*IFSCC 2025 full paper (**IFSCC2025-796**)*

"Redefining Sustainable Cosmetic Emulsions: Natural Deep Eutectic Solvents as key ingredients"

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1. Introduction

As consumer demand for eco-friendly, high-performance products grows, Natural Deep Eutectic Solvents (NaDES) offer a promising avenue for innovation in emulsion design. NaDES are a groundbreaking class of sustainable solvents formed through weak interactions such as hydrogen bonding and Van der Waals forces between natural metabolites like sugars, amino acids, and organic acids [1]. They are notable for their biocompatibility, renewability, and biodegradability. NaDES stand out as viable alternatives to conventional solvents in cosmetic applications [2]. Currently, they are widely being explored as the basis for innovative bio-based active cosmetic ingredients [3, 4]. Our consortium introduces a paradigm shift by considering NaDES as sustainable key components of cosmetic products, focusing on their impact on structure, stability, and performance [5]. Now that NaDES-based extracts were successfully introduced in cosmetic formulations as active ingredients at low concentrations [6, 7], it is interesting to determine if NaDES could become functional or sensory ingredients and be introduced in cosmetic products at high concentrations.

Emulsions are the backbone of various skincare and makeup products like skincare creams, hair masks or foundations. These biphasic systems stabilize immiscible ingredients, typically oils and/or emollients and water, enhancing texture, sensory appeal, and the diffusion of actives in the skin. The feasibility of a hydrophobic NaDES in water was already described in the literature using controversial ingredients like sodium lauryl sulfate and methodologies difficult to scale up like ultrasonication [8], our approach is designed especially for a transfer to cosmetic industry. The study from which this article stems was designed to evaluate the potential of three hydrophobic NaDES with distinct physicochemical and sensory characteristics, and compliant with cosmetic regulations, to serve as the internal phase of an emulsion with water as the external phase. The three NaDES are representative of the combinations most seen in the literature when it comes to hydrophobic NaDES: one based on the combination fatty acid / fatty acid, one based on the combination fatty acid / terpene and fatty acid / polyol [9]. Three types of natural surfactant were evaluated to stabilize the formula. To minimize materials and energy consumption, a Design of Experiment (DOE) approach was used. This short paper contains a sample of the results obtained with one specific NaDES composed of two fatty acids (octanoic acid and lauric acid), combined with a hydrogenated lecithin as a natural surfactant. The proof of concept of the emulsification was established, then this NaDES was incorporated as the oily phase in a COSMOS-certified cream. Its impact on physicochemical and sensory properties was assessed, revealing the unique behavior of this NaDES when interacting with common ingredients like texture agents or preservatives. This research aims to advance the development of next-generation emulsified systems with enhanced performance.

2. Materials and Methods

2.1 NaDES preparation and characterization:

NaDES C8/C12 was prepared by mixing octanoic acid and lauric acid at a specific molar ratio determined thanks to *in silico* prediction (COSMO-RS, data not shown). The mixture was heated at 50°C and stirred by magnetic stirring for 1h until a colorless liquid was obtained. After returning to room temperature, the NaDES is stored for a maximum of 7 days at 20°C in an oven. Various analyses of NaDES, including shear-dependent viscosity at 25°C, calorimetry constant shear viscosity from 15°C to 60°C, density from 15°C to 40°C are performed to control the formation of a NaDES (data not shown). Various instrumental assays, including spreading on artificial skin were performed to characterize C8/C12 NaDES sensory properties. C8/C12 NaDES miscibility with water was studied by NMR. Briefly, C8/C12 was mixed with the same mass of water (50:50 mixture) during an hour then the mixture was decantated during 24h and centrifuged to ensure a complete phase separation. Both phases were analyzed with Bruker® Avance 300 NMR spectrometer using DMSO-*d6* as internal reference. Measurements were done at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR.

2.2 Screening of emulsification feasibility by a design of experiment approach (DOE) :

A central composite design was used to study a ternary system water/ NaDES/ hydrogenated lecithin and to determine both the concentrations and the experimental conditions in which stable emulsions can be obtained. Emulsions were prepared using a common disperser (T25 Ultra-Turrax®, Ika, Germany) with varying experimental conditions (time, temperature, speed). Emulsion stability was assessed using Static Multiple Light Scattering (SMLS, Turbiscan Lab®, Microtrac, France). Emulsions were considered stable after 7 days when they showed a creaming inferior to 5% vol/vol, and coalescence inferior to 5% (evaluated through retrodiffusion variation measurements and oil separation measurements). DOE was generated and treated with Design Expert software (Stat-Ease, USA).

