Preparation of High Internal Phase Emulsions and Their Application in the Field of Daily Chemicals

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Abstract. High internal phase emulsions (HIPEs), which are characterized by a dispersed phase volume fraction of more than 74.05%, exhibit unique structural and rheological properties, making them valuable across various industries. HIPEs have been utilized in food, pharmaceuticals, and daily chemical products due to their high surface area and stability. This review investigates the preparation methods of HIPEs, with an emphasis on the impact of raw materials, emulsification techniques, and conditions on emulsion quality. Additionally, the applications of HIPEs in moisturizing lotions, makeup removers, detergents, and absorbent materials are explored to highlight their potential in the daily chemical sector. Evaluating key factors such as particle size distribution, viscosity, and stability, this study aims to identify opportunities for performance optimization. Although significant progress has been made in HIPE development, further research is necessary to enhance their application potential, particularly in daily chemical products.

Keywords: high internal phase emulsions, preparation, daily chemicals.

1. Introduction

High internal phase emulsions (HIPEs) are characterized as emulsions with a dispersed phase volume fraction exceeding 74.05%, often referred to as superconcentrated emulsions [1]. Due to their large surface area and solid-like rheological properties, HIPEs have attracted significant attention across industries such as food, personal care, and pharmaceuticals. This study aims to review the preparation methods of HIPEs, focusing on the impact of various raw material choices and preparation techniques on the quality of emulsions, with the goal of identifying potential optimization strategies. Additionally, the demand and application of HIPE products in emulsification-related fields will be explored to highlight research gaps and future opportunities.

Currently, known types of HIPEs include oil-in-water (O/W), water-in-oil (W/O), and CO_2-in-water emulsions, with various emulsification techniques such as one-step, two-step, and concentration methods in use. However, limited research exists on the effects of key parameters, such things as raw materials, concentrations, mixing equipment, and emulsification conditions on the quality and stability of emulsions. This study will assess how adjusting these factors can improve the stability and performance of emulsions, with evaluations based on particle size distribution, viscosity, and stability testing.

Most existing research on HIPE applications focuses on the food industry. In this study, we will extend the analysis to daily chemical products, examining the potential of HIPEs in moisturizing and hydrating skincare products, detergents, porous absorbent materials, hair care products, and other daily-use products.

2. Summary of High Internal Phase Emulsions

In general, in an emulsion, the volumetric fraction of the dispersed phase typically ranges from 30% to 50%, where the dispersed phase exists as isolated spherical droplets within the successive phase. Nevertheless, in certain cases, when the volumetric fraction of the dispersed phase gradually increases, the critical density of 74.05% is finally reached. The droplets, which were previously scattered in a more random manner, now become closely packed together and transform into an interconnected spherical arrangement. If the volume fraction is further increased beyond this critical point, the droplets, which were originally arranged in an interconnected spherical shape, are gradually compressed by increasing pressure. As the degree of compression deepens, the shape of the droplet no longer remains spherical, but undergoes significant deformation, gradually changing to a polygonal form. This morphological shift marks the transition into a HIPE (Figure 1). At this stage, the emulsions exhibit unique structural properties due to the tightly packed, deformed droplets.

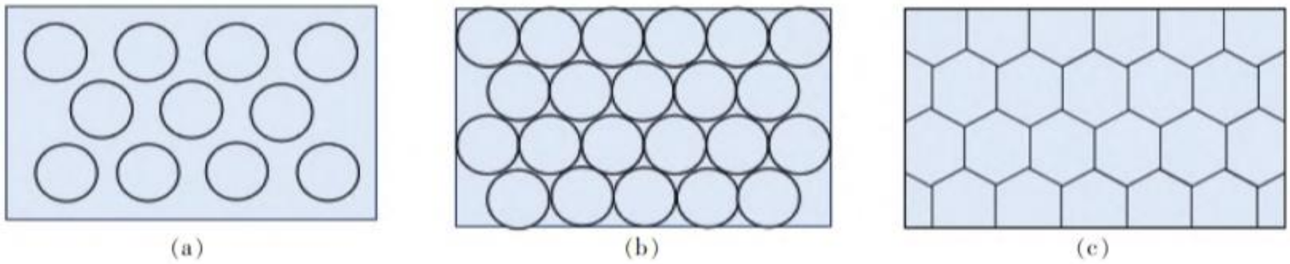

Fig. 1 volume fraction of dispersed phase

(a) between 30% and 50% (b) equal to 74.05% (c) over or equal to 74.05% [1]

