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Factors Affecting the Phase Inversion Process of Alkyl polyglycol ether C16-18/Fatty Alcohol/Oil/Water System

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The change of spontaneous curvature of nonionic surfactants is related to temperature. The phase inversion of the emulsion system is induced by temperature change, which is called phase inversion temperature method. Experiments were carried out in which Ceteareth-12 (Alkyl polyglycol ether C16-18) and Ceteareth-20 (Alkyl polyglycol ether C16-18) were used as hydrophilic emulsifiers and fatty alcohol as lipophilic emulsifiers. It was found that the increase of HLB value of hydrophilic emulsifier, the decrease of fatty alcohol content or the increase of carbon atom number of fatty alcohol led to the increase of phase inversion temperature of the system. The experimental results also showed that when the hydrophilicity of emulsifier system was enhanced, the second phase inversion would be more obvious. The phase inversion temperature of ester oils is generally higher than that of alkane oils.

Keywords: fatty alcohol; phase inversion temperature; ternary phase diagram.

INTRODUCTION

Emulsion is a colloidal dispersion system composed of two immiscible liquids[1]. One phase in the form of droplets is called dispersed phase, and the other phase is called continuous phase. The preparation of emulsion can be divided into high energy emulsification and low energy emulsification in terms of the source of energy. High energy emulsification relies on equipment to provide a lot of energy in a short period of time, which includes high pressure homogenization, microfluidic method, ultrasonic breaking method, etc. In practical application, it consumes a lot of energy and needs special equipment. The input energy density is about 10^8–10^{10} W/kg [2]. Low energy emulsification uses the chemical energy stored in the system to produce fine emulsions with less energy consumption (10^3 w/kg) [3]. The formation of fine emulsions depends on the spontaneous movement of surfactants and low interfacial tension. Low energy emulsification can be divided into two types: spontaneous emulsification[4] and phase inversion[5]. In the process of spontaneous emulsification, a large number of surfactant or solvent molecules are required, which rapidly diffuse from the dispersed phase to the continuous phase, inducing the formation of fine emulsions[4]. Phase inversion emulsification can utilize the chemical energy in the system by changing the spontaneous curvature. The method of changing the composition while keeping the temperature constant in order to change the spontaneous curvature is called phase inversion composition (PIC)[6]. Based on PIC, Sagitani et al.[7] dissolved surfactants in polyols to form D phase and proposed D phase emulsification method. The process of preparing emulsion by changing temperature while maintaining the same composition is called phase inversion temperature (PIT)[8–10]. In PIT emulsification, the hydrophilicity and lipophilicity of non-ionic surfactants change with temperature[11]. Thus W/O emulsion of the system at high temperature will be converted into O/W emulsion in the process of cooling[12]. Compared with PIC and D phase emulsification, PIT emulsification has more advantages in practical application. It has no restriction on the viscosity of oil and the melting point of oil and emulsifier.

The hydrophilic and lipophilic properties of non-ionic surfactants are nearly balanced when the system approaches the phase inversion temperature. The system passes through bicontinuous phase[13, 14] and lamellar liquid crystal phases[15] with low surface tension. The hydrophilic and lipophilic properties of surfactants change with the change in temperature. This results in the change of interfacial tension between emulsifier/water and emulsifier/oil, and induces the change of curvature radius of oil-water interface. Eventually, the emulsion type changes. At high temperatures, the emulsifier has strong lipophilicity, and the interfacial tension between emulsifier and oil is low, and thus the oil phase is easy to act as the external phase. With the decrease of temperature, the emulsifier decreases in lipophilicity and increases in hydrophilicity. The interfacial tension between emulsifier and water is low, and the water phase is easy to act as the external phase. The temperature at which the Hydrophile-Lipophile Balance (HLB)[11] of a nonionic surfactant occurs is called the phase inversion temperature. the factors affecting the phase inversion temperature include: Water-to-Oil Ratio (WOR)[16], Surfactant-to-Oil Ratio (SOR)[17, 18] and inorganic salt[19]. However, in different systems, these factors affect the regularity of the phase inversion process quite differently. In addition to the above factors, fatty alcohols have small hydrophilic heads, which can be adsorbed on the oil-water interface, and often play as an co-emulsifier in the emulsion[20]. In the non-ionic surfactant system, fatty alcohols also have a great influence on the phase inversion temperature and the phase inversion process. In this paper, it was found that the effects of the contents and types of fatty alcohols on phase inversion temperature and the second phase inversion had certain regularity. This may be due to the adsorption of fatty alcohols on the oil/water interface, which contributes to the co-emulsification and affects the microstructure of the emulsion.

In recent years, much attention has been paid to the application of PIT method in formula. However, extensive studies have focused on the occurrence of phase inversion and the influencing factors of phase inversion temperature. However, there are few studies on the change of microstructure of emulsion during phase inversion and the effect of oil type on phase transition

temperature. Ceteareth-12 and Ceteareth-20 are two typical polyoxyethylene ether type nonionic surfactants. Cetearyl alcohol (C16-18 Alcohols) and the hydrophobic groups of these two surfactants have similar structures. In this paper, the influence of the ratio of hydrophilic emulsifier and the type of fatty alcohol on the phase inversion temperature was studied. The change of emulsion structure was analyzed in the second phase inversion. In addition, the effects of alkanes and esters on phase inversion temperature were also studied.

