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Evaluation of the effect of the Organo-bentonite on gelification of Almond oil 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 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. In our study a design of experiments approach was tested using a mixture design to evaluate the effects of the bentone and ethanol on enhancing viscosity of Almond oil. This viscosity was established by sensory analysis, which resulted in a score on a scale from 0 to 10. Formulation of oleogel based on bentone as gellant agent and almond oil seems to improve the viscosity of the formulae.

1. Introduction

Oleogels, also referred to as organogels or lipogels, are defined as the semi-solid formulations, comprising of a 3D network structure of gelator molecules, which immobilizes apolar liquid. Oleogels can be synthesized using a diverse group of gelators and organic solvents [1]. The microstructure of oleogels is characterized by either permanent rigid networks or transient semiflexible meshes, both thermoreversible [2].
The applications of oleogels were investigated in several areas such as organic chemistry, environmental chemistry and also in pharmaceutical and cosmetic fields. The majority of the applications reported in the pharmaceutical area were related to transdermal systems, topical bases and preparations intended for percutaneous absorption [3].
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 [4].
Organoclays, organically modified montmorillonites/smectites, are being extensively used as rheological modifier agent in a number of applications like 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 [5]. They have several health benefits when applied locally over the skin [6].
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 [6, 7].
A polar activator is necessary to promote the dispersion process for obtaining stable dispersion by forming gel structure. The function of polar activator 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 [8].
Almond is a major tree nut crop cultivated mainly in the Mediterranean region and the USA, North to South, under different environmental conditions, mostly on non-irrigated areas of poor soils and receiving little attention from farmers. The climate is primarily Mediterranean, becoming more extreme toward the inland regions and Saharian in the South. The resultant variability in environment and climate has turned into an extensive diversity of almond genotypes in each producing region, due to the fact that about 50% of the almond trees grown in Morocco are seedlings, located primarily in the north and the south [9].

Almond oil contains a substantial quantity of triacylglycerols, which are stored as intracellular oil droplets in the cotyledon tissues of the kernel. Almond oil is composed predominantly of mono and di-unsaturated fatty acids (FA). The major FA in Almond oil is oleic acid, representing 50–80% of the total FA content. Linoleic, palmitic and stearic acids are present at levels of 10–26%, 5–9%, and 1.5–4%, respectively[10].
In this work, Almond 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 [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, 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 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.

2. Experimental details

2.1.*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 Almond oil purchased by Biopur company (Morocco). The almoid oil used in this work was obtained as a commercial product.
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 (Hirschmanntechcolor Germany), magnetic bar, micropipette a 20-200 μl (Finpepette).
The software Design Expert was used for the experimental design and statistical tools.

2.2.*Preparation of the samples*

The formulation of oleogels took place in the laboratory of Galenic Chemistry at the Faculty of Medicine and 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].
Firstly, Bentone powder was prepared by accurately weighing the appropriate quantity, by adding the exact volume of 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 and 100 °C for 10 min. while heating from ambient temperature to 40 °C.
Secondly, after 10 min, a solution of ethanol has been added by micropipette precision under the same conditions, which were tried for 10 min.
The viscosity score is attributed just after the gelification of Almond oil in ambient temperature according to a scale from 0 to 10. Score 0 corresponds to an absence of viscosity, however score 10 allows gel consistency.

2.3.*Experimental design and mathematical modelling*

To define the formulation space for the Almond 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 [14].
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 Almond oil. This provides maximum information from a limited number of experiments. The studied factors were: the amounts of Almond oil (X1 = A), Ethanol (X2 = B) Bentone®34 (X3 = C).To make this experimental design, the lower and upper limits of components were fixed (Table I).

2.4. *Viscosity determination*

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 [15].
The viscosity score is attributed by sensory analysis just after the gelification of Almond oil in ambient temperature according to a scale from 0 to 10. Score zero corresponds to an absence of viscosity, however score 10 allows gel consistency.

Table I. Lower and upper limits of components used to made experimental design.

