

## **Determination of optimal dead sea salt content in a cosmetic emulsion using rheology and stability measurements**

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### **Synopsis**

Dead Sea mud and salts are known for their therapeutic and cosmetic properties. The presence of Dead Sea (DS) salts in different types of cosmetics has affected the stability and the flow properties of the finished products. In this study, an attempt was made to find the optimum Dead Sea salt content in a cosmetic emulsion (model of body cream) using both rheology and stability measurements. The rheological properties were tested during a four-month storage period at three different storage temperatures: 8°C, room temperature, and 45°C. In addition to rheological measurements and centrifuge tests, the conductivities of the emulsion samples were also determined. The centrifuge tests showed that the cream samples containing more than 0.25 wt% of DS salt showed phase separation. The addition of DS salt to the cosmetic emulsion led to two maxima in the emulsion viscosity at salt contents of 0.07 wt% and 0.15 wt%. However, the emulsion samples containing 0.15% of DS salt was considered the optimum sample since it contained the maximum amount of salt and exhibited the maximum viscosity at all tested conditions. It was found that the viscosity of the emulsion is increased with storage time and storage temperature. This behavior was accompanied by a decrease in conductivity. This behavior was explained by water evaporation from the emulsion. However, it has been shown that the presence of DS salt in the cosmetic emulsion significantly reduces the rate of water evaporation. The conductivity measurements reflect the rate of water evaporation, and the presence of DS salt reduces the rate of conductivity. Conductivity is observed to decrease with storage time and temperature.

### **INTRODUCTION**

In Jordan, a growing industry was established to produce different types of cosmetics. Cosmetics that have Dead Sea salts and/or mud in their formulas are the main products of this industry. The Dead Sea is known worldwide to be one of the world's richest sources of salts and minerals. But the presence of Dead Sea salts in various cosmetics has resulted in many problems during the production and in the stability of the end products. A typical problem is the maximum amount of Dead Sea salt that can be added

to the product without affecting stability and consistency. Phase separation is another problem observed in many samples of locally produced Dead Sea creams and mud masks.

Many investigators have reported on the close relationship of emulsion rheology and stability relative to several structural parameters (1–5). Rheological techniques are powerful tools to study the behavior of cosmetic emulsions. Changes in the rheological properties of cosmetic emulsions represent an important early warning of the impending failure of the product (3).

Rheological measurements are now required in various pharmaceutical and cosmetic industries including, but not limited to (a) quality control, (b) storage stability under various weather and transportation conditions, (c) correlation with sensory assessment and consumer evaluation, (d) the effect of formulation on consistency, and (e) prediction of flow behavior under manufacturing or production environment conditions (e.g., pumping, mixing, milling, and packaging). Various cosmetic products have different rheological behaviors. For example, body creams require a high viscosity at rest in order to stay in the hands of the consumer while being taken out of the bottle, but on the other hand, a subsequent shear thinning behavior is required for the ease of spreading and applying the creams onto the skin (6).

Modern Dead Sea cosmetics have been developed to meet the demands of new regulations, technical opportunities, and today's consumer expectation for higher quality standards and proven performance. As an example of the application of this approach, Maor *et al.* (7) describe the development of new cosmetics formulations, based on "osmoter," a special Dead Sea mineral composition, and the evaluation of this formulation effect on the depth of skin wrinkles by a controlled assay.

In this study, body cream (a cosmetic emulsion model) containing Dead Sea salt was compounded using the conventional techniques in emulsion preparation. The addition of salt(s) to the emulsion resulted in a significant change in rheological behavior and stability. For this reason, rheological and stability measurements were used to evaluate the prepared cosmetic emulsion in order to find the optimum content of Dead Sea salt that can produce a stable cream with maximum viscosity.

## MATERIALS AND METHODS

### MATERIALS

The components used in the cream formulation were divided into three groups: water phase, oil phase, and preservative. Oil-phase components were lanolin (pastel) consisting mainly of sterol ( $C_{27}H_{45}OH$ ), petrolatum (white petroleum), paraffin oil, cetearyl alcohol (stied), sodium cetearyl sulphate (lan N), and glycerin stearate. The oil-phase components contribute to 24.1% (wt%) of the total components used in the formulation of the body cream. The water-phase components were propylene glycol (PG), glycerin, Dead Sea salt, and RO water. The preservatives used were 5-chloro-2-methyl 4-iso thiazolin-3-one, 2-methyl 4-iso thiazolin-3-one, propyl paraben, and methyl paraben. Table I shows the percentages of the components used in the formulation of the body cream. The materials used for the body cream formulation were supplied by Ammon Dead Sea Co. (Amman, Jordan), which in turn were exported from Henkle Co. (Germany). The Dead Sea salt consists mainly of  $K^+$  (114500 mg/kg),  $Mg^{+2}$  (81200 mg/kg),

Table I  
Formulation of the Body Cream Used in the Study

| Raw material          | wt%       |
|-----------------------|-----------|
| Paste 1               | 4.0       |
| White petrolatum      | 4.0       |
| Paraffin oil          | 4.0       |
| Stied                 | 4.0       |
| Lan N                 | 4.0       |
| Propyl paraben        | 0.1       |
| Glyceriyl stearate    | 4.0       |
| Propylene glycol (PG) | 4.0       |
| Methyl paraben        | 0.2       |
| Dead sea salt         | 0.0–0.25  |
| Glycerin              | 7.0       |
| Preservative          | 0.2       |
| RO water              | Up to 100 |

$\text{Na}^+$  (25600 mg/kg),  $\text{Ca}^{+2}$  (2000 mg/kg) and  $\text{Cl}^-$  (382100 mg/kg). The complete chemical analysis of the DS salt used can be found in reference 8.

