. It is found that the liquid crystal strucutre is built utilizing a crystalization aid such as trihydroxystearin[7] is quite necessary. As shown in Fig.1 A, a taurine base shampoo is made without trihydroxystearin where no liquid crystals can be found under PLMs. However, with the same base, if adding the crystalline aid, substances are precipitating out under polarized light, which are indicators of crystal structures. The liquid crystal structure can be manipulated and optimized by further adjusting the temperature and the process, as shown in Fig. 1(B) and (C). Uniform Maltese cross patterns are obtained when the temperature is at 95 ℃ during homogenization, whereas a lower temperature of 90 ℃ results in a different crystalline structure.

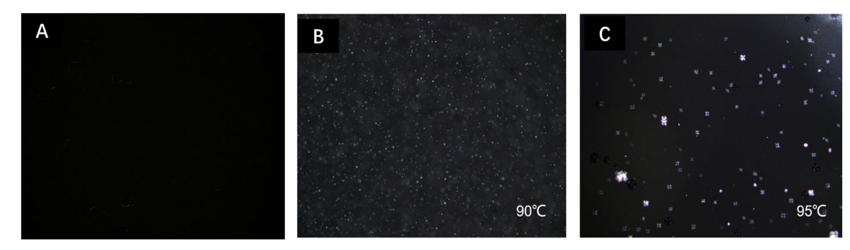

Fig.1 polarized light micrographs of (A) base shampoo without trihydroxystearin, (B) base shampoo made at 90℃ and (C) base shampoo made at 95℃ (all graphs are 10x)

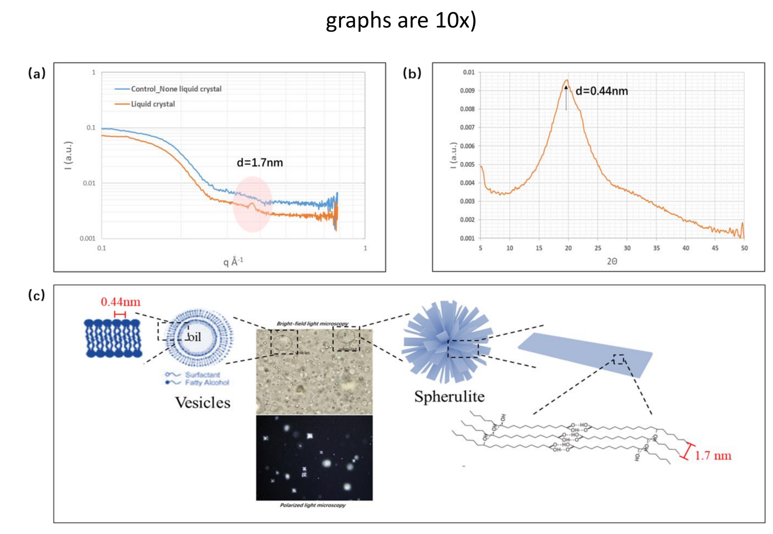

Fig.2 X-ray scattering results: (a) SAXS profiles of a liquid crystal structured shampoo and a control none liquid crystal shampoo, (b) WAXS profile of a liquid crystal structured shampoo, and (c) a schematic microstructure cartoon proposal