MATERIALS AND METHODS

Materials

The raw materials used in the experiment are shown in Table 1.

Preparation of nano-emulsion

The ratio of hydrophilic emulsifier Ceteareth-12 and Ceteareth-20 ranges from 10 : 0 – 0 : 10 (total content 10% w/w), lipophilic emulsifier cetearyl alcohol content 7% (w/w) and 20% (w/w) oil. 10% glycerin is combined with water to form aqueous phase. The two phases are heated to 95 °C respectively (BHS-2 digital display constant temperature water bath, BAI). Under stirring conditions (400 rpm, RW20 DS025, IKA), the aqueous phase is added to the oil phase, and the temperature is reduced after constant temperature for 10 min.

Determination of phase inversion temperature

The determination of phase inversion temperature can be inferred from conductivity[21], absorbance[10] and viscosity[18]. Conductivity can determine the type of continuous phase. The conductivity of the system is 0 μS/cm when oil is continuous phase, and > 5μS/cm when water is continuous phase. The temperature at which the conductivity suddenly changes is the phase inversion temperature.

Use the deionized water preheating conductivity meter (DDS-307A, DJS-1C, Shanghai INESA Scientific Instrument Co., LTD) to insert the probe into the emulsion. At high temperature, the oil is a continuous phase, the system has no conductivity, and the conductivity value is about 0 μS/cm. With the decrease of temperature, the continuous phase gradually changes from oil phase to aqueous phase, and the conductivity increases to the maximum, which marks the end of the phase conversion process. When the conductivity value is constant ≥ 5μS/cm, the temperature is considered to be the phase inversion temperature of the system.

Particle Size Characterization

The nano-particle sizer were measured using Malvern Zetasizer Nano ZS (Malvern Instruments, UK) at 25 °C, by scattering light at 173 °. The scattering angle instrument performed particle sizing by means of a 4 MW laser diode operating at 670 nm. Particle size were measured by dynamic light scattering method to measure the diffusion of particles under Brownian motion at a 173 degree scattering angle, and converts it into particle size and particle size distribution by Stokes Einstein relation. Dilute the sample to 1/200 and add about 1ml to the sample cell. The values of the mean diameter were the averages of results obtained for three replicates.

RESULTS AND DISCUSSION

Emulsifier

Hydrophilic Emulsifier

Polyoxyethylene ether non-ionic surfactants are commonly used as emulsifiers in cosmetics. Their HLB values varied with temperature. Emulsifiers Ceteareth 12 and Ceteareth 20 have high HLB values at low temperature, which is beneficial to the formation of O/W system. However, the HLB value decreases at high temperature, which is beneficial to the formation of W/O system. Firstly, the change of PIT temperature of the two emulsifiers in different proportions was studied. The change of conductivity with temperature is shown in Figure 1, and the change of formula and phase inversion temperature are shown in Table 2.

With the increase of Ceteareth-20 (B2) in the emulsifier, the content of Ceteareth-12 (B1) decreases, the HLB value increased and the phase inversion temperature increases. When the content of B2 in the system was ≥ 8%, the HLB value of emulsifier was ≥ 15.24, and the system was O/W system without phase inversion. In the variation range of HLB value (HLB = 13.4 ~ 15.7), the phase inversion temperature changes greatly (59 ~ 86 °C). With the increase of HLB value by 0.23, the phase inversion temperature would increase by 3–6 °C. B1 and B2 have the same hydrophobic group, that is, cetyl/stearyl, and the HLB values of the two emulsifiers

Table 1. The raw materials adopted in the experiment

INCI Name	Chemical Name	Source
CETEARETH-12	Alkyl polyglycol ether C16-18	BASF SE
CETEARETH-20	Alkyl polyglycol ether C16-18	BASF SE
CETEARYL ALCOHOL	C16-18 Alcohols	BASF SE
GLYCERIN	1,2,3-Propanetriol	IOI
ISOPROPYL MYRISTATE	Isopropyl myristate	Shanghai Dailygreen Chemical Company
ETHYLHEXYL PALMITATE	2-ETHYLHEXYL PALMITATE	BASF SE
CAPRYLIC/CAPRIC TRIGLYCERIDE	Mixed decanoyl octanoyl glycerides	Wilmar Oil Technology Co., LTD
TRIETHYLHEXANOIN	Glyceryl tri(2-ethylhexanoate)	Guangdong Sanhao Technology Co., LTD
ISONONYL ISONONANOATE	7-methyloctyl 7-methyloctanoate	BASF SE
MINERAL OIL		Zhejiang Zhengxin Petroleum Technology Co., LTD
SQUALANE	2,6,10,15,19,23-Hexamethyl-tetracosan	Clariant
ISODODECANE	2-Methylundecane	Guangdong Sanhao Technology Co., LTD
ISOHEXADECANE	2-Methylpentadecane	INEOS

