Research Article

Argan Oleogel: Evaluation of the Effect of the Bentone on Gelling Using a Mixture Design

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ABSTRACT

Oleogels are semisolid systems and consist of a lipophilic liquid phase with a gelling agent. The present study was conducted to demonstrate how the concentration of bentone changes the viscosity of the preparation as the influence of the polar activator included in the composition of the formulae. In our study, a design of experiments approach was tested using a mixture design to evaluate the effects of bentone and ethanol on enhancing viscosity of Argan oil. This viscosity was established by sensory analysis which resulted in a score on a scale from 0 to10. The results showed a significant increase in the viscosity. The analysis of the design space showed that the viscosity of argan oil varies very closely with the concentration of bentone. Formulation of oleogel based on bentone as gellant agent and argan oil seems to improve the viscosity of the formulae.

Keywords: viscosity, argan oil, mixture design, bentone, oleogel.

INTRODUCTION

Cosmetics and several medicinal products are intended to be placed in contact with the various external parts of the human body, or with the teeth and the mucous membranes of the oral cavity. In these cases, they require a consistency suitable for application, and enough viscosity to remain in contact with the application area at least until their objective is achieved. However, ideal topical health care preparations must be easily deformed as a liquid and retain their shape in repose as a solid.[1]

A gel play besides lotions and creams an important role as a vehicle for the topical treatment of the skin. Gels are from a physicochemical point of view dispersed systems. They consist of at least two components: a solid substance, which forms a three dimensional network and a liquid which as a coherent medium is immobilized within the solid matrix, and can be categorized as hydrogels, emulgels, and oleogels or organogels, depending on the polarity of the liquid component.[2]

Oleogels are semisolid systems and consist of a lipophilic liquid phase with a gelling agent. They are a kind of preparations based on vegetable, mineral, or animal oils gelled by gelling agents such as organoclays, silicas.[3] The applications of oleogels were studied in several areas such as organic chemistry, environmental chemistry and also in pharmaceutical and cosmetic fields.[4, 5]

Oleogels are cosmetics themselves because of their lipid composition that serves as a barrier between the skin and the outside ambient. When necessary, they help to regenerate the stratum corneum because of their rich content in fatty acids, which are usually compatible with the epidermis. Nonetheless they are commonly used as vehicles to incorporate active compounds to a therapeutic or cosmetic use.[6]

Organoclays dispersion in organic solvents has been studied for the preparation of the pharmaceutical and cosmetic formulations. Organoclays have several health benefits when applied locally over the skin[1]. Organo-modified-bentonits are mentioned in the literature to be implemented as network forming excipients;[7] they are abundantly used in the production of gels and creams, obtained as colloidal dispersions of clay powders in a given solvent.[8]Organoclays are often used in industry as viscosifers, gelants, oil based paints and coatings, and in waste water treatment, as well as, in pharmaceutical and cosmetic industries[9]may be based on hectorite or bentonits hydrophilic clays (Bentone, claytone) treated with quaternary ammonium.[10, 11]

Bentone organoclays are produced for use in the oil phase. The fatty acid chains attached to the face of clay platelet sallow the dispersion in the organic medium, while edge to edge hydrogen bonding of the platelets (via water bridges) and the interaction of the alkyl chains provide formation for gel structure.[1, 10]

A polar activator is necessary to promote the dispersion process for obtaining stable dispersion by forming gel structure. The function of polar activators is to separate layers from each other and restrict agglomeration in the organic medium. Once these layers are de-agglomerated, they allow the organic groups to free themselves from close association with the clay surface. These organic groups are now free to solvate in the organic liquid.[12]

Argan oil comes from the fruit of the argan tree (argania Spinosa) that naturally grows in Morocco,[13]intended for human consumption but also for therapeutic and cosmetic uses. Various studies, national and international, have shown its many virtues (skin, nutritional, cardiovascular…).[14] Argan oil contains relatively high levels of squalene and α-tocopherol and unsaturated fatty acids, namely oleic and linoleic acids.[15]

In this work, argan oil was used as a lipid phase, and Bentone as a gelling agent. For the formulation of this gel, we based our study on planning experiments. The use of this method of experiments provides predictive models studied responses, and optimal conditions and with minimal testing and maximum credibility.[16]

The viscosity of the gels is evaluated by sensory analysis. The sensory evaluation is a scientific discipline that applies principals of experimental design and statistical analysis to the use of human senses (sight, smell, taste, touch and hearing) for the purposes of evaluating consumer products. It is the most direct method for evaluating and understanding the texture.[17]

The aim of our study is to demonstrate how the concentration of bentone changes the viscosity of the preparation as well as the influence of the polar activator included in the composition of the formulae. Moreover, this study aims to find the most suitable formulation by using a mixture design.

