

Determination of Liquid Paraffin Emulsions' Stability Parameters using Spans as Emulgent

ABSTRACT

Aims: To prepare liquid paraffin emulsions using spans of different grades as emulgent in extensively different concentrations and then determine the formulations' stability parameters.

Study design: The study consulted some literatures to have the basic knowledge before laboratory experiments were conducted.

Place and Duration of Study: This study was conducted in Obafemi Awolowo University Ile Ife, Nigeria laboratory between 2023 and 2024.

Methodology: The characteristic properties of different formulations of liquid paraffin emulsions prepared using spans of different grades as emulgent has been studied. The influence of emulgent of various concentrations (2.5- 30%) on the properties of w/o emulsions containing 30% aqueous phase was examined using dilution, dye-solubility, cobalt chloride tests and Rion viscotester VT-04 to determine melting point and softening determination, creaming profile, viscometric and emulsion type.

Results: The result revealed Span 20 and Span 80 to be light yellowish in colour and hydrophobic in nature while Span 60 was miscible with water when heated to 75 °C. Liquid paraffin emulsions formulated via Spans 20, 80 and 85 were all noticed to be physically stable liquid emulsion products at room temperature. The values of the softening and melting point of the Span 85 based creams were lower (32-33 and 35-36 °C) than those of Span 80 based products (35-36 and 41-43 °C) respectively. The yield values of Spans 20 and Span 80 solid emulsions were observed to be relatively high in the range 3500-4000 P when compared with those of Span 85 based creams having 500-1050 P. Two layers of different densities of the dispersed phase were observed by the emulsion phase. Rapid dispersion of the Spans 20, 80 and 85 stabilized samples 1, 2 and 3 emulsion drops that were placed into distilled water was observed. The other Span based formulations which contain higher concentrations (15-30%) of the emulgent (samples 4, 5, 6 and 7) were also observed to be miscible with water.

Conclusion: In conclusion, the emulgent at various concentrations has positive influence on liquid paraffin emulsions at some friendly conditions.

Keywords: Liquid Paraffin Emulsions, Stability Parameters, Spans, Emulgent, Phase inversion temperature

1. INTRODUCTION

An emulsion comprises two immiscible liquid phases. From these, one is uniformly dispersed and finely divided in the other [1]. The dispersion is such that the dispersed phase comprises small liquid globules dispersed all through a vehicle in which it is immiscible. Also, an emulsion is defined as a heterogeneous system where liquid crystals or liquid droplets are distributed in a liquid. Thus, a mixture that contains two or more liquids that are immiscible is called an emulsion. Emulsions are generally classified as two-phase systems of matter referred to as colloids. Furthermore, a system that possesses a natural potential to be separated into two component phases and is thermodynamically unstable is also referred to as an emulsion [2]. A stable emulsion consists of at least three components. These are (1) the dispersion medium

also called a continuous (or external) phase, (2) the dispersed liquid also referred to as the internal (disperse or discontinuous) phase and (3) the emulsifying agent (emulgent or emulsifier) which is applied as stabilizer to the system. One of the immiscible liquids is often an aqueous liquid while the remaining is oil. Interface is the boundary existing between the continuous and dispersed phases.

Emulsions usually have an appearance that is cloudy due to many phase interfaces scattering light that are present as it travels through the emulsion. When all light is equally distributed, emulsions appear white. Low-wavelength light having higher frequency is dispersed more when the emulsion is dilute, and it thus appears blue which is called the Tyndal effect. The color becomes distorted towards yellow when it is highly concentrated. Emulsions do not form spontaneously due to their usual unstable attribute [3]. Energy applied via stirring, shaking, spraying and homogenizing is required to form an emulsion. As time progresses, emulsions tend to return to the phase stable state which comprises the emulsion [15-17]. The emulsifier type and volume fraction of both phases are the major determinants of an emulsion turning into an oil-in-water emulsion or a water-in-oil emulsion. The continuous and the dispersed phases are adopted for the classification of an emulsion as either conventional or simple. An emulsion having oil distributed within it in the form of droplets in the entire aqueous phase is referred to as an oil-in-water (o/w) emulsion. However, the emulsion becomes water-in-oil (w/o) emulsion when oil is the dispersion medium, and water is the dispersed phase. Pharmaceutical emulsions that are applied in the administration of oral are relevant examples of oil-in-water emulsions [4].