*INCI Name：International Nomenclature Cosmetic Ingredient Name

Table 2. Phase inversion temperature of emulsions prepared with different HLB values in mineral oil system

B1/B2 Content	B1/B2 ratio（w%/w%）	HLB Value	Cetearyl Alcohol Content（w/w%）	Phase Inversion Temperature/℃
10	0/10	15.7	7	O/W Emulsion
	2/8	15.24		
	3/7	15.01		86
	4/6	14.78		83
	5/5	14.55		80
	6/4	14.32		74
	7/3	14.09		70
	8/2	13.86		64
	10/0	13.4		59

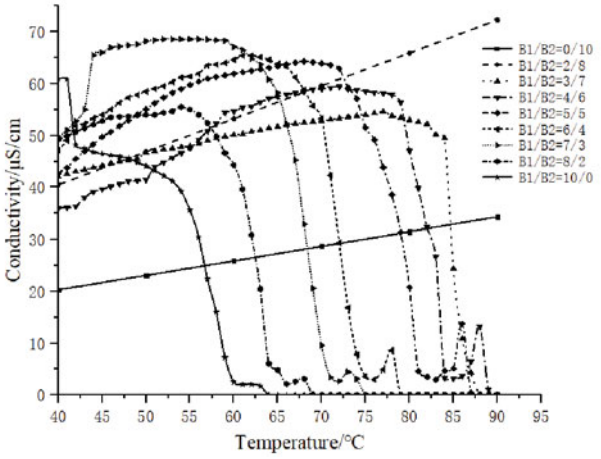

Figure 1. The conductivity of emulsions prepared by PIT method is different from that of emulsifier in the mineral oil system (10% emulsifier, 20% mineral oil, and 7% cetearyl alcohol)

are positively correlated with the number of EO (Epoxyethane). B2 has a larger HLB value, and its proportion increases. With the increase of the content of B2, the affinities between emulsifier and water are improved, and the temperature of the system is increased.

With the decrease of B2 content, the maximum conductivity increases. When the content of B2 was 10%, the maximum conductivity was able to achieved 32 μS/cm. After B2 was replaced by B1, the maximum conductivity could reach 70 μS/cm. The synthetic reaction formula of fatty alcohol polyoxyethylene ether is shown in the following formulas (1) and (2):

$$ROH + H_2C\!-\!CH_2 \xrightarrow{KOH} ROCH_2CH_2OH \quad (1)$$

$$ROCH_2CH_2OH + n\,H_2C\!-\!CH_2 \xrightarrow{KOH} RO(CH_2CH_2O)nH \quad (2)$$

At the end of the reaction, CH_3COOH was used to neutralize KOH. The CH_3COOK generated by the neutralization reaction can explain why the conductivity can be detected of emulsifier solution. The conductivity of 10% emulsifier (B1 : B2 = 7 : 3) was 145 μS/cm (45 °C), and that of 5% emulsifier (B1 : B2 = 7 : 3) was 76 μS/cm (45 °C) . After the emulsion preparation, some impurities may be emulsified and wrapped in the particle, so the maximum conductivity of the system often failed to reach the conductivity value of the hydrophilic emulsifier aqueous solution.

Lipophilic Emulsifier

Cetearyl alcohol is a lipophilic substance. It can be used as emollient in cosmetics, and at the same time help emulsification in oil-in-water system to improve the stability and viscosity of the emulsion. By changing the content of cetearyl alcohol, the change of conductivity with temperature is shown in Figure 2, and the PIT are shown in Table 3.

The results in Figure 2 showed that when the content of cetearyl alcohol was less than 4%, no phase inversion occurred in the system. When the amount of alcohol is more than 5%, the PIT phase inversion process occurred. With the increase of cetearyl alcohol content, the phase inversion temperature gradually decreases. The possible reason is that cetearyl alcohol as an co-emulsifier has a strong lipophilic. In O/W system, it can be used as a co-emulsifier to enhance stability. As an oil, cetearyl alcohol is dissolved in oil phase at high temperature, which increases the proportion of oil phase and is conducive to the stability of W/O system. The formation of stable W/O system at high temperature is the premise of phase inversion in PIT process. The addition of cetearyl alcohol is beneficial to the formation of stable W/O system at high temperature. Experiments have been conducted to further explore the influence law of fatty alcohol and change the type of fatty alcohol, and the results are shown in Figure 3.