2.1. Basic Concepts of High Internal Phase Emulsions

2.1.1. Oil-in-water (O/W) Emulsions

O/W microemulsions are emulsion systems in which oil-phase components are dispersed within a continuous aqueous phase. The emulsifier is positioned at the water-oil interface, where the nonpolar groups at the lipophilic end integrate with the oil phase, and the polar groups at the hydrophilic end interface with the aqueous phase [1]. Typically, O/W emulsions contain 10–25% of the total oil phase and 75–90% of the total water phase. The water phase often includes water-soluble polymer rheology modifiers, such as Hansen's gum, carbomer, magnesium aluminum silicate, or water-soluble cellulose. These agents are used to thicken the emulsion, stabilize suspensions, and assist in emulsification. Additionally, heat-resistant, water-soluble active additives can be incorporated into the water phase and emulsified together during heating.

The oil phase usually consists of various emollient fats and oils, solid fatty alcohols and their esters, and different waxes. Commonly used oils include vegetable oils, synthetic fats, glycerol esters, fatty alcohols, and beeswax [2]. Emulsifiers, which are part of the oil phase, typically account for about 20% of the total oil phase. In oil-in-water systems, emulsifiers are primarily anionic and nonionic surfactants, with hydrophilic-lipophilic balance (HLB) values generally ranging from 8 to 18. Most O/W emulsifiers are nonionic in nature, ensuring stability and emulsification.

2.1.2. Water-in-Oil (W/O) Emulsion

W/O emulsions are systems where the water phase is dispersed within the oil phase and are common in fat-rich formulations. W/O HIPEs are formed when the volume fraction (φ) of the water phase within the W/O emulsion exceeds 0.74. At this point, the dispersed water droplets achieve their highest degree of bulk density and deform into polyhedral shapes. Therefore, W/O emulsions have the highly viscoelastic rheological behavior. Typically, forming W/O emulsions requires the incorporation of large amounts of surfactants to enhance the emulsion's stability. However, the preparation of W/O emulsions is more challenging than O/W emulsions due to the lack of natural hydrophobic stabilizers.

Tai Xiumei et al.’s study has found that to formulate W/O Pickering emulsions, oils and fats with varying polarities can be used.[3] Emulsions prepared from polar oils tend to have smaller particle sizes and better stability, while those made with non-polar oils exhibit larger particle sizes and comparatively reduced stability. Despite these challenges, W/O emulsions, particularly Pickering emulsions, offer promising applications due to their unique stability profiles and structural characteristics.

3. Preparation of High Internal Phase Emulsions

3.1. One-step Emulsification Method

The one-step emulsification method includes techniques such as high-speed shear homogenization, ultrasonic treatment, and hand crank/vortex mixing. Among these, high-speed shear homogenization is the most commonly utilized preparation method. In this approach, the dispersed phase is added to the continuous phase in one go, and the mixture is subjected to high-speed shear forces to create stable HIPEs, with stability achieved through the careful control of shear rate and shear time [1]. This method is favored for its simplicity and ease of operation, making it the most widely applied emulsification technique. Zhai Xiaomei found that, within the same system, multi-structured emulsions prepared via the one-step method exhibited more uniform droplets and higher water content in the inner phase compared to those prepared using the two-step method. The latter resulted in immediate delamination after homogenization due to the altered interfacial adsorption properties of hydrophilic and lipophilic emulsifiers when water was added during the second step of the two-step process. This led to instability in the emulsions produced via the two-step method when W/O emulsions were used as the internal phase. Consequently, the one-step (trans-phase) process was identified as more effective for the preparation of stable multi-structured emulsions [1].

3.2. Two Step Emulsification Method

The two-step emulsification method involves the initial preparation of an emulsion with a low volume fraction of the internal phase using high-energy techniques like microjet, high-pressure homogenization, or ultrasonication. Afterward, the volume fraction of the dispersed phase is increased through low-energy input, typically via high-speed shear, to achieve the formation of HIPEs [4]. By comparing the appearance of emulsions prepared using the one-step and two-step methods after standing at room temperature, Lili Zhang and Chuan-Nu Tang found that the two-step emulsification method significantly enhanced the stability of BSA-stabilized HIPEs, showing improved resistance to the effects of ionic strength [5]. However, when the initial emulsion's particle size becomes sufficiently small, the number of microemulsion droplets increases dramatically within the same volume. This rise in droplet concentration can exceed the threshold for bridging flocculation in HIPEs, causing the emulsions to shift into a more mobile, flocculated state, with a corresponding reduction in elasticity and stability [1]. Consequently, the choice of preparation method should be aligned with the specific properties of the emulsion. While the one-step and two-step methods are conventional approaches for creating HIPEs, new methods are also emerging in the field.