However, internal droplet coalescence within the membrane phase may set in when instability of primary emulsion occurs [18-23]. Their osmotic growth causes external droplets to rupture because of their oil lamella breakdown. The ions of internal droplets determine the drug's appearance when incorporated in the inner aqueous phase inside the outer phase resulting from circumventing the diffusional transfer process [5]. The internal droplets may either coalesce before being expelled or the internal aqueous droplets may be expelled in one step by water passing via diffusion through the oil phase progressively leading to internal droplets shrinkage. The likelihood of the existence of this mechanism in all systems is still vague. However, the reduction in the system free energy is the main driving force that accounts for every step that brought about the w/o interfacial area reduction [6]. This involves the calculation of the change in the system's free energy. Whereas oil drop coalescence causes a large change in the system free energy with a mean diameter of several drops of each emulsion looking to increase for some period and subsequently remain fairly constant thereafter. The internal droplets coalescence does not occur to any level and would not be expected to be a main route of breakdown because these droplets coalescence would cause a large decrease in free energy [7].

Emulsion stability is referred to as an emulsion's ability to repel change in its properties as time progresses. Three types of instability exist in emulsions: creaming, flocculation, and coalescence [8]. Creaming in emulsions occurs when one of its substances migrates to the top (or the bottom, based on the two phase's relative densities) of the emulsion under centripetal force when using a centrifuge or under the impact of buoyancy [9]. Flocculation explains the process via which the dispersed phase comes out of suspension in flakes. Another form of instability is coalescence which occurs when small droplets combine to progressively form larger droplets after bumping into each other [10].

Nonetheless, emulsions can overturn from a w/o to an o/w emulsion or vice versa during sterilization or homogenization procedures. This phenomenon is called phase inversion and can be referred to as an instability form [11-12]. Phase inversion temperature (PIT) is the temperature at which phase inversion occurs. An emulsion stability can also be influenced by

oxidative decomposition and microbial contamination of oils which can be curbed via the addition of suitable antioxidants and preservative agents to the formulation [13]. A stable emulsion exists when a globule preserves its original structure throughout the emulsion's shelf life. Numerous factors affect the emulsion systems stability such as the droplet size, method of manufacture, oil nature, viscosity, pH, disperse phase, emulsion concentration, emulsion type, and electrolytes effects. Emulsion stability as a phenomenon depends on the equilibrium between oil, water, and surfactant. Multiple emulsions as other emulsions are generally thermodynamically unstable [14,24-26]. In this study, emulsions of liquid paraffin were prepared using spans of different grades as emulgent in extensively different concentrations (2.5- 30%) to target w/o emulsions containing 30% aqueous phase. Several complimentary techniques were used to carefully determine the emulsion type produced. Lastly, the determination of emulsion stability parameters was conducted.

2. MATERIAL AND METHODS

In this study, materials used are freshly prepared distilled water, liquid paraffin, cobalt chloride, and Span of 20, 80, and 85 grades. The glassware used includes test tubes, beakers, measuring cylinders, dispensing bottles, cream jars, pipettes, slides, and cover slips. Equipment items used are a hot air oven (Vindon Scientific Ltd), brookfield synchro-lectric viscometer VT-04, light microscope, mettler toledo weighing balance, stopwatch, rion viscotester, mortar and pestle, and spatula.