#### CREAM PREPARATION

The body cream was prepared by adding the oil-phase components and water-phase components at room temperature into two separate jacketed glass vessels. Hot water was circulated into the jackets of the vessels to attain the required temperatures. In order to dissolve all the water- and oil-phase components, the water phase was heated to 75°C, and the oil phase to 80°C under high-speed agitation. The mixing speed was 700 rpm for both the oil and the water phases. When the water and oil phases reached 75°C and 80°C respectively, the water phase was added to the oil phase and the resulting emulsion allowed to cool down to 40°C under slow-speed agitation (400 rpm). The preservative was added at approximately 40°C and the agitation was discontinued. The cream samples were stored in glass beakers at three temperatures: 8°C, room temperature, and 45°C. The rheological properties of the prepared creams were measured at different storage points during a four-month period. In addition to the conductivity measurements of the cream samples, the stability of the prepared creams was investigated using a centrifuge after six weeks from the time of preparation. In order to investigate the reproducibility of the sample preparation, part of the samples was prepared in duplicate.

#### METHODOLOGY

Experiments were performed to study the rheology and stability of the body cream prepared in the laboratory. Rheological studies of the body cream included the study of the dependence of apparent viscosity on shear rate. DS salt concentrations varied from 0.0 to 0.25%. Salt-free cream was used as a control sample, and other samples containing DS salt were compared to this control.

## EQUIPMENT

*Rotational viscometer.* All rheological measurements of the body cream samples were carried out at 25°C using a concentric cylinder viscometer (Haake VT 500, SV1-system). The viscometer has an inner cylinder rotating in a stationary outer cylinder. The SV1-system has a bob with a length of 61.4 mm and a radius of 10.1 mm, and it has a jacketed cup with a radius of 11.55 mm. Body cream samples were placed in the temperature-controlled measurement viscometer and equilibrated to 25°C for ten minutes prior to performing the measurements. The rheological experiments were carried out in duplicate and the reproducibility was  $\pm 4\%$  on average for selected samples.

*Centrifuge.* All stability tests of the body cream samples were carried out using a conventional centrifuge (Hettich Zentrifugen, Germany). Samples were subjected to an accelerated stability test using the centrifuge at 4000 rpm for 30 minutes six weeks from the day of preparation.

*Conductivity meter.* Conductivity measurements of the cream samples were performed with an electrical conductivity meter (Euteoh, Cybercsan 1000, Singapore) at room temperature at different storage periods of four months.

*Stirrers.* A three-bladed impeller was used to mix the oil phase of the cream during preparation (Heidloph, RZR, Germany). It was driven by a variable-speed motor (400–1400 rpm). A two-bladed impeller (Stuart Scientific, SS2, U.K) set at 700 rpm was used for mixing the water phase during cream preparation.

## RESULTS AND DISCUSSION

## CENTRIFUGE TEST

The first body cream stability test was carried out using a centrifuge. Samples were subjected to accelerated stability testing using a centrifuge at 4000 rpm for 30 minutes six weeks from the day of preparation. The aim of this test was to check for phase separation and to examine how homogenous the prepared cream was. Results indicated that all cream samples containing 0.25 wt% of DS salt or less were homogenous, and no change in the sample structure was observed. Samples containing more than 0.25 wt% of DS salt showed a phase separation pre- and post-centrifugation. For this reason, the rheological analysis was limited to the stable samples.

## RHEOLOGICAL PROPERTIES

In this part of the investigation, the effect of added DS salt on the viscosity of the body cream samples was examined by adding different salt concentrations to the standard formula mentioned earlier in the Experimental section. The concentration of the DS salt varied from 0.0 to 0.25 wt%. Creams containing more than 0.25 wt% DS salt were completely unstable.

The effect of DS salt concentration on the apparent viscosity of cream samples stored for one week at room temperature is shown in Figure 1. As can be seen in this figure, the effect of increasing the DS salt concentration from 0.0 to 0.25 wt% on the apparent viscosity can be divided into four regions. In the first region, a decrease in the apparent