3.3. Concentration Method

The concentration method for HIPEs preparation involves creating an initial emulsion with a low internal phase fraction using techniques such as high-speed shear or high-pressure homogenization. The resulting emulsion is then subjected to high-speed centrifugation or vacuum evaporation to remove the excess external phase, ultimately producing HIPEs with the final volume fraction of the internal phase calculated and determined [1]. Although this method is more complex and the precise determination of the oil and water phase volume fractions can be challenging, it offers valuable insights for exploring new preparation methods. Despite its current limited use, the concentration method opens broader research possibilities for innovative approaches to HIPEs preparation.

4. Selection of Raw Materials

4.1. Surfactants

Surfactants stabilize emulsions by reducing interfacial tension or forming a viscoelastic interfacial film. They can be broadly classified into small molecule surfactants and biomolecules. Small molecule surfactants often exhibit kinetic instability, as they adhere weakly at the oil-water interface and are easily displaced, necessitating the use of a large quantity of emulsifiers to stabilize HIPEs. Additionally, the potential toxicity and limited biocompatibility of small molecule surfactants pose concerns that cannot be overlooked [1].

In contrast, biomolecule particles used to stabilize HIPEs are categorized into three groups: (1) polysaccharide particles, such as cellulose, chitin, starch nanocrystals (SNCs), and chitosan; (2) protein particles, including gelatin, peanut proteins, soybean globulin, and whey proteins; and (3) composite particles, such as mellitus protein-chitosan composites and zein alkyd-chitosan composites. Solid particles assembled from natural biomolecules and their complexes serve as excellent stabilizers for HIPEs due to their biocompatibility, low toxicity, and renewability [6].

For instance, Wang Chao et al. [7] demonstrated the preparation of starch granules through nanoprecipitation to stabilize HIPEs containing an 80% volume fraction of soybean oil. The study found that as the concentration of starch granules increased, the size of the emulsified droplets gradually decreased. This suggests that sufficient hydrophobicity was generated on the hydrophilic starch particles, enhancing the affinity between the starch and oil phases, thereby improving the stability of the emulsion.

4.2. Solid Particles (Inorganic & Organic)

Emulsions stabilized by solid particles are referred to as Pickering emulsions. These solid particles possess high adhesion energy, allowing them to adsorb irreversibly at the oil-water interface. Pickering emulsions offer several advantages over conventional HIPEs stabilized by small molecule surfactants: (1) the particles are absorbed at the oil-water interface or self-assemble there. In this way, a rigid layer is formed at the interface of oil-water, which prevents droplets coalescing, Ostwald maturation as well as frosting. (2) Pickering emulsions exhibit long-term stability, with shelf lives ranging from months to years; and (3) compared to small molecule surfactants, colloidal particles not only have less toxicity to humans, but also perform better in terms of environmental protection. [1].

A relevant example of Pickering emulsions is the use of egg yolk spheres, which are natural colloidal structures co-assembled from proteins and lipids. These yolk spheres possess both hydrophilic and lipophilic properties, making them suitable for emulsification. In Xiaoli Liu et al. ‘s study [8], High Pressure Homogenization (HPH) technology is used in the pressure range from 0 to 90 MPa to prepare egg yolk sphere microgels (EYSMs). When applied to an oil-in-water emulsion system, the oil-to-water ratio of the oil-in-water emulsion is set to 11:9. Their study revealed that in egg yolk sphere microgels (EYSMs) produced at different pressures, EYSM (60-EYSM) produced at 60MPa pressure demonstrated excellent emulsification properties. Specifically, the Emulsion Activity Index (EAI) is 2.8 m^2/g and the Emulsion Stability Index (ESI) is 356.6 minutes. The storage stability of the emulsion was enhanced for up to 30 days. Under high-pressure treatment, the lipid content of EYSMs decrease. At the same time, it results in a more uniform protein-lipid profile. Thus, the balance of hydrophilic and hydrophobic sites is improved, resulting in superior emulsification performance. Additionally, the exposure of free sulfhydryl and hydrophobic groups during HPH promoted the formation of -S-S- bonds on the EYSM surface, further enhancing surface hydrophobicity and emulsification capacity.