2.1 EVALUATION OF SPANS PHYSICAL CHARACTERISTICS

The emulgent's physical properties (Span 20, Span 60, Span 80, and Span 85) were examined. Their physical state (liquid or solid), appearance, viscosity, and miscibility with oil or water (liquid paraffin) were evaluated. About 1g of Span 60 and 2 or 3 drops of Span 20, Span 80, and Span 85 were placed in a beaker of distilled water to examine its miscibility at room temperature. Liquid paraffin was used to repeat the procedure. The miscibility of each substance with water and the oil was recorded.

2.2 PREPARATION AND STORAGE OF EMULSIONS

Samples of emulsion (about 100 ml or g each) were prepared using ingredients quantities shown in Table 1. Samples of different Span 20, Span 60, Span 80, or Span 85 as emulgent were prepared. For the preparation of Spans 20, 80, and 85 based emulsions, the liquid paraffin volume was measured into a mortar, and the required quantity of the (span) emulgent was added and mixed in the mortar. Then, 30 ml of water was poured into the mortar content and continuously mixed with a pestle until a stable emulsion was obtained. Span 60 based emulsions were prepared by weighing Span 60 (Table 1) and mixed with the liquid paraffin in a beaker. The mixture was warmed to a temperature of 600 °C on a hot plate to mix and melt the solid Span with the paraffin. When the temperature reached 750 °C, the required amount of water was added and mixed via continuous swirling to form the emulsion. The continuous mixing was stopped when the product was cooled to approximately 400 °C. To determine the creaming profile, 10ml of the freshly prepared liquid emulsion sample was dispensed into a calibrated test tube and the remaining product was poured into a 100 ml dispensing bottle having a tight-fitting screw cap. This was kept at room temperature (28 ± 2 °C) and was adequately labeled for subsequent tests. A sample is packed into a plastic cream jar having well-fitting screw cap lid when a semi-solid preparation was formed after 30 min and kept at room temperature for subsequent tests.

Table 1: Quantities of constituents in emulsion formulations

Sample parameters	Emulsion Sample Code/ Ingredients Quantities						
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Concentration (%w/v) or (w/w) of Span in sample	2.5	5	10	15	20	25	30
Weight of spans (g)	2.5	5	10	15	20	25	30
Volume of water (ml)	30	30	30	30	30	30	30
Volume of liquid paraffin (ml)	67.5	65	60	55	50	45	40

2.3 MELTING POINT AND SOFTENING DETERMINATION

The melting point and softening point of semi-solid samples were evaluated four days after preparation. The melting and softening temperatures were calculated by pacing a small portion (about 3 g) of the sample inside a test tube and a thermometer was dipped into it and placed in a water bath heated by a thermo-regulated hot plate at approximately 10 °C for 2 minutes. The lowest temperature at which the entire product sample in the test tube started flowing as an emulsion, was taken as the melting point. The temperature at which the semi-solid sample started to spread or slip under its weight on the test tube surface was recorded as the softening (or slip) point.

2.4 DETERMINATION OF CREAMING PROFILE

The creaming profile of the 10-ml sample placed in a calibrated test tube was measured daily for one week. The percent creaming was measured as the volume fraction of creamed emulsion, relative to the total sample volume.

2.6 VISCOMETRIC DETERMINATION OF PRODUCT SAMPLES

The viscosity of liquid samples was determined at room temperature (26±10C) using the Brookfield synchro-lectric viscometer (using spindle 3 and 4), while that of the semi-solid samples was measured by the Rion viscotester VT-04, using spindle 2. The shear stress readings (%) of the liquid samples in response to shear rates of 0.3, 0.6, 1.5, 3, 6, 12, and 30 revolutions per minute (rpm) were taken, while the viscosity drop of the semi-solid samples over 30 min was recorded directly from the viscotester.

