Journal of Molecular Liquids 215 (2016) 454–460

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

The effect of Na_2SO_4 concentration in aqueous phase on the phase inversion temperature of lemon oil in water nano-emulsions

Somaye Mashhadi [a], Hamedreza Javadian [a,*], Inderjeet Tyagi [b], Shilpi Agarwal [c], Vinod Kumar Gupta [b,c,**]

[a] Young Researchers and Elite Club, Arak Branch, Islamic Azad University, Arak, Iran
[b] Department of Chemistry, Indian Institute of Technology, Roorkee-247667, India
[c] Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa

ARTICLE INFO

Article history:
Received 11 December 2015
Accepted 12 January 2016
Available online xxxx

Keywords:
Lemon oil
Phase inversion
Emulsification
Surfactant
Na_2SO_4

ABSTRACT

Lemon oil in water (LO/W) nano-emulsions were synthesized using the phase inversion temperature emulsification technique (PIT), which is used as a low-energy method to produce the samples which are stable in the long term. Tween 40 was used as a surfactant and the effect of Na_2SO_4 concentration on the synthesizing method i.e. PIT and the particle size was well investigated and elucidated. The particle size and distribution index of LO/W emulsion measurement were carried out using zeta potential analyzer. To compare the size and stability of nano-emulsions by variations in temperature and time, the transmittance percentage of prepared nano-emulsions with different concentrations of Na_2SO_4 was determined by spectrophotometer UV–Vis at a wavelength of 600 nm. According to the results, with increase in Na_2SO_4 solution concentration from 0.05 to 1 M, a gradual reduction was observed in the PIT from 66 to 49 °C. The optimum temperature was also reduced with increase of Na_2SO_4 concentration in the aqueous phase and the optimum temperature was found to be 9 to 16 °C below the PIT to have the nano-emulsion with more stability. The average drop sizes for nano-emulsions with 0.25 and 0.8 mol/L of Na_2SO_4 in aqueous phase at 25 °C were 9.6 and 11.1 nm, respectively, and the dispersion index were 0.380 and 0.311, respectively.

1. Introduction

Emulsion is a solution in which tiny drops of a liquid (such as oil) are scattered in another liquid (such as water) without mixing (Scheme I). In other words, if two fluids are accumulated so that they are not resolved and come in suspense, it is called emulsion. Emulsions are generally divided into two categories: oil in water (O/W) like ice-cream or milk and water in oil (W/O) like butter and margarine [1,2].

The process of dispersing a material as separate drops in another substance is called emulsification. This particular method should be maintained for a certain time in industrial scale. Emulsions are thermodynamically unstable and may gradually lose their stability. Depending on the drops size, emulsions can be divided into mini or nano-emulsion (10 to 100 nm), micro-emulsion (100 to 1000 nm) and macro-emulsion (0.5 to 100 μm) [2,3]. Their appearance is transparent or semitransparent in sizes ranging from 50 to 200 nm and is milky above 500 nm [4].

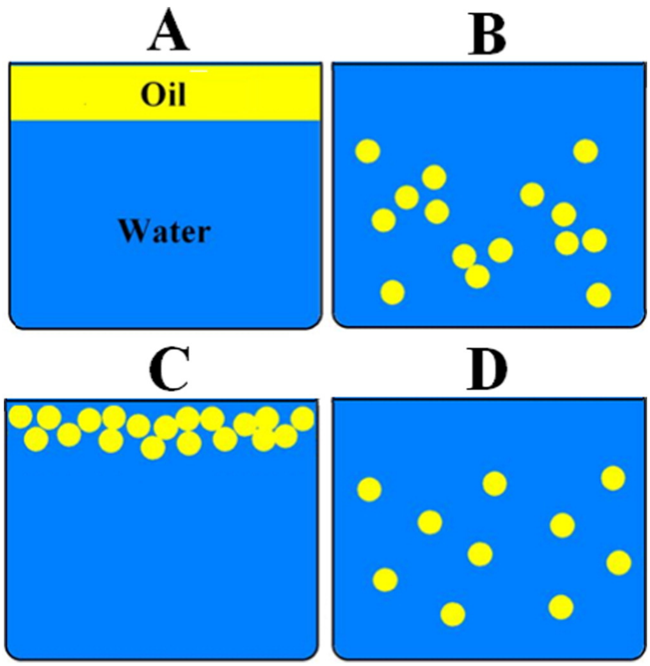
Usage of nano-emulsions is current for the following reasons: (1) Very small drops size, lower weight and Brownian diffusion may be barrier for any clots or deposition of drops, (2) Small drops and high kinetic stability make nano-emulsions appropriate for effective delivery of active agents and the permeation to the uneven texture of the skin, (3) Unlike micro-emulsions that need high surfactant concentration typically in the range of 10–30%, for nano-emulsions, an average concentration of surfactant in the range of 5–10% is sufficient, and (4) Unlike micro-emulsions that they are also transparent and thermodynamically stable, nano-emulsions are only kinetically stable [4–6].

Nano-emulsions have various industrial applications, for example, in the preparing of environment for the polymerization reaction, construction and cosmetic materials (antimicrobial, drug delivery and burn healing) and the chemicals used in agriculture (liquid fertilizers and herbicides). They are non-equilibrium systems and do not form spontaneously. Thus, the energy of a typical mechanical device or chemical potentials is necessary for the formation of such compounds [7–9]. There are two main methods for preparing nano-emulsions: (1) The dispersion techniques in which the high-energy processes are needed and (2) The low-energy or density techniques that are formed by the intrinsic physicochemical properties of surfactants [10–12].

