ORIGINAL ARTICLE

Oleogels based on Vegetable Oil and Synthetic Oil: Evaluation of the Effect of the Bentone on Gelling using a Mixture Design

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Abstract

Introduction: Oleogels are semisolid systems consisting on a lipophilic liquid phase with a gelling agent. **Aim:** The aim of our study is to demonstrate how the concentration of Bentone modifies the viscosity of the preparation as well as the influence of the polar activator included in the composition of the formulas. Moreover, this study aims to find the most appropriate formulation from the results obtained using a mixture design. **Settings and Design:** To define the formulation space for the oil viscosity, we tested an experimental design using software Design-Expert®. **Subjects and Methods:** 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 using two categories of oils: Natural vegetables oils and synthetic oils. This viscosity was established by sensory analysis which resulted in a score on a scale from 0 to10. **Statistical Analysis Used:** The statistical significance of the model has been evaluated by using the analysis of variance. **Results:** The results showed a significant increase in the viscosity. The analysis of the design space showed that the viscosity of different oils varies very closely with the concentration of bentone. Formulation of oleogel based on bentone as gelling agent and oils seems to improve the viscosity of the formula. **Conclusion:** The mixture experimental design indicates clearly that the concentration of bentone determines the viscosity of the studied oils. The influence of variable concentration is a key factor to define conditions to have adequate viscosity.

Key words: Bentone, gelification, mixture design, oleogel, vegetable oil, viscosity

INTRODUCTION

Oleogels have shown promise in edible applications as alternatives to conventional fats.[1] Oleogels have a proven potential in many fields such as environmental chemistry, the pharmaceutical, and cosmetics industries, because the microstructure of oleogels is characterized by permanent rigid networks or transient semi-flexible meshes and both thermo-reversible. This provides a consistency which is suitable for the application, and a sufficient viscosity to remain in contact with the application zone at least until their objective is reached.

Oleogels are gel systems obtained with a gelling agent and a hydrophobic liquid. Interest in this field has increased due to the strikingly rise of the discovery of substances that are able to gel organic solvents.[2]

Organogels are a system composed of an organic liquid and a gelling agent. The organogel classification can be based on the nature of the organic liquids, gelling agents used as well as their intermolecular interactions.[3]

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Organoclays, organically modified montmorillonites/smectites, are being extensively used as rheological modifier agent in a number of applications such as paints, inks, adhesives, greases, and varnishes, as well as in cosmetics, and medicines. The adsorption of organic liquids/media, swelling and thixotropic gel forming ability/behavior of organoclays has been widely studied.[4] They have several health benefits when applied locally over the skin.[5]

Bentone organoclays are produced for use in the oil phase. The fatty acid chains attached to the surface of clay platelet sallow the dispersion in the organic medium, while edge to edge hydrogen bonding of the platelets (through water bridges) and the interaction of the alkyl chains provide formation for gel structure.[5,6]

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.[7]

In vegetable oils, viscosity increases with chain lengths of triglycerides fatty acids and decreases with unsaturation in other words, increase with hydrogenation. Therefore, viscosity is a function of molecules dimension and orientation.[8]

In this work, we chose to work with two categories of oils that have a great presence in the field of cosmetology and pharmacology: The class of natural vegetable oils represented by: Olive oil, castor oil, cade oil, and cottonseed oil; and the class of synthetic oils represented by: Vaseline oil, paraffin oil, and silicone oil.

Both categories of the study represent the liquid phase, and Bentone as a gelling agent. For the formulation of this gel we were based on a planning experiment.

Using this kind of method in experiment provides predictive models, studied responses, and optimal conditions with minimal testing, and maximum credibility.[9-11]

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, and hearing...) for the purposes of evaluating consumer products. It is the most direct method for evaluating and understanding the texture.[12]

The aim of our study is to demonstrate how the concentration of Bentone modifies the viscosity of the preparation as well as the influence of the polar activator included in the composition of the formula. Moreover, this study aims to find the most appropriate formulation from the results obtained using a mixture design.

SUBJECTS AND METHODS

It is an observational and comparative study that aims to evaluate the effect of Benton on oils and compare the profile of natural and synthetics oils.

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.

Vegetables oils: Olive oil was purchased by SOMAPROL Company (Morocco), Cade oil was purchased by COOPER MAROC Company (Morocco), Castor oil was purchased by APOTHICAIRES Company (Morocco), and Cotton seeds oil was purchased by SIGMA-ALDRICH Company (Germany).

Synthetic oil: Vaseline oil was purchased by SOMAPROL Company (Morocco), paraffin oil was purchased by COOPER MAROC Company (Morocco), and silicone oil was purchased by PROLABO Company (France).

The tools used for our preparation were: A stirring and heating plate (VELP scientifica), Thermometer (Brannan, England) weighing machine AA&D Company, limited, graduated burette (Hirschmanntech color Germany), magnetic bar, micropipette a 20–200 µl (Finpepette). All those tools were calibrated.

The software Design Expert was used for the experimental design and statistical tools.

Preparation of the samples

The formulation of oleogels took place in the laboratory of galenic chemistry at the faculty of medicine of pharmacy of rabat. The oleogels formulation *per se* consists of the repartition of three components in tubes of 20 ml.

The Bentone powder was first dispersed thoroughly in an organic liquid using mixing method. An activator polar is then added and mixing continued.[13]

First, Bentone powder was prepared by accurately weighing the appropriate quantity, by adding the exact volume of oil using a graduated burette in the tubes of 20 ml. The dispersion was submitted to a constant magnetic mixing at 500 rpm and 100°C during 10 min. Note that room temperature is increasing from 25°C to 40°C.

Second, after 10 min, a solution of ethanol has been added using micropipette precision inside the initial mixture respecting the same conditions. The new mixture will continue with the same method of agitation during 10 additional min.