2.3 Creams preparation:

A COSMOS (COSMetic Organic and Natural Standard) certifiable chassis cream was selected to be able to measure the formulability of the hydrophobic NaDES in a more complex formula. The same cream containing Caprylic Capric Triglycerides as the oily phase was used as a control. These formulas, reported in Table 1, were produced in triplicate at room temperature with a dual assymetric centrifugation mixer (SpeedMixer®; Hauschild, Germany). First, the aqueous phase was prepared by placing the components in a specific mixing cup, then mixed during 4 minutes at 1800 rpm. Then, the emulsion was made by adding the components of the oily phase (medium chain triglycerides or C8/C12 NaDES, the preservative and the emulsifier) and mixing during 2 minutes at 1800 rpm.

Table 1. COSMOS creams composition (% wt.)

Ingredients	Function	Control	C8/C12 cream
C8/C12 NaDES	Solvent	0	25
Gum mix	Thickener	1	1
Glycerol	Humectant	10	10
Hydrogenated lecithin	Emulsifier	3	3
Capric Caprylic Triglycerides	Emollient	25	0
Dehydroacetic acid/ benzyl alcohol mix	Antimicrobial agent	1	1
Water	Solvent	60	60

2.4 Creams characterization:

Creams were stored in a climatic chamber (Memmert, Germany) at 40°C with 75% humidity for one month. The pH of the creams was measured with a suitable pH electrode. Static Multiple Light Scattering based stability analyses were done with the Turbiscan® instrument (Microtrac, Toulouse, France). The droplet size is also calculated thanks to the software. Rheological characterization was conducted using a Kinexus pro+ rheometer (Netzsch, Germany) equipped with a sanded cone-plate geometry (4° angle, 40 mm diameter, 25°C, aligning with usage conditions).

For sensory analysis [10], creams were spread between a PMMA plaque and a polypropylene sheet using a TAX-T Plus texturometer (Stable Micro Systems, UK). The friction coefficient, as well as the properties of the residual film, were studied on Biody® material using a Frictiometer® FR700 equipped with a plain PTFE disk, a GL 200 Glossymeter® (both Courage-Khazaka, Germany) and TAX-T Plus texturometer with spherical stainless steel probe. Contact angle was measured on the residual film (after 10 circles) with a drop shape analyzer DSA 30 (KrüssGmbH, Germany).

3. Results and discussion

3.1. NaDES characterization

C8/C12 NaDES showed a newtonian rheological behavior and a very low viscosity around 0.008 Pa.S at 25°C,whereas the control oil, Caprylic Capric Triglycerides showed a viscosity of 0.032 Pa.S. The NaDES and the reference oil showed close densities (0.904 and 0.944) and refractive indexes (1.430 and 1.446, respectively). C8/C12 show a very present odor while the reference oil was odorless. It showed a spontaneous spreading value close to 7 $mm^2/\mu L/min$, which bring it closer to ester-based emollients than vegetable oils which in general a lower spontaneaous spreading.

3.2 Proof of concept of NaDES in water emulsions

NMR analysis of 50:50 mixture of C8/C12 NaDES and water showed that no molecular transfer occurred from one solvant to the other (data not shown). The two liquids are then considered immiscible. It was then theoritically possible to create an emulsion between the NaDES and water in adapted experimental conditions of shearing and temperature. DOE was used to prepare C8/C12 in water emulsions using usual lab disperser in different experimental conditions while reducing the number of experiments. The analysis of the results indicated that the better conditions to prepare C8/C12 in water emulsions stabilized with hydrogenated lecithin were, among those tested: i) to dissolve the surfactant in the NaDES at 60°C ii) to disperse the NaDES phase in the aqueous phase during 5 min at 12,000 rpm. It is noticeable that the heating of the phase to 60°C is necessary to dissolve the hydrogenated lecithin either in oils or in NaDES. The yellow zone on Figure 1 shows the concentrations of NaDES and surfactant leading to stable emulsions in these specific conditions, as determined by SMLS. It can be seeen that the ternary system C8/C12 NaDES/ Water/ hydrogenated lecithin can lead in this conditions to physically stable emulsions (7 days) for a large range of concentrations, including concentrated emulsions (internal phase > 30% wt.). Stable emulsions prepared showed a newtonian behavior and a low viscosity (data not shown).

