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Original Article

Experimental design and evaluation of the influence of a glucomannan-based thickener on the characteristics of an oil/water emulsion

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Abstract

Background: The thickening agents are an important part of the cosmetic formulation, offering an opportunity not only to regulate the product viscosity, but also to improve its stability. But, the way to use them and the impact of these natural ingredients on the qualities of the finished product are not always assessed. In this work, a new multifunctional glucomannan-based blend has been evaluated, the aim was to study its influence on the qualities of an oil/water emulsion.

Materials and Methods: To get a rational understanding of this factor, an experimental design approach was adopted. An Optimal design optimized for a second-degree model (Quadratic) with only 12 runs and 1 repeated point was implemented. From the formulation, three ingredients concentrations varied as following; the thickener, a glucomannan-based blend, from 0.6% to 1.2%, one emollient from 3% to 7% and the emulsifier from 3% to 6%. The emulsion was prepared at 70°C and the thickener was added at 50°C. Viscosity measurement, droplets size and stability were analyzed 48 hours following the preparation.

Results: In the final emulsions, in terms of viscosity and stability to centrifugation, the glucomannan-based blend was is the parameter with the strongest impact. As for the droplets size, it was impacted the most, thus in a smaller extend, by the emulsifier concentration. Moreover, a synergistic effect between the emulsifier and thickener was monitored on the droplets size parameter while the concentration of squalene proved little influence. Finally, the optimal concentration of glucomannan-based blend to ensure system stability was determined at 1.2%.

Conclusions: In conclusion, conducting an Optimal design allowed to model the effect of the thickener in formulation as well as the interactions between the monitored ingredients.

Keywords: Glucomannan, Emulsion, Experimental design, Viscosity, Stability

Background

For a few years, there is a trend towards using natural ingredients in cosmetic product instead of chemicals that were used in the past. Accordingly, the world market value for natural cosmetics is expected to increase by roughly 37.8% by 2027.[1] In parallel, in 2018, the world sales of skin care category, was estimated at 134.8 billion dollars according to Grand View Research.[2]

Due to this paradigm shift, natural emulsions are more and more studied on different research axis, such as ingredients[3,4] or from their fabrication process.[5] Usually, the emulsion contains two or more partially or completely immiscible liquids, where the dispersed phase exists as droplets suspended in the continuous phase. The interface between hydrophobic and hydrophilic molecules is intrinsically not stable.[6] For any emulsion system, the choice of a right surfactant[7] is critical because they decrease interfacial tension and slowdown the emulsion breaking such as coalescence. However, the choice of the thickener[8] is also very important to decrease the creaming instability. Despite being simple to prepare from an oily, aqueous base and emulsifier, many parameters come into play and can influence the characteristics of the final emulsion. Design of experiments (DoE) is the way to achieve knowledge on the role of the different parameters. The combination of the experimental findings allowed to gain a deeper insight into the stability of these emulsions, which can be applied to the rational development of new formulations.[9,10] Using experimental design approach[11] is therefore of great help to assess the synergy between a thickener, an emollient

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and an emulsifier, respectively to avoid instabilities, bring sensory properties[12] and make a stable emulsion.[13]

This work deals with the development of emulsions containing a green thickener a glucomannan-based blend. Glucomannan is a polysaccharide composed of 1.4-β-linked D-glucosyl and D-mannosyl residues[14] able to form a network when dispersed in water phase and restrain oil droplets migration during gelation.[15] But there are few studies concerning its application in cosmetic formulation. In this study, an Optimal design (quadratic model) has been conducted to evaluate the effects of ingredients concentration on physical-chemicals parameters.

Materials and Methods

Ingredients

Demineralized water obtained after passage on resins at the laboratory was used. Squalene (Phytosqualan, Sophim); Caprylic/Capric Triglycerides (Labrafac CC, Gatefosse); *Butyrospermum parkii*, Sodium benzoate (Cooper); Cetearyl Alcohol & Cetearyl Glucoside (Montanov 68 Seppic); Glucomannan (and) capric/caprylic triglycerides (and) polyglyceryl-4-laurate (and) xanthan gum (INAGEL Green Inabata-pharmasynthese); were all kindly sampled by the different companies.