Experimental design and mathematical modeling

To define the formulation space for the oil viscosity, we tested an experimental design by using software Design-Expert® that is a statistical tool that enables calculation for factorial designs and drawing graphs for design evaluation.[10,14]

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

To make this experimental design, the lower and upper limits of components were previously fixed [Table 1].

Viscosity determination

The sensory qualities of cosmetic products are studied using discriminatory or descriptive methods which are internationally well known. The sensorial descriptive profile is the essential tool for this experiment, which allows both qualitative and quantitative evaluation of the sensorial characteristics of product panel. The results subsequent to this method allow eliciting a precise sensorial image of this product.[15]

The viscosity score is attributed just after the gelification of oil in an ambient temperature, according to a scale from 0 to 10. Score 0 corresponds to an absence of viscosity, while the score 10 is equivalent to the gel consistency.

Table 1: Mixture design of experiments

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

Statistical analysis

Design Expert software is a statistical tool that permits the calculation of factorial designs and drawing graphs for design evaluation. It can handle many models of experimental design, such as factorial or mixture design. The statistical analysis of variance (ANOVA), the R-squared, the precision and mathematical modeling of the responses by polynomial equation at day 0, day 5, day 10, and day 15 which were carried out by Design Expert.[10,16]

RESULTS

Viscosity of oils

All the oils tested gave a good gelation except the silicone oil which did not give gelling with the Bentone, which will not be treated in the statistical analysis.

All the mixture experiments were conducted in a random order and the Design Expert® Software performed the calculations. The viscosity score results of the 16 mixtures in various ratios of oil, Bentone, and ethanol are shown in Tables 1 and 2.

With viscosity score, mixtures were designed by Design Expert® to explore the feasibility zone, presenting the maximum viscosity score for all oils.

Figures 1–7 represent the experimental domain inside the ternary diagram at different days.

Mathematical modeling

Experiments were carried out to determine the mathematical relationship between the factors influencing the performance and the characteristics of the formulation. A first-order polynomial regression model represented by a linear equation was selected as follows:

$$Y = a1X1+a2X2+a3X3$$

Where Y is the score of viscosity prediction of oils, a1, a2, and a3 are the estimated coefficients from the observed experimental values of viscosity for X1 (oils), X2 (ethanol), and X3 (Bentone). The responses of oils viscosity expressed by the linear equation at day 0, day 5, day 10, and day 15 were as follows.

Olive oil

$Y \text{ day } 0 = -0.008X1-0.07\,X2+0.82X3$
$Y \text{ day } 5 = -0.01X1+0.09X2+0.84X3$
$Y \text{ day } 10 = -0.01X1-0.08X2+0.94X3$
$Y \text{ day } 15 = -0.02X1+0.03X2+1.00X3$

Table 2: Viscosity results of the 16 mixtures

Run	Olive oil				Cade oil				Castor oil				Cotton seeds oil			
	Y: score Day 0	Y: score Day 5	Y: score Day 10	Y: score Day 15	Y: score Day 0	Y: score Day 5	Y: score Day 10	Y: score Day 15	Y: score Day 0	Y: score Day 5	Y: score Day 10	Y: score Day 15	Y: score Day 0	Y: score Day 5	Y: score Day 10	Y: score Day 15
1	2	2	0	0	0	0	0	0	4	4	0	0	0	0	0	0
2	2	2	4	4	2	4	0	0	6	6	0	0	2	2	0	0
3	4	8	8	8	6	6	6	7	8	8	8	8	2	2	0	0
4	4	4	0	0	0	0	0	0	6	6	0	0	0	0	0	0
5	10	10	10	10	10	10	10	10	9	9	8	8	10	10	10	10
6	4	4	4	0	2	2	0	0	4	4	0	0	0	0	0	0
7	4	4	6	6	8	8	8	8	8	8	8	8	4	4	0	0
8	4	4	6	6	8	8	4	4	4	4	4	0	4	4	6	6
9	10	10	10	10	10	10	10	10	8	8	9	9	10	10	10	10
10	10	10	10	10	10	10	10	10	9	8	8	8	10	10	10	10
11	10	10	10	10	8	8	8	8	8	8	8	8	4	6	6	6
12	10	10	10	10	10	10	10	10	9	10	10	10	10	10	10	10
13	10	10	10	10	10	10	10	10	9	10	10	10	10	10	10	10
14	8	10	10	10	10	10	10	10	4	4	6	6	8	10	10	10
15	0	0	0	0	0	0	0	0	2	2	0	0	2	0	0	0
16	0	0	0	0	0	0	0	0	2	2	0	0	0	0	0	0

Run	Vaseline oil				Paraffine oil				Silicone oil			
	Y: score Day 0	Y: score Day 5	Y: score Day 10	Y: score Day 15	Y: score Day 0	Y: score Day 5	Y: score Day 10	Y: score Day 15	Y: score Day 0	Y: score Day 5	Y: score Day 10 5	Y: score Day 1
1	0	0	0	0	0	0	0	0	4	0	0	0
2	2	0	0	0	10	10	10	10	6	0	0	0
3	10	10	10	10	10	10	10	10	6	0	0	0
4	2	0	0	0	8	8	8	0	4	0	0	0
5	8	10	10	10	4	0	0	0	0	0	0	0
6	2	0	0	0	0	0	0	0	4	0	0	0
7	2	0	0	0	0	0	0	0	6	0	0	0
8	2	0	0	0	10	10	10	10	6	0	0	0
9	10	10	10	10	10	10	10	10	4	0	0	0
10	10	10	10	10	4	0	0	0	0	0	0	0
11	10	10	10	10	4	4	0	0	6	0	0	0
12	10	10	10	10	10	10	10	10	6	0	0	0
13	10	10	10	10	10	10	10	10	6	0	0	0
14	10	10	10	10	10	10	10	10	6	0	0	0
15	0	0	0	0	0	0	0	0	4	0	0	0
16	0	0	0	0	4	4	0	0	4	0	0	0

