Stability of Emulsions Prepared by Vapor Condensation

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**Abstract.** Emulsions, consisting of a mixture of two immiscible liquids, one dispersed in another, with an added amphiphilic surfactant, have been extensively used in different areas such as cosmetics, pharmaceutics, material synthesis for new applications, for example thermal energy storage, new cooling systems etc. The current study focuses on emulsion preparation using a novel technique[1], namely water vapor condensation on an oil-surfactant layer containing one or two surfactants. The method was incompletely investigated previously, thus experiments were initiated in order to assess the emulsion stability for different working conditions. Two distinctive configurations were experimentally studied, one, with an adiabatic, constant room temperature bottom and another, with a high, constant temperature bottom. A mixture of two surfactants, Tween 80 and Span 80, was used in different ratios, also, the condensation time and the vapor flowrate were varied. The obtained emulsions stabilities were assessed visually and also, by pH measurements, over couple of week time period. The estimated average emulsion particle size was within the microscale range.

1. **Introduction**

Emulsions are defined as dispersed systems consisting of two immiscible liquids, one referred to as the dispersed or discontinuous phase, spreaded within another, named the continuous phase, stabilized by an amphiphilic surfactant [2]. Based on their droplet size, they can be classified in macroemulsions (mean diameter ranging from 0.1 to 100 µm) [3], microemulsions (100Å - 100 nm) [4] and nanoemulsions (20 - 200 nm) [5]. The various tunable properties of the emulsions make them suitable for application in different fields such as: cosmetics, pharmaceutics, material synthesis for new purposes such as thermal energy storage, new cooling systems etc.

One of the major characteristics of an emulsion is its physical stability consisting of a uniform distribution of the dispersed particles throughout the continuous phase. The stability is visually assessed by simple storage at different temperatures (usually 0-40°C) for 24 h up to 15 days. It can be also evaluated by accelerated aging methods, for example repeated hot-cold cycles or even, centrifugation to establish the emulsion stability index (ESI), many times referred as creaming index (CI), known to have higher values for less stable emulsions. In an emulsion three types of physical instabilities can be encountered: creaming, flocculation and breaking. The creaming consists of two layer separation, one richer in the disperse phase than the other. It can be reduced by decreasing the droplet size, increasing the droplet concentration and even, the system viscosity by addition of different substances such as methylcellulose or paraffin. Flocculation consists of cluster formation due to the aggregation of dispersed phase particles and can be followed by sedimentation. It can be prevented by coating particles with a high charge density surfactant that keeps them separately. Breaking implies phase separation and can be prevented by controlling the factors responsible for creaming and flocculation.
A stable emulsion can be prepared by an appropriate selection of the components and the corresponding optimum quantities, the attainment of the best hydrophilic-lipophilic balance (HLB), appropriate storage conditions, addition of some ingredients that can increase the emulsion stability etc.

The main emulsion preparation techniques are classified in low and high energy methods and have been extensively used to obtain all types of emulsions. Recently, a new technique has been proposed, namely the condensation method consisting in water vapor condensation onto a subcooled oil-surfactant solution [1]. Water droplets nucleate at the oil/air interface and spontaneously disperse within the oil, due to the spreading dynamics. Oil-soluble surfactants stabilize the resulting emulsions. The oil-surfactant concentration controls the spreading behavior as well as the droplet size, the polydispersity and the stability of the resulting emulsions [1].

Despite the discussions related to the emulsion formation mechanism, the major parameters thought to influence the particle size and ultimately, the emulsion stability, have not been investigated. Thus, this study focuses on some preliminary experiments meant to identify these aspects. Commercial sunflower oil, with an added mixture of Tween 80 and Span 80, were used as a base layer for water vapor condensation, in order to obtain emulsions. Among the parameters assumed to influence the emulsion particle size and thus, the emulsion stability, the following were investigated: the vapor flowrate, the condensation time, the surfactant mixture-oil ratio, the emulgator final HLB. Also, two settings with different bottom temperatures were studied.

These data can be used as a starting basis to investigate the vapor condensation technique to obtain high stability emulsions.

2. Experimental setup and measurement procedure. Data analysis

2.1. Materials and sample preparation

Tween 80 (polyoxethylene sorbitan monooleate) and Span 80 (sorbitan monooleate), two high and respectively low hidrophilic-lipophilic emulsifiers, (with HLB=15.0 and respectively, HLB=4.3) from Sigma Aldrich, sunflower oil (SO) bought from a local store and double distilled water were used in this study.

