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Study on the formation and stability of polyol-in-oil emulsion

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Abstract: In this study, the influence of polyols, emulsifiers and oils on the formation and stability of polyol-in-oil (P/O) emulsions was investigated. The interfacial tension in P/O systems is much lower than that of water-oil systems, so polyols and oils showed a greater affinity, which was not conducive to the stability of the emulsion system. High compatibility of the emulsifier and the inner and outer phases was the key to the formation of stable emulsions. Using polyethylene glycol 400 (PEG) as polyol phase, mineral oil or squalane as oil phase and cetyl PEG/PPG-10/1 dimethicone (EM 90) as emulsifier, long-term stable P/O emulsions with homogeneous droplets were successfully prepared.

Keywords: droplet morphology; emulsion stability; interfacial tension; polyol-in-oil emulsions.

1 Introduction

The expansion of the cosmetics market has prompted researchers to develop new functional cosmetic products that are highly effective and safe to use [1, 2]. The production of effective functional cosmetics depends on the properties of their functional ingredients, but is limited by the concentration of ingredients achievable in the application system. Although there are many types of functional raw materials in cosmetics, most of them, which have good antioxidant, anti-radical, whitening and other functions, such as flavonoids, terpenes, polyphenols, etc., are difficult to dissolve in the media of oil and water commonly used in cosmetics [3, 4], which limits the realization of efficacy. Therefore, the preparation of suitable formulations is urgently needed to modify the physical and chemical properties of such water/oil insoluble active ingredients and improve their stability and solubility.

For those functional ingredients which are difficult to dissolve in oil and water, polyols are potential media to solve such dissolution limitations. Polyols are common non-aqueous polar solvents which can form hydrogen bonds and have relatively high dielectric constants [5–7]. In addition, the multiple hydroxyl groups in polyols can form hydrogen bonds, for example hydroxyl, phenol hydroxyl and ketone groups in the functional ingredients [8, 9], which improves the solubility of the ingredient to some extent. Hamill and Petersen [10] first prepared olive oil/polyol emulsions in the 1960s and proposed the concept of “non-aqueous emulsification”. Their alcohol-oil emulsification system attracted considerable attention. Lin et al. [11] encapsulated the skin-lightening agent deoxyarbutin in a non-aqueous emulsified structure using polyol in silicone oil, which effectively improved the coating rate and stability of the agent. In our previous study, polyol-in-oil-in-water (P/O/W) multiple emulsions were first developed in which the internal water phase was replaced by a polyol phase and this was used to encapsulate vitamin C [12, 13]. It was found that the formation of a stable polyol-in-oil (P/O) emulsion was first the key to the preparation of P/O/W multiple emulsions. However, when the internal phase of the multiple structure changed from water to polyol, the interfacial characteristics also changed accordingly [14–17]. The compatibility of the internal and external media and the aggregation behavior of the emulsifier in the polyol system differed from those in aqueous media, which affected the directional adsorption behavior of the emulsifier at the P/O interface and changed the regulating

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strategy of the P/O microstructure. Since then, only a few similar studies have been reported.

In this study, the influence of polyols, emulsifiers, and oils on the formation and stability of P/O emulsions was systematically investigated. The formation of P/O emulsions was characterized according to appearance and microstructure. Recommendations are made for future investigations and preparation of P/O emulsions, and for the practical application of P/O/W multiple emulsions.

2 Materials and methods

2.1 Materials

Glycerol (**GLY**), butylene glycol (**BG**) and propylene glycol (**PG**) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Mineral oil (26#) was supplied by Shanghai Daoxin Co., Ltd. (China). Cetyl PEG/PPG-10/1 dimethicone (**EM 90**) as one of the lipophilic emulsifiers was purchased from Evonik (Germany). Polyethylene glycol 400 (**PEG**) and squalane (**Squ**) were purchased from Clariant Chemicals Ltd. (China). Caprylic/capric triglyceride (**318**), and polyglyceryl-2 dipolyhydroxystearate (**PGPH**) were obtained from BASF (Germany). The sample of PEG-30 dipolyhydroxystearate (**DPHS**) was a gift from Croda (UK). Polyglyceryl-2 isostearate (**IS-201P**) was obtained from SAKAMOTO (Japan).