Cade oil

Y day 0 = −0.01X1–0.23 X2+0.98X3
Y day 5 = −0.01X1–0.20X2+0.96X3
Y day 10 = −0.03X1–0.07X2+1.02X3
Y day 15 = −0.03X1–0.03X2+1.01X3

Castor oil

Y day 0 = 0.02X1+0.03 X2+0.51X3
Y day 5 = 0.01X1+0.13X2+0.52X3
Y day 10 = −0.02X1+0.06X2+0.89X3
Y day 15 = −0.03X1+0.18X2+0.88X3

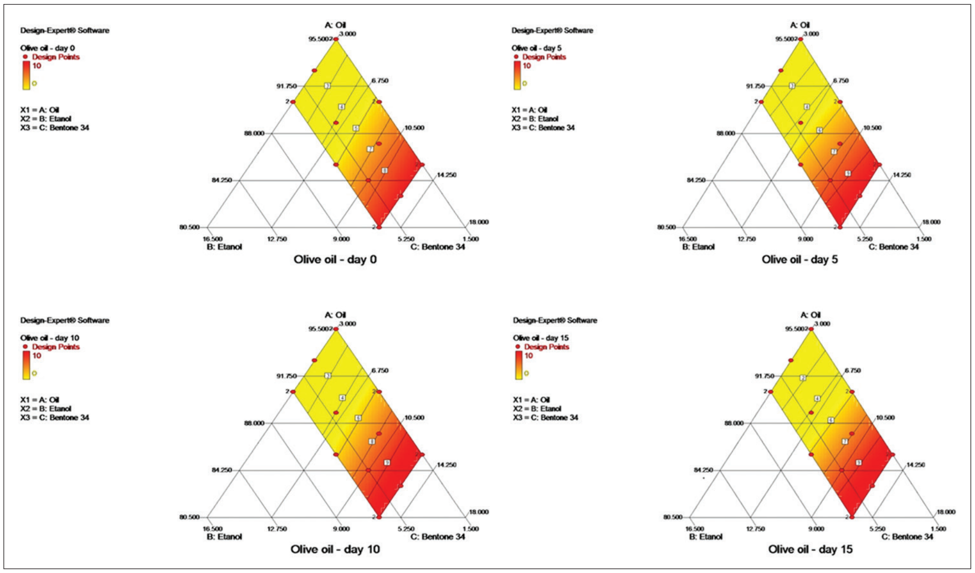

Figure 1: Contours plots and surface plots of estimated viscosity score of olive oil at day 0, day 5, day 10, and day 15

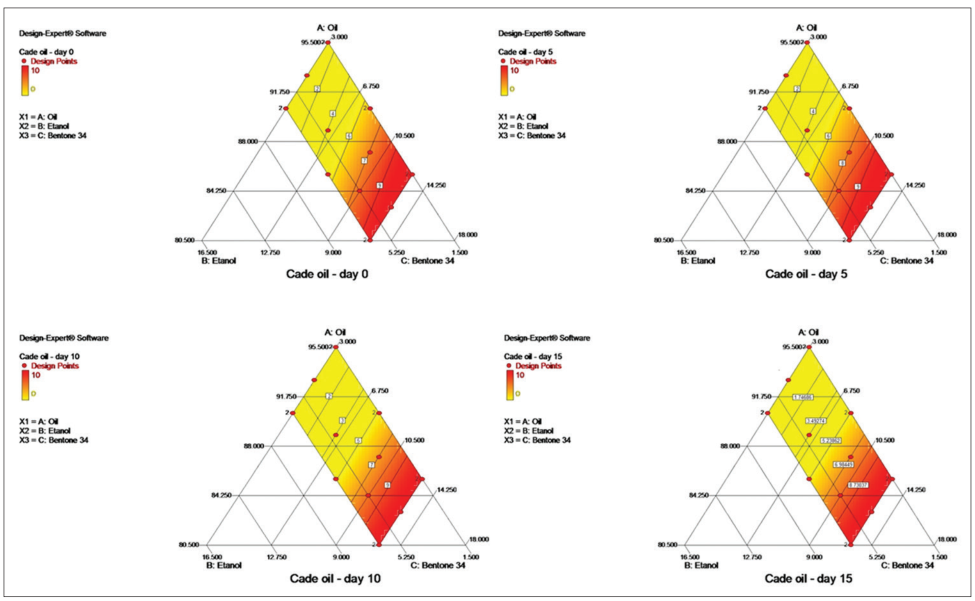

Figure 2: Contours plots and surface plots of estimated viscosity score of cade oil at day 0, day 5, day 10, and day 15

Cotton seed oil

Y day 0 = −0.03X1–0.04X2+0.93X3
Y day 5 = −0.03X1–0.03X2+0.99X3
Y day 10 = −0.03X1–0.07X2+1.00X3
Y day 15 = −0.03X1–0.07X2+1.00X3

Vaseline oil

Y day 0 = −0.03X1+0.41 X2+0.89X3
Y day 5 = −0.05X1+0.43X2+1.01X3
Y day 10 = −0.05X1+0.43X2+1.01X3
Y day 15 = −0.05X1+0.43X2+1.01X3

Paraffin oil

Y day 0 = −0.02X1+1.15X2+0.46X3
Y day 5 = −0.03X1+1.42X2+0.31X3
Y day 10 = −0.03X1+1.31X2+0.36X3
Y day 15 = −0.04X1+1.01X2+0.51X3

Statistical analysis

The statistical significance of the model has been evaluated using the 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 hypothesis on the model parameters.[10-17]

Table 3 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 significance of test hypothesis. The low

