Stable Liquid Paraffin-in-Water Nanoemulsions Prepared by Phase Inversion Composition Method

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Abstract: Oil-in-water nanoemulsions were prepared in the system of water/Span 80−Tween 80/long-chain paraffin oil via the PIC (phase inversion composition) method. With the increase of preparation temperature from 30 ℃ to 80 ℃, the diameter of emulsion droplets decreased from 120 nm to 40 nm, proving the formation of nanoemulsions. By varying the HLB (hydrophilic lipophilic balance) of mixed surfactants, we found that there was an optimum HLB around 12.0 ~ 13.0 corresponding to the minimum droplet size. The viscosity of nanoemulsions clearly increased with droplet volume fraction, f, but the droplet size slightly increased. Significantly, at f ≤ 0.3, the size distribution of nanoemulsions kept constant more than 2 months. These results proved that the viscous paraffin oil can hardly be dispersed by the PIC method at 30 ℃, but the increase in preparation temperature makes it possible for producing monodisperse nanoemulsions. Once the nanoemulsion is produced, the stability against Ostwald ripening is outstanding due to the extremely low solubility of the liquid paraffin oil in the continuous phase. The highly stable nanoemulsions are of great importance in cosmetic applications.

Keywords: Liquid paraffin, Nanoemulsion, PIC, Ostwald ripening, Cosmetics

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1. Introduction

The potential benefits of cosmetic nanoemulsions include optical clarity, good stability to gravitational separation, flocculation and coalescence, and improved absorption and bioavailability of functional components[1]. A deeper understanding of the basic physiochemical properties of nanoemulsions would, therefore, provide key information to better guide formulation and application of nanoemulsion to cosmetics.

Nanoemulsions can be prepared by high or low energy emulsification methods[2–4]. High energy emulsification methods require large mechanical energy generated by high pressure homogenizers or ultrasound generators to produce fine droplets. In contrast, low energy emulsification methods can take advantage of the chemical energy stored in the ingredients and produce the nanoemulsions almost spontaneously, thus have great attraction both in theoretical study and practical application. The change in the spontaneous curvature of surfactants during the emulsifying process has been recognized to be a key factor for the formation of nanoemulsions, which can be achieved either by changing the temperature (phase inversion temperature, PIT method) or by changing the volume fraction of water or oil (phase inversion composition method, PIC method)[2–4]. Paraffin oil has been applied in many cosmetic products as a component of O/W emulsions, mostly as macroemulsions. The formation of paraffin oil emulsions with submicron droplets using the PIC method has occasionally been reported[4,5]. Sagitani et al. suggested that a proper HLB value of the surfactants was a key factor for the formation of emulsion with minimal droplets[5]. Dai et al. observed that the molecular structure of emulsifiers had a great effect on the droplet size of the final emulsions[6]. Fernandez et al. attained paraffin oil nanoemulsions with droplet sizes of 300 ~ 500 nm with surfactant-to-oil weight ratios of 0.364 and 0.5 at 80 °C[4].

In the present work, we obtained paraffin oil-in-water nanoemulsions at different emulsification temperatures using the PIC method. We optimize the droplet size of nanoemulsions by varying the HLB of Tween 80 and Span 80.

2. Materials and Methods

2.1. Materials

The liquid paraffin (Lily 70, cosmetic grade), Sorbitan monooleate (Span 80, cosmetic grade), and polyoxyethylene (20) sorbitan monooleate (Tween 80, cosmetic grade) were obtained from Kukdong Oil & Chem. Ltd, Ilshin wells Co. Ltd. and Croda Chem., respectively. The components of this paraffin oil are light mixtures of alkanes in the C15 to C40 range with specific gravity of 0.831 and viscosity of 11.0 ~ 13.5 cSt at 40 °C. All reagents were used as received without further purification. Water was deionized and Milli-Q filtered.

