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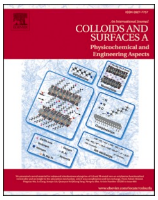

General approach to enhance emulsifying internal phase capacity of low-concentration surfactant—Enlarging head group occupied area

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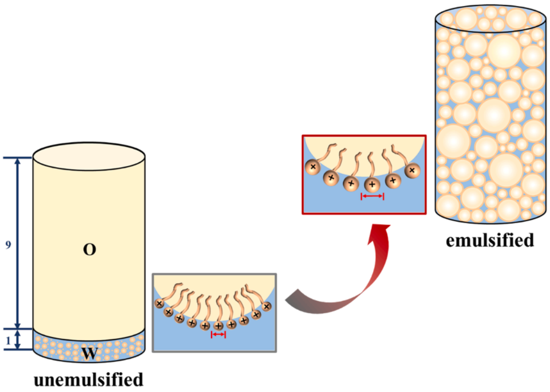
GRAPHICAL ABSTRACT



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ABSTRACT

The high internal phase O/W emulsion is of great importance for a multitude of scientific processes and practical applications. Nevertheless, the preparation of high internal phase O/W emulsion with high-concentration (5–50 wt%) surfactant is costly and eco-unfriendly. It is vital to study the molecular design principles for surfactants to enhance the emulsifying internal phase efficiency. This study revealed a positive correlation between the emulsifying internal phase capacity and the surfactant head group occupied area by grafting short-chain alkyl groups onto the surfactant head group, incorporation of inorganic salt, and mixture of cationic-anionic surfactants. To enhance the emulsifying internal phase capacity of low-concentration surfactant, 0.1–0.2 wt% of electrostatic repulsive amphiphilic molecules or steric hindrance amphiphilic molecules were doped into the 0.3–0.5 wt% surfactant to enlarge the surfactant head group occupied area, thus achieving a heightened emulsifying internal phase capacity of 12 (corresponding to the internal phase content as 92 %). This study proposes the definitive molecular principle for surfactants to enhance the emulsifying internal phase capacity, capable of providing theoretical guidance for a wide range of emulsion application fields. The construction of

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high internal phase emulsion by low-concentration surfactant not only lowers the emulsification cost but also curtails environmental pollution, aligning with the green development concept.

1. Introduction

Stable dispersion of as much as possible oil into aqueous media is of great significance for scientific research of dispersed systems and soft matter [1,2], such as interfacial catalysis [3] and rheological control [4]. Among the numerous dispersed systems, the emulsion is the most representative system for achieving the stable dispersion of high-content oil phase in water phase, which refers to the high internal phase emulsion (HIPE) [5]. The capacity to encapsulate great amount oil renders the HIPE important implications for a range of fields, including food [6], cosmetics [7], pesticides [8] and pharmaceuticals [9]. The structural characteristics of multi-cavity and extensive-interface render the HIPE highly versatile templates for the synthesis of diverse porous materials [10–13]. As the most significant emulsifier for emulsion research and application, applying surfactants to prepare HIPE usually necessitates high surfactant concentration (5–50 wt%) [14], which is costly and eco-unfriendly. Therefore, the objective is to prepare HIPE with low-concentration surfactants, which requires to improve the emulsifying internal phase efficiency of each surfactant molecule.

However, there is still a paucity of fundamental principles which can give direction to surfactant molecular design or combination to achieve high emulsifying internal phase efficiency. In O/W emulsions, an increase in the number of oil droplets emulsified into the water is associated with the enlargement of oil-water interface area which is stabilized by the adsorption of surfactants [15,16]. Thus, the emulsifying internal phase capacity of surfactants is closely related to the adsorption and alignment behaviors of surfactants at the oil-water interface. However, it seems that the conventional surfactant physicochemical parameters are not sufficiently effective to characterize the interfacial behaviors of surfactants. The conventional surfactant critical micelle concentration (*cmc*) is indicative of the capacity of surfactant molecules to form micellar assemblies in the aqueous phase [17], which depends on the solubility of the head group and the hydrophobicity of the tail chain in water phase [18,19] and cannot serve as a representative interfacial characterization parameter. The hydrophilic-lipophilic balance (*HLB*) of surfactants can be employed to ascertain the relative magnitude of the head group hydrophilicity and the tail chain lipophilicity at the oil-water interface [20]. However, the *HLB* has a major limitation as it is difficult to calculate accurately for ionic surfactants with a head group ionization effect or for mixed surfactant systems with a complex molecular structure [21]. So, it is also an inadequate parameter for characterizing the interfacial behaviors of surfactant molecules.