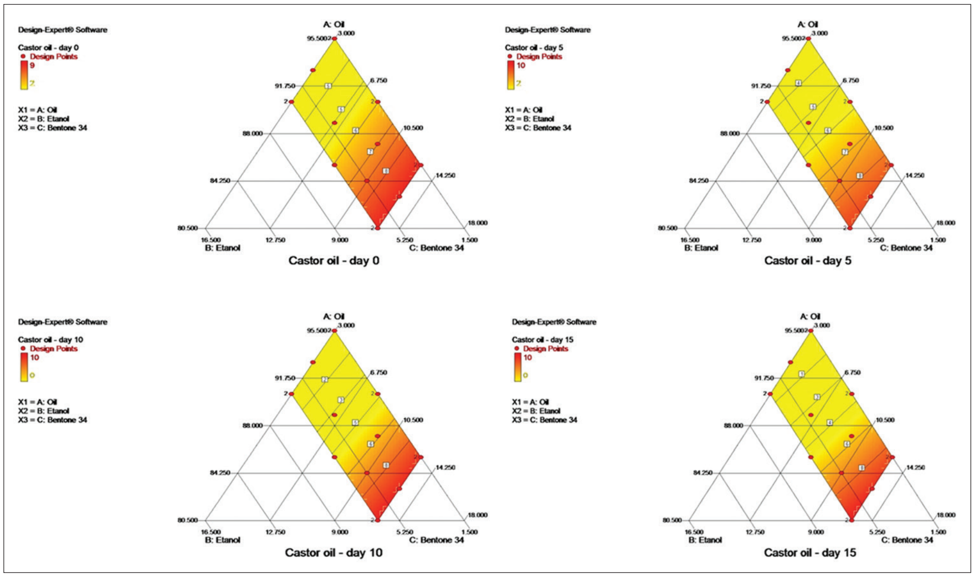

Figure 3: Contours plots and surface plots of estimated viscosity score of castor oil at day 0, day 5, day 10, and day 15

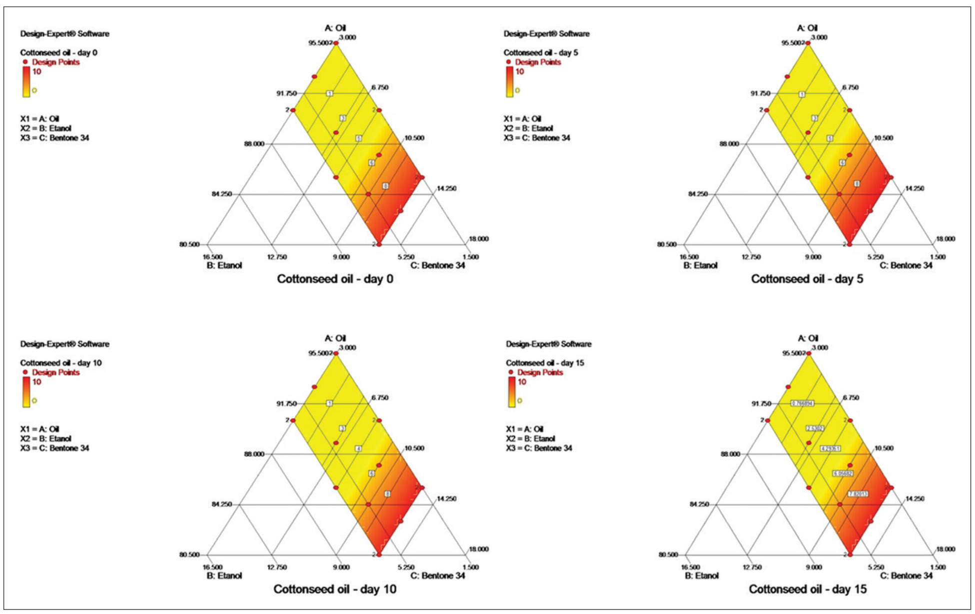

Figure 4: Contours plots and surface plots of estimated viscosity score of cottonseed oil at day 0, day 5, day 10, and day 15

probability score indicates that the model is considered statistically significant.[10-18]

The results show that the model is very significant, except for silicone oil (absence of gelification).

DISCUSSION

For all experiments of different oils, the significance of the statistical analysis at day 0, day 5, day 10, and day 15 shows that the responses of viscosity are modelled successfully. However, this also indicates that if the colloidal structures have been contaminated, statistical analysis could not be significant and the signal will be disturbed by noises.

The results obtained made it possible, first, to see the evolution of the viscosity of the gels in function of the Bentone concentration, and second to analyze several phenomena such as the syneresis phenomenon and the Ripening process, and also to deduce the prediction, by the model of a better viscosity for the different oils studied, and finally, to provide a general prediction point of the proposed matrix.

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.

The ripening process is explained by the fact that the gel obtained during the sol-gel transition still contains a large

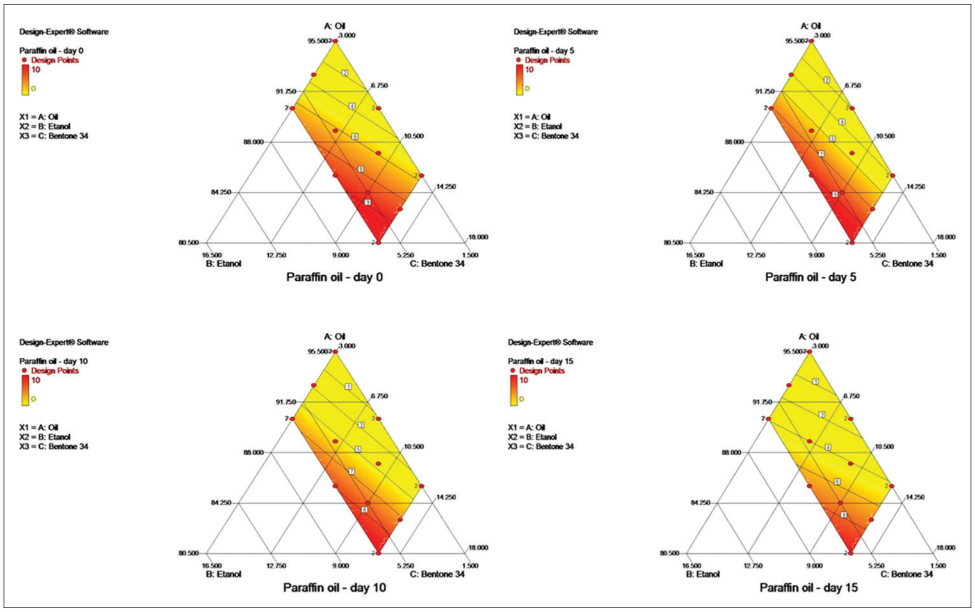

Figure 5: Contours plots and surface plots of estimated viscosity score of paraffin oil at day 0, day 5, day 10, and day 15

