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Short communication

Droplet size and stability of nano-emulsions produced by the temperature phase inversion method

Sher Lin Ee, Xiumei Duan, Jeffery Liew, Q. Dzuy Nguyen*

School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

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Abstract

We studied the formation and stability of *n*-decane in water nano-emulsions produced by the phase inversion temperature (PIT) emulsification method using polyoxyethylene lauryl ether as surfactant. The results obtained indicate that the droplet size and size distribution are strongly dependent on the methods of heating and cooling, and on the final temperature to which the mixture is cooled after phase inversion. Importantly, there exists an optimum storage temperature, at which the nano-emulsions are most stable, and develop ultra-small droplet sizes, ranging from 35 nm to 54 nm, with low polydispersity indices (∼0.2). This optimum temperature is about 20 °C below the PIT, and dependent on the surfactant concentration. Any departure in temperature from the optimum would result in increases in droplet sizes, polydispersity and instability by Ostwald ripening. Furthermore, nano-emulsions destabilized after a long period of storage at different temperatures can be rejuvenated simply by equilibration for a few minutes at the optimum temperature.

Keywords: Nano-emulsions; Emulsion stability; PIT method

1. Introduction

Nano-emulsions are emulsions in which the droplet sizes range typically from 20 nm to 200 nm, which are intermediate between normal emulsions and microemulsions. Because of their small droplet sizes, nano-emulsions appear transparent and are kinetically stable against sedimentation or creaming. Applications of nano-emulsions can be found in many industries, such as polymers, cosmetics, pharmaceuticals, agrochemicals, and microelectronics.

Nano-emulsions are non-equilibrium systems and cannot be formed spontaneously. They may be produced by the dispersion or high-energy emulsification methods which involve high shear mixing, high-pressure homogenization or ultrasonification [1–3]. Nano-emulsions can be formed almost spontaneously by taking advantage of the physicochemical properties of the system. This is the basis of the condensation or low-energy emulsification methods that exploit phase transitions taking place during the emulsification process. One of these methods is the phase inversion temperature (PIT) method, which is based on the changes in solubility of polyoxyethylene-type non-ionic surfactants with temperature [4]. The surfactant is hydrophilic at low temperatures but becomes lipophilic with increasing temperature due to dehydration of the polyoxyethylene chains. At low temperatures, the surfactant monolayer has a large positive spontaneous curvature forming oil-swollen micellar solution phases (or O/W microemulsions) which may coexist with an excess oil phase. At high temperatures, the spontaneous curvature becomes negative and water swollen reverse micelles (or W/O microemulsions) coexist with excess water phase. At a critical temperature, the hydrophilic–lipophilic balance (HLB) temperature, the spontaneous curvature is zero and a bicontinuous microemulsion phase containing comparable amounts of water and oil phases coexists with both excess water and oil phases [5]. The PIT emulsification method takes advantage of the extremely low interfacial tensions at the HLB temperature to promote emulsification. However, coalescence rate is extremely fast and the emulsions are very unstable even though emulsification is spontaneous at the HLB temperature. By rapidly cooling or heating the emulsions prepared at the HLB temperature, kinetically stable emulsions (O/W or W/O, respectively) can be produced with very small droplet size and narrow size distribution [5]. If the cooling or heating process is not fast, coalescence predominates and polydispersed coarse emulsions are formed [6].

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* Corresponding author. Tel.: +61 8 8303 5456; fax: +61 8 8303 4373.
E-mail address: dzuy.nguyen@adelaide.edu.au (Q.D. Nguyen).

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This work studied the formation and stability of *n*-decane in water nano-emulsions produced by the phase inversion temperature emulsification method using polyoxyethylene lauryl ether as surfactant. Different procedures were investigated to develop the best protocol for forming nano-emulsions with the smallest droplet size and lowest polydispersity. In particular, the effects of the final cooling and storage temperature on the droplet sizes and stability were investigated.