Preparation of the emulsions

The oil/water emulsions were prepared by the direct method and their composition are presented in Table 1. The concentrations of squalene, the emulsifier and the thickener, are expressed by the range of variation used in the experimental design.

Briefly, aqueous and oily phases were heated at 70°C then the oily phase was added at 400 rpm to avoid splashing. When the dispersion was obtained the agitation was raised until 1000 rpm then maintained for 10 minutes. The temperature was after decrease at 50°C and the thickener wad added. The agitation was maintained again for 10 minutes before adding the preservative.

Methods of control

All measurements were taken 48 hours after the samples were prepared.

Viscosity measurements

The viscosities tests were performed on a rheometer (M301/ ANTON PAAR plate/plate geometry, Rheocompass software). Data have been collected at 0.1 rpm, 20°C, with the deposit of 3 g of each sample.

Droplets size measurements

The droplets size was analysed with the equipment Turbiscan™ LAB. Measurements were performed at room temperature. Refractive index chosen for oil phase was 1.473 and the one chosen for water phase was 1.333.

Stability observations

Samples have been centrifugated by a MiniSpin Eppendorf centrifuge two days after formulation. Centrifugation has been done at 25°C, 4000 rpm for 5 minutes on 5 g samples. Stable samples were marked “0” and unstable samples were marked “1” for data analysis.

Experimental design

In order to rationally develop an optimal formulation, an experimental design and mathematical model were required. In the present work, the three variables selected were: squalene, emulsifier and thickener. With those 3 factors, an optimal design optimized for a second-degree model (quadratic) with only 12 runs and 1 repeated point was implemented (#1 and #5).

The quadratic model for three parameters is given in equation 1, it has 10 coefficients. It is therefore necessary that the plan includes at least 10 different tests. Hence the optimal design in 12 tests including one repeated (11 different tests - a repeat).

Equation 1 . Quadratic model

$$Y=\theta_0+\theta_a A+ \theta_b B + \theta_c C + \theta_{aa} A^2 + \theta_{bb} B^2 + \theta_{cc} C^2 + \theta_{ab} AB + \theta_{ac} AC+ \theta_{bc} BC \quad (1)$$

The effect of the three variables on emulsion viscosity, droplets size and stability were studied. Experiments were randomly carried out in order to minimize the effects of random error of possible “lurking variables” in the observed responses.

The DOE analysis based on multiple regression models was carried out in the Design Expert® [11-17] software. The independence, Homoscedasticity and normality of the

Table 1. Composition of the different oil/water emulsions

Phase	INCI name	Function	Percentage and range (%)
Aqueous	Aqua	Solvent	QSP
Oily	Squalene	Emollient	3-7
	Caprylic/capric triglyceride	Emollient	2
	Butyrospermum parkii butter	Moisturizer	1
	Cetearyl Alcohol & Cetearyl Glucoside	Emulsifier	3-6
Thickener	Glucomannan (and) capric/caprylic triglycerides (and) polyglyceryl-4-laurate (and) xanthan gum	Thickener	0.64-1.2
Preservative	Sodium benzoate	Preservative	1

data were analyzed and an analysis of variance (ANOVA) performed. The suitability of the models was determined by using coefficient of determination (R2) and the lack of fit test (Flof). Joklegar and May proposed that R2 should be higher than 0.80 to obtain a good fitting.[15]

Results and Discussions

The experimental design technique has received increasing attention in the emulsion field in recent years.[12] The goal is to obtain quality information about factors/variables that affect the properties of emulsions. In a previous nonpublished work, a factorial experimental design was implemented for selection of the percentage and qualities of ingredients adapted to an oil/water system. In this work, a response surface design was performed to evaluate the effects and interactions of significant variables involved. All the results for each different run done are presented in Table 2.

Run were structured accordingly to the use of the optimal quadratic model, with a variation from 3% to 6% for the emulsifier (factor A), from 0.64% to 1.2% for the thickener (factor B) and from 3% to 7% for the emollient (factor C).

Analysis of viscosity

Table 2 shows that the lowest viscosity was 10.02 Pa.s and the highest 31.07 Pa.s, this high value was remarked for a composition with the highest concentration for each ingredient (run 12). The ANOVA performed on viscosity analysis has shown that the quadratic model chosen was significant with *P* value of 0.0011 and R^2 was equal to 0.988.