3.3. Characterization of the NaDES-based cream

Based on the DOE analysis, it was decided to test the introduction of C8/C12 NaDES in a COSMOS frame cream formula to observe the impact of the NaDES on the properties of the cream compared to an oil usually used to prepare creams: Caprylic Capric Triglycerides. To be consistent with the sustainable approach encouraged in this project, a room temperature, low energy process was used to prepare the cream.

Stability of the creams was assessed after 30 days in accelerated aging conditions for both creams : no alteration of organoleptic characteristics was observable. No creaming or oil separation was visible.

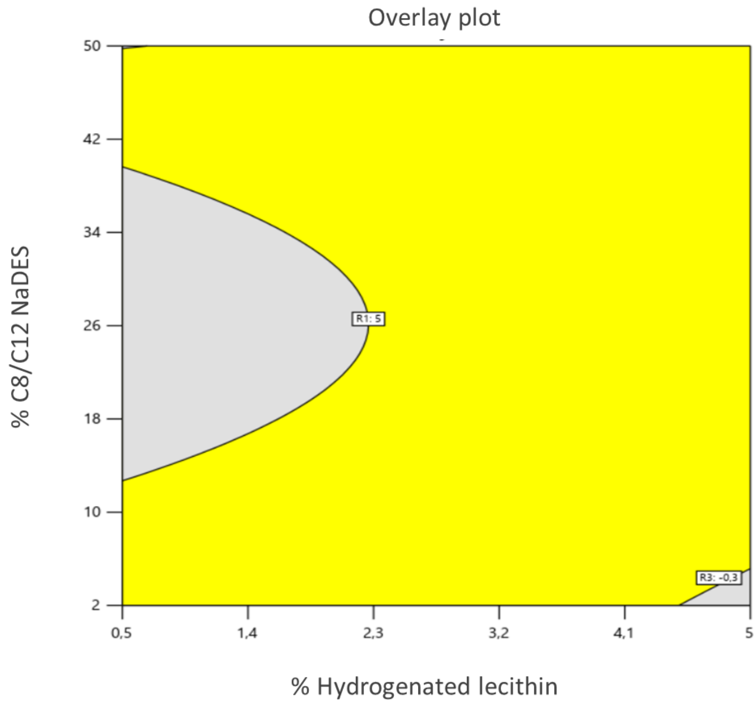

Figure 1. Prediction of stable emulsions based on the ternary system C8/C12 NaDES/ water/ hydrogenated lecithin obtained by the DOE approach. The yellow zone corresponds to the stable emulsions considering the criteria selected (creaming < 5%, coalescence <5%).

The colors of the control and the NaDES-based creams were close, whereas the odor of NaDES-based cream was more pronounced. The pH of the NaDES-based cream was inferior to the one of the control cream, certainly due to the slight solubility of the fatty acids, in particular octanoic acid, in water. Nevertheless, after 30 days in accelerated aging conditions, the pH of the creams were finally close, with ≈ 5.1 for C8/C12 cream and ≈ 5.5 for the control. The pH of the NaDES-based cream is compatible with a skin application.

Concerning rheology (Figure 2), both creams show shear-thinning behavior but C8/C12 creams exhibits lower values of viscosity. This phenomenon is particularly clear at high shear rates. For example, at 0.1 s-1, the viscosity of the NaDES cream is close to 30 Pa.s, while the viscosity of the control cream is close to 220 Pa.s. This decrease in viscosity can be linked to the difference in size droplets between the two formulations. The droplet size was approached by SMLS measurements which implies a calculation leading to an overestimation of the diameter of the droplets. Nevertheless it is interesting to compare the values obtained 24h after preparation. For the cream containing NaDES droplets, the estimated droplet diameter was ≈ 2 µm, whereas it was ≈12 µm for the control cream. On the contrary, the phenomenon is less marked at high shear rates. Indeed, at 1000 s^{-1}, the viscosities are 0.07 Pa.s and 0.12 Pa.s respectively. These results mean that the C8/C12 cream will look less viscous at rest, and may be easier to pick up from the pack compared to the reference cream. During spreading (high shear rates), the difference between both cream should be more difficult to discern.