2. Experimental

2.1. Materials

Emulsions were prepared using *n*-decane (99.5% purity from Sigma–Aldrich), a non-ionic surfactant, poly(oxyethylene)(4) lauryl ether ($C_{12}E_4$) of technical grade (Brij 30, Sigma–Aldrich), and reverse-osmosis water containing 0.01 M NaCl as the aqueous phase. All reagents were used without further modifications.

2.2. Methods

2.2.1. Phase inversion temperature determination

The hydrophilic–lipophilic balance temperature was determined using the electrical conductivity method [7]. The emulsions containing 20 wt% decane and different water and surfactant concentrations were prepared by manual shaking at room temperature (∼20 °C). The emulsion was then heated gradually and the conductivity was measured as a function of temperature. The HLB temperature was determined as the temperature at which the conductivity decreases sharply, corresponding to a phase inversion from oil-in-water to water-in-oil emulsion. This is also defined as the phase inversion temperature.

2.2.2. Emulsification by the PIT method

Oil-in-water nano-emulsions were prepared using a two-step procedure. The oil phase containing the surfactant and the water phase were first heated separately and simultaneously to a temperature of up to 15 °C above the PIT corresponding to the given surfactant concentration. Once that temperature was reached, the water was poured into the oil phase and the mixture was removed from the heating source and allowed to cool naturally at ambient condition to the PIT. The aim of this slow cooling step was to ensure complete solubilization of the oil phase into a bicontinuous microemulsion at the HLB temperature, which is the requirement for formation of nano-emulsions [7]. This step was followed by a rapid quench of the sample to 25 °C by placing it an ice bath. The emulsion was continuously stirred by manual shaking during both cooling stages.

2.2.3. Droplet size and stability determination

Mean droplet size and polydispersity of the emulsions were determined by dynamic light scattering (DLS) technique. The instrument used is the Malvern Zetasizer Nano, Series ZEN 3600 (Malvern, UK), with a 532 nm green laser and a scattering angle of 173°. All size measurements were done in duplicates and the average results were reported in this paper. The stability of the nano-emulsions produced was assessed by measuring the variation of droplet sizes with time of storage at fixed temperatures. The effect of temperature of storage on emulsion stability was investigated by measuring the droplet sizes (after emulsification) at various temperatures with an interval of 1 °C and an equilibration time of 3 min at each interval. A sample volume of 1 ml was used in these measurements.

3. Results and discussion

3.1. Phase inversion temperatures

The phase inversion temperatures determined from conductivity measurements are summarized in Table 1 for the emulsion systems containing 20 wt% decane. The PIT corresponds to the hydrophilic–lipophilic balance temperature of the emulsion system [4]. The results show a gradual decrease in the PIT from 38 °C to 33 °C with an increase in surfactant ($C_{12}E_4$) concentration from 4 wt% to 8 wt%. This dependence of the HLB temperature on surfactant concentration may be attributed to the polydispersity of the commercial surfactant used [8]. With a wide distribution of alkyl chain length and ethylene oxide (EO) units, the chains with the lower EO content would preferentially partition to the oil phase. As surfactant concentration is increased, molecules with short EO chains tend to accumulate at the oil–water interface, resulting in a reduction of the HLB temperature.

3.2. Formation of nano-emulsions by the PIT emulsification method

Different emulsification procedures, based on the phase inversion temperature emulsification method, were investigated to determine the most effective protocol for the system studied. The procedure that produced nano-emulsions with the smallest droplet sizes involves emulsification at a temperature of 15 °C higher than the PIT shown in Table 1 for a given surfactant concentration, followed by a slow cooling of the emulsion to the PIT, and a rapid quench to 25 °C. The resulting emulsions were bluish and transparent in appearance, with the droplet sizes lying in the ranges typical of nano-emulsions. Table 1 summarizes the mean droplet sizes and polydispersity indices for the freshly prepared emulsions measured at 25 °C by the DLS method for the nano-emulsions produced at different surfactant concentrations. It is interesting to note that the mean droplet size of the emulsions at a fixed oil content of 20 wt% decane decreases only slightly from 74 nm to 71 nm with increasing surfactant concentration from 4 wt% to 7 wt% $C_{12}E_4$. The system containing 8 wt% $C_{12}E_4$, however, formed the coarsest emulsion with a mean droplet diameter of 213 nm and with a highly dispersed droplet size distribution. The observed increase in droplet sizes and polydispersity with increasing surfactant concentration does not seem to agree with the general trend that the amount of surfactant determines the interfacial surface area and the size of the emulsion droplets [9]. The discrepancy may be due to instability of the droplets, which were coarsened by coalescence at the final cooling temperature (25 °C). The avail-