2.2 Preparation of P/O emulsions

The P/O emulsions were prepared by the homogeneous emulsification method. 63 g of the respective polyol (PEG, Gly, BG, PG) was added to 37 g of the oil phase containing 30 g of oil and 7 g of the lipophilic emulsifier with rapid stirring at 400 rpm for 5 min at 25 °C. The mixture was then homogenised at 15,500 rpm for 3 min using an Ultra Turrax T18 homogeniser (IKA, Germany) to obtain the respective P/O emulsion. All samples prepared in the study showed good repeatability. The primary formulation of the P/O emulsions is shown in Table 1.

Table 1: Composition of P/O emulsions.

Phase	Ingredient name	Weight percentage (wt.%)
Oil phase	Mineral oil/Squ (squalane)/318 (caprylic/capric triglyceride)	30.0
	EM 90 (cetyl PEG/PPG-10/1 dimethicone)/ DPHS (PEG-30 dipolyhydroxystearate)/ IS-201P (polyglyceryl-2 iIsostearate)/ PGPH (polyglyceryl-2 dipolyhydroxystearate)	0.7–14.0*
Polyol phase	PEG (polyethylene glycol 400)/Gly (glycerol)/BG (butylene glycol)/PG (propylene glycol)	To 100

*unless otherwise specified, the weight percentages of EM 90/DPHS/IS-201P/PGPH defaults to 7 wt%.

2.3 Microscopy analysis of P/O emulsions

Microscopy was used to obtain information on the visible characteristics of the emulsions. An optical microscope (Olympus VR BX 53) with an Olympus LC30 camera and LC micro-measurement software was used for the study. The microscopic analysis was performed according to our previous report [18] with some modifications. Samples for microscopic observation were prepared by carefully spreading a small amount of the creamy emulsion on a microscope slide and placing a glass cover. No pressure was applied to the glass cover to avoid affecting the oil droplets in the emulsions. All samples were observed at room temperature and the representative images were taken at 150× magnification. For droplet size analysis, a random area was selected on the image of each sample, and more than 100 droplets were included. The mean diameter ($d_{3,2}$) was calculated using Eq. (1):

$$d_{3,2} = \frac{\sum_{i=1}^{n} d_i^3}{\sum_{i=1}^{n} d_i^2} \tag{1}$$

2.4 Solubility analysis

Mixtures of emulsifier (15 wt%) and polyols (85 wt%) were prepared in a beaker with a magnetic stirrer at 25 °C to measure the solubility of the emulsifiers in polyols. The appearance of the samples was recorded 24 h after preparation using a digital camera (D810, Nikon, Japan). The images were not further processed.

2.5 Interfacial tension determination

The interfacial tension was measured by a fully automatic surface tension meter (BZY-1, Shanghai Heng Ping Instrument and meter Factory). 15 g polyols and 15 g oils were added one after the other to a 50 ml measuring beaker, left to stand for 30 min and then tested.

2.6 Stability studies

The stability of the P/O emulsions under three different storage conditions was determined by observing and photographing the emulsion structure with a microscope. The samples were stored at high temperature (HT: [50 ± 2] °C), room temperature (RT: [25 ± 2] °C) and low temperature (LT: [−18 ± 2] °C). The structure changes of emulsions were characterized after 1, 7, and 30 days, respectively.

3 Results and discussion

3.1 Effect of the types of polyols

The property of the polyol is an important factor influencing the stability of the emulsion as the polyol is the disperse phase of P/O emulsions. A change in the internal phase alters the interfacial tension between the polyol and