Sunflower oil and a mixture of Tween 80 and Span 80, both measured with a pipette or a graded cylinder, depending on the needed volume, were introduced in a Berzelius glasses and homogenized for couple of minutes, at 500 rpm, using a magnetic stirrer. Afterwards, the glasses were placed in the lab apparatus described below, to enable the water vapour condensation and finally, the emulsion formation. Two types of emulsions were prepared by varying the sunflower oil : water ratios to be either 1:4 or 4:1. Once the assessed time for the desired vapour condensation elapsed, the samples were removed from the experimental apparatus and let to cool, at room temperature. The prepared emulsions were observed right away and also, after 24 h. If no phase separation, creaming or sedimentation occurred within first 24 h, the samples were used to be further analysed. The literature indicates that an emulsion stable for one day, remains usually stable for several days [6].

2.2. Experimental laboratory setup

The set-up used to perform all experiments is presented in Figure 1. A special chamber 1, with a heating jacket 2 (filled with water), was used to store a beaker 3, containing a sunflower oil (SO) layer where, previously, a mixture of the two above mentioned emulgators was stirred. The chamber was sealed with a flange lid 4, fitted with an inlet tube 5, for vapor admission. The whole system was placed on a heating plate 6. A steam generator 7 provided with a pressure gauge 8 and an admission valve 9 was used to provide vapour with an adjustable flowrate measured using a flowmeter 10. Digital thermometers (TR) were used to verify the temperatures within the system.

Two different configurations related to the bottom surface temperature were investigated, while the other conditions were maintained the same, in order to assess the emulsion stability. The first one consisted of an adiabatic, constant room temperature bottom (Tb= 20°C) and the second one, of a high, constant temperature bottom (Tb=90°C). The latter was achieved by placing the chamber onto the heating surface, maintained at a constant temperature, until the steady state regime was attained.
A total of seventeen samples, for different conditions, were prepared and their stability was visually assessed within first 24 h and over couple of days, or even weeks, time period. Also, the emulsion pHs were monitored as a measure of their stability and for the creaming emulsions, the creaming index (CI) was reported.

2.3. Preliminary calculations and data analysis

The emulsifiers were prepared using the surfactants Span 80 and Tween 80 in different weight proportions to have a resulting HLB value of 10\textsuperscript{[7,8]} or 11.6. In order to calculate the needed Span 80 mass concentration, \(c_{sp}(\%)\), to achieve a certain HLB value, the following equation was used:

\[
\frac{c_{sp}}{c_{tw}} = \frac{HLB_{tw} - HLB_{f}}{HLB_{tw} - HLB_{sp}} \cdot 100
\]  

(1)

where the Tween 80 surfactant has a HLB\(_{tw}\)=15, Span 80 HLB\(_{sp}\)=4.3 and the final HLB of the emulsifier obtained by mixing Span 80 with Tween 80, HLB\(_{f}\)=10\textsuperscript{[8]}. Thus, the calculated mass percentage of Span 80 and respectively, Tween 80 are presented in Table 1:

| Det. No. | HLB\(_{f}\) | Span 80 mass concentration (%) | Tween 80 mass concentration (%) | Span 80: Tween80 |
|----------|--------------|---------------------------------|---------------------------------|------------------|
| 1        | 10           | 46.73                           | 53.27                           | 8:9              |
| 2        | 11.6         | 31.78                           | 68.22                           | 1:2              |

The unstable emulsions were characterized by the creaming index defined using the following equation:
\[ CI = \frac{H_C}{H_E} \times 100 \% \]  

with \( H_C \) – the height of cream or aqueous layer and \( H_E \) the total height of the emulsion layer. It is known that the higher the CI value, the lower the system stability \[9,10\].

3. Results and discussions

The investigated values of the emulsifier mixture : oil ratio, the final hidrophilic-lipophilic balance (HLB\( f \)), the water vapour flowrate and the condensation time are presented in Table 2. Also, the last column of the table 2 indicates the final characteristics of the obtained emulsions.