Components	Lower limit (%)	Upper limit (%)
X1: Almond oil	80.50	95.50
X2: Ethanol	1.50	6.50
X3: Bentone 34	3.00	13.00

2.5. *Statistical analysis*

The software Design Expert is a statistical tool that permits calculation for 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, the R-squared, the precision and mathematical modelling of the responses by polynomial equation at D0, D6, D7 D10 and D12 were carried out by Design Expert [16].

3. Results and Discussion

3.1.*Viscosity of Almond oil*

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

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

Run	X1: Almond oil	X2: Ethanol	X3: Bentone	Y: score Day 0	Y: score Day 6	Y: score Day 7	Y: score Day 10	Y: score Day 12
1	95.50	1.50	3.00	1	1	1	1	0
2	88.83	4.83	6.33	4	4	4	4	4
3	85.50	6.50	8.00	4	4	4	4	4
4	90.50	6.50	3.00	2	2	2	0	0
5	85.50	1.50	13.00	10	10	10	10	10
6	95.50	1.50	3.00	1	1	1	1	0
7	90.50	1.50	8.00	5	5	5	7	7
8	90.50	1.50	8.00	5	5	5	7	7
9	83.00	4.00	13.00	8	9	10	10	10
10	85.50	1.50	13.00	10	10	10	10	10
11	87.17	3.17	9.67	6	6	6	8	8
12	80.50	6.50	13.00	10	10	10	10	10
13	80.50	6.50	13.00	10	10	10	10	10
14	84.25	5.25	10.50	8	10	10	10	10
15	93.00	4.00	3.00	2	2	2	0	0
16	90.50	6.50	3.00	2	2	2	0	0

3.2.*Mathematical modelling*

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, D6, D7 D_{10} andD_{12} was selected as follows:

Where Y is the score of viscosity prediction of Almond oil, a_1, a_2 and a_3 are the estimated coefficients from the observed experimental values of viscosity for X1 (Almond oil), X2 (ethanol), X3 (bentone). The response of Almond oil viscosity expressed by a quadratic equation at D_0, D6, D7, D10 and D_{12} was as follows:

$$Yday0 = -2.02X1 + 3.57X2 + 3.08X3 - 0.03X1X2 - 0.02X1X3 - 0.08X2X3$$

$$Yday6 = -0.01X1 - 4.40X2 + 2.93X3 + 0.04X1X2 - 0.02X1X3 + 0.01X2X3$$

$$Yday7 = -0.01X1 - 8.53X2 + 3.50X3 + 0.09X1X2 - 0.03X1X3 + 0.05X2X3$$

$$Yday10 = -0.02X1 - 3.98X2 - 2.31X3 + 0.03X1X2 + 0.03X1X3 + 0.10X2X3$$

$$Yday12 = -0.04X1 - 5.35X2 - 2.90X3 + 0.05X1X2 + 0.04X1X3 + 0.10X2X3$$

With viscosity score, mixtures were designed by Design Expert® to explore the feasibility zone presenting the maximum viscosity score for Almond oil. Figures 1, 2, 3, 4 and 5 represent the experimental domain inside the ternary diagram at different day

These equations predict the score of viscosity of the Almond oil in experimental domain. Also the variation of the score of viscosity coefficient during 12 days.