MATERIALS AND METHODS

Instruments and Reagents

An organically modified bentonite, quaternium-18 bentonite supplied by RiedeL-De Haen with, the commercial name of Bentone® 34. The clay powder had a density value of 1,7; Ethanol supplied by Riedel-De Haen had a density value of 0,788. Cosmetic argan oil purchased by Biopur company (Morocco).

The materials used for the preparation were: a stirring and heating plate (VELP scientifica). Thermometer (Brannan, England) weighing machine AA&D Company, limited, graduated burette (Hirschmann techcolor germany), magnetic bar, micropipette of 20-200 µl (Finpepette).

Preparation of the samples

The formulation of oleogels took place in the laboratory of pharmaceutics at the faculty of medicine of pharmacy of Rabat. The oleogels formulation per se consist of the repartition of three components in tubes of 20 ml.

The Bentone powderwas first dispersed thoroughly in anorganic liquid using mixing method. Ethanol asa polar activator is then added and mixing continued.[8]

The first step Bentone powder was first prepared by accurately weighing the appropriate quantity, by adding the exact volume of argan oil with the help of graduated burette in the tubes of 20 ml. The dispersion is submitted to a constant magnetic mixing at 500 rpm.

After 10 min, a solution of ethanol has been added by micropipette precision under the same conditions, which were tried for 10 min.

Experimental design and mathematical modeling

To define the formulation space for the argan oil viscosity, wetested an experimental design by using software Design-Expert® that is a statistical tool that enables calculation for factorial designs and drawing graphs for designevaluation.[18]

In this article, a D-optimal experimental design (mixture design) was selected to evaluate and model the effects of bentone and ethanol on enhancing viscosity of argan oil. This provides maximum information from a limited number of experiments. The studied factors were: the amounts of argan oil ($X1 = A$), Ethanol ($X2 = B$) Bentone® 34 ($X3 = C$).

Viscosity determination and statistical analysis

The sensory qualities of cosmetic products are studied by employing discriminatory or descriptive methods of international renown. The descriptive sensorial profile is the essential tool for this experiment, which allows the evaluation of qualitative and quantitative concerning sensorial characteristics of product panel. The results subsequent to this method allows to elicit a precise sensorial image of this product.[19]

The viscosity score is attributed by sensory analysis just after the gelification of argan oil in ambient temperature according to a scale from zero to 10. Score zero corresponds to an absence of viscosity, however score 10 allows gel consistency.

The statistical analysis of variance, the R-squared, the precision and mathematical modelling of the responses by polynomial equation at day 0, day 5,day 10 and day 15 were carried out by Design Expert.[20]

RESULTS AND DISCUSSION

Viscosity of argan oil

All the mixture experiments were conducted in random order and the Design Expert® Software performed the calculations. The viscosity score results of the 16 mixtures in various ratios of argan oil, bentone and ethanol are shown in Table I.

The variation of organoleptic characteristics

During the jellification process of argan oil with bentone, an alteration from a light cream solution to a brown opaque semisolid preparation was observed. This change of color has been noticed with the increase of the gelling agent concentration (Bentone® 34). After the jellification occurs, there is no significant alteration on the macroscopic aspect of the gel within increasing concentration of bentone, as shown in Figure 1.

Mathematical modeling

Experiments were carried out to determine the mathematical relationship between the factors influencing the performance and the characteristics of the formulation. A second order polynomial regression model represented by a special quadratic equation at D_0, D_5, D_{10} and D_{15} was selected as follows:

Table I: Mixture design of experiments and viscosity results of the 16 mixtures.

Run	X1: Argan oil	X2: Ethanol	X3: Bentone	Y: score Day0	Y: score Day5	Y: score Day10	Y: score Day15
1	95.50	1.50	3.00	1	1	0	0
2	88.83	4.83	6.33	3	3	3	0
3	85.50	6.50	8.00	5	5	5	0
4	90.50	6.50	3.00	2	2	0	0
5	85.50	1.50	13.00	10	10	10	10
6	95.50	1.50	3.00	1	1	0	0
7	90.50	1.50	8.00	5	5	5	5
8	90.50	1.50	8.00	5	5	5	5
9	90.50	4.00	13.00	10	10	10	10
10	85.50	1.50	13.00	10	10	10	10
11	87.17	3.17	9.67	7	7	7	7
12	80.50	6.50	13.00	10	10	10	10
13	80.50	6.50	13.00	10	10	10	10
14	84.25	5.25	10.50	8	9	10	10
15	93.00	4.00	3.00	1	1	0	0
16	90.50	6.50	3.00	2	2	0	0