**Table 2.** Emulsion composition (S1* prepared at \( T_b=20^\circ C\); S2-S17 prepared at \( T_b=90^\circ C\)).

| Sample number | Surfactant mixture:oil ratio(w) | HLB\( f \) | Condensation conditions | Emulsion stability |
|---------------|---------------------------------|-----------|------------------------|-------------------|
|               |                                 |           | Water vapour flowrate (m\(^3\)/h) | Time (min) |
| S1*           | 1:1                             | 10        | 0.3                    | 5                 | creaming         |
| S2            | 1:1                             | 10        | 0.3                    | 5                 | stable           |
| S3            | 1:1                             | 11.6      | 0.5                    | 5                 | creaming         |
| S4            | 1:1                             | 11.6      | 0.5                    | 5                 | creaming         |
| S5            | 5:4                             | 11.6      | 0.5                    | 5                 | creaming         |
| S6            | 5:4                             | 10        | 0.3                    | 5                 | creaming         |
| S7            | 5:4                             | 10        | 0.5                    | 3                 | creaming         |
| S8            | 5:4                             | 10        | 0.7                    | 2.1               | stable           |
| S9            | 3:2                             | 11.6      | 0.5                    | 5                 | creaming         |
| S10           | 3:2                             | 11.6      | 0.3                    | 5                 | stable           |
| S11           | 3:2                             | 10        | 0.5                    | 3                 | creaming         |
| S12           | 3:2                             | 10        | 0.3                    | 5                 | creaming         |
| S13           | 3:2                             | 10        | 0.7                    | 2.1               | creaming         |
| S14           | 2:1                             | 11.6      | 0.5                    | 5                 | creaming         |
| S15           | 1:2                             | 10        | 0.7                    | 2.1               | stable           |
| S16           | 1:2                             | 10        | 0.5                    | 3                 | stable           |
| S17           | 1:2                             | 10        | 0.3                    | 5                 | stable           |

3.1. The bottom surface temperature

Two identical samples consisting of 10 mL sunflower oil, a mixture of Tween 80 and Span 80, with a resulting HLB\( f \) of 10, were used to establish what surface condition is more suitable to obtain a stable emulsion.

The two emulsions, marked S1, and respectively, S2, obtained by vapour condensation with a constant bottom surface temperature, \( T_b \), of 20°C (room temperature) and, respectively, 90°C (heating plate), are presented in Figure 2 (a) and (b).

A couple of other similar samples were prepared and checked for the bottom temperature influence on the emulsion stability within the first 24 h and yielded the same results. In the first setup, there is a larger temperature difference between the vapour and the liquid layer which would be expected to increase the mass of the condensed vapours on the subcooled substrate, according to a simple heat transfer balance.
However, the condensed vapour mass was similar in the two setups. This suggests that on a cooler substrate, the vapour convection is more enhanced and probably the local rate of condensation becomes larger, thus, more unstable emulsions are obtained.

Thus, once the favorable condition was established, the rest of the prepared emulsions were obtained by vapour condensation on a high temperature substrate.

Pictures of all the other prepared oil-in-water samples are presented in Figure 3 (a1) and (b1) up to (a5) and (b5). The letters (a) and respectively, (b), stand for freshly prepared emulsions and respectively, 24 h after emulsions preparation.

3.2. The vapor flowrate
The vapour flowrate influence on the oil/water emulsion stability was investigated for the same emulgator mixture: oil of 2:3, namely at 0.3 and 0.5 m$^3$/h, for the same time period of 5 minutes (samples S9 and S10, presented in Figure 3 (a2), (b2)).

It was found that the lowest flowrate produced a stable emulsion, while the other one did not render a stable system.

This probably can be explained as follows: a lower vapour flowrate condensing on the liquid layer will induce a more gradual formation and stabilization of the droplets within the liquid layer.

Some of the samples prepared using the lowest vapor flowrate value did not render stable emulsions. (sample S6, as seen in Figure 3(a4), (b4) and sample S12, as seen in Figure 3(a5), (b5)).

