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ScienceDirect
LWT 40 (2007) 1376–1380
LWT
www.elsevier.com/locate/lwt

Continuous preparation of O/W nano-emulsion by the treatment of a coarse emulsion under subcritical water conditions

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Received 14 April 2006; received in revised form 6 September 2006; accepted 7 September 2006

Abstract

A coarse oil-in-water (O/W) emulsion, the oil phase of which was octanoic acid, was prepared at a very low surfactant concentration using a rotor/stator homogenizer. The emulsion was passed in a stainless steel tube immersed in an oil bath at 220 °C at a residence time of 60 s, and then mixed with the surfactant solution to produce a finely dispersed emulsion. The diameter of oil droplets in the fine emulsion was ca. 40 nm at the weight ratio of surfactant to oil of ca. 0.35 or higher.

Keywords: O/W emulsion; Nano-emulsion; Subcritical water; Homogenization

1. Introduction

Water, which maintains its liquid state at elevated temperatures under a pressurized condition, is called subcritical water. The water has two distinct properties, i.e. low relative dielectric constant and high ion product. Because the relative dielectric constant of subcritical water is low (Miller & Hawthorne, 1998), the water acts like an organic solvent that solubilizes hydrophobic substances at relatively high concentrations. Another property of the subcritical water is its high ion product (Clifford, 1998), i.e. high concentrations of hydrogen and hydroxyl ions. Therefore, subcritical water has the possibility to act as an acid or base catalyst (Krammer & Vogel, 2000), and is used for the decomposition of food-related materials (Holliday, King, & List, 1997; Oomori, Haghighat Khajavi, Kimura, Adachi, & Matsuno, 2003; Yoshida, Terashima, & Takahashi, 1999) and woody materials (Adschiri, Hirose, Malaluan, & Arai, 1993; Sasaki, Fang, Fukushima, Adschiri, & Arai, 2000).

The former property of the subcritical water suggested that fatty acids could be solubilized in water at high concentrations. We measured their solubility in the temperature range from 60 to 230 °C, and showed that their solubility at 200 °C or higher temperatures was hundreds-fold or a thousand-fold higher than that at ambient temperature (Khuwijitjaru, Adachi, & Matsuno, 2002; Khuwijitjaru, Kimura, Adachi, & Matsuno, 2004a). Based on these measurements, we devised a novel method to prepare a finely dispersed oil-in-water (O/W) emulsion by mixing water containing a dissolved fatty acid at a high temperature and a surfactant solution, and confirmed the realization of the method (Khuwijitjaru, Kimura, Matsuno, & Adachi, 2004b). However, the method was a batch operation.

In this study, we propose a continuous method to produce the finely dispersed nano-emulsion in a flow system in which a coarse emulsion prepared at a very low surfactant concentration is passed through a tube immersed in an oil bath at usually 220 °C and then mixed with the surfactant solution of a specific concentration. The practicability of the method is shown, and the factors affecting the size of the oil droplets in the emulsion are examined.

2. Materials and methods

2.1. Materials

Octanoic acid was purchased from the Tokyo Chemical Industry, Tokyo, Japan. Decaglycerol monolaurate

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0023-6438/$30.00
doi:10.1016/j.lwt.2006.09.004

(SY-Glyster® ML-750) was supplied by Sakamoto Yakuhin Kogyo, Osaka, Japan. All other chemicals were purchased from Wako Pure Chemical Industries, Osaka, Japan.

2.2. Preparation of O/W emulsion

Octanoic acid was mixed with a dilute ML-750 solution to produce an octanotic acid to ML-750 weight ratio of 150:1. The volume of the mixture was 300 ml contained in a 500-ml glass bottle, and the octanoic acid concentration in the mixture was 15–99 g/l. The mixture was homogenized at 10,000 rpm for 1 min using a rotor/stator homogenizer (Polytron PT20SK, Kinematica, Lucerne, Switzerland). Fig. 1 schematically shows the apparatus used for the continuous preparation of the O/W emulsion. The coarse emulsion, which was gently stirred by a magnetic stirrer (SR200, Advantec, Tokyo) to prevent flotation, was fed to the heating coil by an LC-10ATvp pump (Shimadzu, Kyoto, Japan). The heating coil ($\varnothing$ 1.0 mm × 0.75 m) made of SUS316 stainless steel was immersed in an oil bath (R105HB, Riko Kagaku Sangyo, Chiba, Japan) at 220 °C unless otherwise specified. The oil in the bath was also gently stirred by a magnetic stirrer (HM19G, Koike Seisakusho, Kanagawa, Japan). The residence time of the mixture in the heating coil was regulated at 60, 80 or 100 s; usually, 60 s. The mixture that passed through the coil was then mixed with an ML-750 solution (0.75–75 g/l) fed by another LC-10AS pump (Shimadzu) at a three-way joint. The volume ratio of the coarse emulsion to the ML-750 solution was 1:2. The temperature of the mixture was measured using an inline thermometer (TM-400, Jusco Engineering, Tokyo), and was 31, 32 or 34 °C when the temperature of the oil was 200, 220 or 240 °C, and the residence time of the mixture in the heating coil was 60 s. The mixture was pooled in the effluent reservoir after passing through a back-pressure regulator (High pressure adjustable BPR, Upchurch Scientific, Oak Harbor, WA, USA), which was used to regulate the system pressure at 10 MPa.

