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A NOVEL METHOD FOR RAPID NON DESTRUCTIVE DETERMINATION OF O/W CREAMS STABILITY

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ABSTRACT

A nonconventional method for evaluation of emulsion stability was developed. The method was found to be valid for viscous emulsions and results obtained are in good correlation to conventional methods compared.

The technique is based on electrical conductivity measurements during nondestructive short heating-cooling-heating cycles carried out on cosmetic viscous emulsions. Conductivity curves were obtained on a recorder, where the second heating cycles were lower and almost parallel to the first heating curves. The bigger the conductivity differences between the two heating curves, the lower is the emulsion stability.

A relative Stability Index Δ/h, indicating relative change in conductivity between two cycles was elaborated. This index was usefull in finding out:

- optimal required HLB values for required emulsion
- optimal amount of oily phase
- emulsifier concentration.

INTRODUCTION

The usual methods to determine the stability of emulsions are based on accelerating the separation processes occurring during normal storage conditions. The acceleration is achieved by elevated temperatures, freezing, thaw-freezing cycles, and centrifugation (1).

A large number of investigations were performed in order to determine an emulsion stability by measuring its electrical conductivity under severe conditions.

Holzner (2) made an electrolysis of the emulsions and measured the drop in their conductivity during the three first minutes under a constant voltage, and derived from those results the emulsion stability. Rohel (3) measured the conductivity drop at two temperatures, 20 and 50°C, claiming that in stable systems there is only a slight change in the conductivity at both temperatures. By comparing the distances between the two derived curves he could predict the stability of the emulsion in good agreement with shelf-life tests.

Measurements of conductivity, as a function of temperature using alternating current was proposed by Brandau (4) as a quality control for emulsions in the stage of their preparation. The conductivity was plotted vs. temperature between 20-60°C and a comparison of the obtained curves for different emulsions to a standard curve, allows a good product control of the formed emulsion.

Using alternating current, Birrenbach (5) measured the impedance of creams during a single understructive heating-cooling process. Since the measurement was carried out in non-contact cell, it can be assumed that most impedance is contributed by the capacity of the emulsion. The impedance obtained during the heating process is compared to the cooling process impedance and assuming that the closer the two curves are, the more stable is the emulsion, a prediction of emulsion stability could be made.

Many investigators searched for the relation between the electrical conductivity of a given emulsion and it's stability and in this connection it is worth mentioning Bruggeman's equation (6) concerning the emulsion electrical conductivity and the content of the oil phase:

$$k = k_m (1-\emptyset)\ 2/3$$

where k = electrical conductivity of the emulsion

k_m = electrical conductivity of the continuous phase

$\emptyset$ = concentration of the oil phase for o/w emulsions

Bruggeman's equation is an important contribution to that matter but is completely ignoring any relation of the electrical conductivity to the particle size of the dispersed phase.

The goal of our study was to develop a new technique based on measurements of electrical conductivity to determine the stability of an o/w viscous emulsion prepared with non-ionic emulsifiers.

The principle of the technique is based on electrical conductivity changes of emulsions, during non-destructive short heating-cooling-heating cycles.

Conductivity curves were plotted during the heating-cooling cycle, and by the assumption that the smaller the differences between the curves, the higher the stability of the emulsion. A stability index was defined. This stability index, Δ/h, indicates the relative changes in the conductivity between two heating-cooling cycles.

The method was compared to standard stability tests with good correlation, and the use of the stability index enabled easy comparison of emulsion stabilities, while changing the emulsifier, the oil phase concentration, and the HLB's of the emulsions.

EXPERIMENTAL

Materials:

A basic model cream was used in this studay as follows:

Oily phase:	1. Cetyl Alcohol	4.0%
	2. Acetylated wool Alcohols[1]	2.0%
	3. Triglycerides of caproic acid[2]	4.0%
	4. Emulsifier	0.5-5.0%
Aqueous phase:	5. Aqueous gum solution[3]	20.0%
	6. Demineralized water to	100.0%

The emulsifiers used in this study were:

- Ethoxylated fatty alcohols[4]
- Ethoxylated fatty acids[5]

The aqueous gum extract was obtained from a plant extract.