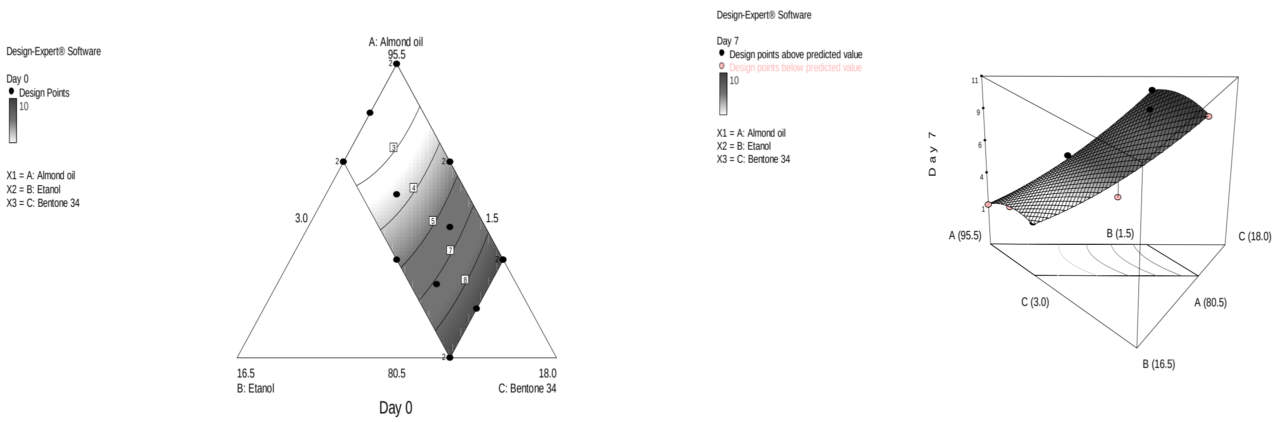

Figure 1: Contours plots and surface plots of estimated viscosity score of almond oil at Day 0.

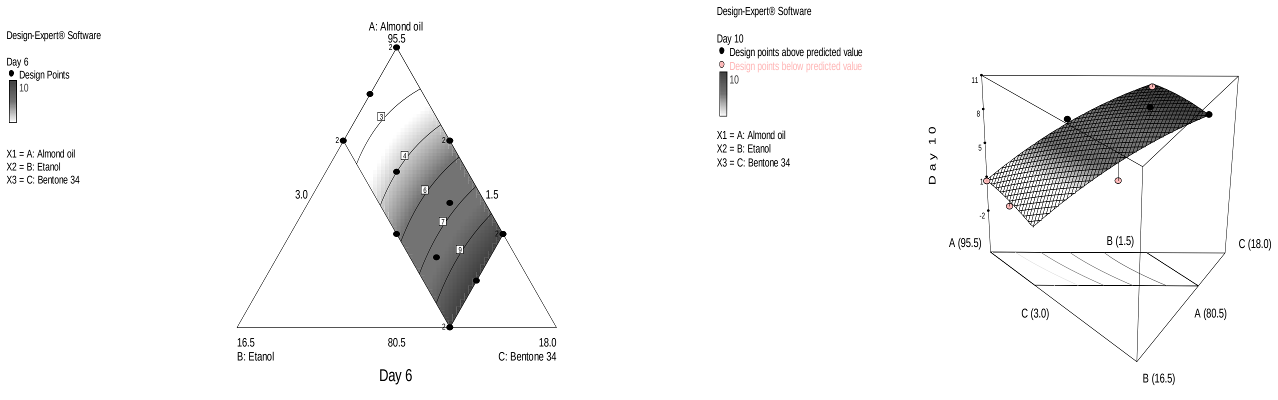

Figure 2: contours plots and surface plots of estimated viscosity score of almond oil at day 6.

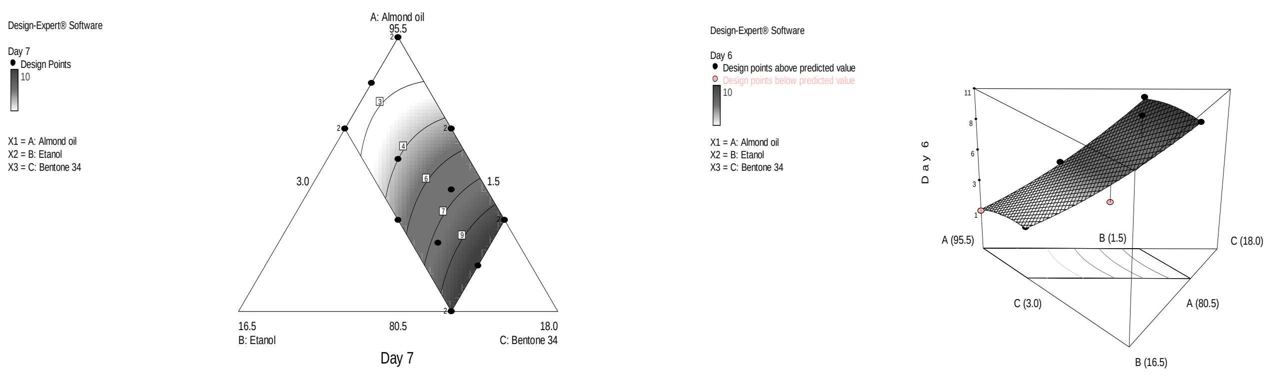

Figure 3: contours plots and surface plots of estimated viscosity score of almond oil at day 7.