Table 1
Phase inversion temperature and droplet characteristics of the system decane/$C_{12}E_4$/water containing 20 wt% decane

$C_{12}E_4$ (wt%)	PIT (°C)	Mean droplet diameter (freshly prepared) at 25 °C (nm)	Polydispersity index at 25 °C
4	38	74	0.301
5	36	72	0.331
7	34	71	0.300
8	33	213	0.575

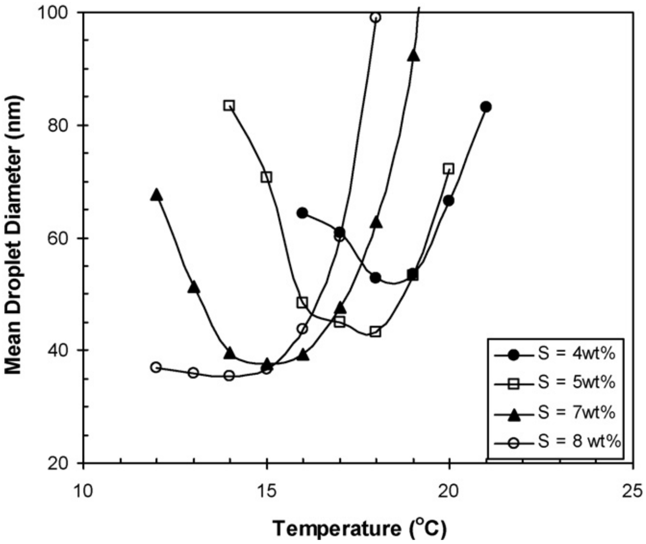

Fig. 1. Effect of storage temperature on mean droplet size for the emulsions formed in the system decane/$C_{12}E_4$/water containing 20 wt% decane with various surfactant concentrations.

able equilibrium phase diagram for water/$C_{12}E_4$/decane at 25 °C [10] indicates that at 8 wt% surfactant and 20 wt% decane, the system would consist of three phases: water, lamellar liquid crystalline phase (continuous) and liquid birefringent (surfactant) phase. Thus an O/W emulsion formed and maintained at this temperature, which is also close to the PIT (33 °C), would be highly unstable as the interfacial tension available would be too low to stabilize the droplets against coarsening due to coalescence.

The effect of temperature on the behaviour of the emulsions produced by the PIT method was further examined by measuring the change in droplet sizes with temperature as the system was cooled after emulsification. The results, shown in Fig. 1 for various surfactant concentrations, clearly indicate the presence of an optimum temperature at which the size of the droplets formed is at minimum. Away from the optimum temperature, any change in temperature will result in an increase in emulsion droplet size and polydispersity due to coarsening by Ostwald ripening and/or coalescence. Both the optimum temperature and the minimum droplet mean diameter decrease with increasing surfactant concentration. As summarized in Table 2, the optimum temperature is approximately 19 °C lower than the PIT corresponding to a given surfactant concentration. The emulsions stored at the optimum temperature have ultra-small droplets (35–54 nm in diameter) with narrower size distributions compared to the emulsions stored at other temperatures. Shinoda and Saito [5] have previously shown that stable and fine O/W type emulsions can be obtained by the PIT method when the PIT of the emulsion system is about 20–65 °C greater than the storage temperature. Consequently, many authors have followed this rule by setting a quench or storage temperature of 25–30 °C below the PIT in the preparation of nano-emulsions [3,11]. While this trend is confirmed in the present study, the results obtained as shown in Fig. 1 further indicate that reducing the temperature below the optimum temperature also leads to coarsening of the emulsion droplets. To the authors' knowledge, the existence of a critical temperature corresponding to optimum storage condition for nano-emulsions produced by the PIT emulsification method has not been previously reported.