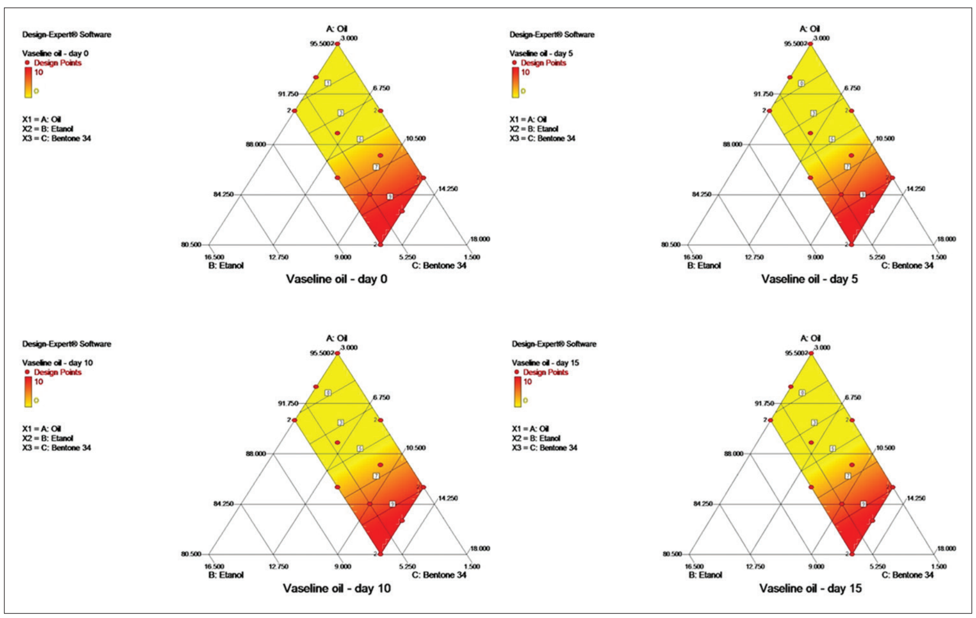

Figure 6: Contours plots and surface plots of estimated viscosity score of vaseline oil at day 0, day 5, day 10, and day 15

fraction of the reactive group and therefore it could continue to develop, in particular, by the condensation reactions between the neighbors groups. The development of these new binding groups increases the degree of cross-linking of the gel, as shown by the increase in the viscosity score of several points.[19] Gelification results from the development of small particles, which grow in number and size, and then join and fill the available space. Ripening takes place through a dissolution/reprecipitation mechanism.

Olive oil

These experiments show an improvement of viscosity by reaching the score 10 with run 5, 9, 10, 11, 12, 13, and 14. For these runs, the gelling agent percentage (Bentone®34) is between 10% and 13% representing, therefore, the maximum value for obtaining a gel of score 10. In comparison with the runs with a lowest score 0, the Bentone®34% is reduced to 3%; this result is observed with the runs 1, 6, 15, and 16.

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

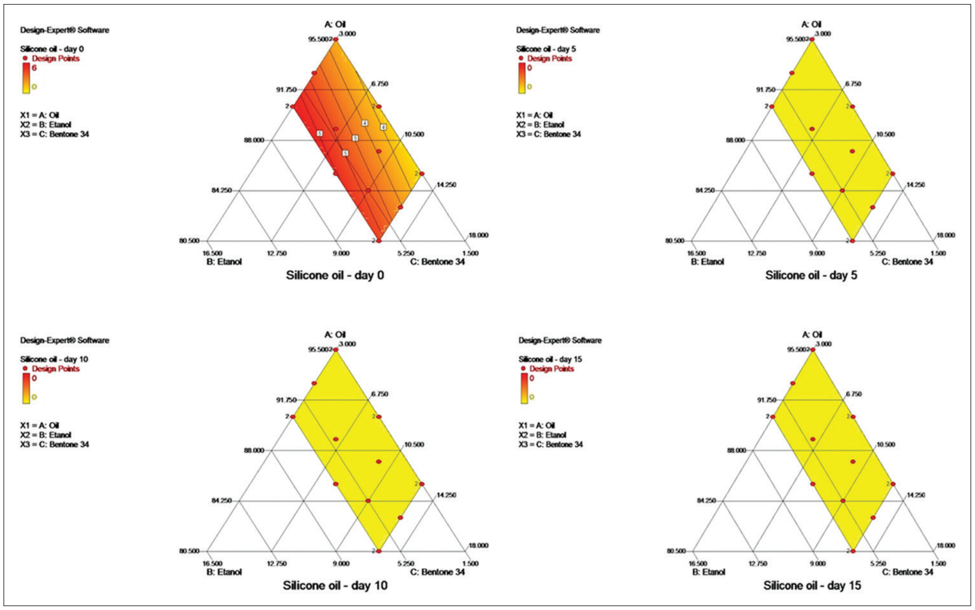

Figure 7: Contours plots and surface plots of estimated viscosity score of silicone oil at day 0, day 5, day 10, and day 15

As shown in Figure 1, the higher proportion of Bentone and Ethanol, the better the viscosity. The optimal mixture consists of 10% of Bentone as seen in our matrix.