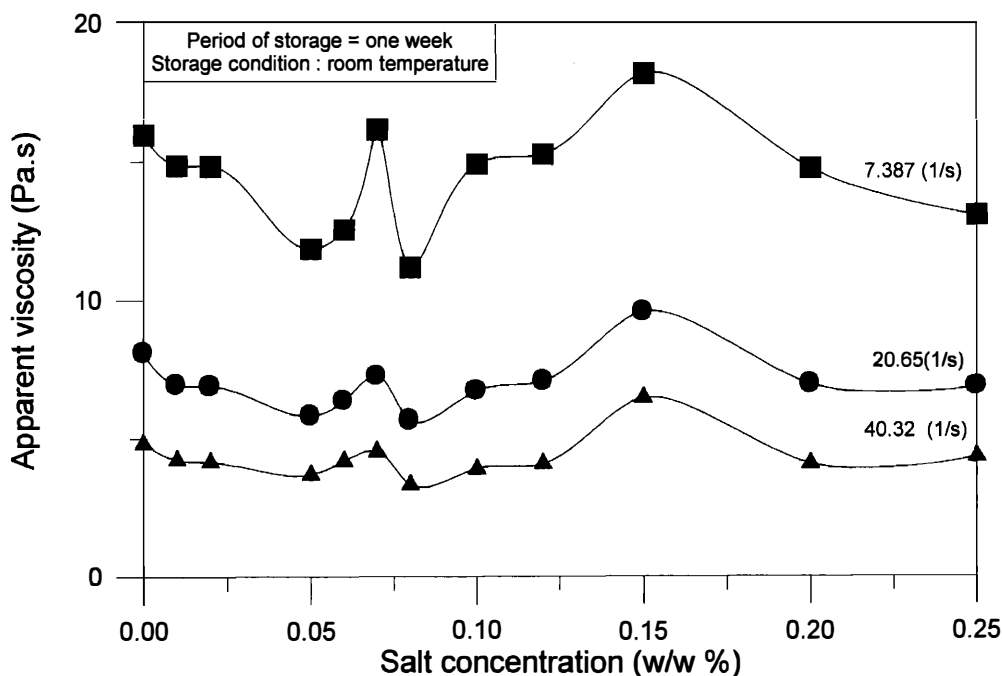


Figure 1. The effect of DS salt concentration on the apparent viscosity of cream samples stored for one week at room temperature and measured at three shear rates: ■ 7.387 (1/sec), ● 20.65 (1/sec), and ▲ 40.32 (1/sec).

viscosity with increasing DS salt concentration from 0.0 to 0.05 wt% was observed, reaching the first minimum point at 0.05%. In the second region, the apparent viscosity increased with DS salt concentration to reach the first maximum in viscosity, which occurred at 0.07 wt% DS salt content. A sharp decrease in the apparent viscosity was then observed, reaching a minimum point at 0.08% DS salt concentration. A higher maximum point than that at 0.0 and 0.07 wt% in the apparent viscosity was reached at 0.15 wt% DS salt concentration. A decrease in the apparent viscosity was noticed in the fourth region when the DS salt concentration was increased from 0.15 to 0.25 wt%. Similar behavior was found for the samples subjected to different shear rates over the entire concentration range, as can be clearly seen in Figure 1.

In order to be sure that the pervious variation of viscosity with salt concentration is real and not a reflection of experimental error, part of the samples was prepared in duplicate. As can be seen in Figure 2, the reproducibility of a sample preparation is very high where the maximum error in the apparent viscosity at a constant salt concentration is less than 4.0%. In addition, Figure 2 shows that experimental error did not affect the general trend of the apparent viscosity of cream samples with the salt concentration.

Based on the function of sodium cetearyl sulfate (anionic emulsifier) used in this system, the oil droplet surface will be surrounded by a negatively charged layer. This layer works as a bridge between the oil and water phases; consequently, the electrostatic repulsion between oil droplets will prevent them from coalescence. Ionization to cations and anions occurs when the DS salt is added. The negatively charged ions (e.g.,  $\text{Cl}^-$ )

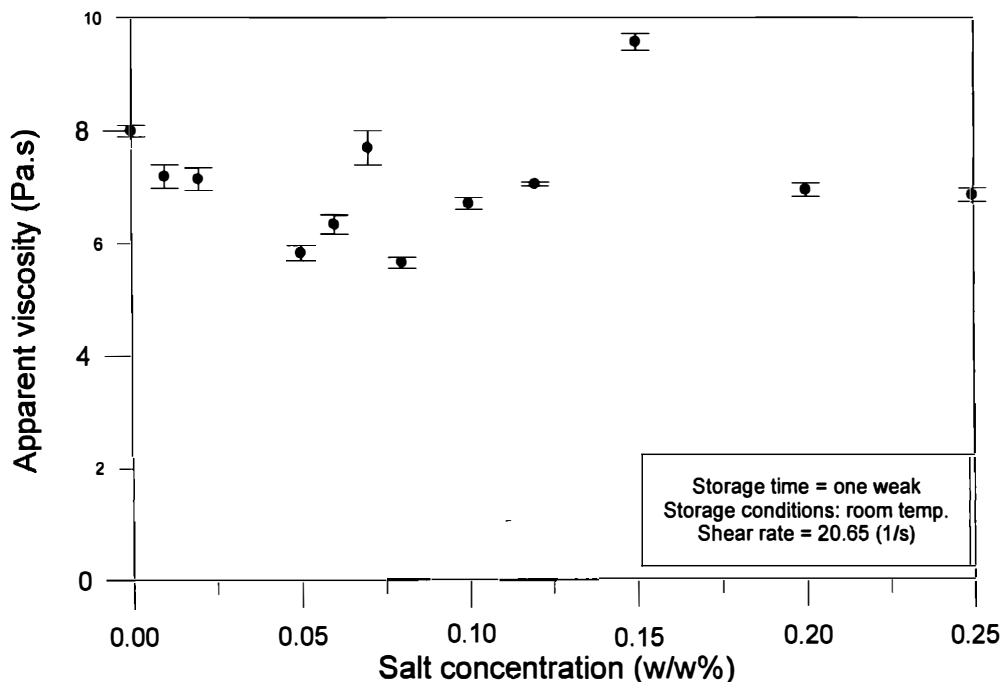


Figure 2. Error bars of the apparent viscosity of the prepared creams measured at shear rate = 20.65 (1/sec).