In this study, conducting the emulsifying internal phase capacity study from the perspective of surfactant head group size was analyzed and proposed. When the head group size changes, the individual surfactant molecule occupied area at the interface will have a notable variation [22], thereby the oil-water interface formed in the emulsion will exhibit a significant discrepancy, which could be reflected in differences in emulsifying internal phase capacity. It would provide valuable insights into the fundamental guideline for surfactant molecular design to enhance the emulsifying internal phase content.

In addition, the emulsion system is thermodynamically unstable, rendering the droplet size susceptible to alterations in preparation conditions [23] and storage time [24]. This uncontrollability presents a significant challenge to the reproducibility and predictability of experimental studies. It is suggested that an ideal emulsion system that is less prone to preparation condition errors and storage time is a prerequisite for the fundamental emulsifying internal phase capacity research.

In a recent study conducted by our research group, the outstanding stable O/W emulsions were successfully prepared using n-hexadecane and water-soluble surfactant solutions. Notably, the emulsions exhibit unchanging properties, including its macro and micro morphology, as well as its droplet size distribution, both within the margins of preparation errors and over the course of a year (Fig. S1). This outstanding stable O/W emulsion can serve as the ideal model system for this study. Based on the model emulsion system, the emulsifying internal phase capacity (*EIPC*) is determined by analyzing the morphology of emulsions with different oil-water ratios in a phase diagram and defining the highest oil-water ratio at which the oil is completely emulsified into the external water. The size of the surfactant head group was regulated by grafting short-chain alkyl groups onto the head group [25]. Meanwhile, the incorporation of inorganic salt and the mixture of cationic-anionic surfactants can modulate the electrostatic interaction between surfactant head groups, thus enabling the regulation of the surfactant head group occupied area at the oil-water interface [22]. Furthermore, the electrostatic repulsive amphiphilic molecules and steric-hindrance amphiphilic molecules were doped to help enlarging the surfactant head group occupied area at the oil-water interface.

The objective of this study is to provide definitive guideline for the design of surfactant molecules to achieve higher emulsifying internal phase capacity, which facilitates a more profound comprehension of the microscopic mechanisms underpinning emulsion behaviors. The improvement of surfactant emulsifying internal phase efficiency can diminish the usage of surfactants to construct HIPE. This not only lowers emulsification cost but also curtails environmental pollution, aligning with the green development concept.

2. Materials and methods

2.1. Materials

The dodecyl amine hydrochloride (DAC), tetradecyl amine hydrochloride (TAC), and hexadecyl amine hydrochloride (CAC) were purchased from MREDA. The dodecyl trimethyl ammonium chloride (DTAC), tetradecyl trimethyl ammonium chloride (TTAC), and hexadecyl trimethyl ammonium chloride (CTAC) were products from Shanghai Dibai Biotechnology. The dodecyl triethyl ammonium chloride (DTEAC), tetradecyl triethyl ammonium chloride (TTEAC), and hexadecyl triethyl ammonium chloride (CTEAC) were synthesized through the reaction of triethylamine with dodecyl chloride, tetradecyl chloride, and hexadecyl chloride respectively, followed by recrystallizing five times from ethanol-acetone [25]. The sodium dodecyl sulfate (SDS) was purchased from Aladdin. The sodium chloride (NaCl) was purchased from Shanghai Dibai Biotechnology. The sodium cholate (SC) was purchased from Rhawn. The adipic acid disodium salt ($C_4(COO)_2Na_2$) was purchased from Macklin. The 1,6-hexanediamine dihydrochloride ($C_6(NH_3)_2Cl_2$) was product from Energy Chemical. The Nile Red was purchased from Beijing konoscience technology. The reagents used were of analytical grade. The n-hexadecane was purchased from Energy Chemical. Aqueous solutions were prepared using Milli-Q water of ~ 18.3 MΩ·cm.

2.2. Emulsion preparation

Precalculated surfactant powder was weighed and then dissolved in Milli-Q water at room temperature. Following this, the hexadecane was added into surfactant aqueous solution with precalculated volumes, resulting in a biphasic liquid with water-oil stratification. Emulsification of the biphasic liquid was performed at room temperature at 1000 rpm (5 gear) for 30 min using a magnetic stirrer (C-MAG HS7, IKA, Germany). All the emulsions were stored at room temperature before further characterization.

