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Ultrasonic assisted formation and stability of mustard oil in water nanoemulsion: Effect of process parameters and their optimization

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ABSTRACT

The present work reports the ultrasound assisted preparation of mustard oil in water nanoemulsion stabilized by Span 80 and Tween 80 at different operating conditions. Effects of various operating parameters such as HLB (Hydrophilic Lipophilic Balance) value, surfactant volume fraction (φ_S), oil volume fraction (φ_O) and power amplitude were investigated and optimized on the basis of droplet size and stability of nanoemulsions. It was observed that minimum droplet size of about 87.38 nm was obtained within 30 min of ultrasonication at an optimum HLB value of 10, φ_S of 0.08 (8%, v/v), φ_O of 0.1 (10%, v/v) and ultrasonic power amplitude of 40%. The stability of the nanoemulsion was measured through visual observation and it was found that the unstable emulsions got separated within 24 h whereas, stable emulsions never showed any separation until 90 days. In addition to that, the kinetic stability of the prepared nanoemulsions was also assessed under centrifuge and thermal stress conditions. The emulsion stability was found to be unaffected by these forces as the droplet size remained unchanged. The ultrasound prepared emulsion was found to be long term stable even after 3 months of storage at ambient conditions without any visual evidence of creaming and phase separation and also remained kinetically stable. FTIR analysis of the emulsions at different sonication conditions was carried out to examine the possible impact of ultrasonically induced chemical effects on oil structure during emulsification and it was found that the oil molecular structure was unaffected by ultrasonication process. The present work illustrates the formation and stability of mustard oil in water nanoemulsion using ultrasound cavitation which may be useful in food and cosmetic based applications.

1. Introduction

Nanoemulsions are gaining more interest due to their wide applications in food industries, pharmaceuticals, cosmetics, etc. because of their several benefits. Due to the nano droplet size, nanoemulsions retain long term stability i.e. up to several months and years [1] as compared to other conventional emulsions. Prior to the application of nanoemulsions, their characteristics and stability are to be well established. Mainly the emulsion stability against the various breakdown processes including coalescence, flocculation, creaming and Ostwald ripening, pose a great limitation against its use and synthesis [2].

In food applications, nanoemulsions are found as a novel system for delivery of various nutraceuticals. Nanoemulsions have potential to improve the solubility and bioavailability of many food active compounds and therefore serve as a carrier for the delivery of lipophilic active compounds in food applications [3,4]. In pharmaceuticals, nanoemulsion is suitable for drug delivery because of its ability in solubilizing the non-polar active compounds [5–7]. In cosmetics, nanoemulsions can be used for synthesis of skin and hair care products.

A nanoemulsion is a non-equilibrium system (i.e. thermodynamically unstable) and hence cannot be formed spontaneously [2]. Also, large amounts of emulsifiers are avoided in food, pharmaceuticals, and cosmetics based nanoemulsions. Therefore nanoemulsions require some desired amount of energy either in the form of agitation or mechanical disturbances to assist the emulsification process thus breaking the interface and reducing the emulsion droplet size [8]. Generally, high speed agitators and high pressure homogenizers are preferred for the preparation of nanoemulsions but these techniques consume high energy and have less control over the particle size distribution and stability of emulsions [8,9]. On the other side, Ultrasound method is found to be an efficient technique for the preparation of nanoemulsions that has better control over the characteristics of emulsions [9–12]. When ultrasound waves are transferred through the liquid medium, they create cavitation phenomena which comprise of the

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formation, growth and implosive collapse of microbubbles/cavities in the liquid medium. This transient collapse conditions generate a localized hot spot region consisting of very high temperature up to 5000 K and pressure up to 1000 bar [13]. Such intense cavitation conditions can initiate the desired physical transformation during emulsification. Ultrasound based emulsification occurs in two ways [14,15], first the generation of droplets in the acoustic field and second the creation of intense turbulence and microjets during asymmetric cavity collapse which cause the break up and dispersion of droplets in the continuous phase. Many studies proved the capability of ultrasound for producing the nanoemulsion of droplet sizes below 100 nm [8,9,16–18]. The emulsion having lower droplet size possesses long term stability. Therefore ultrasound can effectively control the particle size distribution as well as improve stability of the emulsions. Moreover, many studies have reported that ultrasound assisted nanoemulsions are proven to be suitable systems for the encapsulation and delivery of various drugs and food active compounds [8,17,19–23].

In the last decade, many studies have reported the use of ultrasound cavitation for the formation of Oil in water nanoemulsions using different essential edible oils such as coconut oil [9], sunflower oil [16], flaxseed oil [8,17], basil oil [18]. These oils mainly consist of the essential fatty acids, vitamins, etc. and therefore emulsions derived from these oils can be used to deliver bioactive compounds in food applications. As per the author's knowledge, few studies have been reported on the formation of mustard oil in water nanoemulsions using ultrasonication [24–26] however analysis of the kinetic and long term stability of this nanoemulsion system have not been studied which is the novel aspect of this work. Therefore, in the present study, the point of interest was the evaluation of kinetic stability of ultrasonically prepared mustard oil in water nanoemulsions under centrifugal and thermal stress conditions which is not reported in the literature. Another aim of the study was to evaluate the influence of ultrasound induced chemical effects on the prepared nanoemulsions.

