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Development of sophorolipid-chitosan pickering O/W emulsion formulations

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Abstract

Sophorolipids (SL) are well-known biosurfactants produced by the yeast *S. bombicola*, generally in a complex mixture between its lactonic and open acidic forms, both being partially acetylated. To overcome this issue, by alkaline hydrolysis we generate a fully acidic, non-acetylated, form of SL. This acidic SL has a pH-responsive behaviour and above pH 6 can form complex coacervates with high-molecular weight chitosan by a simple mechanism of electrostatic attraction between the negative and positive forms of SL and chitosan, respectively. SL-chitosan complex coacervates are able to stabilize O/W emulsions by a Pickering mechanism. We show here their application in the formulation of O/W emulsions containing cosmetics-relevant raw materials, oils, preservatives and vitamins.

Keywords: Biosurfactants Sophorolipids; Chitosan; Complex coacervates; Pickering emulsion

Introduction

Microbial biosurfactants are broadly intended as amphiphilic molecules obtained by the fermentation process of sugars and vegetable oils by specific yeast and bacteria (Figure 1).[1,2] Considering the more stringent regulations combined with the worldwide consumers' concerns for health and environment, biosurfactants are the obvious eco-friendly option to develop potentially commercial alternatives to petrochemical surfactants, especially in the field of cosmetics,[3,4] a field of application which is quite old.[5]

Among the most widely known biosurfactants, sophorolipids are one of the most attractive classes. They are produced from the yeast *S. bombicola*, with interesting production rates and high titers. [6] Despite their apparent complex mixture of congeners, they can be easily hydrolyzed into one main, non-acetylated C18:1 acidic, congener, with well-characterized

physicochemical properties (Figure 1). Along the years, sophorolipids have been studied within the context of cosmetics, [7] antimicrobial agents[8] or soft materials.[9] In this regard, sophorolipids are known to have surface-active properties and they are suitable for stabilizing oil-in-water emulsions. [10] Nevertheless, compared to conventional surfactants, there have been only a few studies of sophorolipids' emulsifying ability. Koh *et al.* have shown that sophorolipids' interfacial performance is best achieved in a formulation composed of the lactonic and acidic forms, [11–14] rather than each individual congener. However, the interfacial performance remains relatively low. [12] The poor emulsifying performances were attributed to the bolaform, double hydrophilic, nature of acidic sophorolipids, and to the poor surface-active character of lactonic sophorolipids. The surface charge of sophorolipid micelles is pH-dependent [15] and the micellar structure itself does not have a well-defined hydrophilic-hydrophobic character. [16] For these reasons, they developed a series of sophorolipid-ester derivatives, with enhanced emulsifying performances [11–14] on paraffin (alkane-based), almond (triglycerides-based), or lemon (cyclic and partially hydrophilic terpenes) oils.

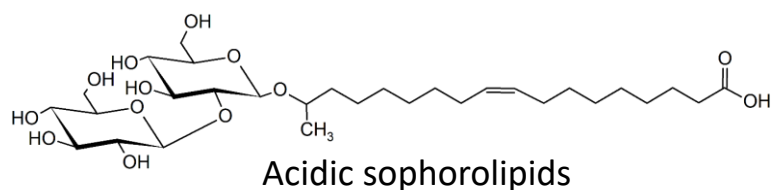


Figure 1 – Acidic sophorolipids (SL) only are employed for this work.

To avoid chemical modification, we have recently developed a new method to prepare O/W emulsions from a combination of acidic SL and chitosan, a worldwide known food and cosmetic grade biopolymer, derived from shrimp's shells.[17] In this new technology, negatively-charged SL micelles and positively-charged chitosan attract each other, forming complex coacervates [18] in the form of stable colloids in water. Complex coacervates have shown to diffuse at both air-water and oil-water interface and behave as colloidal emulsifiers via a Pickering effect, the latter being a mechanism of stabilizing the oil-water interface by means of solid, semi-solid or soft particles, generally observed for solid mineral particles, but not form soft complex colloids. The technology was tested with dodecane-water solutions and the emulsions were shown to be stable in time (months).

In this work, we show how this same technology can be applied to a wide range of raw materials, typically employed in cosmetic products, thus paving the way to potentially

interesting cosmetic formulations based on sophorolipids. The emulsions are prepared with alkane, ester or silicone oils, with and without classical preservatives and vitamins and their stability is tested again time up to 28 days at room temperature.