In order to examine the effect of the passage of the coarse emulsion through the HPLC pump and the coil without heating on the size of the oil droplets in the emulsion, the operation at room temperature was also carried out.

For comparison, the mixture of octanoic acid and the ML-750 solution, the concentrations of which were adjusted to the same ranges as those for the continuous preparation, was homogenized at 10,000 rpm for 1 min using the Polytron PT20SK homogenizer. The size distribution of the oil droplets in the emulsion was then measured.

2.3. Size distribution of oil droplets in emulsion

The size distribution of the oil droplets in an O/W emulsion was measured using a laser diffractive particle size analyzer (SALD-2100, Shimadzu, Kyoto). The median diameter was calculated on a volume-based distribution. When the diameter measured by the analyzer was less than 100 nm, the size distribution was measured again using a dynamic light-scattering photometer (DLS-5000D, Photal Otsuka Electronics, Osaka) at 632.8 nm from a He–Ne laser light source and at a 90° angle. The refractive index and viscosity of the solvent necessary for the calculation of the droplet diameter were measured using a highly sensitive refractometer (DRM-1039, Photal Otsuka Electronics) and a TVE-20L viscometer (Toki Sangyo, Tokyo), respectively.

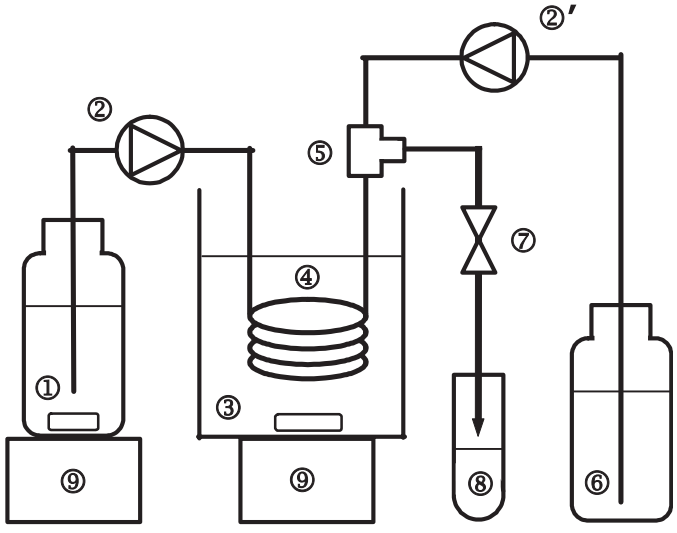

Fig. 1. Schematic diagram of the experimental apparatus: ① reservoir of a coarse O/W emulsion; ② and ②' HPLC pumps for delivery of the coarse emulsion and aqueous surfactant solution, respectively; ③ oil bath; ④ heating coil; ⑤ three-way joint; ⑥ reservoir of aqueous surfactant solution; ⑦ back-pressure regulator; and ⑧ sample collector.

3. Results and discussion

3.1. Preparation of fine emulsion

Fig. 2(a) shows the median diameters of the oil droplets in the emulsions prepared at various surfactant concentrations by the proposed and conventional homogenization methods. The temperature of the oil bath was 220 °C and the residence time in the tube immersed in the bath was 60 s. The emulsions were prepared at the residence times of 80 and 100 s, and no significant difference in the diameters was observed among the emulsions prepared at the different residence times. Therefore, the residence time of 60 s was adopted throughout this study. Because the coarse emulsion is shear-stressed by the piston-type HPLC pump and in the tube in the proposed system, there is the possibility that the shear-stress makes the oil droplets small without heating. Therefore, the coarse emulsion was, for comparison, treated in the system operated at ambient temperature. The octanoic acid concentration was 5.0 g/l in every case.