2.3. Emulsion characterizations

The macro morphology of emulsions was taken by digital camera. The microscopic structure of emulsions was observed by optical microscopy (OM) and confocal laser scan microscopy (CLSM). In the OM measurements, the emulsion sample was put on a glass plate with a cover glass and observed by optical microscopy (BX51, Olympus, Japan). Data of digital video was transferred to a computer through a video capture board, and was recorded into JPG images using the software. In the CLSM measurements, the oil phase was stained by Nile Red (red fluorescent). A drop (about 10 μL) of the stained emulsion sample was sealed between two slides, ready for CLSM observation. A TCS-sp inverted confocal laser scanning microscope (Leica, Germany) was used to conduct experiments in florescence and differential interference contrast (DIC) modes. Laser Scanning Confocal images were performed on Nikon A1R-simicroscope.

2.4. Emulsion droplet size measurement

The droplet size of emulsion was measured using Mastersizer (Malvern Instruments Ltd, Malvern, UK). The 0.5 mL emulsion sample was added into 800 mL deionized water, after being diluted homogeneously, the droplet size distribution was measured and then the average droplet size can be calculated. The emulsion dilution stability experiments demonstrated that the emulsion droplet size remained almost unchanged when the emulsion was diluted with the addition of water (Fig. S2). The average droplet size was obtained by averaging three measurements. In the case of emulsions incorporating inorganic salts, the water used to dilute the emulsion sample was an aqueous solution with the same inorganic salt concentration as the emulsion, which can avert any potential impact of fluctuations in salt ion concentration during the dilution process on emulsion droplet size.

2.5. Calculation of the surfactant head group size

The molecular structure of the surfactant was initially delineated using Gauss View software. The molecular configuration at the lowest energy state was then calculated by utilizing the Gaussian software, employing the optimization mode. The head group size of the surfactant molecule was measured by annotating the atomic spacing, based on the molecular configuration at the lowest energy state.

3. Results and discussion

3.1. Emulsion diagram and emulsifying internal phase capacity (EIPC)

With the surfactant concentration in aqueous solutions as horizontal axis and the oil/water volume ratio as vertical axis, the prepared emulsions were depicted in a diagram, as illustrated in Fig. 1a. Emulsions in the diagram can be classified into three types: emulsion with water dropping out (light blue), perfectly stable emulsion (deep blue), and oil-water separation (black), as illustrated in Fig. 1b. The oil is totally emulsified within the emulsions in first two types (region 1), whereas the oil remains unemulsified in the third type (region 2). The emulsions in region 1 were confirmed to be O/W emulsions by staining the oil phase and observing the micromorphology (Fig. 1c). To characterize the maximum amount of oil emulsified by surfactant, the highest oil/water volume ratio at a certain surfactant concentration in region 1 was defined as the emulsifying internal phase capacity (*EIPC*) of this surfactant at this concentration, as described in Eq. 1. Given that the focus of this study is the effect of surfactant molecular structure on the *EIPC*, subsequent studies will compare *EIPC* of different surfactants at the same concentration.

$$EIPC = V_\mathrm{O}/V_\mathrm{W}(\mathrm{critical}) \tag{1}$$

3.2. Effect of surfactant head group occupied area on EIPC

The *EIPC* of surfactants with different head group occupied area was studied. The head group sizes of DAC, DTAC, and DTEAC were 1.64 Å, 4.22 Å, and 6.29 Å respectively (Fig. 2a). The pH of the DAC aqueous solution was measured as 3.7 (see Tbl. S1a), ensuring its complete presence in the ionic form. The surfactant interfacial adsorption theory posits that an increase of the surfactant hydrophilic head group can engender a decrease of the surfactant adsorbance quantity of per unit area, corresponding to that a single surfactant molecule occupies larger interfacial area [22]. With all the surfactant concentration in aqueous phase was maintained at 30 mmol/L, the $EIPC_{(\mathrm{DTEAC})}$ was identified as 8, followed by $EIPC_{(\mathrm{DTAC})}$ at 5, and $EIPC_{(\mathrm{DAC})}$ was found to be the lowest at 2. While changing the surfactant tail chain as tetradecyl or hexadecyl, there exhibited the similar trend with $EIPC_{(\mathrm{TTEAC})} > EIPC_{(\mathrm{TTAC})} > EIPC_{(\mathrm{TAC})}$ and $EIPC_{(\mathrm{CTEAC})} > EIPC_{(\mathrm{CTAC})} > EIPC_{(\mathrm{CAC})}$ (Fig. 2b). Besides, the *EIPC* study on anionic surfactants with varying head group size