Experimental Section

Chemicals

Non-acetylated acidic sophorolipids ($M_w = 622 \text{ g.mol}^{-1}$) are purchased from Amphistar (Belgium). High molecular weight (HMW) practical grade chitosan, from shrimp shells, ($MW = 190000\text{-}375000 \text{ Da}$) is purchased from Sandream Impact LLC. All oils are purchased according to their INCI number given in Table 1.

Preparation of complex coacervate solutions

SL and chitosan stock solutions are prepared separately by dissolving each compound's appropriate amount in Milli-Q-grade water. Both are prepared at 0.15 wt% in mQ-grade water. The pH of both solutions is adjusted in the range 5.8-6.0 by mean of a 1 M NaOH solution (generally, few μL are necessary for typical volumes of 1 mL). Then, equivalent volumes of SL and chitosan stock solutions are mixed together with final concentrations (C) of $C_{\text{SL}} = 5 \text{ mg/mL}$, $C_{\text{Chitosan}} = 1.4 \text{ mg/mL}$.

Preparation of emulsions

A known volume fraction of the oil, $\Phi_{\text{oil}} = 0.7$, is mixed with a given fraction of the SL-chitosan complex coacervate solution, $\Phi_{\text{complex}} = 0.3$, to prepare a biphasic system. The mixture is then subjected to a high-speed homogenization (rotor-stator) using an Ultra-Turrax homogenizer (IKA® T25 Basic Werke) with a dispersing element of 25 mm (stator diameter) to obtain a homogeneous emulsion. Homogenization is maintained for 1 min at a constant speed of 13500 rpm with the vial's vertical movements along the rod.

Optical microscopy

To visualize the emulsion droplets, images are acquired using Motic BA210E Microscope, non-polarized light, x40.

Stability study

To determine the stability of the emulsion, the sample is characterized by eye observation: whiteness of the emulsion, presence or absence of supernatant. A score is given: 1, the emulsion is stable; 2, average stability; 3, the emulsion is not stable.

Results and discussion

Emulsion formation

In a recent publication, we have shown that SL micelles form complex coacervates in water when mixed with chitosan above pH 6.[18] The complex coacervates are able to stabilize via a Pickering mechanism an O/W emulsion over months when employed in a 30:70 v:v (coacervates:dodecane) mixture with dodecane. [17] Dodecane not being an interesting material for cosmetic applications, several other oils were tested under the same conditions. To broaden the palette, alkanes, esters and silicon oils have been tested and major results are given in Table 1. For this work, the emulsions were analyzed using a simple optical microscope and rated arbitrarily between 1 and 3 according to their visual quality. A score of 1 is attributed to good emulsions, as shown in Figure 2, left, while a note of 3 was attributed to poor emulsions, as shown in Figure 2 right. The emulsions stability was also tested after 28 days at room temperature (about 23°C), a typical standard for formulation studies in cosmetics.

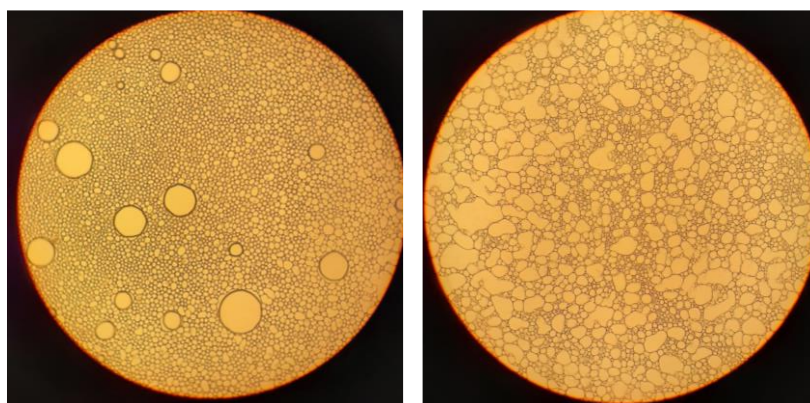


Figure 2 – Typical optical microscopy images of a good, rated 1, (left) and poor, rated 3, (right) emulsion

It was found that other alkanes, like isododecane, isohexadecane and squalane also provide good emulsions (score of 1) with long-term stability at 28 days, in agreement with dodecane. On the other hand, mixed C15-C19 alkanes do not form an emulsion, suggesting a detrimental influence of the impair number of carbon atoms in the chain. Although alkanes are not interesting products for the cosmetic industry, these results show promising potential for

the sophorolipid-based formulation. For this reason, other emollients, more classically used in cosmetics, were employed.