Run	1	15	4	2	3	7	11	14	5	9	12
Aspect											

Figure 1 : Influence of the concentration on the aspect of oleogels.

$$Y = a1.X1 + a2.X2 + a3.X3 + a12.X1.X2 + a13.X1.X3 + a23.X2.X3$$

Where Y is the score of viscosity prediction of argan oil, a_1, $a_2$and a_3 are the estimated coefficients from the observed experimental values of viscosity for X1 (argan oil), X2 (ethanol), X3 (bentone). The response of argan oil viscosity expressed by a quadratic equation at D_0, D_5, D_{10} and $D_{15}$was as follows:

$$\text{Yday0} = -0{,}01X1 + 2{,}02X2 + 2{,}95X3 - 0{,}01X1X2 - 0{,}002X1X3 - 0{,}06X2X3$$

$$\text{Yday5} = -0.01X1 + 0{,}09X2 + 2{,}95X3 + 1{,}22X1X2 - 0{,}01X1X3 - 0.03X2X3$$

$$\text{Yday10} = -0{,}04X1 - 4{,}90X2 + 0.08X3 + 0{,}05X1X2 + 0{,}01X1X3 + 0{,}06X2X3$$

$$\text{Yday15} = -0{,}01X1 - 9{,}35X2 + 5{,}72X3 + 0{,}1X1X2 - 0{,}05X1X3 + 0{,}05X2X3$$

With viscosity score, mixtures were designed by Design Expert® to explore the feasibility zone presenting the maximum viscosity score for argan oil. Figures 2, 3, 4 and 5 represent the experimental domain inside the ternary diagrammatic different days.

These equations predict the score of viscosity of the Argan oil in experimental domain. Also the variation of the score of viscosity coefficient during 15 days.

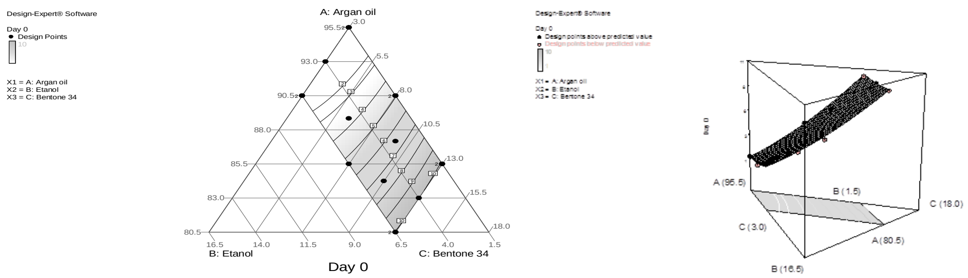

Figure 2: Contours plots and surface plots of estimated viscosity score of argan oil at Day 0.

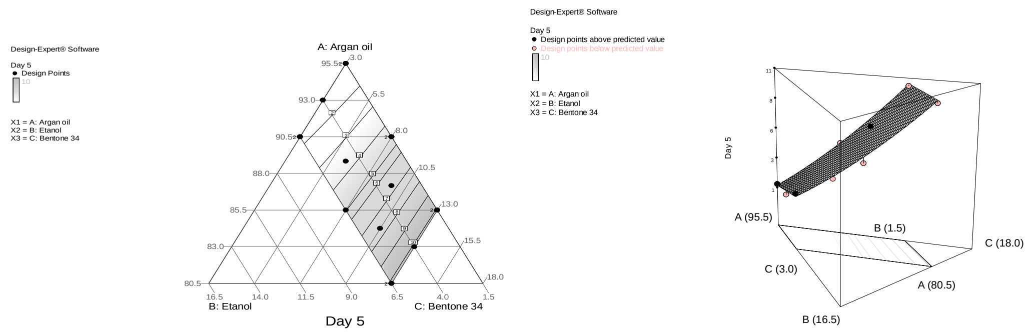

Figure 3: Contours plots and surface plots of estimated viscosity score of argan oil at Day 5.

