Study on the stability and rheological behavior of almond Oil microemulsion

Shengkun Yan¹,², Na Kong³, Jiapeng Yang⁴ and Lijun Yin²,*

¹Agricultural Mechanization Institute, Xinjiang Academy of Agricultural Sciences, Urumqi, China
²School of Food Science and Nutrition Engineering, China Agricultural University, Beijing, China
³Science and technology project service center of Xinjiang, Urumqi, China
⁴School of Control Engineering, Xinjiang Institute of Engineering, Urumqi, China

*Corresponding author: lijun_yin@cau.edu.cn

Abstract. In this study, the formation mechanism of almond oil microemulsion were studied to provide a theoretical basis for the development of almond oil microemulsion. First by the stability of almond oil microemulsion test results show that the system in different conditions of centrifugal (5000, 10000 r/min), storage temperature (-18 ℃, 4 ℃, 25 ℃ and 37 ℃ and 105 ℃) and salinity (0.1, 0.5, 1.0 mol/L) and P H (PH = 1,5,9,13) conditions, have good stability, high light transmittance, almond oil microemulsion system stability is good. Finally, the formation mechanism of almond oil microemulsion was studied, and it was concluded that the n values of almond oil microemulsion prepared by different types of surfactants were all less than 1, all were pseudoplastic fluids, and the shear viscosity decreased with the increase of shear rate. The n values of almond oil microemulsion prepared with different n-butanol contents were all less than 1 and were pseudoplastic fluids. The shear viscosity decreased with the increase of shear rate, and the order of K values was: 1:2 > 1:3 > 1:4. This study has certain theoretical guiding significance to further study the formation mechanism of almond oil microemulsion and the development and production of microemulsion.

1. Introduction

Almond oil is not only a kind of fine edible oil, but also a kind of high grade lubricating oil, which can be used as the important raw material of high grade paint coating, cosmetics and high grade soap, and can also extract essence and vitamins [1-3]. Almond oil is rich in protein, unsaturated fatty acid, vitamin, inorganic salt, dietary fiber and trace elements needed by human body. It has the functions of moistening lung, strengthening stomach and supplementing physical strength. Its amygdala is a natural anti-cancer active substance.

The study shows that the surface embedding technology can reduce the oxidation rate of oil microemulsion technology as the embedding technology of the latest development of technology, is a translucent to transparent system of thermodynamic stability, particle size between 1 ~ 100 nm, the composition of microemulsion for oil, surface active agent, surfactant and water, which is mainly the
function of stable surfactant and surfactant. A large number of studies have been carried out on microemulsion at home and abroad, such as Amar, et al., which developed lutein microemulsion with a load of up to 4% and mainly composed of lemon oil, ethanol, glycerin, Tween-80 and water. Cing-chen Cai et al. prepared oil-in-water microemulsion using kiwi seed oil, Twin-80, Span-80 and water, and measured the shelf life of kiwi seed oil microemulsion[4]. Wu Hongyan et al. prepared oil-in-water microemulsion with evening primrose oil as the oil phase, Tween 80 and lauric acid, and analyzed its stability. Zheng Minying et al. studied the preparation of fish oil microemulsion rich in DHA. In the preparation of walnut oil microemulsion[5], Man Yanan et al. prepared walnut oil microemulsion mainly composed of walnut oil, Tween 80, anhydrous ethanol and sucrose solution[6-7]. In this study, almond oil was used as raw material to study the stability and formation mechanism of almond oil microemulsion, so as to provide a theoretical basis for the development of almond oil microemulsion.

2. Materials and Methods

2.1. Material and equipment
Almond oil: self-made, extracted by cold pressing method at low temperature. Tween-20, Tween-40, Tween-60, Tween-80, Tween-20, Tween-80, ethanol, 1, 2-propanediol, n-butanol, hydrochloric acid, sodium hydroxide, sodium chloride: Analytically pure, Sinopac Chemical Reagent Co., LTD. Low temperature cold pressing: imported small spiral cold pressing machine; Electronic balance: ME104E, Mettler Toledo Instrument Co., LTD. Digital display thermostatic incubator: Shanghai Jinpeng Analytical Instrument Co., LTD. Uv-visible spectrophotometer: UV-2102PCS, Unico (Shanghai) Instrument Co., LTD. Centrifuge: Hettich; Electric thermostatic blast drying box: DhG-9140A, Shanghai Yiheng Technology Co., LTD. Nanometer analyzer: Marvin, UK.