The experimental results showed that the longer the carbon chain of fatty alcohol was, the higher the phase inversion temperature would be. The phase inversion temperature of decanol system was 57 °C and that of octadecanol was 75 °C. In this experiment, the mineral oil has a low solubility in decanol. For the complex emulsifier system, this phenomenon may be related to the amount of substance. When the same mass of fatty alcohol was added, the relative molecular weight of long chain fatty alcohol was large, which makes the amount of substance small. Then the increasing number of carbon atom of fatty alcohol raises the molar ratio of hydrophilic emulsifier to lipophilic emulsifier. In the

Table 3. Phase inversion temperature of emulsion prepared with different content of cetearyl alcohol in mineral oil system

B1/B2 Content	B1/B2 ratio（w%/w%）	HLB Value	Cetearyl Alcohol Content（w/w%）	Phase Inversion Temperature/℃
10	7/3	14.09	5	80
			6	74
			7	70
			8	67
			9	65
			10	57

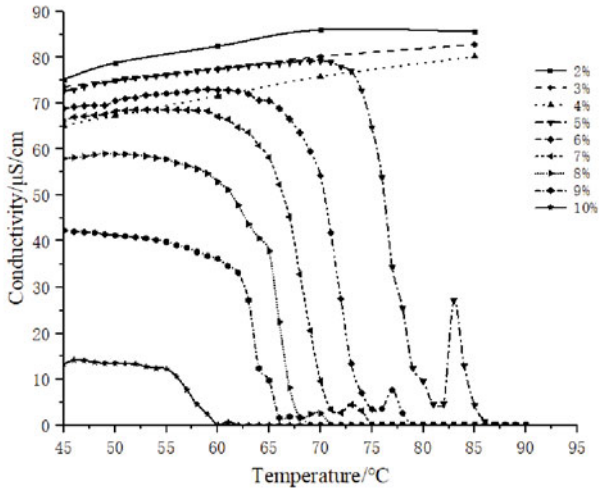

Figure 2. The conductivity of different content of cetearyl alcohol in the mineral oil system is prepared by PIT method (2–-10% fatty alcohol, 10% emulsifier, 20% mineral oil)

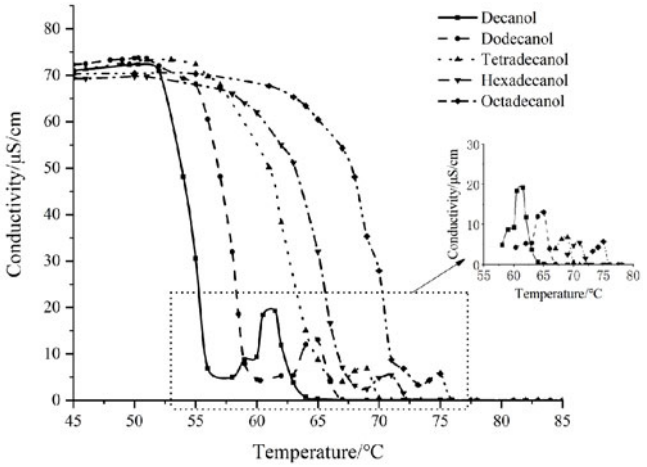

Figure 3. The conductivity of different types of fatty alcohols in the mineral oil system is prepared by PIT method (7% fatty alcohol, 10% hydrophilic emulsifiers, 20% mineral oil)

end, the increasing hydrophilicity of emulsifier system increases the temperature of phase inversion.

In the cooling process, a change in conductivity may occur before the complete conversion to oil-in-water emulsion, called the second phase inversion, which may happen due to the presence of liquid crystal phase[15]. The addition of aliphatic substances could induce significant structural changes of the system. For instance, the system changed from lamellar phase to anti-hexagonal phase[22] when the content of vitamin K1 grew. As the HLB value decreased, the conductivity peaks also decreased. This may be related to the weakening of the liquid crystal, because fatty alcohols are amphiphilic substances with CPP > 1, and the increase of the content of fatty alcohols is beneficial to the formation of reverse micelles.

Therefore, it is speculated that because the strength of the liquid crystal is weakened, the second phase inversion decreases with the increase of carbon atom number. The results showed that the long hydrophobic group of fatty alcohol was difficult to promote the stratified and ordered arrangement of emulsifier.

In addition to structural changes that may cause second phase inversion, the supposition that the lipophilic emulsifier migrates during the cooling process can be confirmed as follows. The lipophilic emulsifiers are difficult to have hydrogen bonding at high temperature and dissolve in the oil phase. With lower temperature, the arrangement of the hydrophilic emulsifiers on the oil-water interface is no longer close. This increases the probability of contact between lipophilic emulsifiers and water molecules, making lipophilic emulsifiers migrate to the oil-water interface, strengthening the interface film, and generating the second phase inversion in the process of temperature drop. With the drop of temperature, the interaction between emulsifier and water is further strengthened, which makes the system phase inversion happen again and completely be changed into water continuous phase.

The Content of Emulsifier

In this system, the hydrophilic emulsifier is composed of B1 and B2, and the lipophilic emulsifier cetyl stearol is used as co-emulsifier. In practical application, the lower the amount of emulsifier to stabilize the emulsion is much desired. An experiment has been conducted to determine the ratio between emulsifiers, and change the content of emulsifier system. The measured conductivity data is shown in Figure 4, and the phase inversion temperature is shown in Table 4.