2.7 DETERMINATION OF EMULSION TYPE

The emulsion type of samples was determined by the dilution, dye-solubility, and cobalt chloride tests. For the dilution test, 10 ml of distilled water placed in a beaker was mixed with about 1 g of the semi-solid samples or two drops of the liquid sample and approximately 10ml of liquid paraffin at room temperature. The spontaneous miscibility was observed when the mixture was thoroughly shaken in the beaker. For the dye solubility test, one drop of well-mixed liquid emulsion sample was placed on a glass slide, and methylene blue powder or Sudan IV powder was dusted on the slide and mixed with the sample. A cover slip was used to cover the slide and observed under the light microscope. The color of the dye taken up by the emulsion continuous or dispersed phase was noted, showing the phase in which the dye was soluble. The cobalt chloride test was carried out by dipping a strip of filter paper inside

the cobalt chloride solution and dried. Then 1 or 2 drops of the emulsion sample were placed on the treated filter paper to observe a change in the color change.

3. RESULTS AND DISCUSSION

3.1 PHYSICAL PROPERTIES OF THE EMULGENTS

At room temperature, the colour of Span 20 and Span 80 were observed to be light yellowish and are hydrophobic liquids in nature. They appear miscible with liquid paraffin but immiscible with water at room temperature. Their respective viscosity was measured at 8.1 and 8.3. Span 85 was also light yellowish at room temperature of 26 °C and was hydrophobic liquid. However, it becomes a semi-solid or viscous liquid at a very low temperature of ≤ 20 °C). At room temperature, it is also miscible with liquid paraffin but immiscible with water. Span 60 was observed to be a pale white amorphous crystalline solid (granules) at room temperature. At room temperature, it is neither miscible with water nor liquid paraffin. However, a formation of a homogenous mixture occurred resulting from span dissolution in liquid paraffin heated to a temperature of 60 °C. This mixture was observed not to separate on cooling. Span 60 miscibility with water was influenced only via heating the water to 75 °C. However, when the mixture was cooled to room temperature, the separation of the span from the aqueous mixture was noticed.

3.2 PHYSICAL PROPERTIES AND STABILITY OF SPAN-STABILIZED LIQUID PARAFFIN EMULSIONS

The preparations of Span 60 were liquid-based emulsion products when cooled to 40 °C. The uniformity of samples 4, 5, 6, and 7 of the Span 60 based emulsions was based on a semi-solid product. These formulations solidified on cooling to room temperature after dispersion into cream jars. The solid products also had a persistent and multi-phase appearance signifying the absence of homogenous mixing of oil and aqueous –phases. Sample 4 (15% w/w Span formulation) revealed significant separation of an excess oil phase (the un-emulsified) above a solidified emulsion phase after 1 hour of preparation. The liquid Span 60 based products (i.e. samples 1, 2, and 3 consisting of 2.5, 5.0, and 10 %w/v Span 60) were unstable and cracked between the periods of 1 hour after preparation.

On the other side, liquid paraffin emulsions formulated via Spans 20, 80, and 85 were all noticed to be physically stable liquid emulsion products at room temperature. This observation was maintained for about 30 min after preparation. After that, all the Spans 20, 80, and 85 emulsions consisting of 25 or 30 %w/w of the emulgent (i.e. Samples 6 and 7) changed to semi-solid. The Spans 20, 80, and 85 liquid paraffin products (samples 1 to 5) were liquid emulsions while samples 6 and 7 were solid emulsions.

Table 2 presents the solid product's softening and melting temperatures. The values of the softening and melting point of the Span 85 based creams were lower (32-33 and 35-36 °C) than those of Span 80 based products (35-36 and 41-43 °C) respectively. These were lower values than those of Span 20 based products. The melting and softening temperatures of Span 20 were observed to be temperature range for each determination.

Table 2: Melting and softening temperatures of solid span-stabilized emulsions

Span	Span concentration (%w/w)	Softening temperature (°C)	Melting temperature (°C)
Span 20	25	47 – 49	50 – 52
	30	48 – 50	51 – 52
Span 80	25	35	41
	30	36	43
Span 85	25	32	35
	30	33	36

3.3 SPAN BASED EMULSIONS VISCOMETRIC PROPERTIES

The viscometric properties of the liquid (samples 1-5) emulsions and span-stabilized solid (samples 6 and 7) are presented in Table 3. The yield values of Spans 20 and Span 80 solid emulsions were observed to be relatively high in the range of 3500-4000 P when compared with those of Span 85 based creams having 500-1050 P. The highest viscosity limit measured by spindle 2 of the RION viscotester was 4000 P. The Span 20 based sample 7 product which contains 30% w/w emulgents was noticed to be so hard because its yield was greater than 4000 and the subsequent viscosity measurement could not be determined by the equipment. However, viscosities ranging between 4 cP and 5 cP were recorded for the liquid span stabilized emulsion as compared to an unusually high viscosity of 212 cP. This was revealed by the Span 80 based sample 5 formulation.