move toward the negatively charged layer. This results in an increase in the ionic strength of the negatively charged layer and subsequently capturing more water molecules in the void space between the aggregated oil droplets. This may explain the increase in the viscosity of the cream upon the addition of salt. The appearance of maximum viscosity may be explained by the concentration at a certain salt level where a maximum capacity of the layer for the anionic charge is reached. As more DS salt is added, positively charged ions (e.g.,  $\text{Na}^+$ ,  $\text{Mg}^{+2}$  . . .) start neutralizing some of the negative charge. This action results in a weaker bridge, resulting in water molecules with lower attraction. Thus, the oil droplets will have a greater tendency to coalesce, resulting in a reduction in the apparent oil-phase volume. The viscosity reduction of the body cream samples is the result of a decrease in the apparent phase volume of the dispersed droplets.

The explanation for the appearance of two maxima in the apparent viscosity at 0.07 and 0.15 wt% DS salt concentration (see Figure 1) might be attributed to the presence of different ions (e.g.,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , . . .) with different ionic strength in the added DS salt. Silvander *et al.* (9) investigated the effects of electrolyte addition to a cosmetic emulsion. Monovalent sodium chloride had practically no influence on viscosity. Calcium chloride, on the other hand, had a large impact on viscosity, even at low concentrations. The resulting increase in viscosity was due to flocculation that led to an increase in apparent phase volume. A similar behavior was obtained with magnesium chloride, with the difference that the maximum in viscosity was shifted to higher electrolyte concentrations. This was interpreted as such because magnesium bound more strongly to the hydration water than did calcium.

An additional point of interest is the decrease in viscosity when the salt concentration increased from 0.0 to 0.05 wt%. This small effect is due to the decrease in electrostatic screening length and is often referred to as a secondary electroviscous effect (9).

On the other hand, a decrease in the apparent viscosity of body cream samples with different DS salt concentrations was observed as the shear rate was increased (see Figure 1). This implies that the cream behaves like a shear thinning material.

Figures 3 and 4 show the effect of DS salt on apparent viscosity for samples stored at room temperature at different storage periods. It can be clearly observed that the apparent viscosity of cream samples increased with storage time and that this effect was more pronounced at high storage time (two and three months). In a similar study, Korhonen *et al.* (3) studied the effect of storage time on the rheological behavior of creams with four different surfactant combinations. They found that the viscosity (consistency) of the cream decreased during storage, suggesting that other factors have affected our creams in the increase of viscosity with storage time. This phenomenon can be attributed to the evaporation of water from the emulsion. Evaporation of the water-continuous phase causes compression of the emulsion, with progressive distortion of the oil drops and thinning of the water films separating them (10). To verify this result, the weight of two cream samples, one with DS salt and one salt-free, was observed. As can be seen in Figure 5, the weight of the cream samples decreases with storage time because of water evaporation. It is interesting to see in Figure 5 that the rate of water evaporation decreases in the presence of DS salt. This can explain the results presented in Figure 4, where the salt-free sample exhibits maximum viscosity after three months of storage.

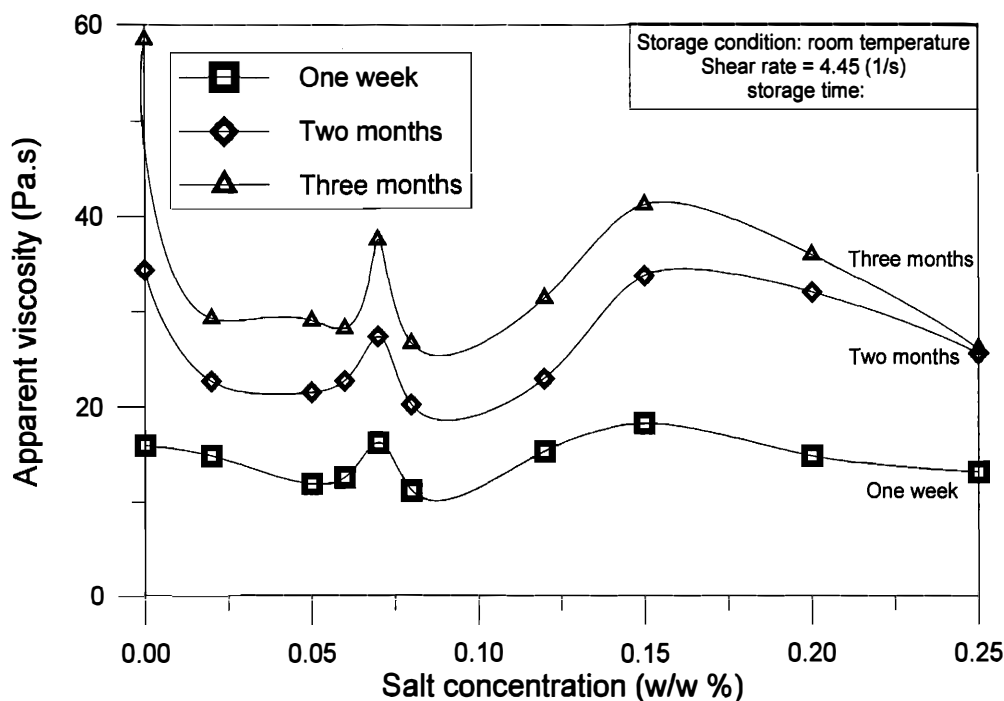


Figure 3. The effect of DS salt concentration on the apparent viscosity of cream samples stored for different periods at room temperature.