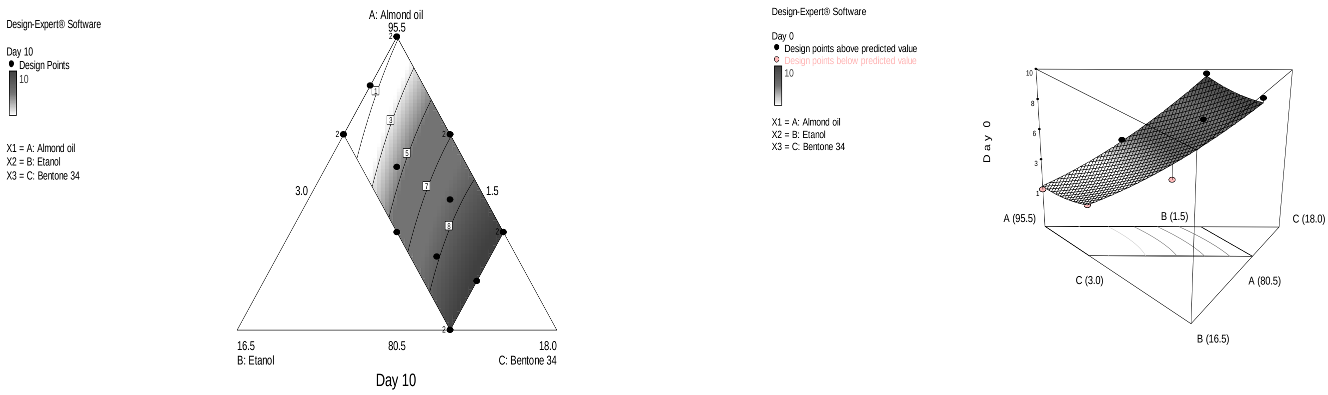

Figure 4: contours plots and surface plots of estimated viscosity score of almond oil at day 10.

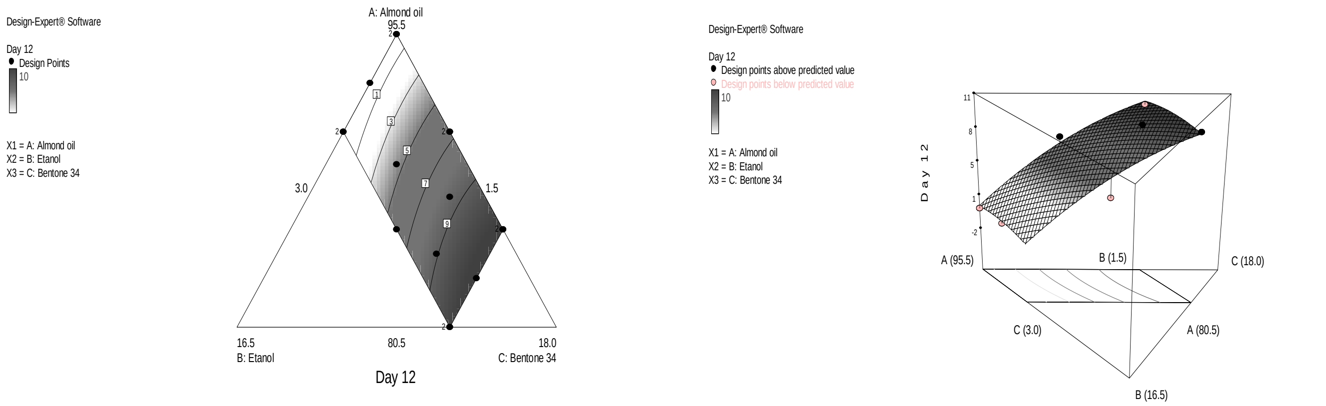

Figure 5: contours plots and surface plots of estimated viscosity score of almond oil at day 12.