Table 3: Viscometric properties of emulsion samples

Span-type used	Liquid samples					Solid samples			
	Sample Code/ Viscosity value (cP)					Yield value/ Terminal viscosity (P)			
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6		Sample 7	
Span 20	6.0	5.0	6.6	21.1	*13.9	3500/	1600	>4000	ND
Span 80	4.6	4.3	6.6	30.4	212.2	3500/	1000	3750/	750
Span 85	5.0	3.8	5.0	18.3	78.3	500/	280	1050/	780

3.4 SPAN-STABILIZED EMULSIONS CREAMING PROPERTIES

As expected, creaming was obvious only in the liquid formulations. Tables 4, 5, and 6 present the percentage creaming of the oil and aqueous phases of the emulsions for spans 20, 80, and 85 respectively. The volume ratio of the resultant percent emulsion phase is also presented. Two layers of different densities of the dispersed phase were observed by the emulsion phase. The lower-density phase was observed to be larger in volume than the higher-density phase and the lower-density phase was above the higher-density phase. Minimal (below 9%) and non-existence of oil phase creaming was noticed in most of the Spans 20, 80, and 85 products and was experienced only in samples 1, 2, or 3. Samples 4 and 5 revealed no oil phase creaming. However, the percent aqueous-phase creaming was higher (up to 40% in Span 85 based emulsions) as presented in Table 6, and happened in samples 1, 2, 3, and 4, but not in sample 5. The sample 5 formulations which contain 30% w/w Spans 20, 80 or 85 emulgent revealed no oil or aqueous phase creaming throughout the 7 days under which it was examined in which the emulsion phase was 100% throughout the examination period.

Table 4: Percent creaming of Span 20-stabilized liquid emulsions

Days		1	2	3	4	5	6	7
Sample 1	Oil phase	3	3	3	3	3	3	3
	*Emulsion phase	12,60	12,60	12,60	6,66	6,66	6,66	6,66
	Aqueous phase	25	25	25	25	25	25	25
Sample 2	Oil phase	0	3	3	3	3	3	3
	Emulsion phase	69	66	66	66	66	66	66
	Aqueous phase	31	31	31	31	31	31	31
Sample 3	Oil phase (ml)	0	0	0	0	0	0	0
	Emulsion phase	72	66	66	63	63	63	63
	Aqueous phase	28	34	34	37	37	37	37
Sample 4	Oil phase	0	0	0	0	0	0	0
	Emulsion phase	98	96	93	90	90	90	90
	Aqueous phase	2	4	7	10	10	10	10
Sample 5	Oil phase	0	0	0	0	0	0	0
	Emulsion phase	100	100	100	100	100	100	100
	Aqueous phase	0	0	0	0	0	0	0

Table 5: Percent creaming of Span 80-stabilized liquid emulsions

Days		1	2	3	4	5	6	7
Sample 1	Oil phase	3	6	9	9	9	9	9
	*Emulsion phase	3,66	3,60	3,54	3,54	3,54	3,54	3,54
	Aqueous phase	28	31	34	34	34	34	34
Sample 2	Oil phase	3	6	6	6	6	6	6
	*Emulsion phase	3,75	3,69	3,66	3,66	3,66	3,66	3,66
	Aqueous phase	19	22	25	25	25	25	25
Sample 3	Oil phase (ml)	0	3	3	3	3	3	3
	Emulsion phase	72	63	60	60	60	60	60
	Aqueous phase	28	34	37	37	37	37	37
Sample 4	Oil phase	0	0	0	0	0	0	0
	Emulsion phase	99	98	97	96	96	96	96
	Aqueous phase	1	2	3	4	4	4	4
Sample 5	Oil phase	0	0	0	0	0	0	0
	Emulsion phase	100	100	100	100	100	100	100
	Aqueous phase	0	0	0	0	0	0	0