Furthermore, Xu Wei et al. [9] demonstrated that Pickering emulsions, which are stabilized by solid particles encapsulating droplets at the interface between two phases, effectively mitigate the toxicity and biocompatibility concerns associated with conventional emulsions stabilized by small molecular surfactants.

5. Characterization and Evaluation

5.1. Determination of High Internal Phase Emulsion Type

The type of emulsion can be identified by observing how the HIPE behaves when introduced into water and oil phases. If the emulsion remains insoluble in oil, settles unchanged in the oil phase, and disperses uniformly in water, it is classified as an O/W emulsion. Conversely, if the emulsion disperses uniformly in oil, it is a W/O emulsion.

For instance, as demonstrated in a study by Nie Xiaohua, Wang Lingyun, and Huang Baozhu, the dispersion method was used to determine the type of emulsion in a DHA/EPA-rich structured lipid HIPE. The HIPE did not disperse in oil and maintained its original form but dispersed effectively in water (Figure 2). This observation confirmed that it was an oil-in-water (O/W)-based high internal phase emulsion [10].

Fig. 2 (a) soybean oil (b) distilled water [10]

5.2. Micromorphological Testing

Using an optical microscope, the prepared high internal phase emulsion (HIPE) droplets were first carefully placed on a slide. Then a coverslip was used to cover it to avoid air bubbles or emulsion build-up. Finally, it was placed on the stage for photo documentation.

As demonstrated in Fig., Yanyan Zhao, Xingxing Lu, and Qi Yin et al. observed that, based on micromorphological photos, the droplet diameter of P-SPI-stabilized HIPEs was smaller. With the increase in the oil phase volume fraction, the reduced distance between the droplets contributed to the emulsion gradually transforming into a more elastic, gel-like structure (Figure 3). This transition reduced the tendency for relative sliding, thereby improving the stability of the emulsion. The electrostatic repulsion and aggregation between oil droplets facilitated the rearrangement of the gel network, which indicated the formation of HIPEs with enhanced gel-like properties [11]

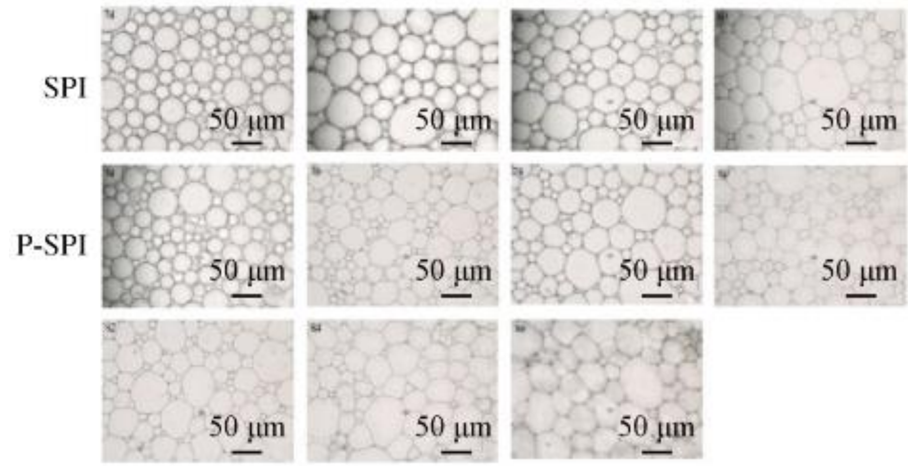

Fig. 3 Comparison of P-SPI-stabilized HIPEs droplets and SPI-stabilized HIPEs [11]

5.3. Rheological Properties

The rheological properties of high internal phase emulsions (HIPEs) were tested using a rheometer at a temperature of 25±1°C, with a 1.0 mm gap between the plates, following established literature guidelines [12]. The tests included strain scanning. When the frequency is fixed at 1.0Hz and the strain is in the range of 0.001 to 1.0, the storage modulus (G') and the loss modulus (G") are measured. Frequency scanning is also included. It assessed elastic and viscous moduli using a fixed strain of 0.5% and a frequency range of 0.1 to 10 Hz. Additionally, steady-state shear tests were conducted to observe changes in viscosity at a shear rate of 0.1 to 100 s^{-1} at 25 °C.

Jiang Lianzhou, Sun Yuanda, and Zhong Mingming's rheological analysis indicated that Pickering HIPEs exhibited elastic-dominated viscoelasticity. As frequency increased, both the elastic and viscous moduli of the emulsions grew, with the energy storage modulus (G') being significantly larger than the loss modulus (G'), suggesting the formation of a gel network structure (Figure 4) [13].

