Stability of Lipid Nanoparticles For Hair Conditioning Formulations

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Abstract: Candelilla wax-in-water nanoemulsions stabilized by Span 80/Tween 80 were prepared by the phase inversion composition (PIC) method. Stable nanoemulsions with droplet diameters below 50 nm could be formed when the hydrophilic–lipophilic balance (HLB) values were between 13.5 and 14.5, surfactant concentration was 5.0 wt%, and the surfactant-wax ratio was 1:1. Increased emulsification temperature and cooling rate were found to improve the emulsion properties. Process of PIC (adding aqueous phase to the wax phase) produced smaller droplet size nanoemulsion compared to the process of adding wax phase to the aqueous phase. The stability of these nanoemulsions was assessed by following the change in droplet diameters with time of storage at room temperature (∼25 °C). The size remained constant during 2 months storage time.

1. Objective

In the present work, we prepared candelilla wax-in-water nanoemulsions using the low-energy PIC method, and investigated the effects of HLB value, surfactant concentration, emulsification temperature and emulsification route.

2. Methods and Results

Emulsions were prepared from a mixture of candelilla wax and surfactants by slowly adding EDTA-2Na aqueous solution with gentle agitation using a magnetic stirrer. The addition rate of aqueous solution was kept constant at approximately 1.0 mL/min. The emulsification temperatures were kept at 65–80 °C. The concentration of candelilla wax in all emulsions was kept constant at 5.0 wt%, while the surfactant concentration was varied from 2.0 to 12.5 wt%.
The size and distribution of nanoemulsion droplet were determined by dynamic light scattering (ELS-8000, Otsuka, Japan). A 200 mW green laser ($\lambda = 532$ 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.

### 3.1. Determination of required HLB for preparing of candelilla wax emulsions

Stable emulsions, especially where synthetic surfactants are used, are best formulated with emulsifiers or a combination of emulsifiers having HLB values close to that required of oil phase. To attain a much greater degree of the droplet stability, a combination of hydrophilic and lipophilic emulsifiers is often used, which are thought to align alongside each other imparting more rigidity and strength to the emulsifier film [12]. Emulsions were prepared initially with 90 wt% aqueous phase, 5 wt% candelilla wax and 5 wt% emulsifier blend of Tween 80 and Span 80 at HLB values ranging from 11.8 to 14.8 to determine the 'required HLB' of the candelilla wax. The mixed HLB values were calculated by the following equation:

$$HLB_{\text{mix}} = HLB_T \times T + HLB_S \times S \ (1)$$

where $HLB_T$, $HLB_S$ and $HLB_{\text{mix}}$ are the HLB values of Tween 80 (15.0), Span 80 (4.3) and the mixed surfactants, and $T$ and $S$ are the mass percentages of Tween 80 and Span 80 in the mixed surfactants, respectively. All the HLB values used were obtained at 25 °C. The photograph of nanoemulsions as a function of HLB is shown in Fig. 1. HLB values between 13.5 and 14.5 were found to be suitable for small droplet size of nanoemulsions. Nanoemulsion stability is often estimated by the average size of the droplets, so the droplets size was also measured. The droplets size of emulsions with smallest size below 40 nm was attained at HLB 14.0, beyond which the droplet size increased. So we chose HLB 14.0 as the candelilla wax's required HLB as stable candelilla wax O/W nanoemulsions with droplet size below 40 nm were obtained within this region. The combination of Tween 80 and Span 80 within the required HLB region may improve the rigidity and strength of the emulsifier film around the wax droplets.

### 3.2. The influence of surfactant concentration for preparing of candelilla wax nanoemulsions

For the nanoemulsions prepared with a constant HLB (14.0, with the weight ratio of Span 80/Tween 80 = 0.1/0.9), Fig. 3 shows the size of nanoemulsion as a function of the surfactant concentration. The size of droplets was rather constant with the surfactant concentration, because the HLB of surfactant determines the size of droplet of emulsions.
3.3. The influence of temperature for preparing of candelilla wax nanoemulsions