Method of Preparation:

For all experiments the same method was used: dropwise addition of small amounts of the aqueous solution to the oily phase at approximately 70°C, till inversion. Then the rest of the aqueous phase was added at one portion while vigorous stirring. The obtained emulsion was cooled to ambient temperature while vigorous stirring.

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[1] "Acetulan" manufactured by "Amerchol", U.S.A.

[2] "Myritol" by "Henkel", Germany.

[3] Secrecy agreement with a pharmaceutical company prevents us from giving full name and source of structure.

[4] "Brijs" / Atlas Europol S.P.A. or Capitol City Corp.

[5] "Myrjs" / Atlas Europol S.P.A. or Capitol City Corp.

Determination of emulsion stability

While the emulsions were still fresh a measurement of the particle size distribution (P.S.D.) was handled using a Carl Zeiss polarizing microscope. Each result was an average of several measurements.

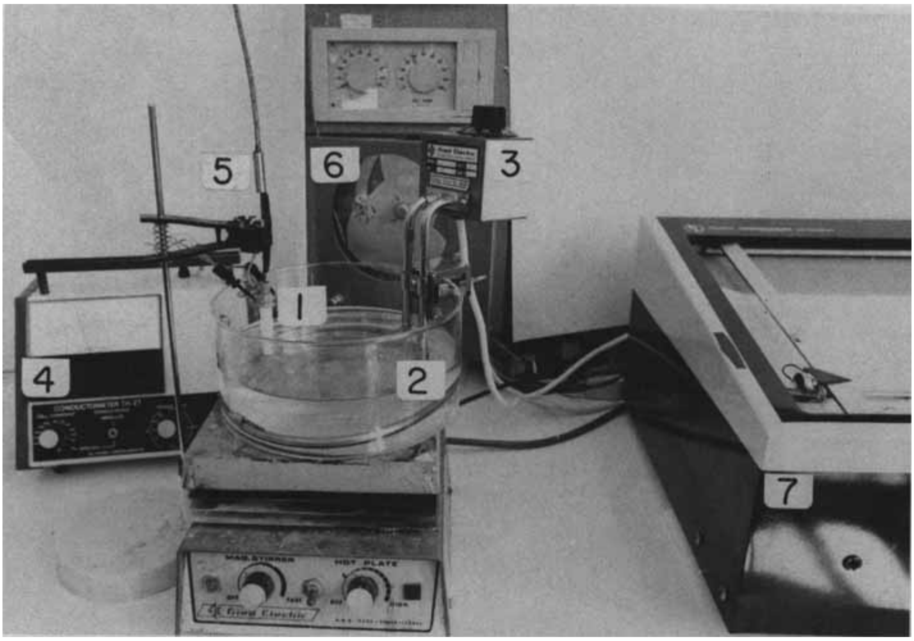

FIGURE I

Separation temp. measurement apparatus

1. electrodes cell
2. water bath
3. heating element
4. conductometer
5. thermocouple
6. temperature controller
7. x-y recorder

Separation temperature measurements were carried out using the apparatus shown in Fig.I.

Electrical conductivity tests were carried out using the apparatus shown in Fig.II.

The above machinery was mainly composed of temperature controller (West Gardian), Conductivity Cell and El-Hama Conductometer. The temperature was measured by a thermocouple placed in the bottom of the conductivity cell. The conductivity was measured in a cell equipped with electrodes at the bottom. This