The perturbation graphic (Figure 1) represents the influence of the concentration of ingredients A (emulsifier), B (thickener) and C (emollient) on the studied parameter; viscosity. It shows a medium and positive influence of emulsifier and emollient on viscosity. This graphic also exhibits that the thickener has the greatest impact on the response. Figure 2 illustrates the three-dimension response surface curves at different level of thickener. These three dimensions (3D) plots and their respective contour plots provide a visual interpretation of the interaction between two other factors. When the level of thickener increases from 0.64% to 1.2%, the viscosity of emulsions increases from 10 Pa.s to 30.s on average with a small influence of the other emulsion constituents

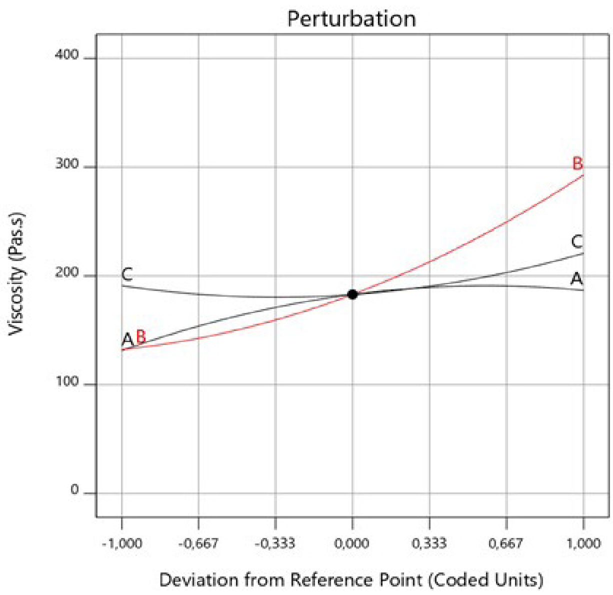

Figure 1. Viscosity and perturbation graphic A (emulsifier) B (thickener) ou C (emollient).

Analysis of droplets size

The average diameter of the droplets measured in Turbiscan® shows a relatively small range of variation with values between 2.02 µm and 3.76 µm. The ANOVA performed on droplets size analysis has shown that the quadratic model chosen was significant with *P* value of 0.0007% and the R^2 was equal to 0.9955.

Table 2. Factors studied in the experimental design and results for the different responses

Run	Factor 1 A: Emulsifier (%)	Factor 2 B: Thickener (%)	Factor 3 C: Emollient (%)	Response 1 Viscosity (Pa.s)	Response 2 Droplet size (µm)	Response 3 Index of stability
1	4.5	0.92	5	167.99	2.26	1
2	5	0.827	7	201.35	2.83	1
3	3	0.64	7	122.68	3.31	1
4	3	1.2	3	237.01	2.86	1
5	4.5	0.92	5	192.67	2.54	1
6	4	0.64	3	122.84	2.42	1
7	3	0.827	4.33	100.25	3.16	1
8	6	0.64	5.667	145.83	2.78	0
9	3	1.2	7	307.60	3.74	0
10	5	1.2	4.33	297.77	2.21	0
11	6	0.92	3	211.46	2.02	0
12	6	1.2	7	310.36	2.67	0

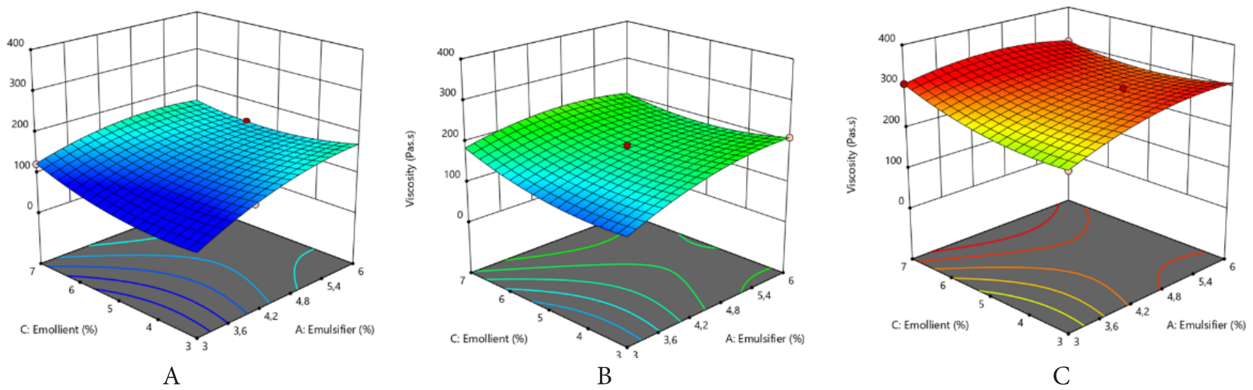

Figure 2. Response surface 3D plots of values of viscosities. (A) 0.64%, (B) 0.92%, (C) 1.2% of thickener.