2.2. Preparation of nanoemulsions

Before emulsification, the surfactants (Span 80 and Tween 80) were dissolved into the oil phase under magnetic stirring. The surfactant–oil mixture and water were placed separately in a water bath at the desired temperature. Then the water phase was added dropwise to the oil solution. After the emulsification, the samples were cooled at room temperature (~ 25 °C). The influence of composition parameters, including the oil-to-surfactant weight ratio (O/S) and the droplet volume fraction (ϕ), was investigated systematically. Moreover, the formation of nanoemulsions depends not only on composition variations but also on preparation conditions[7,8]. Therefore, the experimental parameters were maintained constant at a stirring rate of 400 rpm and an addition rate of 2 mL/min.

2.3. Droplet size determination

Nanoemulsion droplet size and distribution were determined by dynamic light scattering (ELS-8000, Otsuka, Japan). A 200 mW green laser (λ = 532 nm) with variable intensity was used, and measurements were carried out at room temperature with a scattering angle of 90 °. The droplet size was measured directly without dilution.
The average radius were calculated from the intensity autocorrelation data with the cumulant method. The time-intensity correlation functions were analyzed by the CONTIN method[9].

2.4. Long-term stability test

The long term stability of nanoemulsions was assessed by measuring the change of droplet size with time of storage. The samples were kept sealed at room temperature.

2.5. Viscosity

The viscosity of nanoemulsions was measured by DV-E viscometer (RT, Brookfield, USA) using a #4 spindle and a rotational speed of 60 rpm at 25 ℃.

3. Results

3.1. Effect of emulsification temperatures at fixed composition

The schematic diagram and photograph of the nanoemulsions as a function of the preparation temperature is shown in Figure 1. The turbidity of emulsions is decreased as increasing the emulsification temperature. In Figure 2, droplet diameter decreases from 113.9 to 43.2 nm with the increase of emulsification temperature at a constant composition (O/S = 1 : 1, φ = 0.1). The droplet size decreases with the increase of emulsification temperature from 30 to 80 ℃ and remain unchanged with a further increase in the temperature. L. Yu et al. reported that nanoemulsions cannot be obtained at low temperature due to the relatively high interfacial tension and the high viscous resistance of the oil phase. With the increase of preparation temperature, the amount of surfactant molecules adsorbed at the O/W interface increases gradually. At elevated temperatures (≥ 70 ℃), the surfactant adsorption reaches saturation[10].

3.2. Effect of HLB on emulsification at elevated temperature

As stated above, the droplet size distributions remain unchanged when the emulsions are prepared at 70, 78, and 85 ℃. The temperature of preparation is fixed at 70 ℃ for further investigations. In this section, we examined the influence of HLB value and O/S on nanoemulsion formation. When the emulsion is stabilized by a mixture of nonionic surfactants, the mixed HLB value is considered to be the algebraic average of the HLB value of the individual surfactants.

In other words, the variation in the mixed HLB values was calculated according to the relationship

$$\text{HLB}_{\text{mix}} = \text{HLB}_A \times \%_A + \text{HLB}_B \times \%_B$$

where HLB_{mix} is the HLB value of the mixed surfac-
Figure 3. Droplet diameter as a function of the HLB value for samples with O/S = 1 : 1, $\phi = 0.1$ and preparation Temp. = 75 °C.

Figure 4. Droplet diameter as a function of the oil/surfactant weight ratio at HLB = 12.0.

The droplet diameter of samples with HLB 10.5 and 13.1 shows 233.7 and 46.5 nm, respectively. However, we obtained macroemulsions below the HLB of 10.5 and above 13.1. These macroemulsions were unstable and show creaming patterns within several days.

In our system, the droplet volume fraction, given by the oil volume fraction plus the surfactant volume fraction, was varied from 0.05 to 0.5 (Figure 5). The droplet diameter remains less than 350 nm when O/S is fixed at 1 : 1. The droplet size increases gradually as the volume fraction increases. However, in case of volume fraction 0.4 and 0.5, we cannot measure the droplet size.
As the volume fraction increases from 0.05 to 0.4, the viscosity of nanoemulsions gradually increases. The viscosity of 0.4 (ϕ) is measured 60 cP by a #4 spindle and a rotational speed of 60 rpm using DV-E viscometer. However, the viscosity of a volume fraction of 0.5 increases dramatically and translucent gel is observed. It is thought to be a phenomenon caused by liquid lamellar phase formation rather than inner phase interaction.