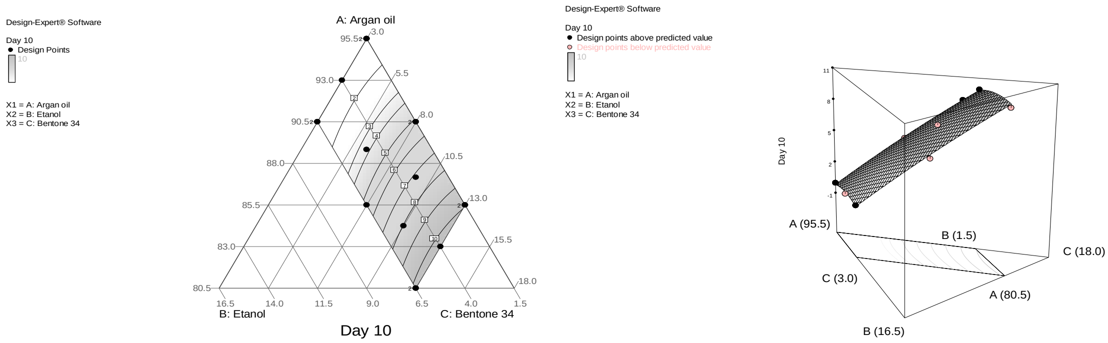

Figure 4: Contours plots and surface plots of estimated viscosity score of argan oil at Day 10.

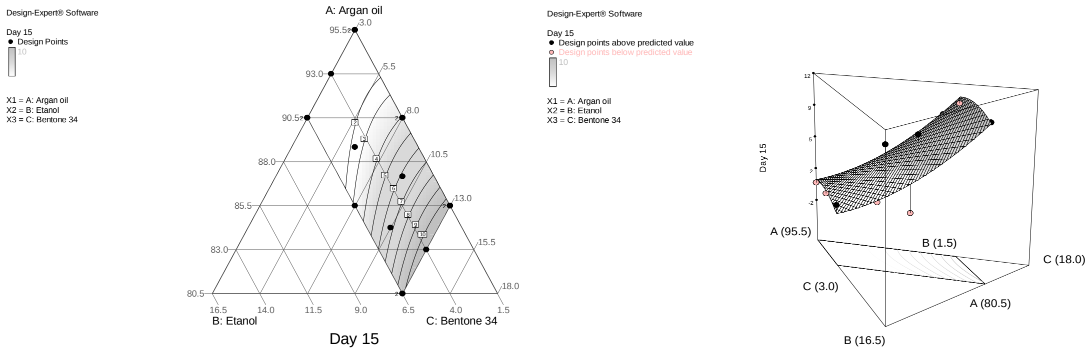

Figure 5: Contours plots and surface plots of estimated viscosity score of argan oil at Day 15.

Table II: Significance of the results and mathematical model used.

	Mathematical model	$F_{0,05}$	P value	Significance for alpha at 5%	R-squared (R^2)	Precision
D_0	Quadratic	281.17	<0,0001	Significant	0.9929	39.782
D_5	Quadratic	120.72	<0,0001	Significant	0.9873	26.049
D_{10}	Quadratic	107.92	<0,0001	Significant	0.9818	24.156
D_{15}	Quadratic	19.15	<0,0001	Significant	0.9055	10.952

Statistical analysis

The statistical significance of the model has been evaluated by using the analysis of variance (ANOVA). It is a statistical technique which subdivides the total variation in a set of data in linked components for the aim of testing the hypotheses on the model parameters[21]. Table II shows the results of the ANOVA.

Score F is a link of two independent estimations for the experimental error. Associated to this report, the value of the probability P quantifies the probability of making a mistake by linking an effect with a given factor. This score also provides the exact level of the significant of hypothesis test. The results show that the model is very significant evidence, the same as score F ($F_{D0\ model}$= 281,17 $F_{D5\ model}$=120.72 $F_{D10\ model}$ =107.92 and $F_{D15\ model}$=19.15) and low probability score (p<0,0001). The low probability score indicates that the model is considered statistically significant.[22]Values under 0.05 % were considered statistically significant. The R-squared beyond 0.90 is in reasonable agreement. Precision measurements of the signal to noise ratio should be greater than 4our ratios are beyond 10.95.

Model and results analysis

The significance of the statistical analysis at D_0, $D_{5,}$ D_{10} andD_{15} shows that the responses of viscosity are modeled successfully. However, this indicates that if the colloidal structures have been contaminated, statistical analysis could not be significant and the signal will be disturbed by noises.

These experiments show an improvement of viscosity by reaching the score 10 with run 5, 9, 10, 12 and 13. For these runs, the gelling agent percentage (bentone®34) is 13% representing therefore the maximum value for obtaining a gel of score 10. In comparison with the runs with a lowest score1, the Bentone®34 percentage is reduced to 3%; this result is observed with the runs 1, 6 and 15.

It is observed that the degree of gel stability and viscosity of this argan oil–organoclay dispersion increased with the increase of bentone concentration from 3 to 13 %. As explained earlier, the magnitude of interaction between argan oil and quaternary ammonium cations increases with the increase of the concentration of bentone in the dispersions. Therefore, the bentone contributes, to a bigger formula stability by increasing its viscosity.