Mustard oil is mainly obtained from the mustard seeds at low temperature (40–60 °C). It is widely used as cooking oil in India and is being considered as heart friendly oil. This oil protects against heart diseases which may be attributed to the presence of omega 3 polyunsaturated fatty acids. Like other edible oils, mustard oil is also rich in alpha-linolenic acid which reduces the cholesterol levels and consequently the risks of heart diseases. Alpha-linolenic acid is an essential fatty acid that is known to support cell, nerve & cognitive skills development in children and cardiovascular functions in humans [17,27]. Hence mustard oil is considered to be a safe and healthy edible oil. Moreover, mustard oil based cosmetics are found to be more favorable and protective for skin, as the oil contains high level of Vitamin E which protects against UV rays and other pollutants. Also, mustard oil possesses anti-bacterial and anti-fungal properties that effectively prevent skin infections [28]. Therefore, mustard oil based nanoemulsion can be better utilized in cosmetics and food applications.

In the present study, mustard oil in water nanoemulsions were prepared using ultrasound cavitation and stabilized by combination of Span80 (S80) and Tween 80 (T80) surfactants. The main objective of the present study was to evaluate the kinetic stability of the emulsions formed at the optimum operating condition and to study, the effect of various parameters such as HLB, surfactant fraction (φ_S), oil volume fraction (φ_O) and ultrasound power on emulsion properties. The kinetic stability of prepared emulsions has been evaluated under the centrifugal and thermal stress conditions. The present work also report the role of ultrasound induced chemical effects on the oil molecular structure of prepared nanoemulsion using FTIR analysis.

2. Materials and methods

2.1. Materials

Refined mustard oil was obtained from the local market. The surfactants Span 80 and Tween 80 were obtained from TCI Chemicals, India. Deionized water (Ultrapure, Thermofisher) was used for the preparation of all formulations. All the materials were used in experiments without any further purification.

2.2. Methods

2.2.1. Preparation of emulsion

The nanoemulsion was prepared using mustard oil as an internal phase in deionized water and the formulations were stabilized by the addition of surfactant Tween 80 and Span 80. Primarily the surfactants Tween 80 and Span 80, at the required HLB were premixed with deionized water and the mixture was heated up to 45 °C for the complete dissolution of surfactants. After cooling the mixture to room temperature, mustard oil was added dropwise into the mixture for the formation of an emulsion in a complete batch of 100 ml. The prepared formulations were further subjected to sonication for 30 min using Ultrasonic processor (VCX 750, Sonics, USA) that operated at 20 kHz with a maximum power output of 750 W. The schematic of experimental set up is shown in Fig. 1. To prevent overheating and temperature rise during the ultrasonication process, an ice bath was used to maintain the temperature difference (before and after sonication) at ⩽5 °C. The experiments were conducted at different HLB values (8, 9, 10, and 11) for getting the minimum droplet size and a stable emulsion. The desired HLB values can be calculated as given in Eq. (1):

$$HLB_{RESULTANT} = (HLB_{T80} \times V_T) + (HLB_{S80} \times V_S) \quad (1)$$

where $HLB_{RESULTANT}$, HLB_{T80} and HLB_{S80} are the HLB of mixed surfactant, Tween 80 (HLB:15.0) and Span 80 (HLB:4.3) respectively and V_T and V_S are the volume percentage of T80 and S80. HLB is a useful parameter in the selection of surfactant or emulsifier. The surfactants with lower HLB (<7) are favorable for water in oil emulsification whereas surfactants with higher HLB (>7) are favorable for the preparation of oil in water emulsion [13]. Therefore in order to obtain higher extent of stability of the prepared oil in water nanoemulsions, HLB value was varied from its lower to higher value

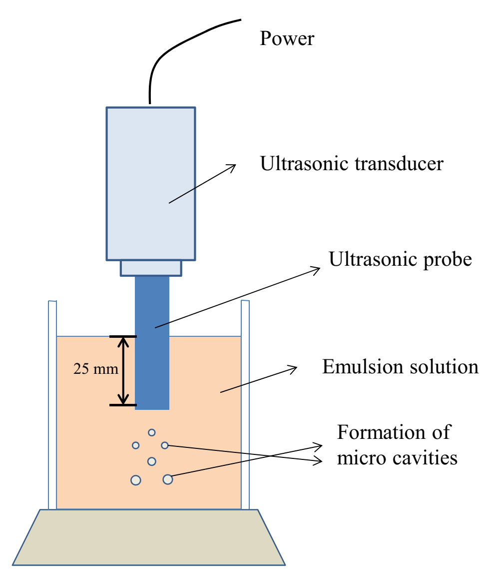

Fig. 1. The schematic of experimental set up (ultrasonic processor).