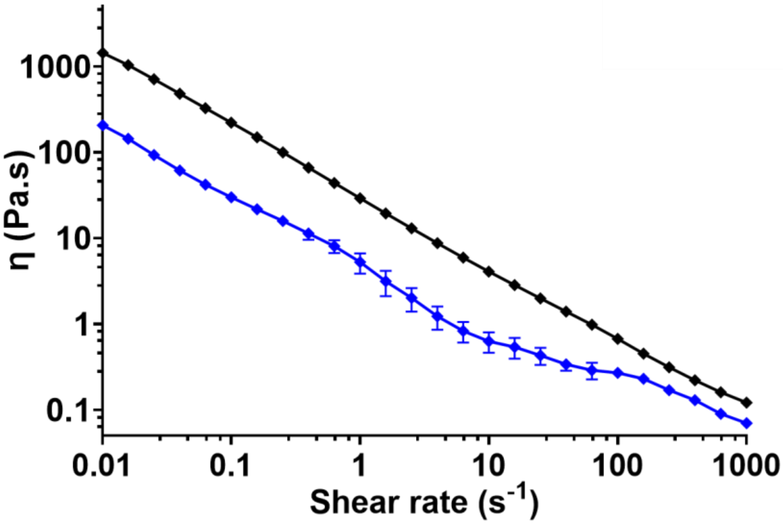

Figure 2: Flow properties of control (black line) and C8/C12 NaDES-based cream (blue line).

3.4 Instrumental sensory evaluation of the creams

Numerous studies have established a correlation between instrumental measurements and the sensory properties of a cream as evaluated by panelists. This approach was chosen for a fast preliminary evaluation of NaDES-based creams. Sensory properties were defined during its application on artificial skin (spreading properties evaluated by texturometry and friction using biometrical probes), and after application—that is, the properties of the residual film (measurements performed with probes such as a glossmeter for glossyness properties; texturometry for stickiness; and contact angle measurements, which are related to skin interaction and penetration) [11]. Table 2 highlights results obtained with the control cream containing triglycerides as the internal phase, and the cream formulated with C8/C12 NaDES.

Regarding spreading properties, the friction force (circular spreading) and spreading force values (linear spreading) indicate that both creams have a lubricating effect, making them easy to apply on the skin. However, the C8/C12 NaDES-based cream is less lubricating than the reference cream during linear spreading, but more lubricating in the case of circular spreading. As for the residual film properties after application, the cream formulated with C8/C12 NaDES seems to deliver more glossyness immediately after application and after 5 minutes of drying, compared to the control. It also seems that this NaDES helps reducing the sticky feeling after application compared to the control cream. Finally, the contact angle values show that both creams enable the formation of a hydrophilic residual film, ensuring good interaction with the skin and effective penetration. However, the use of NaDES improves these properties compared to triglycerides.

Table 2: Instrumental measurements of Control and C8/C12 Nades-based creams ensory properties (properties of the polymer-based skin models used for measurements are provided as a comparison)

	Biody®	**Polypropylene sheet**	**Control**	**C8/C12 cream**	**Sensory correspondence**
Spreading force (positive area in g.s)	-	1416±19	1004±33	1262±33	Application
Friction force (UA)	226.3±26.8	-	92.3±7.1	75.5±7.5	
Gloss at T0min (UA)	5.2±0.3	-	11.9±2.1	16.4±1.6	After application
Gloss at T5min (UA)	5.2±0.3	-	9.7±2.0	10.4±1.2	
Gloss with DSC at T0min (UA)	2.8±0.3	-	9.6±1.0	14.3±1.6	
Gloss with DSC at T5min (UA)	2.8±0.3	-	7.5±2.3	8.3±1.2	
Stickiness (negative area in g.s)	-0.003± 0.001	-	-0.491± 0.048	-0.157± 0.025	
Contact angle (°)	123.8±2.4	-	25.7±2.9	11.8±0.4	

4. Conclusion

The results presented in this short paper are extracted of a larger study demonstrating the possibility to prepare emulsions with an internal phase constituted of hydrophobic NaDES of various natures. Specifically, a DOE approach demonstrated that C8/C12 NaDES can be emulsified with water and stabilized by hydrogenated lecithin using a commonly available homogenizing device in mild experimental conditions comparable to those used to emulsionnate oil in water. When combined with a mix of thickening agents at low concentration (1%), these emulsions can be transformed in creams at room temperature using low-energy consuming processes. NaDES-based creams show specific rheological and spreading properties. Considering NaDES can be obtain with various components from biorefinery, our consortium's work is revealing a whole range of new cosmetic formulas combining performance and eco-responsibility.

5. References

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