This investigation thus further demonstrates the important effects of temperature on the decane–water nano-emulsions studied even after emulsification has taken place. The results suggest that the nano-emulsions need to be kept at the optimum storage temperatures, corresponding to their surfactant concentrations, to remain in the nano-size state. Increasing or decreasing the storage temperature from the optimum temperature will lead to an increase in droplet sizes due to coarsening by Ostwald ripening and/or coalescence. Significantly, the change in droplet sizes with temperature was found to be reversible with the emulsions studied. For example, the data in Table 3 were obtained with the emulsion systems which were kept at two different non-optimal temperatures (25 °C and 11 °C) for 12 h before returning to their optimum temperatures. After a 3-min equilibration at the optimum temperatures, the measured droplet sizes indicate that all systems were able to revert to the initial nano-size condition.

Table 2
Optimum temperature and droplet characteristics of the system decane/$C_{12}E_4$/water containing 20 wt% decane as a function of surfactant concentration

$C_{12}E_4$ (wt%)	PIT (°C)	Optimum temperature (°C)	Mean droplet diameter at optimum temperature (nm)	Polydispersity index at optimum temperature
4	38	19	54	0.234
5	36	18	43	0.192
7	34	15	38	0.231
8	33	13	35	0.200

Table 3
Study of reversibility of the emulsions systems subjected to changes in temperature and storage conditions

Surfactant concentration (wt% $C_{12}E_4$)	4	5	7	8
Optimum temperature, T_{Opt} (°C)	19	18	15	13
Thermal history	Mean droplet diameter (nm)			
Initial at T_{Opt}	54	42	41	38
Heated to and stored at 25 °C for 12 h	119	178	238	5440
Cooled to T_{Opt} and equilibrated 3 min	52	46	45	46
Cooled to and stored at 11 °C for 12 h	59	85	N/A	N/A
Reheated to T_{Opt} and equilibrated 3 min	60	44	N/A	N/A

3.3. Emulsion stability

The stability of the nano-emulsions produced was assessed by measuring the change in droplet sizes with time of storage at (a) room temperature (∼20 °C), and (b) optimum temperature corresponding to the surfactant concentration. As shown in Fig. 2, droplets in the emulsions stored at the optimum temperatures experienced considerably slower growth rates than droplets stored at room temperature. For both storage conditions, the droplets generally grow faster in emulsions containing higher surfactant concentrations. This effect of surfactant concentration on droplet growth in nano-emulsions is well known, as shown previously in other studies [8,9].

The main mechanism responsible for the destabilization of nano-emulsions is often attributed to Ostwald ripening, which arises from the difference in solubility between droplets of different sizes [3]. In this process, larger droplets grow in size at the expense of smaller droplets due to molecular diffusion of the oil through the continuous phase. The droplet growth rate, ω, due to Ostwald ripening, can be obtained by the Lifshitz-Slezov and Wagner (LSW) theory [12]:

$$\omega = \frac{dr^3}{dt} = \frac{8}{9}\frac{C_\infty \gamma V_m D}{RT} \quad (1)$$

where r is average droplet radius, t the storage time, C_∞ the bulk phase solubility, γ the interfacial tension, V_m the molar volume of the oil, D the diffusion coefficient in the continuous phase, R the gas constant, and T is the absolute temperature.

Eq. (1) predicts a linear relationship between r^3 and t, with the gradient being the Ostwald ripening rate ω. Fig. 3 shows plots of r^3 for the nano-emulsions as a function of time over a 1-month period at two different storage conditions. For the emulsions stored at room temperature (20 °C), the plots are linear only for surfactant concentrations of 4 wt% and 5 wt%, indicating that Ostwald ripening is the driving force for instability. At higher surfactant concentrations, the volume of the droplets stored at 20 °C tends to increase exponentially with time (Fig. 3a), which suggests that droplet coalescence by flocculation is the possible mechanism for destabilization [13]. For the emulsions stored at optimum temperatures, Ostwald ripening is the dominant mechanism for instability as evidenced by the linearity of the r^3–t plots at all surfactant concentrations (Fig. 3b).