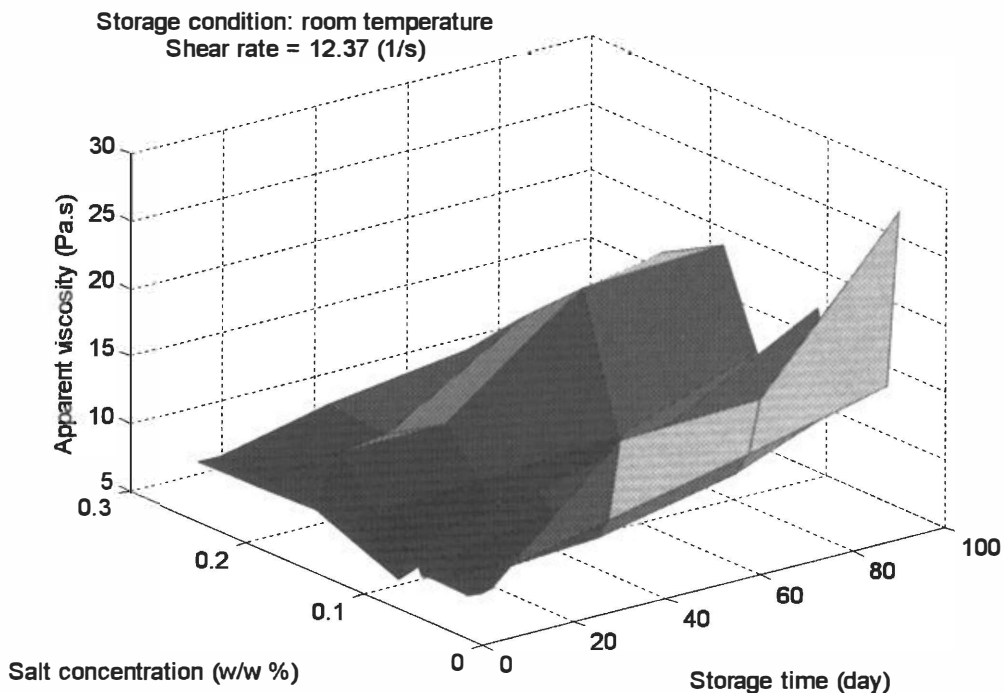


Figure 4. The effects of DS salt concentration and storage time on the apparent viscosity of cream samples stored at room temperature.

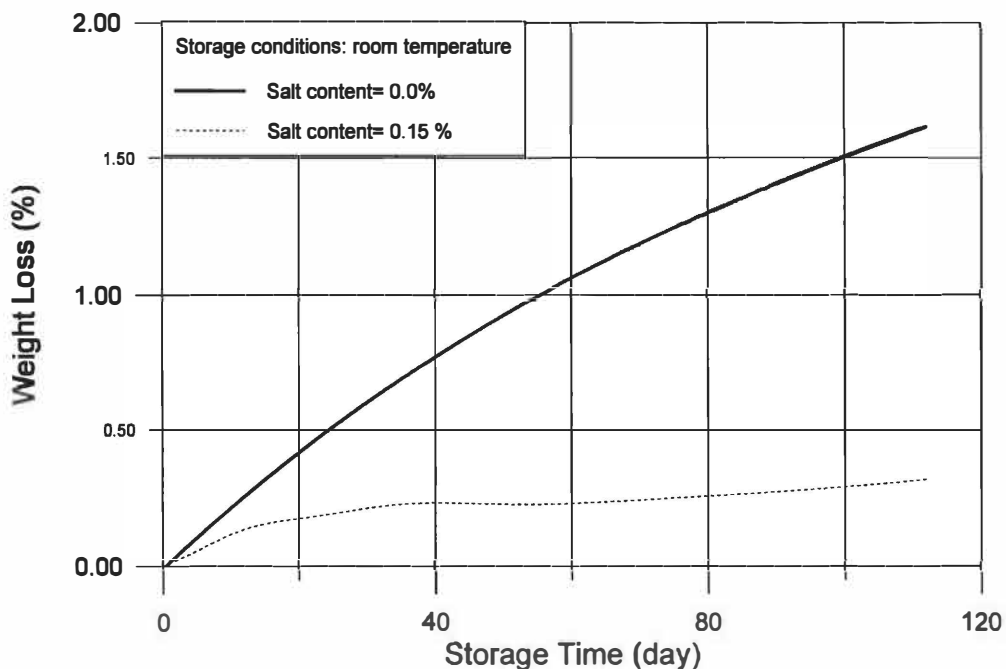


Figure 5. Weight losses in cream samples as a function of storage time.



Aranberri *et al.* (10) found that in emulsion systems with added salt, water evaporation virtually ceased before all the water present was lost, probably as a result of oil-drop coalescence resulting in the formation of a water-impermeable oil film at the emulsion surface.

A control experiment was conducted on a sample placed in a closed container where no change in weight was observed. In addition, the viscosity of this sample did not show significant change. This result supports our previous hypothesis that the increase in cream viscosity with storage time is caused by the evaporation of water from the emulsion.

The samples containing 0.07 and 0.15% DS salt showed a maximum viscosity over the entire range of storage time tested. With the increase in storage time, the two maxima showed less increase in apparent viscosity than in the salt-free sample.