2.2. Methods

2.2.1. Preparation of almond oil microemulsion. Elect GB2760-2014 allows the surfactant and surfactant, the formula of almond oil microemulsion: Tween60 is obtained and is HLB = 14 and Span40 mixture of mixed surfactant, n-butyl alcohol to help surfactant, k = 2, almond oil (k = 2)/water/emulsifier mixture = 1/4/7, loads of almond oil is 11.2% in this system, and the product appearance is transparent and clear. The average particle size of almond oil microemulsion system was 56.53 nm.

2.2.2. Centrifugal stability method for microemulsions. The almond oil microemulsion was centrifuged at different rotational speeds (8000, 12000 r/min) for 10 min to observe the state of the microemulsion. If it was still clear and transparent or translucent, the absorbance of the microemulsion was compared with that of the microemulsion at room temperature. Transmittance T was calculated according to formula

$$T \% = \frac{A_0}{A_1} \times 100 \quad (1)$$

T -- transmittance (%); A₀ -- Absorbance of microemulsion before centrifugation; A₁ -- Absorbance of microemulsion after centrifugation.

2.2.3. Temperature stability method for microemulsion. Microemulsions were stored at different temperatures (-18 °C, 4 °C, 25 °C, 37 °C and 105 °C) for 6h. After being restored to room temperature, their absorbance was measured at 550 nm and compared with the absorbance of microemulsions at room temperature. Transmittance was calculated according to formula (1).
2.2.4. Method for salinity stability of microemulsion. NaCl aqueous solution with concentration of 0.1, 0.5, 1.0 mol/L and mixed solution of almond oil microemulsion were respectively prepared, and their absorbance was measured at 550 nm. The absorbance was compared with that of the microemulsion at room temperature, and the light transmittance was calculated according to formula (1).

2.2.5. pH stability method of microemulsion. An appropriate amount of microemulsion was added with 0.2mol /L HCl or 0.2mol /L NaOH to adjust PH to 1, 5, 9, 13, and its absorbance was determined at 550 nm. The absorbance was compared with the absorbance of the microemulsion at room temperature, and the transmittance was calculated according to formula (1).

2.2.6. Research methods on the influence of co-surfactant types on the flow curve of almond oil microemulsion. Steady-state scanning was carried out by rheometer to investigate the influence of water content of 58%, Km=2, oil: emulsified mixture =1:4 (W/W) and co-surfactants of n-butanol, 1, 2-propylene glycol and ethanol on the flow curve of almond oil microemulsion.

2.2.7. Research methods for the influence of N-butanol content on the flow curve of almond oil microemulsion. The influence of water content of 58%, n-butanol as co-surfactant, Km=2, oil: emulsified mixture =1:2 (W/W), 1:3, 1:4 on the flow curve of almond oil microemulsion was investigated by steady-state scanning.

2.2.8. The relationship between shear rate and shear stress. Loury study that the relationship between shear rate and shear stress can be expressed by the power law equation:

\[ \tau = K \gamma^n \]  

\( \tau \) - shear stress, Pa; \( K \) - consistency coefficient, Pa·s; \( \gamma \) - shear rate, s⁻¹; \( n \) - flow index.

3. Results and Discussion

3.1. Study on the stability of almond oil microemulsion

3.1.1. Centrifugal stability of microemulsions. If the microemulsion system is not stable enough, particle aggregation will occur during the placement process, the particle size will gradually increase, and the final system stratification. The speed of this process is an important index to evaluate the stability of microemulsion system. In order to observe the stability of microemulsion in a short time, centrifugation is usually used to accelerate the change. The centrifugation results of the samples at different rotating speeds are shown in Table 1. It can be seen from Table 1 that the centrifugation at different speeds did not stratify the microemulsion system. The increase of centrifugal speed and the decrease of transmittance indicate that the particles are aggregated to some extent. However, the light transmittance is high in general, and the degree of particle aggregation is very small. Therefore, it is considered that the microemulsion system has high centrifugal stability.

| Speed, r/min | Layering yes or no | Light transmittance, % |
|-------------|--------------------|------------------------|
| 8000        | no                 | 94.58                  |
| 12000       | no                 | 97.12                  |
| blank       | no                 | 98.60                  |

3.1.2. Temperature stability of microemulsion. According to 2.2 test method, almond oil microemulsion was placed at -18 °C, 4 ºC, 25 ºC, 37 ºC and 105 ºC respectively, and the
microemulsion penetration rate is shown in Figure 1. The figure 1 shows that almond oil microemulsion after high temperature treatment (105 °C), light transmittance than other low temperature condition, the stratification, but after normal temperature, microemulsion again clear, the main reason is that in the Tween with temperature rise and the decrease of hydrogen bond and the hydrophilicity is reduced, which reduces the stability of the microemulsion system. And were treated with low temperature (-18 °C and 4 °C) of almond oil RuTou light rate declined, because temperature effect on the strength of the hydrogen bonding interaction are obvious, but the low temperature processing of micro RuTou light rate is greater than 95%, explain the stability of the microemulsion is good, at room temperature (25 °C and 37 °C), the microemulsion system maintained a high light transmittance, almond oil microemulsion system shown under the condition of different temperature, good stability.