The content of emulsifier was the sum of the hydrophilic emulsifier B1/B2 and 1618 alcohol. When the emulsifier content was ≤ 5%, there was no phase inversion in the investigated temperature range, and the continuous phase of the system was water. With the increase of emulsifier content, the phase inversion temperature decreased (Table 4). When the emulsifier content was 8%, the phase inversion temperature was 88 °C. The emulsifier content increased to 15%, and the phase inversion temperature decreased to 68 °C. With the increase of SOR (surfactant: oil ratio) (0.4–0.75), B1 and B2 with high EO content would be adsorbed to the oil / water interface, while cetearyl alcohol was more dispersed from the interface to the oil. Cetearyl alcohol is beneficial to stabilizing W/O system, thus resulting in a decrease of

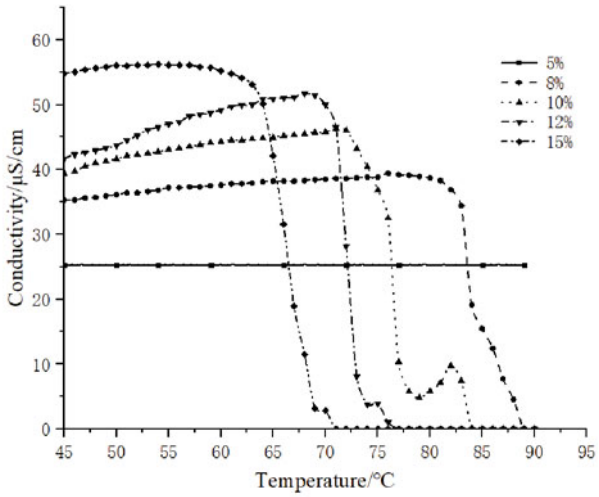

Figure 4. Conductivity of different emulsifier contents in mineral oil system (Fatty alcohol: hydrophilic emulsifiers = 1:1, 20% mineral oil)

Table 4. Phase inversion temperature of emulsion prepared with different content of emulsifier and cetearyl alcohol in mineral oil system

B1/B2 Content	B1/B2 ratio（w%/w%）	HLB Value	Cetearyl Alcohol Content（w/w%）	Phase Inversion Temperature/℃
2.5	7/3	14.09	2.5	O/W Emulsion
4			4	88
5			5	83
6			6	73
7.5			7.5	68

temperature. The formation of O/W system requires the main emulsifier to be more hydrophilic. This increased the oil phase content and reduced the phase inversion temperature. The second phase inversion was the most obvious when the emulsifier content was 10%.

There may be three reasons for the decrease of phase inversion temperature when the total content of emulsifier increases. (1) The increase of total content of emulsifier reduces the proportion of water phase, or the addition of cetearyl alcohol increases the oil phase ratio. (2) The increase of the amount of cetearyl alcohol does not have the property of co-emulsifier to form O/W at high temperature, which is more conducive to the stability of W/O system. (3) The increase of B1 and B2 content improves the viscosity of the system, leading to the lag of PIT phase inversion process.

The lipophilic emulsifier disperses from the boundary to the oil, which increases the oil phase content and reduces the phase inversion temperature. That is because the increase of lipophilic emulsifier will reduce the phase inversion temperature by reducing the affinity between oil-water interface and aqueous phase. The second phase inversion will be more obvious when the affinity between oil phase (oil + surfactant) and aqueous phase is enhanced by increasing the proportion of emulsifiers with high HLB value, reducing the content of lipophilic emulsifiers, and using short chain fatty alcohols.

Oil

Cetearyl alcohol is 7%, and some ester oil systems will not change phase. Therefore, 10% cetearyl alcohol is used as lipophilic co emulsifier. The oil is 20% and emulsifier is 10% (B1:B2 = 7:3). The effect of oil type on phase inversion temperature was studied.

Alkane

Firstly, the effects of 7#, 10#, 15#, 26# and 32# mineral oils on phase inversion temperature were investigated. The main component of mineral oil is saturated alkane. The larger the number, the greater its viscosity and the much larger the average relative molecular mass. The change of conductivity with temperature is shown in Figure 5. The phase inversion temperature and the particle size of the emulsion are shown in Table 5.

As the average relative molecular mass of mineral oil increases, the phase inversion temperature (Table 5) and maximum conductivity (Fig. 5) increase. The experimental data in the literature shows that after the conductivity reaches the maximum, the conductivity value remains unchanged with the decrease of temperature. However, after the conductivity of the system reached the highest point, the value began to decline. The viscosity increases with the decrease of temperature. The ability of transmitting current is weakened, resulting in the decrease of conductivity. For a certain non-ionic emulsifier, the