During the recent decades, researches have been based on low-energy processes to produce nano-emulsions. The low-energy methods are divided into two ways: (1) The method of producing spontaneous emulsification and (2) The phase inversion temperature (PIT). Studies have shown that these two systems are very close [13–16].

* Corresponding author.
** Corresponding author at: Department of Chemistry, Indian Institute of Technology, Roorkee-247667, India.
E-mail addresses: Hamedreza.javadian@yahoo.com (H. Javadian), vinodfcy@gmail.com, vinodfcy@iitr.ac.in (V.K. Gupta).

http://dx.doi.org/10.1016/j.molliq.2016.01.045
0167-7322/



Scheme I. (A) Two liquids not yet emulsified form two separate phases, a layer of oil on top of a layer of water. (B) The liquids have been stirred vigorously, initially the water layer and oil layers have formed an emulsion. (C) The unstable emulsion progressively separates back into two distinct layers (phases). (D) A stabilized emulsion with the addition of an emulsifier.

PIT is determined by several methods in which one of them is visual. Above this temperature, the emulsion is thin and watery and below this temperature the emulsion is white, opaque and thick. PIT can also be measured by measuring conductivity. The third way is determining by the pH. Above the PIT, the pH is unstable, while below the PIT, the pH is quite stable. In fact, above the PIT, oil pH is measured. According to scientists' studies, the migration of dual molecules from the oil phase to the water phase is possible with sudden changes in temperature. In other words, when the system is initially at a temperature above the PIT, with sudden dilution in order for temperature reduction to lower than PIT, a sudden change occurs in phase from W/O to O/W. In fact, this process represents that the formation of emulsions by surfactants can be controlled by temperature [13,17].

The surfactants are fats that have the dual properties of lipophilic (fat-loving) and hydrophilic (water-loving) (Scheme II). Surface tensions are reduced by surfactants between the two phases that are normally inaccessible, so the two phases would be able to form an emulsion [18–21]. In fact, the purpose of using surfactants is to prevent separation and stabilize the emulsion. Surfactants have different lipophilic and hydrophilic powers and their balance is called HLB, whose value is from 0 to 20 [22–55]. A surfactant with high lipophilic strength has low HLB value, while a surfactant with high hydrophilic strength has high HLB value (Scheme III).

As a result, although the emulsification goes to HLB temperature, but emulsions are very unstable. By rapid cooling or heating (30–25 °C) of emulsions prepared at HLB temperature, kinetically stable emulsions are generated with very small dimensions in the form of O/W or W/O, respectively. If the cooling or heating process is not quick enough, the concentration is preferred and coarse poly-dispersed emulsion is formed [56].

In this study, phase inversion temperature emulsification method (PIT) was used to prepare nano-emulsions of lemon oil in water (LO/W). The changes in the PIT and the drops size were investigated by the changes in Na_2SO_4 concentration in the aqueous phase. The drops size and dispersion index of LO/W were measured by zeta potential analyzer. The transmittance percentage of prepared nano-emulsions with different concentrations of Na_2SO_4 was determined by spectrophotometer UV–Vis at a wavelength of 600 nm to compare the size and stability of nano-emulsions by variations in temperature and time.

2. Methods

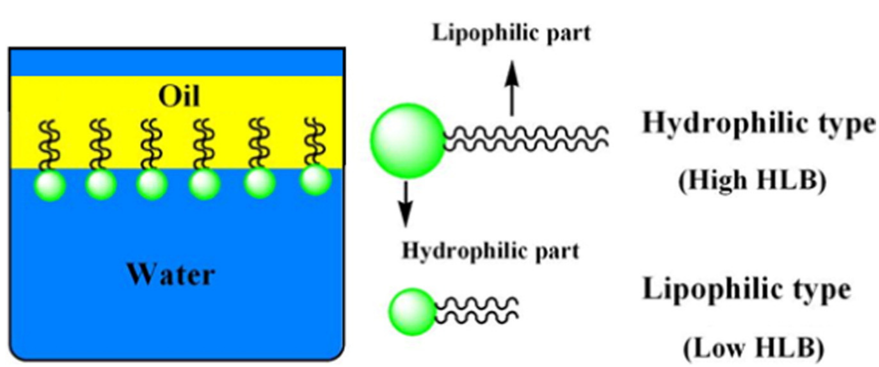
2.1. Materials

Lemon oil was used as oil phase and preparation of nano-emulsions was done by Tween 40 as non-ionic surfactant and Na_2SO_4 purchased from Merck. Deionized water was used to prepare aqueous phase with different concentrations of Na_2SO_4 (0.05, 0.1, 0.25, 0.5, 0.8 and 1 M).

2.2. Experimental operations

2.2.1. Determining the PIT

The PIT was determined by two methods of visual and electrical conductivity by conductivity meter. Emulsions with weight percentage of 20% oil, 7.5% surfactant and 72.5% Na_2SO_4 solution with different concentrations (0.05, 0.1, 0.25, 0.5, 0.8, and 1 M) were prepared by handy shaking at the lab temperature. Each of the prepared emulsions was placed on stirrer separately and heated gradually. Phase changes were visually tracked and conductivity (μs/cm) was measured as a function of temperature (°C). The first emulsions were thin and in white mode. At the PIT, emulsions became turbid and concentrated. There has been a maximum sudden drop in conductivity at this temperature. The HLB temperature was considered as average, maximum and minimum temperature of conductivity and determined as inverse temperature emulsion phase of O/W to W/O [57–60]. The apparatus for the PIT measurement was similar to the one used by Jiri Pohlodek [61].



Scheme II. The structure of a surfactant.