Table 6: Percent creaming of Span 85-stabilized liquid emulsions

Days		1	2	3	4	5	6	7
Sample 1	Oil phase	9	9	9	9	9	9	9
	Emulsion phase	66	66	66	66	66	66	66
	Aqueous phase	25	25	25	25	25	25	25
Sample 2	Oil phase	6	6	6	6	6	6	6
	Emulsion phase	51	48	48	48	48	48	48
	Aqueous phase	43	46	46	46	46	46	46
Sample 3	Oil phase (ml)	3	6	6	6	6	6	6
	*Emulsion phase	3,63	3,57	3,57	3,57	3,57	3,57	3,57
	Aqueous phase	31	34	34	34	34	34	34
Sample 4	Oil phase	0	0	0	0	0	0	0
	Emulsion phase	69	63	60	60	60	60	60
	Aqueous phase	31	37	40	40	40	40	40
Sample 5	Oil phase	0	0	0	0	0	0	0
	Emulsion phase	100	100	100	100	100	100	100
	Aqueous phase	0	0	0	0	0	0	0

Note: * = Double values in a data cell indicate the emulsion phase having a lower-density (larger value) and a higher-density (smaller value) portion.

3.5 EMULSION TYPE OF SPAN-STABILIZED LIQUID FORMULATIONS

With reference to the cobalt chloride test adopted, all the emulsion formulations prepared using Spans 20, 80, or 85 were oil-in-water (o/w) and possessed an aqueous continuous phase because they turned the paper pink from the previous blue color.

With reference to the dilution test, rapid dispersion of the Spans 20, 80, and 85 stabilized samples 1, 2, and 3 emulsion drops that were placed into distilled water was observed. However, droplet formation that sank to the bottom of the oil inside the beaker was noticed when other emulsion drops were put in the liquid paraffin without mixing with the liquid paraffin. The other Span based formulations which contain higher concentrations (15-30%) of the emulgent (samples 4, 5, 6, and 7) were also observed to be miscible with water. They were produced spontaneously and were gradually dispersed in water. However, no form of dispersion was observed when any of these samples were put in the beaker containing liquid paraffin even at severe mixing for proper agitation.

4. CONCLUSION

The characteristic properties of different formulations of liquid paraffin emulsions prepared using spans of different grades as emulgent have been studied. The influence of emulgent of various concentrations (2.5- 30%) on the properties of w/o emulsions containing 30% aqueous phase was examined. The result revealed Span 20 and Span 80 to be light yellowish in colour and hydrophobic in nature while Span 60 was miscible with water when heated to 75 °C. Liquid paraffin emulsions formulated via Spans 20, 80, and 85 were all noticed to be physically stable liquid emulsion products at room temperature. The values of the softening and melting point of the Span 85 based creams were lower (32-33 and 35-36 °C) than those of Span 80 based products (35-36 and 41-43 °C) respectively. The yield values of Spans 20 and Span 80 solid emulsions were observed to be relatively high in the range of 3500-4000 P when compared with those of Span 85 based creams having 500-1050 P. Two layers of different densities of the dispersed phase were observed by the emulsion phase. Rapid dispersion of the Spans 20, 80, and 85 stabilized samples 1, 2, and 3 emulsion drops that were placed into distilled water was observed. The other Span based formulations which contain higher concentrations (15-30%) of the emulgent (samples 4, 5, 6, and 7) were also observed to be miscible with water. In conclusion, the emulgent at various concentrations has a positive influence on liquid paraffin emulsions at some friendly conditions.

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