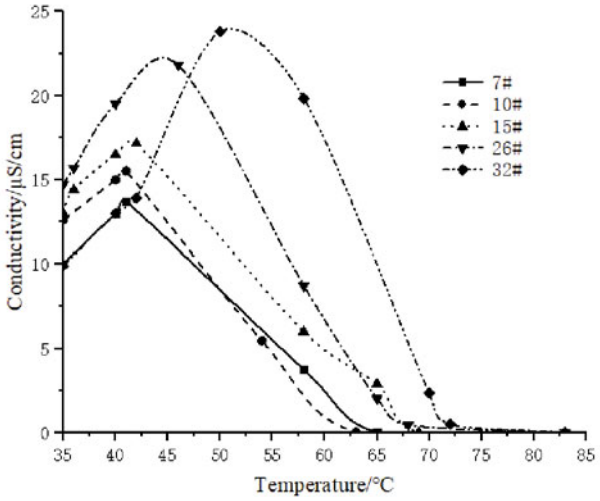

Figure 5. The conductivity of different number of mineral oils was prepared by PIT method (20% mineral oil, 10% cetearyl alcohol, 10% hydrophilic emulsifier, B1:B2 = 7:3)

Table 5. The phase inversion temperature and particle size of different mineral oils prepared by PIT method

	Number/#	Phase inversion temperature/℃	Z-Average /nm
Mineral Oil	7	57	362.2
	10	55	338.2
	15	60	311.3
	26	62	208.2
	32	67	210.6

higher the solubility of alkanes, the lower the phase inversion temperature[23]. In this experiment, as the serial number goes up, there is greater similarity between the structure of mineral oil and emulsifier hydrophobic group. Under the same oil-water ratio, it was more conducive to the preparation of O/W system, so the phase inversion temperature increased.

Branched alkanes have the advantages of enhancing product performance, such as excellent solubility and oxidation stability. It is widely used in cosmetics. The effects of three branched alkanes (Isododecane, Isocetane and squalane) on phase inversion temperature were investigated. The conductivity changes with temperature as shown in Figure 6. The phase inversion temperature and the average particle size of the emulsion are shown in Table 6.

At the same mass, the phase inversion temperature has no relationship with the molecular weight of branched alkanes. The phase inversion temperature of isocetane was the highest and the particle size was the smallest among the three oils. The maximum conductivity of branched alkanes was lower than 20 μS/cm, which was lower than that of mineral oil system.

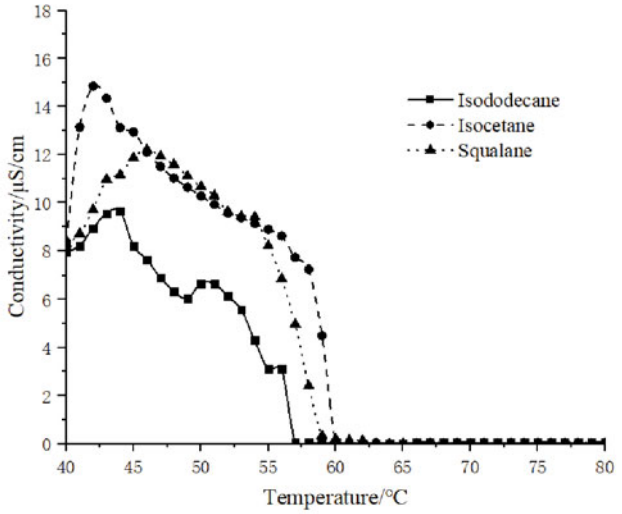

Figure 6. The conductivity of different branched alkanes was prepared by PIT method (20% branched alkane, 10% cetearyl alcohol, 10% hydrophilic emulsifier, B1:B2 = 7:3)

Table 6. The phase inversion temperature and particle size of different branched alkanes prepared by PIT method

Chemical name	Relative molecular mass	Phase inversion temperature/°C	Z-Average /nm
Isododecane	170.33	54	439.6
Isocetane	226.44	59	369.9
Squalane	422.81	57	424.8

Ester Oil

Ester oil has good moisturizing effect and is widely used in cosmetics. The effects of Isopropyl Myristate (IPM), Isononyl Isononanoate (ININ), Ethylhexyl Palmitate (2-EHP), Triethylhexanoin (GTEH) and Caprylic/Capric Triglyceride (GTCC) on the phase inversion temperature of were investigated.

In Figure 7, the viscosity of the emulsion made from GTEH is largest than that of the other four oils, which led to a slower rise in conductivity. When the conductivity was greater than 5 μS/cm, the phase inversion temperature was 78 °C. After phase inversion, the viscosity of the system increased and the conductivity