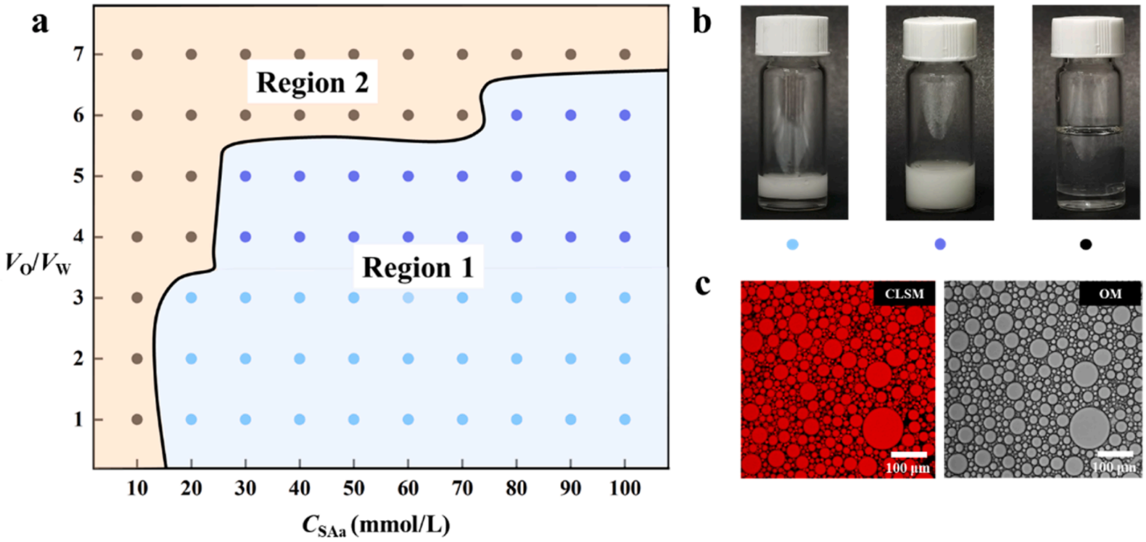

Fig. 1. (a) Emulsion diagram of DTAC. (b) Macro morphology of three types of emulsion. (c) Micrographs of the emulsion in region 1 by CLSM and OM (the sample emulsion corresponds to C_SAa of 50 mmol/L and $V_\mathrm{O}/V_\mathrm{W}$ of 3).