#### EFFECT OF STORAGE TEMPERATURE

In this part of our investigation the effect of storage conditions was studied. Body cream samples were stored up to four months at (i) room temperature, (ii) 45°C, and (iii) 8°C. The concentration of the Dead Sea salt varied between 0.0 and 0.15 wt%. Figure 6 shows the effect of storage temperature on the apparent viscosity of the cream samples stored for one week. An increase in the apparent viscosity at constant shear rate with increasing storage temperature can be clearly observed. The increase in the viscosity of

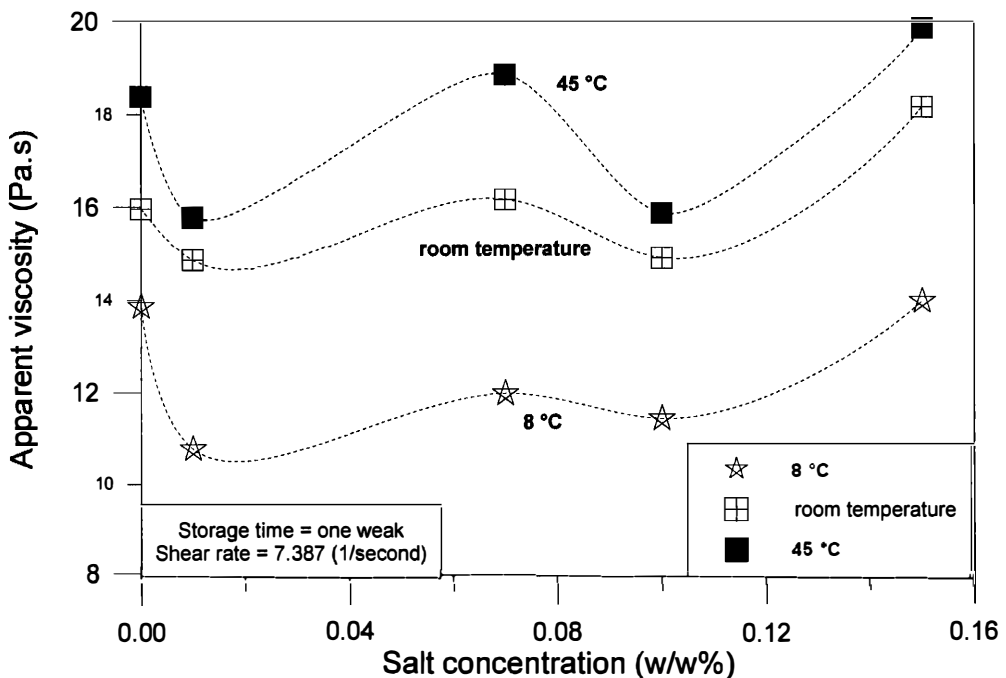


Figure 6. The effect of DS salt concentration on the apparent viscosity of cream samples stored for one week at different temperatures.

creams with increasing storage temperature may be due to the increase in the rate of water evaporation. With increasing storage temperature, the evaporation of water increases, resulting in a viscosity increase. In a similar study, Korhonen *et al.* (3) found that the consistency of a cream containing a non-ionic surfactant, PG 25 soya sterol and sorbitan trioleate, increased with increasing storage temperature.

At longer storage periods a clear effect of the storage temperature on the viscosity of the salt-free sample can be seen, where a significant increase in the apparent viscosity is observed (see Figure 7). The salt-free sample stored for two months at 45°C showed the highest viscosity beyond the viscosity range that can be measured by the viscometer. The effect of increasing the storage temperature on the viscosity of the salt-free sample was more pronounced than that observed for the salted sample. However, the salt-free samples showed a higher rate of increase in apparent viscosity with storage time than that observed for the salted samples.

#### CONDUCTIVITY MEASUREMENTS

The conductivity test is a rapid method for determining the stability of creams based on the change in the physical characteristics of the cream (11). Conductivity measurements of cream samples were performed at room temperature and over various storage periods up to four months.

Conductivity values of the creams increased as the amount of added DS salt was increased. This may reflect the higher level of free ions within the cream samples as the