Ripening process

After 5 days, and starting from Bentone "run number 3 and run number 14" concentration, we have observed an increase of viscosity as shown by Figure 1. This leads to the assumption that the remaining free platelets take more time to find a disposable site in the structure.

Syneresis phenomenon

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

As expected, the syneresis decreased with an increase in Bentone concentration for all these gels: 2, 3, 5, 7, 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 olive oil gel gave additional points. The proportions of the various components bringing the maximum of viscosity are: Olive oil (83.50%), ethanol (4.50%), and Bentone® 34 (12%).

Cade oil

These experiments show an improvement of viscosity by reaching the score 10 with run 5, 9, 10, 12, 13, and 14. 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 score 0, the Bentone®34% is reduced to 3%; this result is observed with the runs 1, 2, 4, 6, 15, and 16.

It is observed that the degree of gel stability and viscosity of this cade oil - organoclay dispersion increased with the increase of Bentone concentration from 3% to 13%. As explained earlier, the magnitude of interaction between cade 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.

As shown in Figure 2, the higher proportion of Bentone and ethanol, the better the viscosity. The optimal mixture consists of 13% of Bentone as seen in our matrix.

Ripening process

After 15 days, and starting from Bentone 34 "run number 3" concentration, we have observed an increase of viscosity as shown by Figure 2. This leads to the assumption that the remaining free platelets take more time to find a disposable site in the structure.

Syneresis phenomenon

In the run number 8, although we notice a degradation of the gelification in the time, we are not able to observe a syneresis phenomenon, and this is due to the color and organoleptic aspect of the mixture.

Prediction point

The prediction by the model of a better viscosity of cade oil gel gave additional points. The proportions of the various

Table 3: Significance of the results and mathematical model used for oils

Oil	Day	$F_{0,05}$	*P* value	Significance for alpha at 5%	R^2	Precision	Mathematical model
Olive oil	Day 0	30.42	<0.0001	Significant	0.8239	11.590	Linear
	Day 5	27,87	<0.0001	Significant	0.8108	11,335	
	Day 10	53.80	<0.0001	Significant	0.8922	15.386	
	Day 15	91.01	<0.0001	Significant	0.9333	19.817	
cade oil	Day 0	80.93	<0.0001	Significant	0.9256	20.049	
	Day 5	95.64	<0.0001	Significant	0.9363	21.596	
	Day 10	65.84	<0.0001	Significant	0.9101	16.717	
	Day 15	60.17	<0.0001	Significant	0.9025	15.715	
Castor oil	Day 0	11.08	<0.0001	Significant	0.6303	6.808	
	Day 5	11.30	<0.0001	Significant	0.6348	7.522	
	Day 10	36.03	<0.0001	Significant	0.8471	12.703	
	Day 15	25.24	<0.0001	Significant	0.7951	11.291	
Cotton seeds oil	Day 0	74.53	<0.0001	Significant	0.9197	17.597	
	Day 5	100.56	<0.0001	Significant	0.9392	20.297	
	Day 10	30.43	<0.0001	Significant	0.8239	11.324	
	Day 15	30.48	<0.0001	Significant	0.8239	11.324	
Vaseline oil	Day 0	27.90	<0.0001	Significant	0.8110	12.824	
	Day 5	24.11	<0.0001	Significant	0.7876	11.838	
	Day 10	24.11	<0.0001	Significant	0.7876	11.838	
	Day 15	24.11	<0.0001	Significant	0.7876	11.838	
Paraffin oil	Day 0	9.66	<0.0001	Significant	0.5978	8.592	
	Day 5	7.91	<0.0001	Significant	0.5489	7.286	
	Day 10	5.38	<0.0001	Significant	0.4526	6.197	
	Day 15	4.63	<0.0001	Significant	0.4159	5.998	

components bringing the maximum of viscosity are: Cade oil (83.5%), ethanol (4.2%), and Bentone® 34 (12.3%).

Castor oil

These experiments show an improvement of viscosity by reaching the score 9 with run 5, 9, and 10, and the score 10 with run 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 9 and 10. For the runs 10, the polar activator (ethanol) represents 6.5%, whereas it represents 1.5% for the runs of score 9.

In comparison with the runs with a lowest score 0, the Bentone percentage is reduced to under 8%; this result is observed with the runs 1, 2, 4, 6, 8, 15, and 16.

It is observed that the degree of gel stability and viscosity of the cade oil - organoclay dispersion increased with the increase of Bentone concentration from 8% to 13% with a small influence of the polar activator. As explained earlier, the magnitude of interaction between castor 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. The polar activator provides an additional contribution to the viscosity of the dispersion and consequently the creation of a new internal phase.[20]

As shown in Figure 3, the higher proportion of Bentone and ethanol, the better the viscosity. The optimal mixture consists of 13% of Bentone as seen in our matrix.

Ripening process

After 10 days, and starting from Bentone "run number 9 and run number 14" concentration, we have observed an increase of viscosity as shown by Figure 3. This leads to the assumption that the remaining free platelets take more time to find a disposable site in the structure.

Syneresis phenomenon

The increase of gelification is represented by a gel rigidification; 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, 4, 6, 8 15, and 16. As expected, syneresis decreased with an increase in Bentone concentration for all these gels: 3, 5, 7, 9, 10, 11, and 14 this phenomenon was significant at a concentration of 3%.

Prediction point

The prediction by the model of a better viscosity of castor oil gel gave additional points. The proportions of the various components bringing the maximum of viscosity are: Castor oil (80, 50%), ethanol (6.50%), and Bentone 34 (13%).

Cotton seeds oil

These experiments show an improvement of viscosity by reaching the score 10 with run 5, 9, 10, 11, 12, 13, and 14. For these runs, the gelling agent percentage (Bentone®34) is between 10.5 and 13% representing, therefore, the maximum value for obtaining a gel of score 10. In comparison with the runs with a lowest score 0, the Bentone®34% is reduced to 3%; this result is observed with the runs 1, 6, 15, and 16.