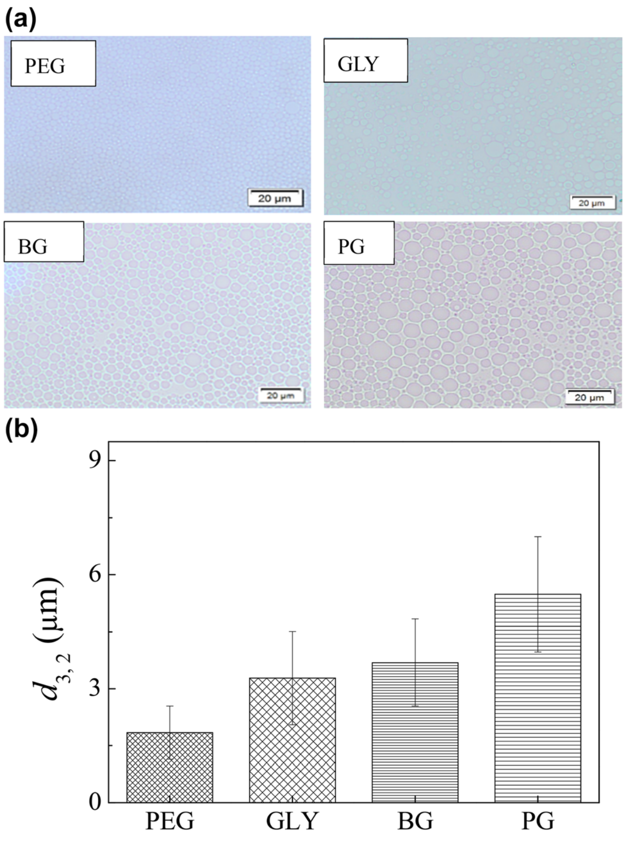

Figure 1: (a) Optical micrographs and (b) Z-average diameter ($d_{3,2}$) of P/O emulsions containing different polyols; **PEG**: polyethylene glycol 400; **Gly**: glycerol; **BG**: butylene glycol; **PG**: propylene glycol.

Table 2: Stability of P/O emulsions containing different polyols.

Polyol	1 day			7 days			30 days		
	HT	RT	LT	HT	RT	LT	HT	RT	LT
PEG	++	++	++	+	++	++	−	+	+
GLY	++	++	++	+	+	+	−	−	+
BG	++	++	++	+	+	++	−	−	+
PG	++	++	++	+	−	+	−	−	+

−, poor (good phase separation); +, moderate (slight phase separation); ++, excellent (no oil phase separation).

the oil phase as well as the adsorption behavior of the emulsifier at the P/O interface [19, 20]. The effects of PEG, Gly, BG and PG on the morphology and stability of P/O emulsions were studied. Optical micrographs (a) and Z-diameter ($d_{3,2}$) (b) of the different emulsions after 24 h are shown in Figure 1.

As shown in Figure 1a, the droplets of the P/O emulsions prepared with PEG are the smallest and most uniform, while the droplets of the emulsions prepared with Gly under the same conditions show a clear polydispersity. PEG has fewer hydroxyl groups than the other polyols, which means that less PEG adsorbs to the hydrophilic chains of EM 90 and the volume of hydrophilic groups is smaller. In addition, the droplet size of PG was higher than that of PGE after 24 h, showing that smaller hydrophilic groups tend to form smaller P/O droplets. Significantly, the P/O droplets were less distinct than conventional W/O droplets in this microscopic study, probably due to the similar refractive indices of mineral oil (26#) and polyols. According to references [21, 22], the refractive index of mineral oil (26#) is 1.466, and the refractive indices of polyols are 1.460–1.467 (PEG), 1.470–1.475 (Gly), 1.440 (BG), and 1.431–1.433 (PG). The stability of the P/O emulsions up to 30 days is shown in Table 2.

As shown in Table 2, emulsions prepared with PEG remained stable after 30 days at room temperature, while emulsions prepared with Gly, BG, and PG were observed to have different degrees of emulsion instability during storage, eventually leading to phase separation. However, all emulsions were unstable after 30 days at high temperature (Table 2). It can be assumed that the Ostwald ripening, coalescence and flocculation of P/O emulsions occured during storage, especially at high temperature [23, 24].

The directional adsorption of emulsifiers at interfaces is a key factor in the formation and stability of emulsions [25]. The adsorption behavior of the emulsifier at the interface is affected by its chemical structure and also depends on the weak interactions (such as Van-der-Waals forces, π-π-interactions, and hydrogen bonding [26]) between the emulsifier and the internal and external phases. To investigate the interactions between emulsifier (EM 90), polyol and oil, the solubility of the emulsifier in different polyols and the interfacial tension of polyol and oil were studied. As shown in Figure 2, EM 90 has the best solubility in glycerol, producing a homogeneous, turbid mixture. PEG gives a cloudy polyol phase and an upper emulsifier