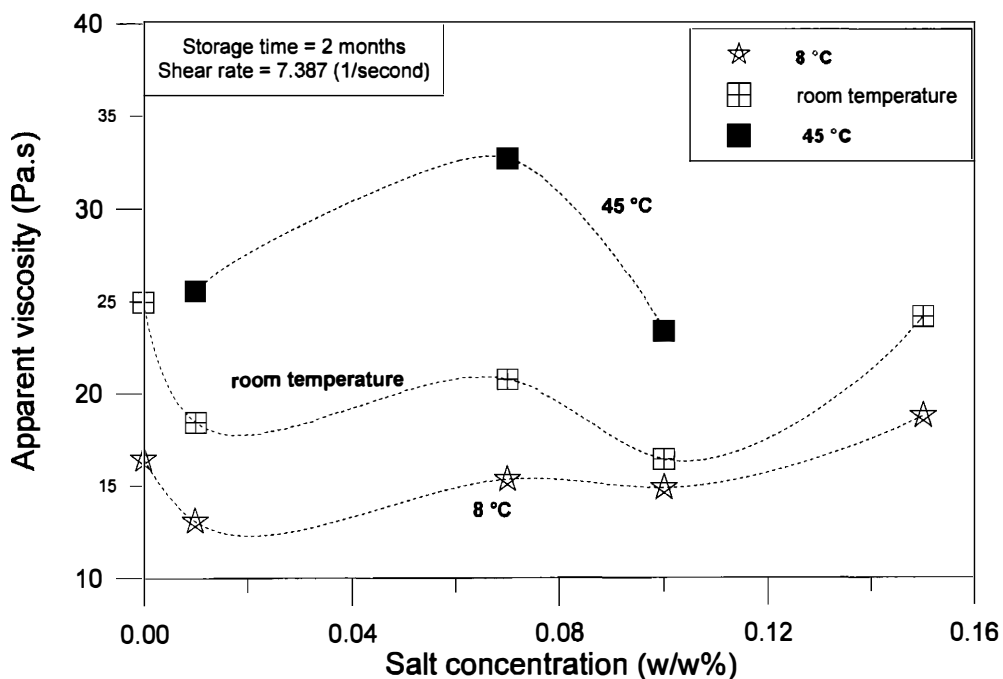


Figure 7. The effect of DS salt concentration on the apparent viscosity of cream samples stored for two months at different temperatures.

amount of added DS salt was increased (12). This behavior can be observed in Figure 8. A sudden change in conductivity curves can be seen at salt concentrations of 0.07 and 0.15 wt%, corresponding to the observed maximum viscosities. This result suggests that the added ions to the system at these concentrations have a more pronounced effect on the emulsion structure, leading to an increase in viscosity, than does the free water, which leads to an increase in conductivity.

A decrease in the conductivity values of body cream samples with storage time up to four months can be also seen in Figure 8. This is an expected result of water evaporation during the storage period.

As shown in Figure 9, the conductivity of the salt-free cream stored for four months decreases with the storage temperature. The conductivity values of the body cream samples decreased during the four months of storage over the entire range of storage temperatures. A decrease in the conductivity values with increasing storage temperature at constant storage time can be clearly observed. A low conductivity value reveals that there is more lamellar water and less free water in the cream, which can be seen as an increase in the viscosity of the cream (13). The largest change in conductivity during storage was observed for the sample stored at 45°C. This cream previously had a maximum viscosity related to the increase in water evaporation at this condition.

Figure 10 shows that the conductivity of a body cream sample containing 0.07% DS salt content decreases with both storage time and storage temperature. The largest and the sharpest changes in conductivity during storage were observed for the sample stored at 45°C, which exhibited a maximum viscosity, as shown previously.

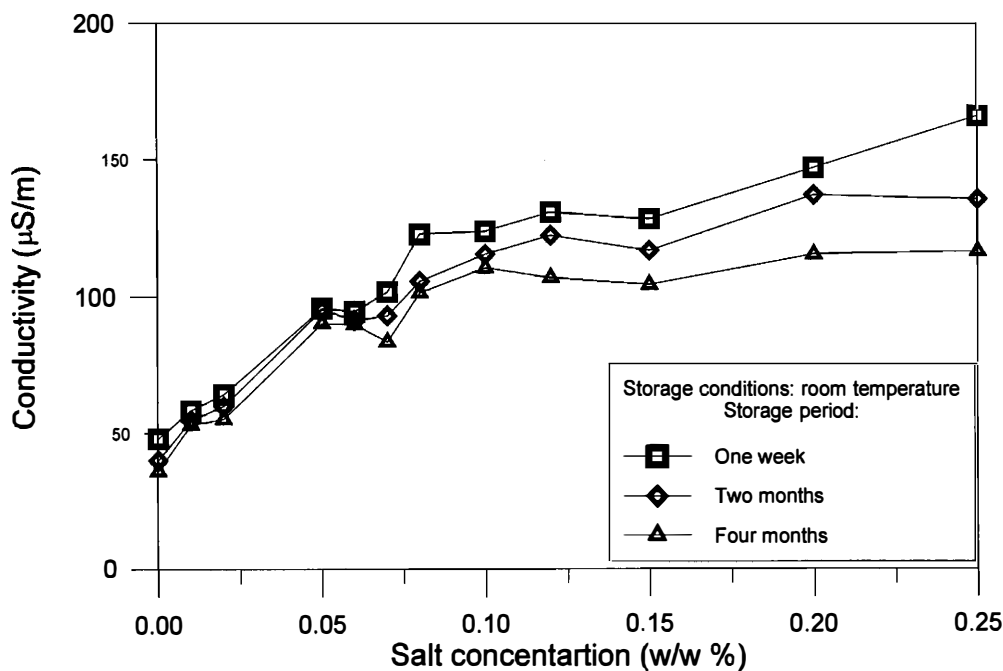


Figure 8. The effect of DS salt concentration on the conductivity of body creams stored for different periods at room temperature.