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

As shown in Figure 4, the higher proportion of Bentone and ethanol, the better the viscosity. The optimal mixture consists of 13% of Bentone as seen in our matrix.

Ripening process

After 10 days, and starting from Bentone 34 "run number 8, run number 11, and run number 14" 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.

Syneresis phenomenon

The increase of gelification is represented by a gel rigidification; 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: 2, 3, 7, and 15.

Prediction point

The prediction by the model of a better viscosity of cotton seeds oil gel gave additional points. The proportions of the various components bringing the maximum of viscosity are: Cotton seeds oil (83.2%), ethanol (4.2%), and Bentone 34 (12.6%).

Vaseline oil

These experiments show an improvement of viscosity by reaching the score 10 with run 3, 5, 9, 10, 12, 11, 13, and 14. For these runs, the gelling agent percentage (Bentone®34) is between 8% and 13% representing, therefore, the maximum value for obtaining a gel of score 10. In comparison with the runs with a lowest score 0, the Bentone®34 percentage is reduced to 3%; this result is observed with the runs 1, 2, 4, 6, 7, 8, 15, and 16.

It is observed that the degree of gel stability and viscosity of this Vaseline oil - organoclay dispersion increased with the increase of Bentone concentration from 3% to 8%. As explained earlier, the magnitude of interaction between Vaseline 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. As shown in Figure 5, the higher proportion of Bentone and ethanol, the better the viscosity. The optimal mixture consists of 8% of Bentone as seen in our matrix.

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 optimal score value of our matrix (Vaseline oil gel) was observed with run 3 that contain a optimal value of Bentone 8% and ethanol 6.5%.

Prediction point

The prediction by the model of a better viscosity of Vaseline oil gel gave additional points. The proportions of the various components bringing the maximum of viscosity are: Vaseline oil (84%), ethanol (4.4%), and Bentone 34 (11.6%).

Parrafin oil

These experiments show an improvement of viscosity by reaching the score 10 with run 2, 3, 7, 8, 9, 12, 13, and 14. For these runs, the gelling agent percentage (Bentone®34) is between 8% and 13% representing, therefore, the maximum value for obtaining a gel of score 10. In comparison with the runs with a lowest score 0, the Bentone percentage is reduced to 3%; this result is observed with the runs 1, 4, 5, 6, 10, 15, and 16.

It is observed that the degree of stability and viscosity of the gel of this dispersion of pips paraffin oil - organoclay increased with the increase in the concentration of Bentone of 3–8% accompanied by an increase in the activator which must constitute at least one-quarter of the quantity of Bentone. As explained earlier, the magnitude of interaction between paraffin oil and quaternary ammonium cations increases with the increase of the concentration of Bentone in the dispersions. Therefore, the Bentone contributes, to bigger formula stability by increasing its viscosity. The polar activator provides an additional contribution to the viscosity of the dispersion and consequently the creation of a new internal phase. Increasing in the proportion of Bentone and ethanol to obtain it is favorable to a higher viscosity because the optimum composition [Figure 6], which has allowed to gel the Vaseline oil, contains an optimal quantity of Bentone (8%) and ethanol (1/4 quantity of Bentone) in our matrix. 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%.

Prediction point

The prediction by the model of a better viscosity of paraffin oil gel gave additional points. The proportions of the various components bringing the maximum of viscosity are: Paraffin oil (85.4%), ethanol (4.6%), and Bentone 34 (10%).

For both Vaseline and paraffin oils, we observed that the gelification are well determined and that there is neither syneresis phenomenon nor ripening process.

Silicone oil

For the experiments conducted, there is no run that could reach the gelification point. We suggest that other trial runs with other matrix must be launched to explore possibilities to find an optimal gelification point [Figure 7].

Model analysis

Considering the coefficients a1 (oil), a2 (ethanol), and a3 (Bentone) given by our model's viscosity equation at day 0, it has been noticed that a3 is the most dominant coefficient that affects oil viscosity. In addition, important values of viscosity are seen when Bentone proportions are high.

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.[20]

Taking into account that organo-bentonites are clays partially covered by alkyl ammonium molecules adsorbed at their surface, the structure and, consequently, the flow behavior 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.[21]

The analysis by infrared spectroscopy [Figure 8] confirmed the presence of alkyl ammonium ions in Bentone®34 by cations exchange. Characteristic bands intercalated surfactant (valence vibration bands of the methylene group (CH2) of the long chain to 2921 cm^{-1} and 2849 cm^{-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/oil gel formed and the viscosity and gel strength of the system increased.[22]

The analysis of three dimensional model 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.

The analysis of results of all runs lead to the below three major ascertainments:

- The runs numbers 12 and 13 gave good results for all natural and synthetic oils. This result is even confirmed with former studies using almond and argan oils.[10,11]