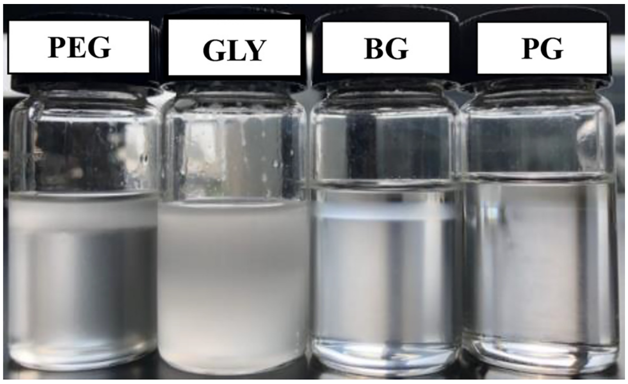

Figure 2: Compatibility of different polyols with EM 90 emulsifier.

phase. EM 90 has the worst solubility in PG and BG, giving an almost transparent lower polyol phase.

The interfacial tension between oil and water was 30.67 mN/m in the absence of the emulsifier. The results showed that the interfacial tension between mineral oil and the polyols was much lower than that at the W/O interface (9.80 mN/m in the case of PEG) (Table 3). The interfacial tension is proportional to the Laplace pressure, which is related to the energy required to form small droplets. An ultralow interfacial tension means that it is easier to form smaller droplets under the action of emulsifiers. However, an ultra-low interfacial tension also means that the good affinity between the two phases can lead to migration between the continuous and dispersed phases if the barrier of the emulsifier phase is not strong enough. Therefore, polyols with good affinity for oil and with a moderate solubility with lipophilic emulsifiers are more conducive to the production of small and stable P/O droplets. Therefore, PEG was chosen as the inner polyol phase for the subsequent experiments.

3.2 Effects of emulsifiers

Lipophilic emulsifiers play a key role in the formation of P/O emulsions, as they adsorb directionally at the polyol-oil interface and stabilise it [27]. The adsorption behavior of the emulsifier changes when the internal phase changes from water to polyols, resulting in different emulsification properties. For this reason, four types of conventional W/O emulsifiers were investigated: cetyl PEG/PPG-10/1 dimethicone (**EM 90**), PEG-30 dipolyhydroxystearate (**DPHS**), polyglyceryl-2 isostearate (**IS-201P**), and polyglyceryl-2 dipolyhydroxystearate (**PGPH**). Their chemical structures are illustrated in Figure 3 and the P/O emulsions prepared using these emulsifiers are shown in Figure 4.

As shown in Figure 3, IS-201P and PGPH are polyglycerol emulsifiers with different hydrophilic alkyl groups. The emulsions prepared with IS-201P and PGPH were unstable and phase separation is observed after 24 h (cf. Figure 4). Possibly, the intermolecular forces between polyglycerol groups and PEG are too weak to achieve the equilibrium between polyol and lipophiles required for the system. Delamination is more pronounced in the P/O system with IS-201P than in that with PGPH. DPHS is an A-B-A block polymer, with the hydrophobic groups consisting of polyhydroxystearic acid and the hydrophilic groups consisting of polyethylene oxide. DPHS could not be used as a lipophilic emulsifier in the PEG/mineral oil system because the hydrophilic groups in DPHS and PEG are too similar. As can be seen in Figure 4, a homogeneous system is formed that contains only bubbles (cf. Figure 4). However, the P/O system prepared using EM 90 shows uniform and stable emulsion droplets, which can be attributed to its moderate affinity with oils and polyols. EM 90 has a particular "comb-like" structure with multiple polyether and alkane branches which are evenly distributed on both sides of a polysiloxane skeleton. This unique structure and desirable solubility results in the

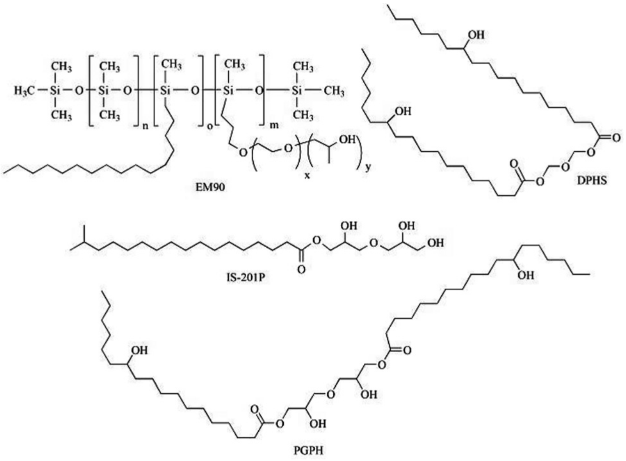

Figure 3: Chemical structure of different lipophilic emulsifiers.