3.4. High Stability

Ostwald ripening is usually considered to be the major destabilization mechanism of nanoemulsions. It arises from the fact that oil solubility increases with decreasing droplet size. Large droplets grow at the expense of small ones in polydisperse emulsions due to molecular diffusion of the oil through the continuous phase. The rate of Ostwald ripening, \( \omega \) can be obtained by LSW (Lifshitz – Slezov – Wagner) theory\[20\]

\[
\omega = \frac{dr^3}{dt} = 8\gamma C_\infty V_m D/9RT
\]

where \( r \) is the average droplet radius, \( t \) is the storage time, \( C_\infty \) is the bulk phase solubility, \( \gamma \) is the interfacial tension, \( V_m \) is the molar volume of the oil, \( D \) is the diffusion coefficient of the oil phase in the continuous phase, \( R \) is the gas constant, and \( T \) is the absolute temperature. Equation 2 predicts a linear relationship between the cube of the radius and time.

The main limitation for developing nanoemulsion applications is the relatively low stability. When the emulsification was produced by high energy methods, the stability of nanoemulsions could be improved by increasing the oil viscosity, corresponding to the decrease in \( C_\infty \). The size distributions of these nanoemulsions have not changed over months\[21\]. But the disadvantages of these methods are the high energy cost and viscous heating\[22\]. For instance, the high-pressure homogenizers generally work in the pressure range between 50 and 100 MPa\[23\]. When nanoemulsions were prepared using low energy methods, the effect of carbon number of various n-alkanes on nanoemulsion formation and stability has been investigated\[24\]. The Ostwald ripening is suppressed by the increase in carbon chain length of oil owing to the decrease of its solubility in water\[24\]. Nevertheless, the initial droplet size increases with the increase in hydrocarbon alkyl chain length due to the increase in the interfacial tension and oil viscosity. In brief, it is difficult to obtain highly kinetically stable nanoemulsions with remarkably small droplet sizes by low energy methods.

The stability of these nanoemulsions was assessed by following the change in droplet diameters with time of storage at room temperature (\( \sim 25 ^\circ C \)). The size distributions of nanoemulsions prepared at elevated temperatures have not changed over a week. In addition, nanoemulsions prepared within the experimental O/S region (Figure 6) also remained stable during the same storage
time. In recent literature it has been presented that the Ostwald ripening rate could be reduced by the addition of a second, less soluble, component to the dispersed phase[20]. In Figure 7, we presented the change of droplet size of different HLB. The size remained constant during the same storage time. It is deduced that the components with long-chain hydrocarbons could help enhance the stability against Ostwald ripening. Figure 8 also shows the effect of droplet volume fraction on the stability of nanoemulsions stored at ambient temperature. Moreover, we assessed the change in droplet size over 2 months. The size of nanoemulsion droplets (Figures 6-8) have not changed over 2 months (Data was not shown). From the above result we concluded that when nanoemulsion composed with less soluble oil was formed, the size remained constant.

4. Conclusion

Paraffin oil-in-water nanoemulsions have been obtained by the PIC method at elevated temperatures. The increase in preparation temperature decreases the droplet diameter of nanoemulsions. The droplet diameter is mainly governed by the structure of microemulsion during the emulsification process. In brief, nanoemulsions could be obtained over a wide range of temperature and droplet volume fractions. Once formed at elevated temperature, the size distributions of nanoemulsions have not changed over 2 months. The PIC method at elevated temperature is an attractive alternative for preparation of nanoemulsions since this method leads to formation of higher inner phase volume nanoemulsions with long-term stability. These results lead to applying liquid paraffin nanoemulsions in cosmetic vehicles.

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Reference

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