![Figure 1](image_url)

**Figure 1** Temperature stability of almond oil microemulsion

3.1.3. Salinity stability of microemulsions. According to 2.2 test method, almond oil microemulsion was treated with NaCl aqueous solution of different concentrations, and the microemulsion penetration rate was shown in Figure 2. In the microemulsion system, when the salt content increases, the surfactant and oil meet under the action of "salting out", the double electric layer is compressed, thus the repulsive force drops, and the oil droplets are easy to approach the interfacial film, which shows that the O/W microemulsion solubilized oil ability is enhanced. As can be seen from Figure 2, the light transmittance of the microemulsion decreased after different salinity treatment, but the light transmittance of the microemulsion was also greater than 94%, indicating that the microemulsion had higher stability. The difference of almond oil microemulsion in different salinity was not large, which indicated that the stability of almond oil microemulsion system was good under different salinity conditions.
3.1.4. **PH stability of microemulsion.** According to 2.2 test method, the changes of light transmittance of almond oil microemulsion under different PH conditions were studied, as shown in Figure 3. As can be seen from Figure 3, the microemulsions were all clear and transparent after being treated with almond oil microemulsions at different PH values without stratification. Under different PH conditions, the light transmittance of the microemulsions was different, but the light transmittance of the microemulsions was also greater than 95%, indicating that the stability of the microemulsions was high. Because Tween is a non-ionic surfactant, its hydrophilicity is less affected by PH changes, so different PH treatments have less impact on the microemulsion, thus proving that almond oil microemulsion has higher stability.
3.2. Study on rheological properties of almond oil microemulsion system

3.2.1. Influence of co-surfactant types on the flow curve of almond oil microemulsion. The fixed water content was 58%, $K_m=2$, and oil: emulsified mixture = 1:4 (W/W). The influence of co-surfactants n-butanol, 1, 2-propylene glycol and ethanol on the flow curve of almond oil microemulsion was investigated, and the results were shown in Figure 4. It can be seen from figure 4 that different co-surfactants have different effects on the flow curve of almond oil microemulsion, and the order of shear viscosity is as follows: n-butanol $>$, 2-propylene glycol $>$ ethanol, which is consistent with the viscosity of the three co-surfactants. It can be seen from figure 4 that the shear stress increases with the increase of shear rate. Equation (2) was used to fit the fluid curves under different co-surfactant conditions in Figure 4 to obtain the rheological characteristic parameters $K$ and $n$ of the almond oil microemulsion system, as shown in Table 2. The table 2 shows that three help surfactant of almond oil microemulsion preparation by the value of $n$ is less than 1, are pseudoplastic fluid, shear viscosity decreases with the increase of shear rate, the main reason is that when the shear rate is low, branched molecules that intertwine, high viscosity, and with the increase of shear rate, molecule branched chain perfectly aligned along the direction of the shear, the direction of the system with reduced viscosity, $K$ value, the size of the order are: n-butyl alcohol $>$ ethanol $>$ 2 - propanediol, because ethanol is relatively small molecular weight, viscosity is low, so its consistency coefficient is low. The experiment shows that the shear rate has an important effect on the processing of the material, and the homogenization of the system can be improved by thinning the material through shear homogenization.

![Figure 4](image-url)  
*Figure 4 Effects of different co-surfactants on the flow curve of almond oil microemulsion*