The obtained water/oil emulsions (samples S15, S16, S17, as seen in Figure 4), no matter the vapour flowrate, of 0.3,0.5,0.7 m$^3$/h, have a relatively good stability and are characterized by a much higher viscosity (mayonnaise consistency) in comparison to the oil/water emulsions.
(a1) S3-stable, S4-creaming, S5-creaming (b1) S3-creaming, S4-creaming, S5-creaming

(a2) S9-creaming, S10-stable (b2) S9-creaming, S10-stable (a3) S14-creaming (b3) S14-creaming

(a4) S6-creaming, S7-stable, S8-stable (b4) S6-creaming, S7-creaming, S8-stable

(a5) S11-creaming, S12-creaming, S13-creaming (b5) S11-creaming, S12-creaming, S13-creaming

**Figure 3.** Oil/water emulsions, samples S3 up to S13 (a) freshly prepared; (b) 24h after preparation.

**Figure 4.** Water/oil emulsions, samples S15, S16, S17, 5 days after preparation.
3.3. The condensation time period
As the condensation time period increases, larger amounts of steam can be incorporated in the liquid substrate. However, for the emulsion stability, the data seem to indicate that the condensation time is a less important factor in comparison to the vapour flowrate.

3.4. Surfactant mixture:oil ratio
It is expected that a higher amount of surfactant mixture in the emulsion, provided the other experimental conditions are the same, would increase the emulsion stability due to the increase of the interfacial area (smaller diameter particles) and decrease of the interfacial tension. In Table 2, the investigated samples S1 to S14 (w/o emulsions) are ordered in ascending order of the surfactant:oil ratio values. Stable emulsions were obtained at all investigated ratios, however, one can observe that these values correspond to lower vapor flowrates, suggesting that the latter is a key parameter for stability.

3.5. Hidrophilic-lipophilic balance
It is known that a mixture of low and high HLB surfactants (hidrophilic- lipophilic balance) determines more stable emulsions since choosing different surfactant ratios allows for HLB tuning. As stated before, a HLB value around 10 was reported as suitable for a stable oil-water emulsion, however some of the prepared emulsions using vapour condensation did not exhibit good stability at this HLB value. Another HLB value of 11.6 was investigated for different parameter values, as seen in Table 2. In this case the Span80:Tween80 ratio was 1:2. However, stable or unstable emulsions were obtained for both HLB values, thus a clear conclusion cannot be drawn for now.

3.6. Emulsion stability
The emulsion stability was assessed visually right after their preparation, after the first 24 h and also, for the next couple of weeks.

An accelerated thermal stability test consisting of repeated increasing-decreasing temperature cycles was applied to the stable emulsions in an Eccocell 55 BMT oven. The temperatures were increased from 20°C to 50°C followed by cooling at the same rate. Five cycles were applied in each case and the emulsion stability was confirmed for samples S2, S8, S10, S15, S16, S17. For the unstable emulsions, the creaming index, calculated using equation (2), and measured after several days when its value maintained constant, is presented in Table 3:

| Sample number | S1  | S3  | S4  | S5  | S6  | S7  | S9  | S11 | S12 | S13 | S14 |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| CI(%)         | 27.57 | 30.00 | 28.57 | 20.00 | 18.60 | 65.12 | 20.00 | 16.22 | 31.82 | 46.34 | 20.00 |

These data seem to indicate that higher creaming index values, of 65.12% and respectively, 46.34%, are obtained in case of larger condensing vapour flowrates of 0.5 and respectively, 0.7 m³/h.

3.7. Emulsion pH
The pH values of the obtained emulsions were monitored from the initial moment for several days. It was found that the stable emulsions are characterized by an almost constant pH (graphs S8, S10, S11 in Figure 5), while the unstable emulsions are characterized by a decreasing pH value (graphs S2, S6, S7, S12, S13) especially in the first days after preparation.
4. Conclusions
The stability of the emulsions prepared by condensation of water vapor on an oil liquid layer, containing a mixture of two surfactants, was investigated. The experimental study examined the influence of some of the parameters thought to be important in this technique. The obtained data seem to indicate that a lower condensing vapor flowrate renders, in most cases, more stable emulsions, even at lower surfactant mixture:oil ratio. Values of 10 and 11.6 of the hidrophilic-lipophilic balance, corresponding to a Span80: Tween 80 ratio of 8:9 and respectively, 1:2 did not seem to indicate any major difference in the obtained emulsions stabilities. Repeated heating-cooling tests operated on stable emulsions did not change their appearance and structure. Measured pH values for stable emulsions within 2-3 days after preparation remain almost constant while for the unstable emulsions, they tend to decrease.

5. References
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