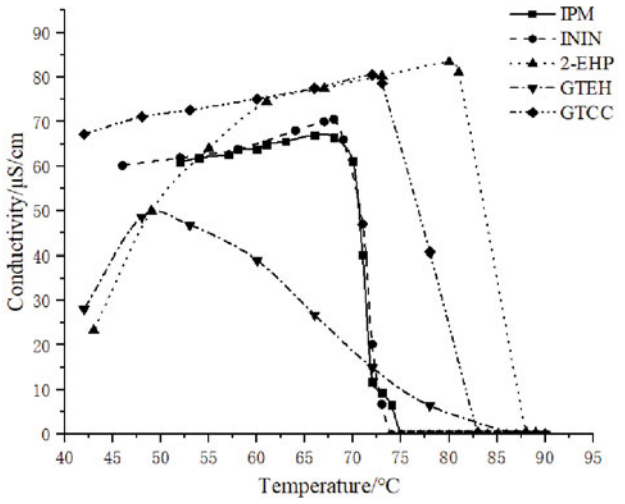

Figure 7. The conductivity of different ester oil was prepared by PIT method (20% oil, 10% cetearyl alcohol, 10% hydrophilic emulsifier, B1:B2 = 7:3)

decreased. In Table 7, the particle size of the emulsion was independent of phase inversion temperature, and the temperature of 2-EHP was between GTCC and GTEH. The particle size might be related to the complexity of structure. Triglycerides (GTCC and GTEH) have complex structures, so the size of the emulsion was larger than monoester (IPM, ININ and 2-EHP). Triglycerides have low interfacial tension, strong affinity with water, less driving force of interfacial contraction, and are easy to form droplets with large curvature.

Table 7. The phase inversion temperature and particle size of different ester oil prepared by PIT method

Chemical name	Relative molecular mass	Phase inversion temperature/°C	Z-Average /nm
ISOPROPYL MYRISTATE（IPM）	270.45	74	127.5
ISONONYL ISONONANOATE（ININ）	284	73	145.9
ETHYLHEXYL PALMITATE（2-EHP）	368.64	81	199.0
TRIETHYLHEXANOIN（GTEH）	470.68	78	457.3
CAPRYLIC/CAPRIC TRIGLYCERIDE（GTCC）	470.68 or 554.84	85	554.6

When the viscosity of the system increases, the maximum conductivity decreases. For example, the viscosity of the emulsion made of alkane oil is higher than that of the ester oil. The stage of low conductivity and smooth curve corresponds to the stage of rising viscosity of the system. The particle size and the viscosity of the system may be related. The viscosity of the emulsion made from 26# and 32# mineral oil is lower than that of other types of mineral oil, and the emulsion size is small. Similar phenomenon occurs in ester oils. No comparison can be made between different oil types. The viscosity of ester oil emulsion is lower than that of alkanes. However, the particle size of GTEH and GTCC is larger than that of alkane system. The affinity between ester oil and aqueous is higher than alkanes. Therefore, the phase inversion temperature of ester oil system is generally higher than alkanes. The phase inversion temperature of emulsion prepared by GTEH and GTCC is higher than that of most systems, but their particle size is the largest in all oils. Mineral oil 32# is the smallest particle size in mineral oil system, and its phase inversion temperature is also the highest in mineral oil system.

Ternary phase diagram

The preparation of ternary phase diagram can understand the interaction and influence between the three components by changing the ratio of different components. Then the ratio of phase inversion process can be determined. By comparing the types of emulsions under high and low temperature conditions, we can understand the law of phase inversion temperature change caused by the change of different components. The ternary phase diagram can show the phase inversion behavior of emulsion in different proportions, which provides important reference and guidance for the design of emulsion products. The ternary phase diagrams of different oils and fats under different emulsifier ratios are shown in

Figure 8. The ratio (B1: B2: Cetearyl Alcohol) is 7:3:7 in Figure 8(A) and Figure 8(C); while the ratio (B1: B2: Cetearyl Alcohol) is 3:7:7 in Figure 8(B) and Figure 8(D). In Figure 8, the gray area is the region where phase transformation occurs, and the Roman numerals are the system types at high temperature.

Figures 8 (A) and (B) demonstrate that an increase in the ratio of emulsifier to oil (emulsifier : oil = 3:7→10:0) leads to a higher minimum water content required for phase inversion in the emulsion, rising from 25% to 55%. Within the range of ratios between emulsifier : oil = 3:7 and 5:5, once the emulsion reaches a proportion capable of undergoing phase inversion, if the water content exceeds 55%, a stable W/O system cannot be formed under high temperature conditions. However, in the B1/B2 = 7/3 mineral oil system, phase inversion can still occur even at very high water contents (water content ≥95%).

Figures 8 (C) and (D) indicate that by increasing the hydrophilicity of the emulsifier system, an IPM system can achieve a milk-to-oil ratio as high as 6:4 during PIT formation. As the ratio changes from surfactant: oil = 3:7→10:0, this case shows an increased minimum water content required for phase inversion from 40% to 65%. Under identical SOR conditions, compared with other systems, IPM system requires lower initial water content for phase inversion. For example, when using a SOR of 6:4, a mineral oil-based system would need at least around 45% humidity level to undergo PIT while an IPM-based system only requires 40%.

By increasing the proportion of hydrophilic emulsifiers, the minimum water content required for phase inversion temperature (PIT) at the same oil-to-water ratio can be reduced. Additionally, the polarity of fats also decreases this minimum water content requirement for PIT at the same oil-to-water ratio. It is worth noting that, except in extreme cases (≥98%), whether phase inversion occurs or not is generally unaffected by the water content, which aligns with the findings presented in this chapter.