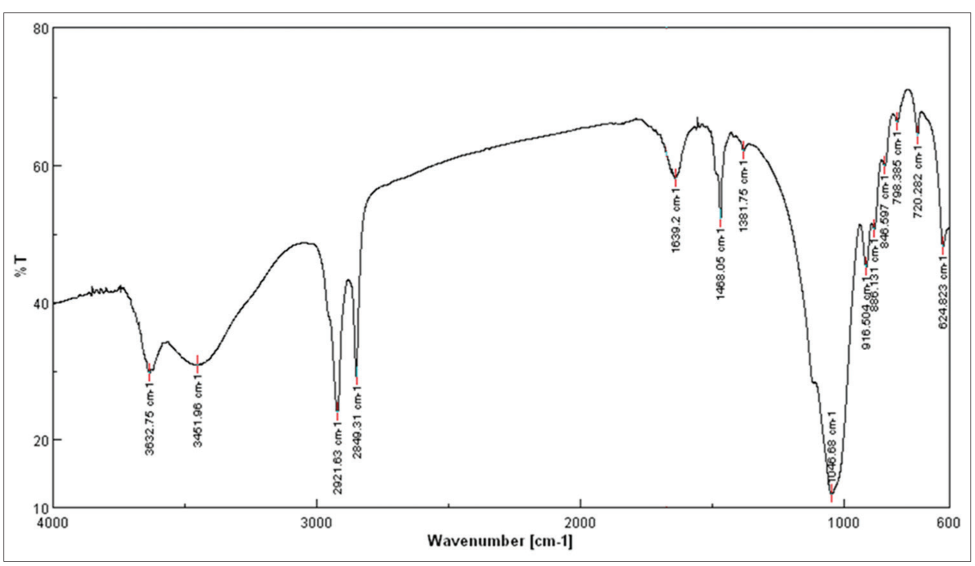

Figure 8: Infrared spectra of bentone®34

- Therefore, the proportion (oil: 80.5%, ethanol: 6.5%, and Bentone: 13%), which corresponds to above runs (12 and 13), can be considered as reference for all oil gelification activity.
- For natural oils, same runs lead to an intermediate gelification statutes, while for synthetic oils either we have gelification or not. This might be explained by the molecule structure of the two types of oils.

CONCLUSION

The experimental design of the mixture clearly indicates that the concentration of Bentone determines the viscosity of the oils studied. The influence of the variable concentration is a key criterion for defining conditions for an adequate viscosity. A gelling domain is in common between the different oils with a defined concentration of Bentone, the polar activator and oil remain usable.

REFERENCES

1. O'Sullivan CM, Barbut S, Marangoni AG. Edible oleogels for the oral delivery of lipid soluble molecules: Composition and structural design considerations. Trends Food Sci Technol 2016;57:59-73.
2. Almeida IF, Bahia MF. Evaluation of the physical stability of two oleogels. Int J Pharm 2006;327:73-7.
3. Kirilov P, Le Cong AK, Denis A, Rabehi H, Rum S, Villa C, *et al*. Organogels for cosmetic and dermo-cosmetic applications. Evaluation 2015;6:30-6.
4. Bhatt J, Somani RS, Mody HM, Bajaj HC. Rheological study of organoclays prepared from Indian bentonite: Effect of dispersing methods. Appl Clay Sci 2013;83-4:106-14.
5. Viseras C, Aguzzi C, Cerezo P, Lopez-Galindo A. Uses of clay minerals in semisolid health care and therapeutic products. Appl Clay Sci 2007;36:37-50.
6. Matsuzaki F. Section 1 - Cosmetics. Gels Handbook. Burlington: Academic Press; 2001. p. 45-6.
7. Patel HA, Bajaj HC. Natural and Synthetic Layered Materials as Cosmetic Ingredients. Focus on Aminocacides, Peptides and Hi-tech Ingredients; 2010. p. 31-5.
8. Santos J, Santos I, Souza A. Effect of heating and cooling on rheological parameters of edible vegetable oils. J Food Eng 2005;67:401-5.
9. Rahali Y, Pensé-Lhéritier AM, Mielcarek C, Bensouda Y. Optimization of preservatives in a topical formulation using experimental design. Int J Cosmet Sci 2009;31:451-60.
10. Yachi L, Elalaoui Y, Bouatia M, Cherkaoui N, Laatiris A, Rahali Y. Argan oleogel: Evaluation of the effect of the bentone on gelling using a mixture design. Int J Pharm Sci Rev Res 2017;43:49-55.
11. Bennis S, Yachi L, Elalaoui Y, Bouatia M, Cherkaoui N, Laatiris A, *et al*. Evaluation of the effect of the organo-bentonite on gelification of almond oil using a mixture design. JMES 2017;8:2506-12.
12. Hayakawa F, Kazami Y, Ishihara S, Nakao S, Nakauma M, Funami T, *et al*. Characterization of eating difficulty by sensory evaluation of hydrocolloid gels. Food Hydrocoll 2014;38:95-103.
13. Lionetto F, Maffezzoli A. Rheological characterization of concentrated nanoclay dispersions in an organic solvent. Appl Rheol 2009;19:23423.
14. EL Alaoui Y, Sefrioui R, Bensouda Y, Rahali Y. Solubilization of acetaminophen using phospholipids and nonionic surfactants optimized by exeprimental design. J Chem Pharm Res 2014;6:39-46.
15. Pensé-lhéritier AM. Recent developments in the sensorial assessment of cosmetic products: A review. Int J Cosmet Sci 2015;37:465-73.
16. Rahali Y, Saulnier P, Benoit JP, Bensouda Y. Exploring ripening of nanocapsules and émulsions in parenteral nutritional mixtures by experimental design. J Drug Deliv Sci Technol 2013;23:255-60.
17. Myers RH, Montgomery. DC, Anderson-Cook CM. Response Surface Methodology, Process and Producet Optimization using Design Experiment. 3th ed. New York: Willey; 2009.
18. Sadok AH, Moulai-Mostefa N, Bouda A. study of the influence of formulation factors on properties viscoelastics of a carbopol gel. Rev Sci Technol Synthèse 2013;26:96-102.
19. Vega AJ. Study of structural evolution of silica gel using 1H and 29Si NMR. J Non-Cryst Solids 1989;111:153-66.
20. Hermoso J, Martinez-Boza F, et Gallegos C. Influence of aqueous phase volume fraction, organoclay concentration and pressure on invert-emulsion oil muds rheology. J Ind Eng Chem 2015;22:341-9.
21. Hermoso J, Martinez-Boza F, Gallegos C. Influence of viscosity modifier nature and concentration on the viscous flow behaviour of oil-based drilling fluids at high pressure. Appl Clay Sci 2014;87:14-21.
22. Zhuang G, Zhang Z, Sun J, Liao L. The structure and rheology of organo-montmorillonite in oil-based system aged under different temperatures. Appl Clay Sci 2016;124-5:21-30.

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