Candelilla wax, the dispersed phase used in this study, is solid at room temperature. During the emulsification process, the temperature is increased to melt the candelilla wax for easier emulsification. Temperature can affect the viscosity and the cohesive force of the candelilla wax, so we prepared emulsions at different temperatures to investigate the effect of temperature. In Fig. 4, the photograph of emulsions produced by varying the emulsification temperature is shown. The transparency of emulsions is increased as the emulsification temperature is increased. Fig. 5 shows clearly that the size of emulsion droplets is decreased with temperature increasing from 65 to 80 °C. This is because the viscosity and cohesive force decreases with increasing temperature, which is beneficial to emulsification. Rousseau [13,14] showed that the crystallization regimes of the paraffin wax could affect the emulsion's properties. Hence we changed the cooling rate to study the effect of the crystallization. For the emulsion prepared at 80 °C, one part of it was cooled at ambient temperature, and the other part was cooled in an ice-bath. The diameter of emulsion droplets and photograph are shown in Fig. 6. As expected, the emulsion cooled in the ice-bath had smaller particle size, 38.4 nm. It is thought that wax droplets may partially coalesce when the temperature is higher than its melting point, the ice-bath method can shorten the time when the emulsion is partially melted, and so it facilitates formation of emulsions with smaller droplet size.

3.4. The influence of emulsification route for preparing of candelilla wax nanoemulsions

Two different emulsification methods were compared in this study: addition of aqueous phase to a surfactant solution in oil (PIC method, A); addition of oil to an aqueous phase (method B). As shown in Figure 7, stable candelilla wax emulsions cannot be obtained by method B, while the PIC method can produce emulsions with small droplet size. This is consistent with previous studies [3,4]. The reason for this is that during the PIC process the emulsion system undergoes a change from a W/O emulsion to an O/W emulsion, and multiple emulsion, bicontinuous or lamellar structure may be formed during this process [4]. The PIC method is a catastrophic phase inversion process, which is induced by a change in the water-to-oil ratio. We showed droplet size distribution and polydispersity index determined by dynamic light scattering Figure 8.

3.5. Emulsion stability

The stability of these nanoemulsions was assessed by following the change in droplet diameters with time of storage at room temperature (≈ 25 °C). In Figure 9, 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 crystal in room temperature could help enhance the stability against Ostwald ripening.
3. Discussion and Conclusion

Phase inversion composition method was used to prepare candelilla wax-in-water emulsions stabilized by Span 80/Tween 80. The formation of emulsions was evaluated in relation to HLB, surfactant concentrations, temperature and processing parameters. Stable nanoemulsions with droplet diameters below 50 nm could be formed when the hydrophilic–lipophilic balance (HLB) values were between 13.5 and 14.5 and the surfactant-wax ratio was 1:1. Increased emulsification temperature and cooling rate were found to improve the emulsion properties. The emulsion prepared with optimum emulsification parameters was quite stable and with an average droplet diameter below 50 nm. We also found that there was big difference of diameter of emulsion droplets between addition of aqueous phase to wax phase(A) and addition of wax to aqueous phase(B). Candelilla wax used as the oil phase of the nanoemulsion was a crystallizable oil phase, which was better for emulsion stability.

Acknowledgements

This study was supported by a grant of the Korea Healthcare technology R&D Project, Ministry of Health & Welfare, Republic of Korea. (Grant No. HN12C0056)

Reference


Fig. 1. Photograph of nanoemulsions as a function of HLB values with 5.0 wt% candelilla wax and 5.0 wt% surfactants prepared by PIC method at 80 °C.

Fig. 2. Droplet diameter as a function of HLB values for nanoemulsions with 5.0 wt% candelilla wax and 5.0 wt% surfactants prepared by PIC method at 80 °C.
Fig. 3. Droplet diameter as a function of surfactant concentration for emulsions with 5.0 wt% candelilla wax prepared at 80 °C with an HLB value of 14.0.

Fig. 4. Photograph as a function of emulsifying temperature for emulsions with 5.0 wt% candelilla wax and 5.0 wt% surfactants prepared at an HLB value of 14.0.
Fig. 5. Droplet diameter as a function of emulsifying temperature for emulsions with 5.0 wt% candelilla wax and 5.0 wt% surfactants prepared at an HLB value of 14.0.

Fig. 6. Droplet diameter as a function of cooling rate for emulsions with 5.0 wt% candelilla wax and 5.0 wt% surfactants prepared at an HLB value of 14.0.

Fig. 7. Droplet diameter as a function of emulsification route for emulsions with 5.0 wt% candelilla wax and 5.0 wt% surfactants prepared at an HLB value of 14.0.
Fig. 8. Droplet size distribution and polydispersity index: (A) slow cooling, (B) fast cooling, (c) method A, (D) method B determined by dynamic light scattering (ELS-8000).

Fig. 9. Droplet diameter as a function of time for samples with different HLB and stored at 25 °C (O/S=1:1). ■: 11.8, ●: 12.9, ◇: 13.4, ●: 14.0, ○: 14.4, □: 14.8.