Table 1 – Emulsification potential and emulsion stability of Pickering emulsions prepared from acidic sophorolipids and HMW chitosan complex coacervates in the presence of various oils.

INCI	Family	Formula	Note Emulsion Day 0	Stability Day 28
Squalane	alcane	C ₃₀ H ₆₂	1	YES
Isododecane	alcane	C ₁₂ H ₂₄	1	YES
C15-19 Alkane	alcane	Mix C ₁₅ /C ₁₉	3	No
Isohexadecane	alcane	C ₁₆ H ₃₄	1	YES
Octyldodecanol	alcanol	C ₂₀ H ₄₂ O	1	YES
Rapeseed oil	biobased		1	YES
Simmondsia Chinensis (Jojoba) Seed Oil	biobased	C ₂₀ abundant	1	No
Dicaprylyl Carbonate	ester	C ₁₇ H ₃₄ O ₃	3	No
Caprylic/Capric Triglyceride	ester	C ₂₄ H ₄₈ O ₈	2	No
Cetearyl Isononanoate	ester	C ₂₅ H ₅₀ O ₂	2	No
Glyceryl undecylenate	ester	C ₁₄ H ₂₆ O ₄	3	No
Diisopropyl Sebacate	ester	C ₁₆ H ₃₀ O ₄	1	YES
Coco-Caprylate/Caprates	ester	C ₄₂ H ₈₄ O ₄	3	No
Cyclopentasiloxane	silicone	C ₁₀ H ₃₀ O ₅ Si ₅	1	No
Dimethicone	silicone	(C ₂ H ₆ OSi) _n	1	YES
PPG-3 Myristyl Ether	ether	C ₁₇ H ₃₆ O ₂	2	No

Octyldodecanol is a branched chain alcohol having medium spreading emollient, commonly used in lipsticks. Emulsification data in Table 1 show that adding an alcohol function to a long branched alkyl chain does not modify the good outcome of the emulsion, which is stable after 28 days, thus suggesting that long chain alcohols could also be employed in the formulation. Following the same approach, a number of cosmetics-relevant esters were tested, like dicaprylyl carbonate, cetearyl isononanoate or diisopropyl sebacate. These and others listed in Table 1 are good skin softeners, commonly used in anti-age and solar cream or foundation formulations, among others. It was found that most common ester emollients, like dicaprylyl carbonate, caprylic/capric triglyceride or cetearyl isononanoate do not allow

producing a good emulsion, which is in turn poorly stable in time. Diisopropyl sebacate, on the contrary, is able to form a good and stable emulsion. Although more work is needed to better understand these empirical results, it could be possible that conformational issues of the aliphatic chain with respect to the intermediate position of the ester bond play a role against the emulsion's stability. Similar poor emulsification results are obtained with an ether, PPG-3 myristyl ether, typically employed in deodorant sticks. The partial polarity of the emollient seems to play a significant role against emulsion stability.

Finally, two silicones (generally used to lower surface tension in dermocosmetic products), linear and cyclic, and two biobased oils, rapeseed (rich in C18 mono and polyunsaturated) and Jojoba seed (rich in long chain, C20 and C22, fatty acids) oil, were tested. It was found that linear silicone and rapeseed oil provide good and stable emulsions, differently than cyclic silicone and Jojoba oil.

Conclusion

This work shows a first tentative to develop emulsion formulations entirely based on a biosurfactant, acidic sophorolipids. Control of the interactions between sophorolipids and a biopolymer, chitosan, drives the formation of a colloidal solution of complex coacervates, which can stabilize the oil-water interface through a Pickering effect, the latter describing a mechanism of stabilizing the oil-water interface by means of solid, semi-solid or soft particles. At a proportion of 70% emollient and 30% coacervate aqueous solution, good and stable Pickering emulsions can be formed. This empirical work provides a non-exhaustive list of cosmetics-relevant emollients, which can be used in biosurfactant-based formulations for cosmetics. It is found that most alkanes, but also dimethicone (silicone), diisopropyl sebacate (ester) and rapeseed oil (vegetal oil) can be used to prepare emulsions stable up to 28 days at room temperature.

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