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Process optimization and stability of D-limonene-in-water nanoemulsions prepared by ultrasonic emulsification using response surface methodology

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ABSTRACT

D-limonene in water nanoemulsion was prepared by ultrasonic emulsification using mixed surfactants of sorbitane trioleate and polyoxyethylene (20) oleyl ether. Investigation using response surface methodology revealed that 10% D-limonene nanoemulsions formed at S_0 ratio (D-limonene concentration to mixed surfactant concentration) 0.6–0.7 and applied power 18 W for 120 s had droplet size below 100 nm. The zeta potential of the nanoemulsion was approximately −20 mV at original pH 6.4, closed to zero around pH 4.0, and around −30 mV at pH 12.0. The main destabilization mechanism of the systems is Ostwald ripening. The ripening rate at 25 °C ($0.39\ m^3\ s^{-1} \times 10^{29}$) was lower than that at 4 °C ($1.44\ m^3\ s^{-1} \times 10^{29}$), which was in agreement with the Lifshitz–Slezov–Wagner (LSW) theory. Despite of Ostwald ripening, the droplet size of D-limonene nanoemulsion remained stable after 8 weeks of storage.

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1. Introduction

D-limonene (4-isopropenyl-1-methylcyclohexene), a major flavor component extracted from citrus fruits, is used widely as flavor additive in cosmetics, foods, and other consumer products. Many literatures have demonstrated that D-limonene had bactericide, antioxidant, chemo-preventative and therapeutic activities [1]. But D-limonene is susceptible to oxidative degradation that results in the loss of lemon-like flavor under normal storage condition [2]. D-limonene is also insoluble in water at neutral pH. Therefore, emulsion technology is probably a good method to solubilize, encapsulate and protect this component.

There are a number of literatures which provide information for the formation of nanoemulsions of D-limonene/water systems. However, less has been done on the emulsion stability. Nanoemulsions were emulsions with droplet size between 20 and 200 nm [3]. Due to its small droplet size, nanoemulsions appear transparent or translucent, and were more stable against aggregation, flocculation, coalescence and Ostwald ripening compared with microemulsions. The physicochemical properties of nanoemulsions are interesting for practical applications because of its small droplet size and long term stability. Nanoemulsions are used in agrochemicals for pesticide delivery [4], in cosmetics as vehicles for personal care or skincare products [5], in fragrance as matrix to encapsulate the volatile compounds [6], and in beverages to give the products an opaque appearance and suitable aroma [7].

The use of ultrasound to prepare nanoemulsions is a recent development. Ultrasound is able to produce nanoemulsions with the advantage of less occurrence of "over processing" [8,9], and the ultrasonic emulsions are less polydispersed and more stable as compared with that prepared by other mechanical devices [10,11]. The ultrasonic emulsification involves two mechanisms [12]. Firstly, an acoustic filed produces interfacial waves to break the disperse phase into the continuous phase. Then, the formation of acoustic cavitation collapses micro-bubbles into smaller droplets by the pressure fluctuations. Formation of nanoemulsion droplets is controlled by the interaction between droplet breakup and droplet coalescence. Although ultrasound applied excellent shear force for droplet breakup, the rate of droplet coalescence is determined by the surface activity and concentration of surfactant [13].

The best nanoemulsions are prepared at optimum hydrophilic–lipophilic surfactant combination and concentration [14]. Combination of surfactants can provide different chain length distributions for forming and stabilizing the nanoemulsions. Paraffin oil in water nanoemulsions have been obtained by using the mixed surfactants Tween 80/Span 80 [15]. Isohexadecane O/W nanoemulsions could be obtained using mixed surfactant C12E4/C12E6 with 4 or 8 wt.% concentrations [11].

The main objective of this study was to systematically investigate the influence of ultrasonic emulsification conditions on the droplet size of D-limonene nanoemulsions, and to optimize the conditions for preparing D-limonene nanoemulsions with smallest droplet size using response surface methodology (RSM). In addition, the stability of D-limonene nanoemulsions under different storage times and temperatures were also examined.

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2. Materials and methods

2.1. Materials

D-limonene (ρ = 840 kg/m^3, RI = 1.487) was a product of Merck (Darmstadt, Germany). Reagent grade sorbitane trioleate and polyoxyethylene (20) oleyl ether with an average HLB number of 1.8 and 15.0, respectively, were supplied by Sigma (Deisenhofen, Germany). Ethylene glycol used as a co-surfactant in emulsion system was obtained from Merck. Water used in this study was deionized and Milli-Q (Millipore Corporation, Molsheim, France) filtered.