3.3. *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 [17]. Table III 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 ($F_{D0\ model}$= 61.58 $F_{D6\ model}$=39.04 FD7 $_{model}$= 50.54 $F_{D10\ model}$ =75.09 and $F_{D12\ model}$=74.54) and low probability score (p<0,0001). The low probability score indicates that the model is considered statistically significant [18]. Values under 0.05 % were considered statistically significant. The R-squared beyond 0.93 is in reasonable agreement. Precision measurements of the signal to-noise ratio should be greater than 4: our ratios are beyond 20.94.

Table III: 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
D0	Quadratic	61.58	<0.0001	Significant	0.9528	18.660
D6	Quadratic	39.04	<0.0001	Significant	0.9269	15.217
D7	Quadratic	50.54	<0.0001	Significant	0.9429	17.718
D10	Quadratic	75.09	<0.0001	Significant	0.9611	21.216
D12	Quadratic	74.54	<0.0001	Significant	0.9608	20.491

3.4. *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, 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 1, the Bentone®34 percentage is reduced to 3%; this result is observed with the runs 1 and 6.

It is observed that the degree of gel stability, and viscosity of this Almond oil–organoclay dispersions increased with the increase of Bentone concentration from 3 to 13 %. As explained earlier, the magnitude of interaction between Almond oil and quaternary ammonium cations increases with he 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 [19].

Increasing the proportion of the bentone and ethanol together is in favor of higher viscosity as the optimum composition (figures 1, 2, 3, 4 and 5), which permitted to gellify the Almond oil, contains the maximum of bentone in our matrix.

Considering the coefficients a_1 (Almond 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 Almond oil viscosity. However, high values of viscosity are observed with high proportions of bentone.

Taking into account that organobentonites 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 [20].

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 interspace. Finally, bentone /Almond oil gel formed and the viscosity and gel strength of the system increased [21].

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 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.

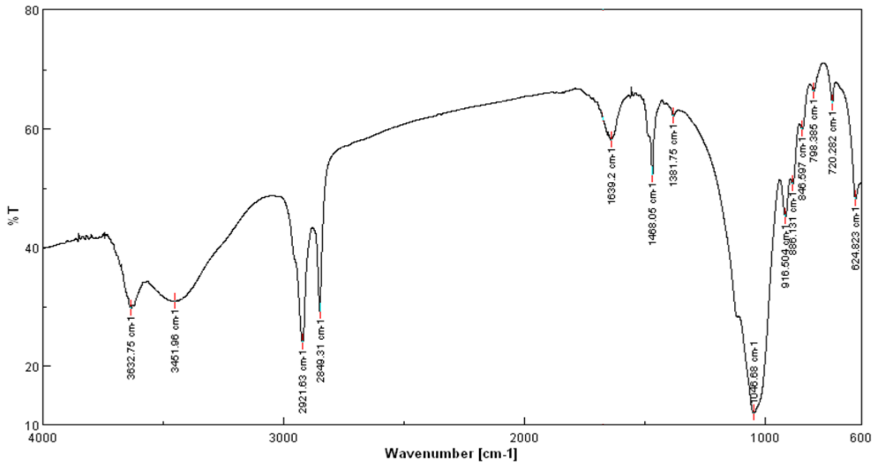

Figure 6: Infrared spectra of Bentone®34.

3.5. *Ripening process*

After 7 days, and starting from Bentone®34 « 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 thatthe 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 9 and run number 14 » [22].
Gelification results from the formation of small particles, which grow in number and size and then join together to fill the available space. Ripening takes place through a dissolution/reprecipitation mechanism.

3.6. *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 with run number 4. 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.

Conclusions
The gelification process was found to be a complex phenomenon affected by several parameters such as the percentage of gelling agent, the percentage of the polar activator and the nature of oil. The study shows that, the percentage of the bentone has a significant effect on gelation.
The mixture experimental design indicates clearly that concentration of Bentone determines the viscosity of the studied Almond oil. The influence of variable concentration is a key criterion in order to define conditions to have adequate viscosity.

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