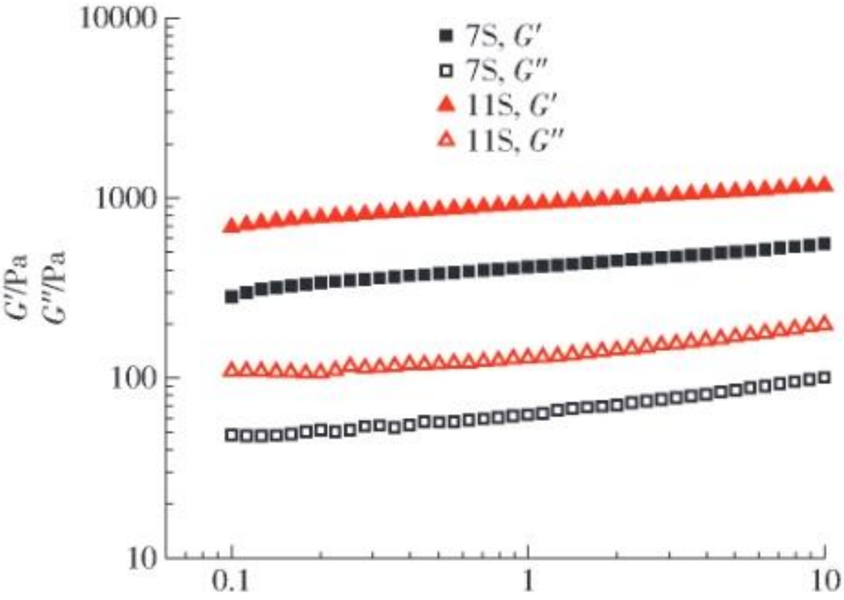

Fig. 4 Rheological diagrams [13]

5.4. Stability Testing

The storage and thermal stability of the high internal phase emulsions were assessed based on established literature methods. The emulsions were stored at three different temperatures: (-5±1) °C, (25±1) °C, and (40±1) °C for 24 hours. After this period, the appearance and microstructure of the emulsions were examined once they returned to room temperature to evaluate any changes in stability [12].

6. Application of High Internal Phase Emulsions in the Field of Daily Chemicals

6.1. Moisturizing Emulsions

Compared to cream-based skincare products, lotions offer a lighter, more refreshing feel on the skin. High internal phase gel emulsions used in oil-in-water skincare lotions provide a moisturizing effect with a high oil content that is quickly absorbed upon contact with the skin. The oil film formed post-application effectively locks in moisture. With low viscosity and a moderate pH, these emulsions demonstrate excellent stability under external conditions such as storage, heating, freezing, and centrifugation. They are ideal for encapsulating, stabilizing, and delivering hydrophobic bioactive ingredients. Additionally, due to their high oil content, they offer greater carrying capacity than conventional emulsions [14].

6.2. Makeup Remover Oils, Detergents

Gel-type makeup remover oils are typically high internal phase oil-in-water gel emulsions. These products exhibit the characteristics of a strong gel, offering good stability, a light scent, uniform color, and an effective makeup removal experience. Similarly, common detergents also utilize oil-in-water emulsions. In this case, the detergent, as the dispersed phase, encapsulates oil and grease, removing them from surfaces. The water phase then wets the surface to prevent the oil phase from re-adhering, ensuring a clean finish [15].

6.3. Preparation of Porous Absorbent Materials for Hygiene Products

Porous materials with absorptive function are prepared by high internal phase emulsion method, which acts as a conductive layer to promote core absorption and fluid distribution capability, transferring the fluid from its initial receiving region to the unused equilibrium region of the absorbent core, which allows for better reception of subsequent fluids [16].

7. Conclusion

This paper summarizes the types of high internal phase emulsions and concludes that the key factors for the preparation of high internal phase emulsions lie in the selection of raw materials as well as the selection of preparation methods and summarizes that high internal phase emulsions can be used for moisturizing lotions, make-up removing oils, detergents, and hygienic multi-vacuum absorbing materials, etc., in the field of daily chemicals. At present, although significant achievements have been made in the method of preparation as well as application development, which have been widely used in the fields of materials, food, biomedicine and chemical industry, there are still limitations in the application in the field of daily chemicals, and it is necessary to further optimize the performance of high inner phase emulsions and broaden their other applications in the field of daily chemicals hereafter.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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