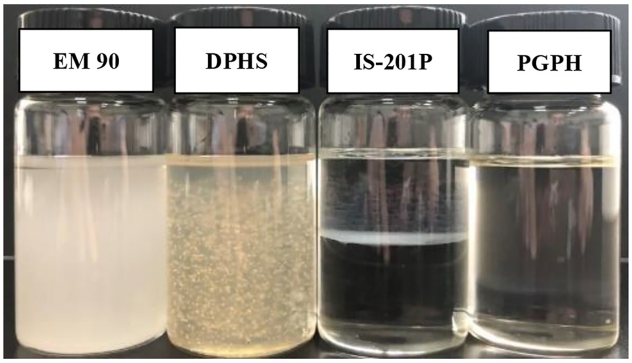

Figure 4: Appearance after 24 h of P/O systems formed with different emulsifiers; **EM 90**: cetyl PEG/PPG-10/1 dimethicone; **DPHS**: PEG-30 dipolyhydroxystearate; **IS-201P**: polyglyceryl-2 isostearate; **PGPH**: polyglyceryl-2 dipolyhydroxystearate.

Table 3: The interfacial tension between mineral oil and polyols.

Polyols	Interfacial tension (mN m^{-1})
PEG	9.8
GLY	15.6
BG	10.3
PG	10.6

stable adsorption of EM 90 at the P/O interface. EM 90 was chosen as the most suitable hydrophobic emulsifier.

Regarding the effects of the hydrophobic emulsifier on the formation of P/O emulsions, our hypothesis that the cross-sectional area of the hydrophilic head group and the length of the hydrophobic tail chain change with the changing properties of the medium was confirmed [28]. The aggregate morphology of the emulsifier at the alcohol-oil interface changed when the internal phase changed from water to polyol, which in turn affected the emulsion formation. This confirmed the need to evaluate the type of emulsifier used in P/O emulsion formation in this study.

The effect of emulsifier concentration on the formation and stability of P/O emulsions was also investigated. Micrographs of emulsions prepared with 0.7, 3.5, 7.0, 10.5, and 14.0% EM 90 are shown in Figure 5 and their stability over 30 days is described in Table 4. The concentration of this hydrophobic emulsifier does not have a major influence on the morphology of the P/O emulsions after 24 h. The size of the polyol droplets decreases slightly with increasing emulsifier concentration (cf. Figure 5). However, the differences in stability became significant over the following 30 days. As shown in Table 4, emulsions prepared with less than 3.5% emulsifier are unstable after 7 days, while those containing 7% or more emulsifier are unstable after 30 days at room temperature. The higher the emulsifier concentration, the less oil phase separates and floats on the surface, and the more stable the system. Only emulsions made with 10.5% or more emulsifier remain stable for 30 days. Therefore, the concentration of 10.5% EM 90 was chosen for subsequent experiments.

Table 4: Stability of P/O emulsions containing different concentrations (*c*) of EM 90 emulsifier.

c (EM 90)	1 day			7 days			30 days		
	HT	RT	LT	HT	RT	LT	HT	RT	LT
0.7%	++	++	++	–	–	+	–	–	+
3.5%	++	++	++	–	–	+	–	–	+
7.0%	++	++	++	+	+	++	–	–	+
10.5%	++	++	++	+	+	++	–	+	+
14.0%	++	++	++	+	+	++	–	+	+

–, poor (severe phase separation); +, moderate (slight phase separation); ++, excellent (no oil phase separation).