2.2. Nanoemulsion preparation

Nanoemulsions consisted of D-limonene, mixed surfactant, deionized water and co-surfactant. The concentrations of D-limonene in emulsion systems were 10 wt.%. The HLB value of the mixed surfactant used in this study was adjusted at 12. The co-surfactant concentration was fixed at 1%. The ratio of D-limonene concentration to mixed surfactant concentration was expressed as S_0 ratio, which varied from 0.26 to 0.94. All emulsions were prepared in two stages. The coarse emulsions were prepared by Polytron (PT-MR 3000, Kinematica AG, Littau, Switzerland), and then further emulsified by ultrasonic process. The Polytron blended the D-limonene, mixed surfactant, co-surfactant and deionized water together via the rotor/stator system, in which samples are drawn into the center of the generator tip, mixed and pressed through the narrow gap between the rotor and stator, and forced out between the teeth of the stator to form a coarse emulsion. Ultrasonic emulsification was performed by using a 20 kHz Sonicator 3000 (Misonix incorporated, Farmingdale, New York) with a 20 mm diameter tip horn. The tip of the horn was symmetrically placed in the coarse emulsion, and the process was carried out at various preset ultrasonic applied powers for different emulsification times controlled by the software of the device. During emulsification, the difference of temperature from initial coarse emulsions to final emulsion was not more than 20 °C. Each experiment was triplicated.

2.3. Droplet size determination

Emulsion droplet size was determined by dynamic light scattering using Nanotrac 150 (Microtrac Inc. Montgomeryville, PA). To avoid multiple scattering effects, all emulsion samples were diluted to 10% with deionized water before the measurement. A refractive index of 1.487 was used for D-limonene. Emulsion droplet size was estimated by the average of three measurements and presented as mean diameter of the volume distribution (*MV*).

$$MV = \frac{\Sigma V_i d_i}{\Sigma V_i} \tag{1}$$

where V_i is the volume percent between droplet sizes; d_i is diameter of droplets.

2.4. Experimental design

RSM was used to study the effects of the independent variables: applied power (X_1), time (X_2) and S_0 ratio (X_3) on the droplet size of D-limonene nanoemulsions. The experiments were designed according to the central composite design (CCD) using a 20 factorial and star design with three central points as shown in Table 1. Individual experiments were carried out in random order. A second-order polynomial equation was used to express the droplet size (Y) of the nanoemulsions as a function of the independent variables as follows:

Table 1
Droplet size of D-limonene nanoemulsions obtained from central composite design.

Experiment number	Variables			Droplet size (nm)	
	X_1	X_2	X_3	Experimental	Predicted
1	12	90	0.4	105	137
2	24	90	0.4	122	141
3	12	150	0.4	119	143
4	24	150	0.4	101	129
5	12	90	0.8	59	55
6	24	90	0.8	58	54
7	12	150	0.8	54	60
8	24	150	0.8	52	49
9	7.9	120	0.6	70	53
10	28.1	120	0.6	71	66
11	18	70	0.6	73	85
12	18	170	0.6	77	71
13	18	120	0.26	444	458
14	18	120	0.94	243	263
15	18	120	0.6	24	31
16	18	120	0.6	33	31
17	18	120	0.6	24	31
18	18	120	0.6	24	31
19	18	120	0.6	25	31
20	18	120	0.6	24	31

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 \tag{2}$$

where a_0 is a constant, a_i, a_{ii} and a_{ij} are the linear, quadratic and interactive coefficients, respectively. The coefficients of the response surface equation were determined using STATISTICA 7.0 (StatSoft Corporation, Oklahoma, USA).

2.5. Transmission electron microscopic analysis

The morphology of D-limonene nanoemulsion was visualized by using the transmission electron microscope (TEM). Samples (50 μL) were added to 200-mesh formwar-coated copper TEM sample holders (EM Sciences, Hatfield, PA, USA). The samples were then negatively stained with 50 μL of 1.5% (w/v) phosphotungstic acid for 10 min at room temperature. Excess liquid was blotted with a piece of Whatman filter paper. The TEM samples were observed with JEOL JSM-1200EX II transmission electron microscope (Peabody, MA, USA) equipped with 20 μm aperture at 67 kV.

2.6. Storage stability

The stability of nanoemulsions was determined by measuring the change of droplet size every week during storage at 4 and 25 °C for 14 weeks.

2.7. Electrophoretic properties

The electrophoretic properties of emulsion droplets were measured by using the Zetasizer nanosystem (Malvern instrument Ltd., UK). The zeta potential (ζ) calculated by Smoluchowski's equation was used to represent the electrophoretic properties:

$$\zeta = \frac{4\pi\eta}{\varepsilon}\frac{v}{U/L} \tag{3}$$

where, η and ε are the viscosity and dielectric constant of water, respectively, v is the mobile velocity of the oil droplets in the electric field, U is the voltage and L is the distance between the two electrodes. The pH values of emulsions were adjusted with 0.01 M NaOH or 0.01 M HCl using autotitrator (Malvern Instrument Ltd., United Kingdom) and the effect of pH on the zeta potential of

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