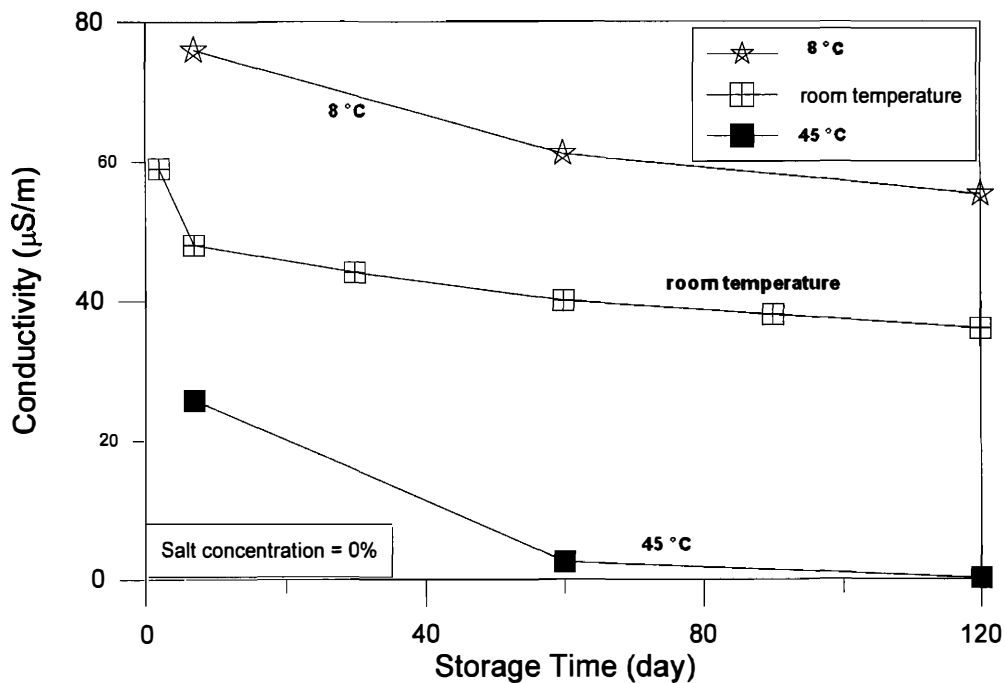


Figure 9. The effect of storage time on the conductivity of a salt-free cream sample stored at different temperatures.

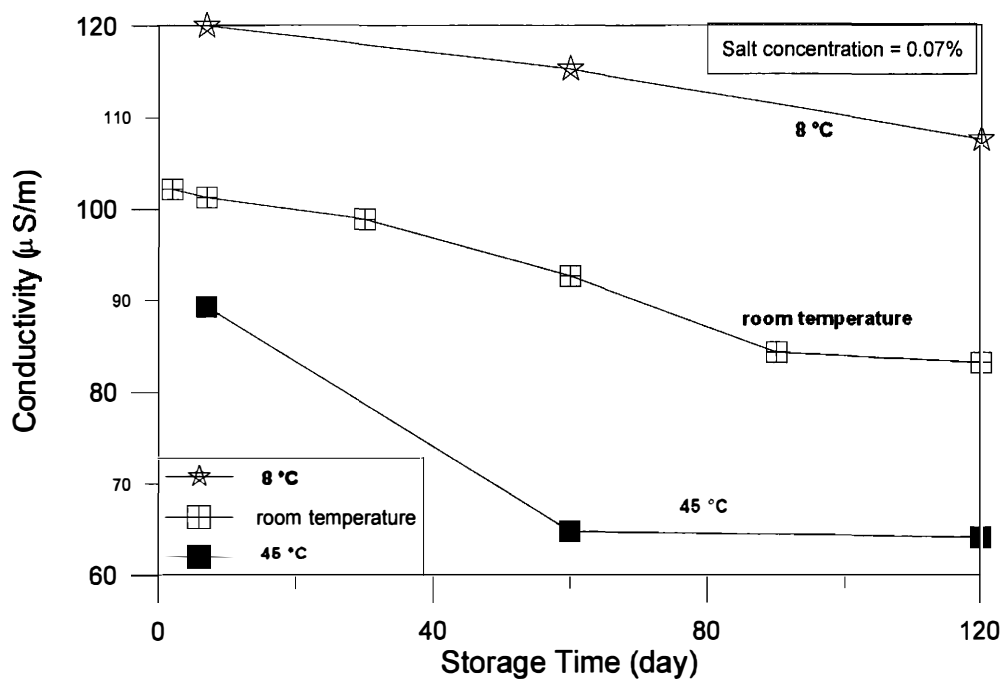


Figure 10. The effect of storage time on the conductivity of a cream sample containing 0.07% DS salt and stored at different temperatures.

Comparison of Figures 9 and 10 reveals that the decrease in conductivity of the salt-free sample with storage time is more pronounced than that of the salted sample. This supports our previous results, that the rate of water evaporation in the salt-free sample is greater than that in the samples with added salt. This result is confirmed by the results of weight measurement, where the weight loss in the salted sample is less than the weight loss in the salt-free sample (see, for example, Figure 5).

## CONCLUSIONS

The addition of Dead Sea salt to a cosmetic emulsion has a large impact on viscosity even at low concentrations. The obtained two maxima in viscosity are due to the presence of different monovalent and divalent ions in the DS salt. The resulting increase in viscosity was due to flocculation that led to an increase in the apparent dispersed-phase volume. The cream samples containing more than 0.25 wt% of DS salt showed phase separation. Emulsion samples containing 0.15% of DS salt exhibited the maximum viscosity under all test conditions, and therefore, were considered the optimal sample. The evaporation of water from the emulsion samples led to increased viscosity with storage time and storage temperature. In addition, the presence of DS salt in the cosmetic emulsion significantly reduced the rate of water evaporation. It was also found that the conductivity of the emulsion decreased with storage time, reflecting the decrease in free water. However, the presence of DS salt reduced the rate of conductivity decrease.

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