3.3 Effect of oils

As an external phase of the P/O system, oil also plays an indispensable role in influencing the formation and stability of emulsions by affecting the arrangement of the emulsifier in the interfacial film and the initial interfacial tension at the P/O interface [29]. To investigate the mechanism of the effect of oils on stability, three types of oil were studied: straight-chain alkane (mineral oil), branched-chain alkane (Squ) and ester oil (caprylic/capric triglycerides). Figure 6 shows microscopic images of emulsions prepared with these oils. Their stability over 30 days is described in Table 5. As the microscopic images of the emulsions show, the microstructure of the emulsions is clearly different depending on the type of oil. The emulsion droplets are fine and uniform when prepared with the straight-chain alkane (mineral oil) and the branched-chain alkane (Squ), whereas they are very

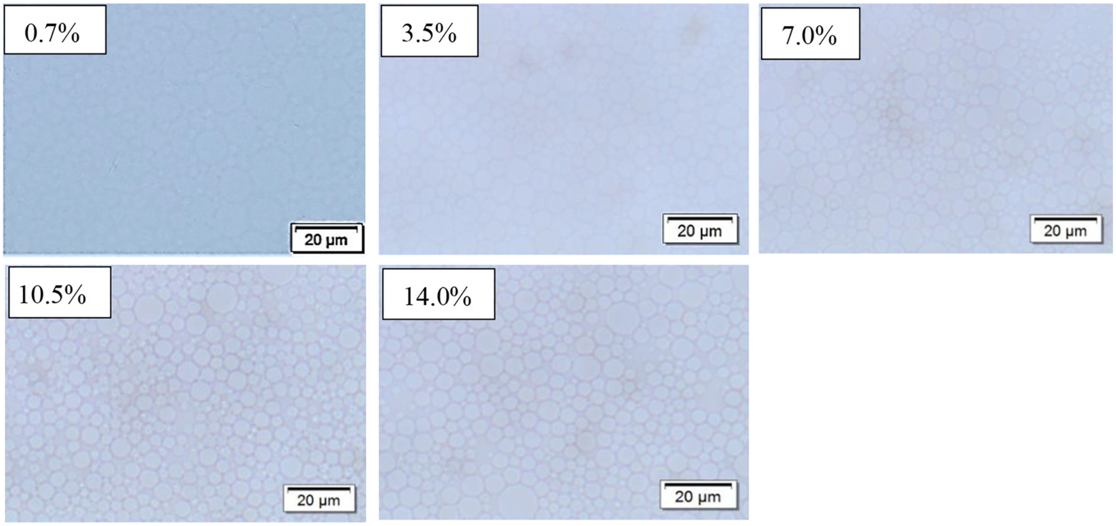

Figure 5: Optical micrographs of P/O emulsions (PEG as the inner polyol phase) prepared with various concentrations of EM 90 emulsifier.

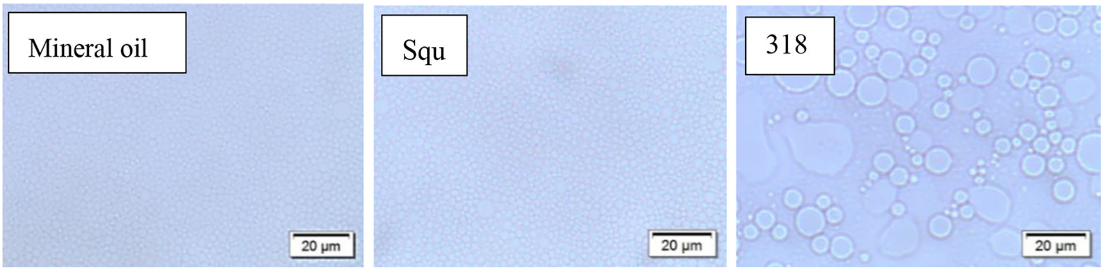

Figure 6: Optical micrographs of P/O emulsions prepared with different oils (PEG as the inner polyol phase); **Squ**: squalane; **318**: caprylic/capric triglyceride.

heterogeneous with the ester oil 318. Table 5 shows that the emulsions prepared with mineral oil and Squ are stable for up to 30 days at room temperature and high temperatures, while the emulsion with oil 318 shows a considerable instability after only one day. The small polyol particles in the 318 system gradually merge into larger particles and a strong phase separation is observed.