When polar molecules, such as ethanol, are added to the organoclay suspension, there is an additional contribution to the viscosity of the dispersion as a consequence of the production of a new internal phase.[23]
Increasing the proportion of the bentone and ethanol together is in favor of higher viscosity as the optimum composition (figures 2, 3, 4 and 5), which permitted to gellify the argan oil, contains the maximum of bentone in our matrix.

Considering the coefficients a_1 (argan oil), a_2 (ethanol) and a_3 (bentone) given by our model's viscosity equation at day0, it has been noticed that a_3 are the coefficient that affects the most argan oil viscosity. How ever, high values of viscosity are observed with high proportions of bentone.

Taking into account that organo bentonites are clays partially covered by alkyl ammonium molecules adsorbed at their surface, the structure and, consequently, the flow behaviour of these dispersions may be related to the interactions developed between the organophilic ions and the solvent, the organic chain density between platelets and the chemical nature of the medium. These interactions, which normally increase with clay concentration, lead to an increase in viscosity, as it has been pointed out above.[24]

The analysis by infrared spectroscopy (Figure 6) confirmed the presence of alkyl ammonium ions in bentone®34 by cation exchange. Characteristic bands intercalated surfactant (valence vibration bands of the methylene group (CH2) of the long chain to 2921cm-1 and 2849cm-1) showing the effectiveness of the cation exchange. Thus the alkyl chains were easily to enwind each other, resulting physical attraction. In addition, oil molecules would also intercalate into the inter space. Finally, bentone /argan oil gel formed and the viscosity and gel strength of the system increased.[25]

The weakest score value of our matrix was observed with run 1 and run 6 that contain a lower limit of bentone 3% and ethanol 1,5%.

The analysis of model 3D shows a correlation between bentone's concentration and ethanol in the formula and

the improvement of dispersion's viscosity; however, this impact becomes no more significant for a certain level of each component, we can consider the existence of an optimum essay of bentone.

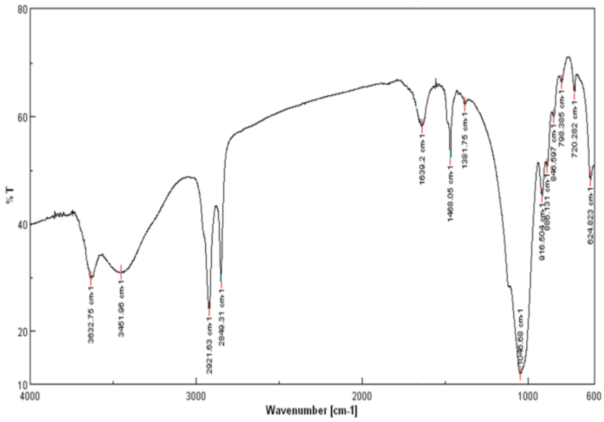

Figure 6: Infra red spectra of bentone®34.

Ripening process

After 10 days, and starting from bentone 34 « run number14 » concentration, we have observed an increase of viscosity as shown by figure 4. This leads to the assumption that the remaining free platelets take more time to find a disposable site in the structure.

The obtained gel during the sol-gel transition still contains an important fraction reactive group. So it could continue to develop, especially, by the condensation reactions between the nearby groups. The formation of these new groups of links increases the reticulation degree of gel, as shown by the increase of viscosity score « run number 14».[26] Gelificationresultsfrom the formation of small particles, which grow in number and size and then join together to fill the available space. Ripening takes place through adissolution/reprecipitation mechanism.

Syneresis phenomenon

The increase of gelification is represented by a gel rigidication; with the ultimate stage, the syneresis phenomenon produces the contraction of the gel and exudation of a part in the liquid phase. This phenomenon has been observed in following runs: 1, 2, 3, 4, 6, 15 and 16.

Syneresis of oil from the formed gel is a natural phenomenon during which unbound excess oil comes out from the formed gel matrix. This is an undesirable phenomenon, which can be reduced by the selection of appropriate concentration of bentone.

As expected, syneresis decreased with an increase in bentone concentration for all these gels: 5, 7, 8, 9, 10, 11, 12, 13 and 14; this phenomenon was significant at a concentration of 3%.

Prediction point

The prediction by the model of a better viscosity of argan oil gel gave additional points. The proportions of the various components bringing the maximum of viscosity are: argan oil (82, 30%), ethanol (5, 30%) and bentone 34(12, 40%).

CONCLUSION

The mixture experimental design indicates clearly that concentration of bentone determines the viscosity of the studied argan oil. The influence of variable concentration is a key criterion in order to define conditions to have adequate viscosity.

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