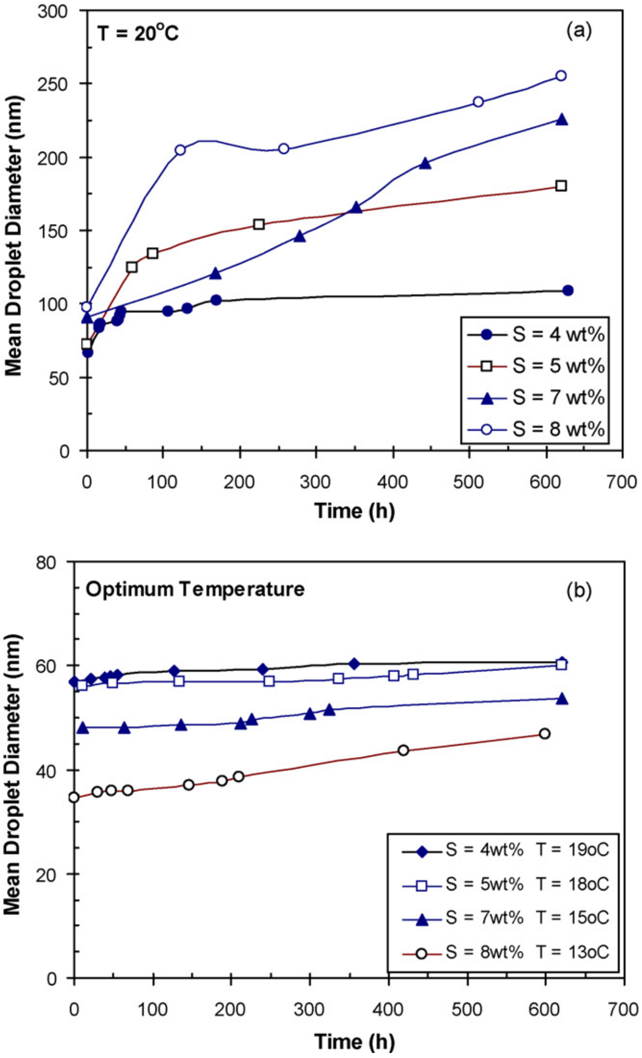

Fig. 2. Change in mean droplet diameter as a function of time in the system water/$C_{12}E_4$/decane at 20 wt% decane and different surfactant concentrations. Emulsions stored at (a) room temperature, 20 °C and (b) optimum storage temperatures.

The Ostwald ripening rate, ω, determined from the slopes of the linear plots are summarized in Table 4. It may be seen that ω generally increases with increasing surfactant concentration, as agreed with previous studies [8,9]. For the emulsions stored at optimum temperatures, ω rises gradually from 2.0×10^{-30} m^3 s^{-1} to 3.6×10^{-30} m^3 s^{-1} as $C_{12}E_4$ concentration is increased from 4 wt% to 8 wt%. Much higher ripening rates were obtained for the emulsions containing 4 wt%

Table 4
Initial droplet radii and Ostwald ripening rates as function of surfactant concentration and storage temperature

$C_{12}E_4$ (wt%)	T_{Opt} (°C)	r_0 (nm) at 20 °C	PI at 20 °C	r_0 (nm) at T_{Opt}	PI at T_{Opt}	ω ($\times 10^{30}$ m^3 s^{-1}) at 20 °C	ω ($\times 10^{30}$ m^3 s^{-1}) at T_{Opt}
4	19	34	0.409	27	0.234	41	2.0
5	18	36	0.535	22	0.192	242	2.1
7	15	80	0.454	20	0.231	N/A	2.8
8	13	102	0.707	18	0.200	N/A	3.6