As expected, the perturbation graphic (Figure 3) shows an important impact of emulsifier on droplets size. Its effect presents a marked decreasing curve (A) on the graph, when emulsifier concentration increases.

The concentration of the thickener has a moderate influence on droplets size when the surface agent is between 4.5 and 6%. There is therefore a synergistic effect between the two ingredients, which is confirmed in the ANOVA model with a value of 0.006 for the AB interaction. It can be visualized on the two-dimensions (2D) graphs representation, in the right part of the schema (visible by the circle, Figure 4A).

Analysis of stability

The stability analysis was carried out using a centrifuge to accelerate the creaming phenomenon in accordance to the Stokes' law (equation 2).

$$\upsilon = \frac{2}{9}\frac{(\rho_p - \rho_f)}{\mu} gR^2 \qquad (2)$$

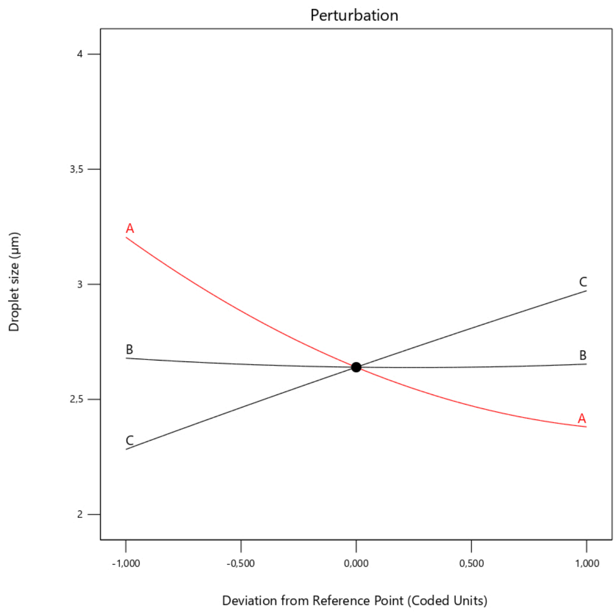

Figure 3. Droplet size - Perturbation graphic A (emulsifier) B (thickener) ou C (emollient).

where g is the gravitational field strength (m/s^2), R is the radius of the spherical particle (m), ρp is the mass density of the particles (kg/m^3), ρf is the mass density of the fluid (kg/m^3), μ is the dynamic viscosity (kg/(m*s).

Stable or unstable qualitative results have been transformed into a 0 for stable and 1 for unstable. Five tests were found to be stable out of the 12. The chi-square test performed on stability results has shown that the multivariate model chosen was significant for the factor A with *P* value of 0.03881, for the factor B with *P* value 0.03472 and for the interaction effect AB with *P* value 0.01332. The A factor (emulsifier) and the B (thickener) was both positively correlated with stability. However, this experiment plan is optimal for a quantitative response, not for a binary response. In fact, the risks of errors of this model are not fully controlled. This model is probably biased.

Figure 5 illustrates the contour plot at different level of the thickener. At 6% of emulsifier, regardless of the level of the other factors, the emulsion is qualified as a 0. (translating stability to centrifugation). On the other hand, if the emulsifier concentration is lower, it is important that the thickener is at its highest level (1.2%) to ensure stability. This can be explained in the increase in viscosity, which increases the value of the denominator in the Stokes equation. Nor should we overlook the decrease in the size of the droplets obtained by a synergistic effect between the thickener and the emulsifier.

Conclusions

Glucomannan is rarely used in the formulation of cosmetic oil/water emulsion and therefore it remains difficult to provide the adequate concentrations in the case of the development of such products. The experiment design is an effective way to understand the influence of formulation or process factors. In this study, it was possible to demonstrate statistically the positive influence of the thickener on the viscosity and stability of the formulas prepared.