The interfacial tension between polyol-oil phases without emulsifiers was also determined and evaluated with the aim of understanding the role of each component in the emulsion formation and stability. The initial interfacial tension in the PEG-318 system was only 3.2 mN/m, in the PEG-mineral oil system 9.8 mN/m and in the PEG-Squ system 8.8 mN/m (cf. Table 6). All values are much lower than those of water-oil systems, which are typically greater than 30 mN/m. It can be seen that a certain interfacial tension difference is necessary for the formation and stability of the oil-polyol systems, although it was assumed that the lower the interfacial tension, the easier the emulsification.

Solubility is another indicator of affinity that more accurately describes the intermolecular forces between two substances [30]. To comprehensively investigate the compatibility of oils, emulsifiers and polyols in the formation and stability of emulsions, the solubility parameters of these components were calculated using the Fedors group contribution method [31]. The results are summarised in Table 7. When comparing the interfacial tension and

Table 5: Stability of P/O emulsions prepared with different oils (Squ: squalane; 318: caprylic/capric triglyceride).

Time (day)	1			7			30		
	HT	RT	LT	HT	RT	LT	HT	RT	LT
Mineral oil	++	++	++	+	+	++	−	+	+
Squ	++	++	++	+	+	++	−	+	+
318	+	+	+	−	−	−	−	−	−

−, poor (severe phase separation); +, moderate (slight phase separation); ++, excellent (no oil phase separation).

Table 6: Interfacial tension in P/O emulsions containing PEG and different oils.

Oil type	Interfacial tension (mN m^{-1})
Mineral oil	9.8
Squ	8.8
318	3.2
Oil E	2.4

Table 7: Solubility parameters of emulsion components estimated by the Fedors method.

Ingredient name	Solubility parameter
PEG	11.28
EM 90	8.79
Hydrophilic group of EM 90	10.45
Hydrophobic group of EM 90	8.27
Mineral oil	7.91–8.06
Squ	9.56
318	12.53
Water	21.03

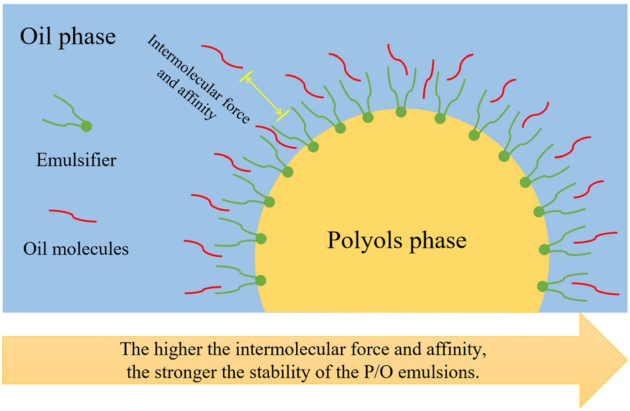

Figure 7: Schematic illustration of the effect of oils on P/O emulsion stability.

solubility parameter data, it is noticeable that the interfacial tension is lower when the solubility parameters of the hydrophobic or hydrophilic chain of the emulsifier are similar to those of the oil phase, which can be explained by the fact that a stable and complete interfacial layer is formed, which in turn leads to the formation of a more stable P/O emulsion (schematically shown in Figure 7).

4 Conclusions

In this article, various factors influencing the formation and stability of P/O emulsion systems were systematically investigated. The type of polyol was a particularly important factor in the formation and stability of the emulsion. The greater the interfacial tension between the mineral oil and the polyol, the larger or more non-uniform the droplets tended to become. PEG proved to be an optimal polyol in this system as it had good affinity for the oil, moderate solubility with lipophilic emulsifiers and produced small and stable P/O droplets. To obtain a stable emulsion, it was important that the hydrophilic or hydrophobic groups of the emulsifier had good compatibility with the polyols and oils present in the system.

Abbreviations

BG	butylene glycol
DPHS	PEG-30 dipolyhydroxystearate
EM 90	cetyl PEG/PPG-10/1 dimethicone
GLY	glycerol
IS-201P	polyglyceryl-2 isostearate
PEG	polyethylene glycol 400
PG	propylene glycol
PGPH	polyglyceryl-2 dipolyhydroxystearate
Squ	squalene
318	caprylic/capric triglyceride.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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