| Co-surfactant   | $K$    | $n$    | $R^2$    |
|-----------------|--------|--------|----------|
| Ethyl alcohol   | 10.62  | 0.9692 | 0.9996   |
| 1, 2 - propylene glycol | 15.214 | 0.9795 | 0.9912   |
| n-butyl alcohol | 32.051 | 0.8965 | 0.9959   |
3.2.2. Effect of N-butanol content on the flow curve of almond oil microemulsion. The fixed water content was 58%, n-butanol was used as co-surfactant, $K_m=2$, and the influence of oil: emulsified mixture =1:2 (W/W), 1:3 and 1:4 on the flow curve of almond oil microemulsion was investigated, as shown in Figure 5. From Figure 5, different levels of n-butyl alcohol with almond oil microemulsion flow curve is different, the influence of shear stress increases with the increase of shear rate, n-butyl alcohol content is higher, the convex to the shear stress axis flow curve, and with the increase of the amount of n-butyl alcohol, shear viscosity of microemulsion system is reduced, indicating that helps the surfactant and surfactant to form the interface membrane, reduce the interfacial tension and the repulsive force between molecules, increased liquidity, to make more beneficial to the formation of emulsion, as a result, the experiment proved to help to reduce the dosage of surface active agent, surfactant to system played an important role in the formation.

Equation (2) was used to fit the fluid curves under different n-butanol contents in Figure 5 to obtain the rheological characteristic parameters $K$ and $N$ of the almond oil microemulsion system, as shown in Table 3.

3.2.3. Effect of N-butanol content on the flow curve of almond oil microemulsion. The fixed water content was 58%, n-butanol was used as co-surfactant, $K_m=2$, and the influence of oil: emulsified mixture =1:2 (W/W), 1:3 and 1:4 on the flow curve of almond oil microemulsion was investigated, as shown in Figure 5. The table 3 shows that different n-butyl alcohol content of almond oil microemulsion preparation by $n$ values are less than 1, are pseudoplastic fluid, shear viscosity decreases with the increase of shear rate, $K$ value, the size of the order are: 1:2>1:3>1:4, because as the emulsifying mixture ratio increases, viscosity decreased, so the consistency coefficient decreases.

![Figure 5](image-url)  
**Figure 5** Effects of different n-butanol content on the flow curve of almond oil microemulsion

| Oil: Emulsified mixture | $K$   | $n$    | $R^2$  |
|------------------------|-------|--------|--------|
| 1:2                    | 47.438| 0.8519 | 0.9877 |
| 1:3                    | 36.552| 0.8807 | 0.9935 |
| 1:4                    | 32.051| 0.8965 | 0.9959 |
4. Conclusion
In this study, the stability and formation mechanism of almond oil microemulsion were studied to provide a theoretical basis for the development of almond oil microemulsion.

(1) The stability of almond oil microemulsion test results show that the system under different centrifugal conditions (8000, 12000 r/min), storage temperature (-18 °C, 4 °C, 25 °C and 37 °C and 105 °C) and salinity (0.1, 0.5, 1.0 mol/L) and pH (PH = 1, 5, 9, 13) conditions, have good stability, high light transmittance, almond oil microemulsion system stability is good.

(2) The n values of almond oil microemulsion prepared by butanol, 1, 2-propanediol and ethanol were all less than 1 and all were pseudoplastic fluids. The shear viscosity decreased with the increase of the shear rate. The order of K values was as follows: n-butanol > 2-propanediol > ethanol; The n values of almond oil microemulsion prepared with different n-butanol contents were all less than 1, which were pseudoplastic fluids. The shear viscosity decreased with the increase of the shear rate. The order of K values was: 1:2 > 1:3 > 1:4.

This study provides a theoretical basis for the wide application of almond oil microemulsion and has a certain theoretical guiding significance for the further development of almond oil products.

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References
[1] Pramote K, Yukitaka K, Pyuichi M, et al. Preparation of finely dispersed O/W emulsion from fatty acid solubilized in subcritical water, Journal of colloid and interface science, 2004, pp. 192-197
[2] Lin C C, Lin H Y, Chen H C, et al. Stability and characterization of phospholipid-based curcumin encapsulated microemulsions, Food Chem, 2009, pp. 923-928
[3] Flanagan John, Singh Harjinder. Microemulsions: A Potential Delivery System for Bioactives in Food, Critical Reviews in Food Science and Nutrition, 2006, pp. 211-237
[4] Garti N, Clement V, Fanun M, et al. Sucrose ester microemulsions, Mol. Liq., 1999, pp. 3945-3956
[5] Kabir H, Aramaki K, Ishitobi M, et al. Cloud point and formation of microemulsions in sucrose dodecanoate systems, Colloid Surface A, 2003, pp. 65-74
[6] Parris N, Joubran R F, Lu D P. Triglyceride microemulsions—Effect of nonionic surfactants and the nature of the oil, J. Agric. Food Chem. 1994, pp. 1295-1299
[7] Amar I, Aserin A, Garti N. Solubilization patterns of lutein and lutein esters in food grade nonionic microemulsions, J. Agric. Food Chem., 2003, pp. 4775-4781