In B1/B2/1618 alcohol systems, when the emulsifier system exhibits higher hydrophilicity, polar fats increase the minimum oil-to-water ratio for PIT. This phenomenon may be attributed to a significant presence of 1618 alcohol within the system: some 1618 alcohol adsorbs on interfacial membranes as co-emulsifiers while excess 1618 alcohol remains in an oily phase - effectively augmenting actual fat content.

CONCLUSION

For fatty alcohol polyoxyethylene ether system, the phase inversion temperature and the influencing factors in the PIT process were studied, and the main conclusions were as follows: When the HLB value of hydrophilic emulsifier is increased or the content of lipophilic emulsifier is decreased, the phase inversion temperature of the system will increase and the second phase inversion becomes more obvious. The decrease of the amount of fatty alcohol will increase the phase inversion temperature of the system. When using mineral oil to study the effect of emulsifier on PIT, increasing the affinity of emulsifier to water can make the second phase inversion more obvious. The second phase inversion may be related to the migration of emulsifier from

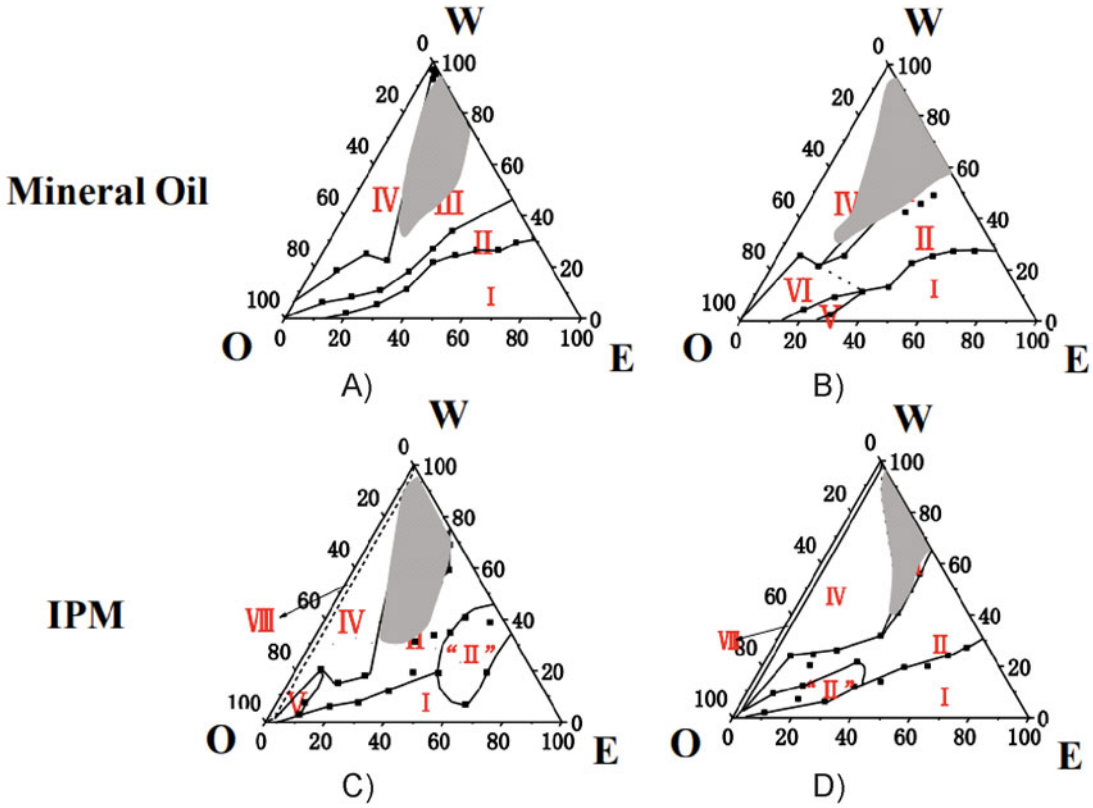

Figure 8. The ternary phase diagrams of different oils and fats under different emulsifier ratios (I: W/O microemulsion (colorless and transparent in appearance), II: W/O nano-emulsion, II: W/O crude emulsion, IV: O/W emulsion, V: two-phase mixing zone (oil, O/W), VI: Three-phase mixing zone (oil, O/W, solid), VII: two-phase mixing zone (W/O, solid), VIII: oil-water two-phase)

oil to the oil-water interface. The conductivity of the system without the second phase inversion when 10% cetyl alcohol is used, which may be related to the high content of lipopile emulsifier and the high viscosity of the system. When the type of oil was changed, there was still no the second phase inversion, which indicates that the second phase inversion was affected more by the type and structure of emulsifier. The influence of oil on the second phase inversion needs further investigation. The particle size of emulsion prepared by monoester and mineral oil is smaller than that of branched alkane and triglyceride. There is no definite relation between emulsified particles and phase inversion temperature. The factors affecting the particle size of emulsion prepared by PIT method need to be further studied. With proper emulsifier and oil ratio, the phase inversion process can still occur even at high water content.

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