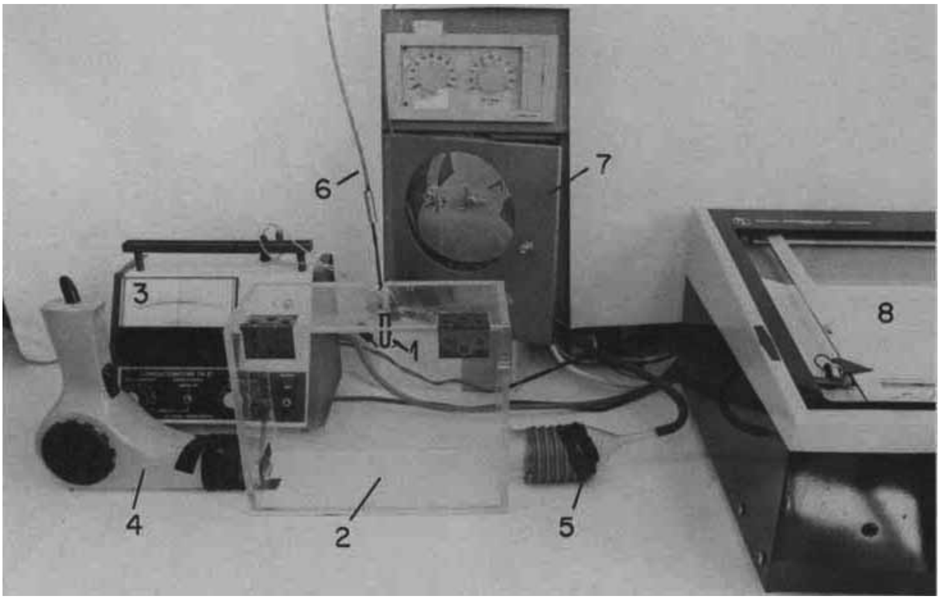

FIGURE II

Λ/h index determination system

1. electrodes cell
2. air chamber
3. conductometer
4. warm air
5. cold air
6. thermocouple
7. temperature controller
8. x-y recorder

placement of the electrodes prevents a measurement of the conductivity which is the result of creaming, or floating air bubbles.

RESULTS AND DISCUSSION

Fig III demonstrates a typical conductivity curve obtained from a heating-cooling-heating cycle, carried out immediately after preparing the semi-solid oil in water emulsion. It can be clearly seen that as expected there is an increase in emulsion conductivity drops to a value lower than in the first curve. In the second heating cycle the conductivity was always lower than

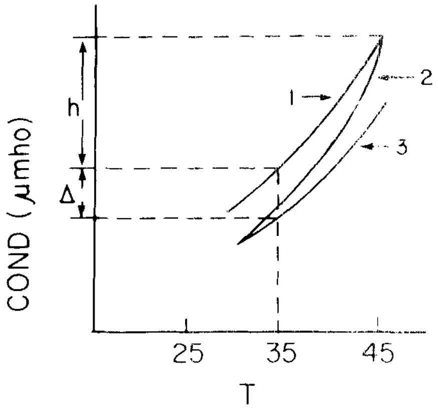

FIGURE III

A typical conductivity vs. temp curve

1. conductivity vs. temperature curve during the first heating process.
2. conductivity vs. temperature curve during the cooling process.
3. conductivity vs. temperature curve during the second heating process.

in the first heating cycle. The change in the conductivity within the 35-45°C was measured and named h, and the interval within the two heating curves at 35°C was also measured and named Δ (the temperature 35°C was chosen arbitrarily). h and Δ are specific and characteristic to each emulsion.

It has been assumed that emulsion having the two heating curves with the smallest interval (gap) will be the more stable.

In order to facilitate comparison between any two given emulsions with different starting conductivity it was decided to define the value of Δ/h which is indicative of the relative stability index. The smaller the relative stability index, the more stable is the emulsion (Fig. III).

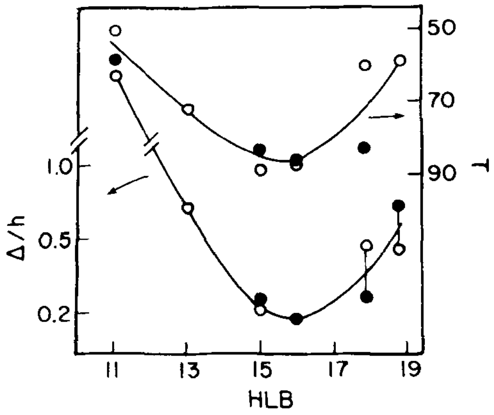

FIGURE IV

Δ/h index and separation temp. vs. HLB

Δ, O: two identical series of emulsions, prepared by different Myrj emulsifiers (3%), at constant oil phase concentration (Ø=0.1).