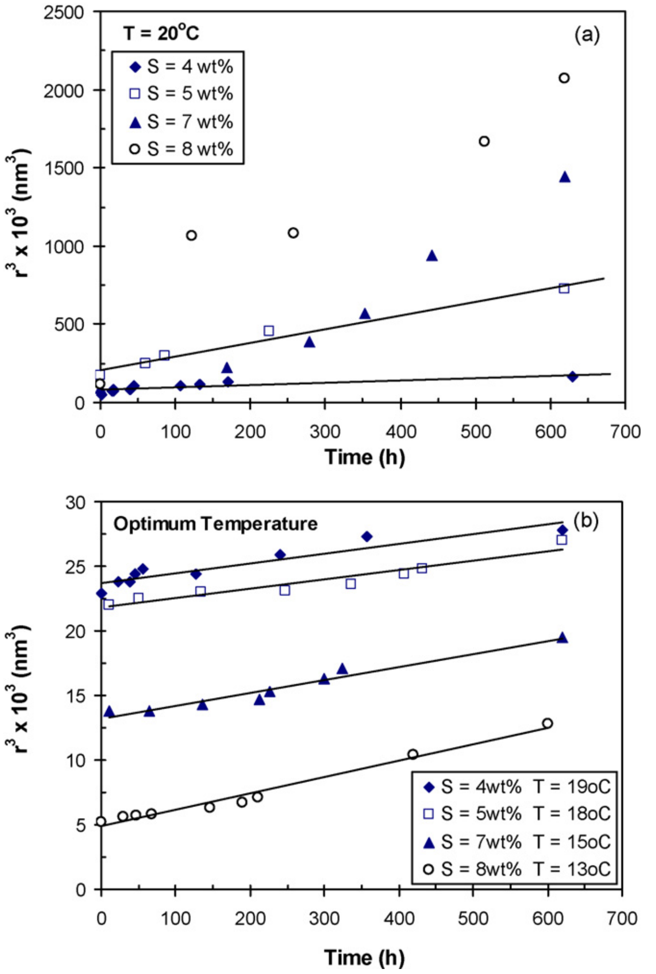

Fig. 3. Plots of r^3 as a function of time in the system in the system water/$C_{12}E_4$/decane at 20 wt% decane and different surfactant concentrations. Emulsions stored at (a) room temperature, 20 °C and (b) optimum storage temperatures.

and 5 wt% $C_{12}E_4$ stored at 20 °C, which show a stronger dependence on surfactant concentration. Izquierdo et al. [8] reported an Ostwald ripening rate of 20.9×10^{-27} m^3 s^{-1}, determined at 25 °C, for a 20 wt% decane–water emulsion containing 4 wt% $C_{12}E_4$. This value, which is consistent with our results, represents some two orders of magnitude higher than that for the same emulsion stored at 20 °C and, four orders of magnitude greater than that measured at the optimum storage temperature.

The factors that favour Ostwald ripening include polydispersity of the emulsion droplets and high surfactant concentrations. As Table 4 shows, the emulsions stored at 20 °C have high polydispersity indices (>0.4) compared to those stored at optimum temperatures (~0.2), hence the increased difference in the droplet sizes in the former would enhance the ripening rate by increasing the Laplace pressure gradient as driving force for diffusion. Increasing surfactant concentration leads to a larger number of micelles formed, which results in a higher molecular flux for oil transport between droplets [8]. The observed increase in Ostwald ripening rate with increasing $C_{12}E_4$ concentration, however, is small in the emulsions stored at optimum temperatures compared to that in the emulsions stored at 20 °C. Therefore, by producing and keeping the nano-emulsions at the optimum storage temperatures, it is possible to retard the destabilizing effect due to Ostwald ripening.

4. Conclusions

The present study shows that for nano-emulsions produced by the PIT method, there exists an optimum temperature at which stable and finely dispersed nano-sized droplets can form. The emulsions stored at the optimum temperatures, which are dependent on the non-ionic surfactant concentration, can retain the nano-sized state with smallest droplet sizes, lowest polydispersity indices, and superior stability compared to the emulsions stored at other temperatures. Furthermore, nano-emulsions, which have been destabilized after prolonged storage at non-optimal temperatures, can be restabilized by returning them to the optimum temperatures. This effect appears to be thermally reversible.

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