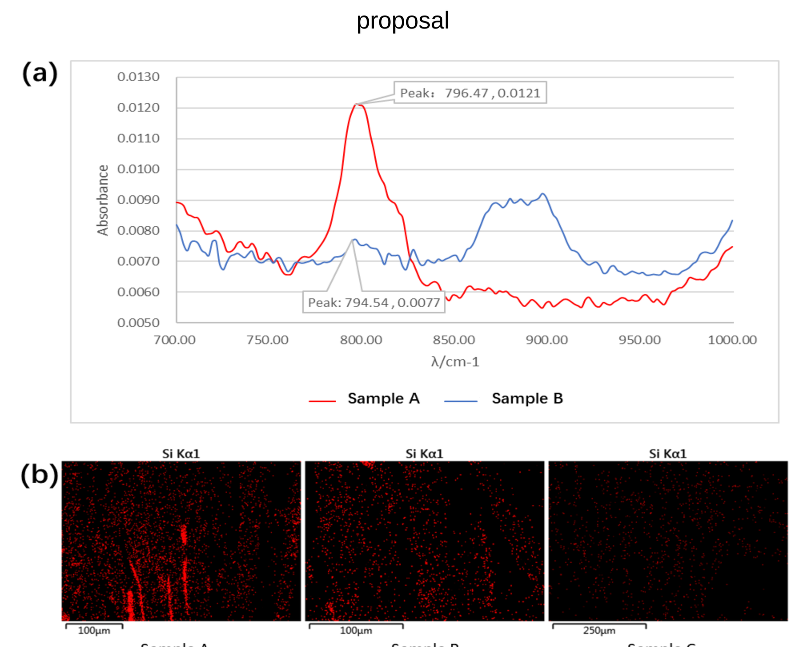

Fig.3 Silicone deposition on wool swatch: sample washed with liquid crystal shampoo (sample A), with conventional carbomer shampoo (sample B), and a blank shampoo without silicone (sample C): (a) FTIR-ATR silicone spectra, and (b) Si distribution graphs via SEM-EDS

To look into the microstructure deeper, SAXS/WAXS measurements are carried out on the liquid crystal shampoo sample A and a control sample without any structures under PLMs. The SAXS and WAXS profiles are plotted as Fig.2 (a) and (b) respectively. In Fig.2(a), liquid crystal structure shampoo has a distinct diffraction peak at 1.7nm, which seems to correspond to a specific characteristic length scale of the trihydroxystearin spherulites. By contrast, the control none crystalline shampoo does not show any peaks across the SAXS profile. Additionally, in Fig.2(b), a very strong interference peak at 0.44nm, which is close to some reported characteristic bi-layer length scale induced by C16 fatty alcohol and co-surfactant in the literature. Combined with the PLMs and BLMs micrographs, a rough schematic cartoon is proposed to describe the interesting dual-liquid crystal shampoo structure, as shown in Fig.2(c).

Study results also show that the dual-structure liquid crystal shampoo has excellent stability and suspension ability. Dual-structure liquid crystal shampoo is compatible with ingredients such as mica, ZPT, glitters, and silicone emulsions, etc., with no need for other additional thickening agents or suspension agents. Compared with the traditional system, the foaming of dual-structure liquid crystal shampoo have apparent advantages, including fast-foaming speed, larger foaming volume, and longer half-life (more stable foam). In addition, the conditioning performance of the dual-structure liquid crystal shampoo is generally improved, especially for the wet sensorial aspects, including wet combing and wet hair suppleness. Both expert evaluations and instrumental tests confirmed that shampoos containing liquid crystal structures are superior.

The hydrophobic silicone deposition is verified and compared via FTIR-ATR measurements. On wool swatch, typically, the absorption peak at 795~800cm-1 corresponds to silicon deposition[6]. Again, sample A is compared with sample B in Fig. 3(a). It is shown that the liquid crystal shampoo sample A has a much larger silicone deposition peak than the conventional carbomer sample B. The content of Si and C elements on the wool swatches are scanned by SEM-EDS as shown in Fig.3(b). So, much larger silicone deposition is found in the liquid crystal shampoo sample A than sample B (the Si content of Sample A is 1.39%, sample B is 0.57%, and sample C is 0.08%).

The depositon efficacy of hydrophilic conditioning polymer and hydrophobic silicones are compared between the reported dual-strucutre liquid crystal shampoo and the conventional carbomer shampoo. It is confirmed that the efficacy of both hydrophilic and hydrophobic active delivery onto hair and scalp is enhanced by the liquid crystal shampoo.

Conclusions:

We report a unique dual-structure liquid crystal taurine shampoo system to achieve an easy formulation process, excellent formulation stability, suspension ability, excellent conditioning performance, and delivery of both hydrophilic and hydrophobic actives. This study provides a pathway for better applications of taurine surfactants in rinse-off cosmetics.

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