The validity of the proposed method is demonstrated through a series of emulsions, which were prepared at different HLB's, emulsifier concentration, and oil phase concentration.

1. Determining the HLB Value

The required HLB value for the system, was determined in a series of emulsions, containing 3% emulsifiers from the Myrj series. Those emulsifiers were chosen because of the similarity of their hydrophobic group to the main component of the oil phase, Cetyl Alcohol.

In Fig. IV, there is a comparison of the stabilities of the emulsions, which were tested by two methods: the Δ/h value, and the separation temperature of the emulsion. The correlation between those two tests is very clear: the lowest Δ/h value (0.2), is obtained at HLB=16, which gives the emulsion with the highest separation temperature (88°C). Checking of particle

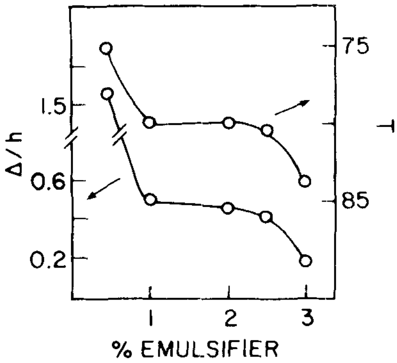

FIGURE V

Δ /h index and separation temperature, vs. emulsifier concentration for emulsions prepared at HLB = 13.7 (combination of Brij 52-58), and Ø=0.1.

size distribution by microscope, shows that the smallest particles (0.5 μm), were observed at HLB=16.

2. Determining the Optimal Emulsifier Concentration

A series of emulsions prepared at HLB=13.7, were prepared by a combination of Brij 52-58 emulsifiers, at different concentrations.

Fig. V shows that the most stable emulsion was prepared at 3% emulsifier concentration, having Δ/h index close to 0.2. The same result is obtained by the separation temperature stability test, and by checking the particle size distribution: the smallest particle sizes are achieved at 3% emulsifier concentration, and the highest separation temperature (84°C). It is worth noticing that there is a rapid drop in Δ/h values, up to 1% emulsifier, where an emulsion having a considerable stability is achieved, (separation temperature above 80°C).

3. Determining the Optimal Oil Phase Concentration (Ø)

The stability of emulsions having different oil concentrations was studied, maintaining the HLB and the emulsifier concentration constant.

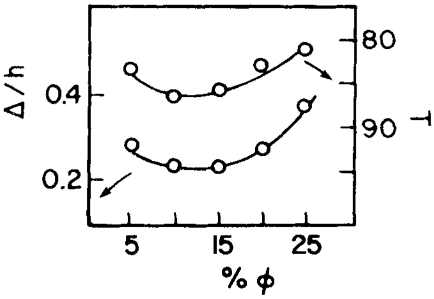

FIGURE VI

Δ/h index and separation temperature, vs. oil phase concentration (Ø), for emulsions prepared at HLB=15.7 (Brij 58), and constant emulsifier concentration (3%).

It can be seen, that by the Δ/h value, the most stable emulsions are prepared at 10-15% oil phase concentration (Fig. VI) while changing Ø from 5 to 25%, the change of Δ/h value is small: only from 0.2 to 0.4. The same results are obtained by separate temperature tests, and here again, there is only a small difference between the separation temperature (about 5°C). The finest particles were observed at 5-10% oil phase concentration.

SUMMARY

From these results, it is clear that the proposed method for evaluation of emulsion stability, is valid for viscous emulsions, the results which are obtained by this method are in good correlation to other methods. By using the Δ/h index, it is possible to determine the required HLB for an emulsion, the optimal amounts of the oil phase, and emulsifier concentration. This method is tested now on various kinds of emulsions, in order to study the scope and limitations of the new proposed method.

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