Competing Interests

None.

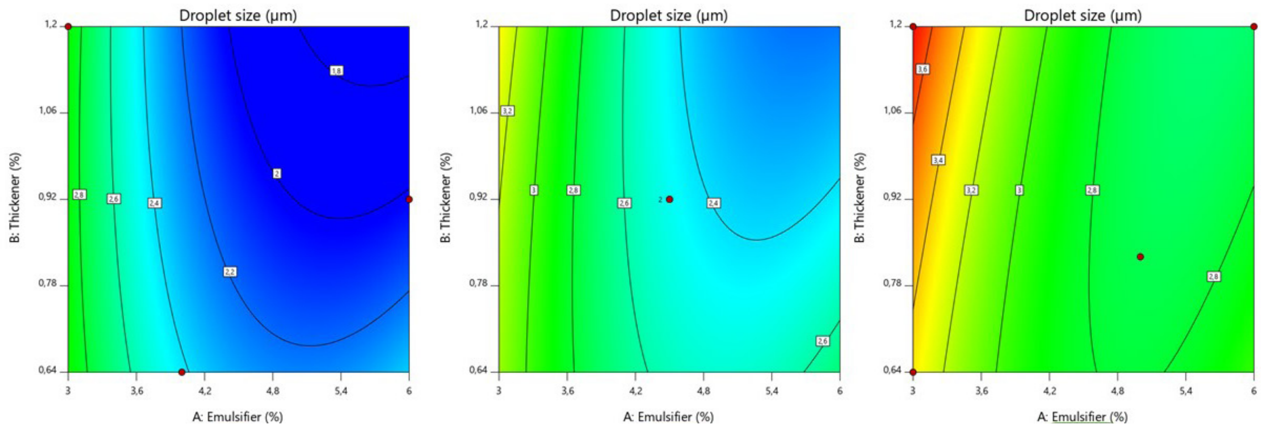

Figure 4. Response surface 2D plots of values of droplet size. (A) 0.64%, (B) 0.92%, (C) 1.2% of thickener.

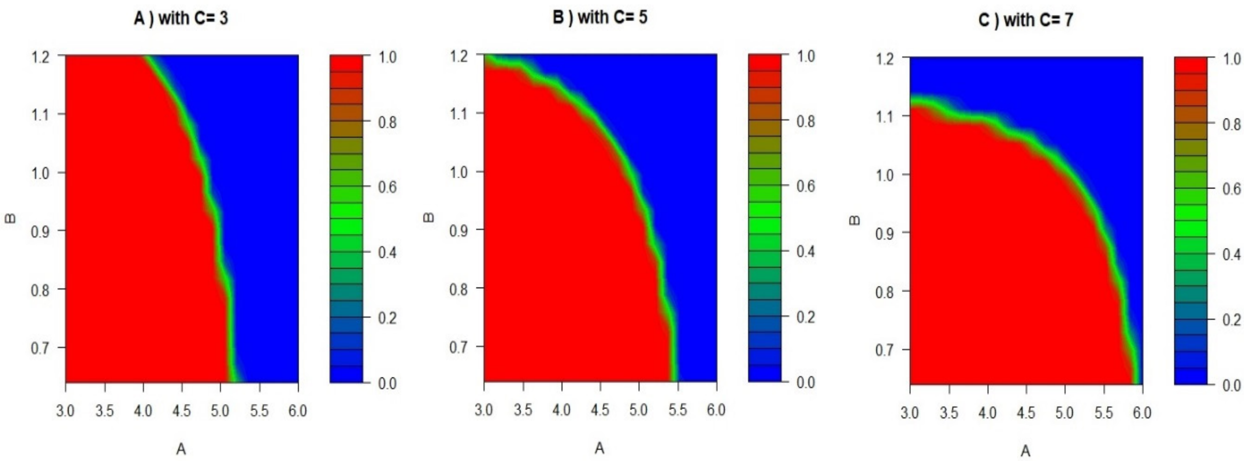

Figure 5. Contour plot of probability values of stability. (A) 3%, (B) 5%, (C) 5% of emollient and A (emulsifier) and B (thickener).

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Founding Sources

None.

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