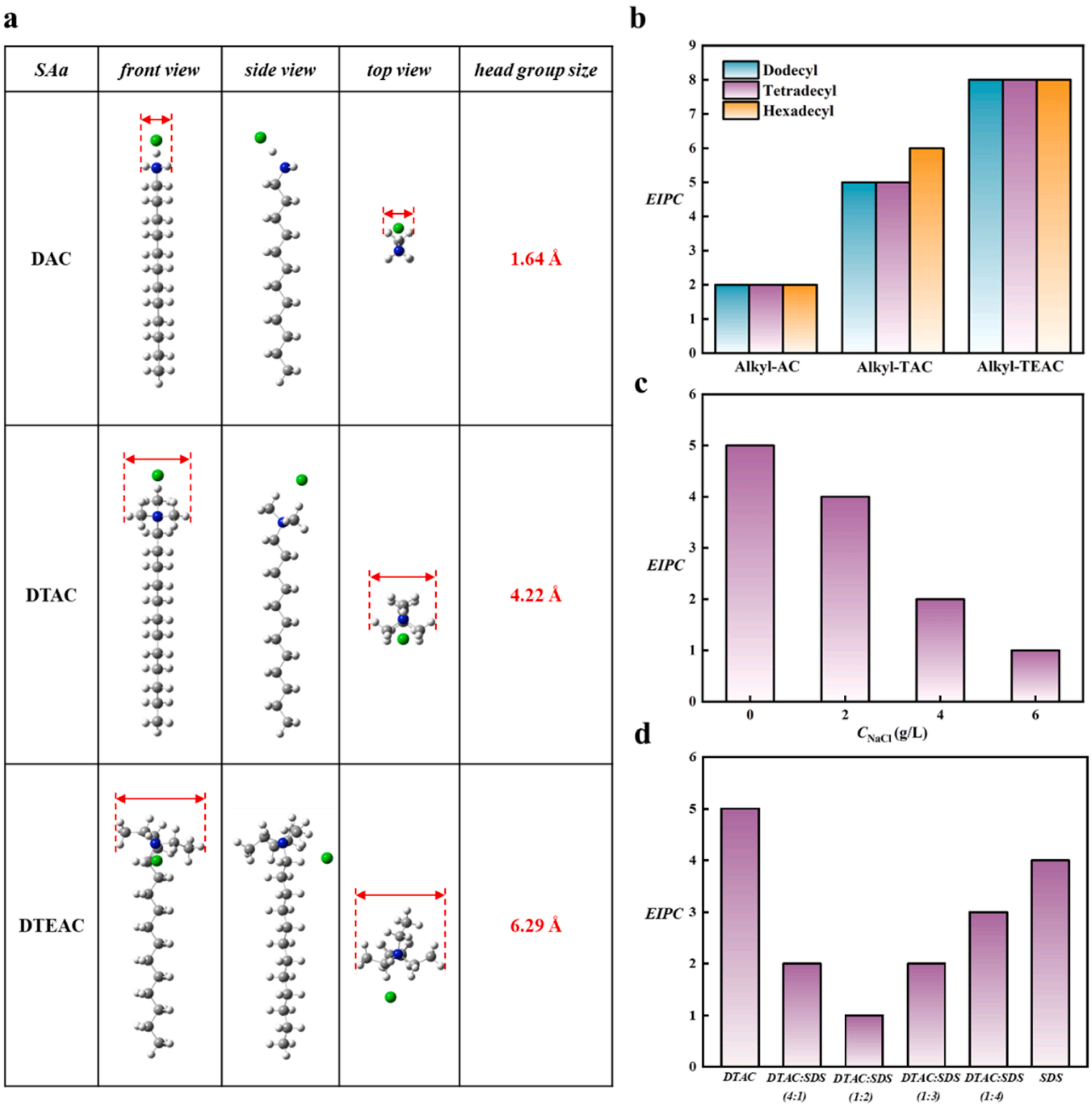

Fig. 2. (a) The three-dimensional molecular structures and head group sizes of DAC, DTAC, and DTEAC. (b) Emulsifying internal phase capacity (*EIPC*) of surfactants with various head group sizes (the surfactant concentration was constant at 30 mmol/L). (c) *EIPC* of 30 mmol/L DTAC with varied addition of NaCl. (d) *EIPC* of 30 mmol/L DTAC/SDS mixtures.

revealed a consistent pattern (Fig. S3). It can be concluded that the surfactant with a larger head group exhibited higher *EIPC*.

To gain further insight into the relationship between *EIPC* and surfactant head group occupied area, the NaCl was added into the DTAC aqueous solution to regulate the surfactant head group occupied area. In accordance with the surfactant interfacial adsorption theory [22], the incorporation of inorganic salts into ionic surfactants has been demonstrated to result in the presence of additional counterions within the adsorption layer and the weakening of the electrostatic repulsion between the ionic head groups, which leads to a closer arrangement of surfactant molecules, corresponding to that a single surfactant molecule occupies smaller interfacial area. With the 2, 4, and 6 g/L of NaCl respectively added to the 30 mmol/L DTAC aqueous solutions, it was observed that the $EIPC_{(\mathrm{DTAC})}$ decreased with the NaCl addition increasing (Fig. 2c). Thus, it can be proposed that the reduction of the surfactant head group occupied area was correlated with the decrease in the *EIPC*.

Moreover, electrostatic attraction interaction between head groups of cationic and anionic surfactants can lead to a closer arrangement of surfactant molecules, also corresponding to a smaller occupied area of single surfactant molecule [22]. In the Fig. 2d, when the molar ratio of DTAC and SDS approached 1: 1, corresponding to the stronger electrostatic attraction interaction between head groups and the smaller occupied area of single surfactant molecule, the *EIPC* was lower. Thus, it can be proposed that the reduction of the surfactant head group occupied area was correlated with the decrease in the *EIPC*.

3.3. Oil-water interface area in emulsions corresponding to the EIPC

In an O/W emulsion, an increase of *EIPC* indicates that more oil droplets are emulsified into the water, which can correspondingly result in an increase of the oil-water interface between the oil droplets and the external water [16]. Meanwhile, the oil-water interface requires the adsorption of surfactant molecules to reduce the interfacial energy, thereby ensuring the stability of emulsions [26]. Consequently, the higher *EIPC* of a surfactant system is corresponded to the greater surfactant interfacial adsorption layer area. With the fixed surfactant concentration, this can be achieved with larger interfacial occupied area of single surfactant molecule.

The investigation focused on the oil-water interface area in emulsions that corresponded to the *EIPC* of surfactants. Through measuring the emulsion droplet diameter distribution (n_i, d_i), the area average diameter ($\overline{d_s}$), as described in Eq. 2, and the volume average diameter ($\overline{d_v}$), as described in Eq. 3, can be calculated. Based on the total oil volume, the total oil-water interface area in the emulsion can be calculated, as described in Eq. 4. The calculated results were listed in Tbl. S2.

$$\overline{d_s} = \sqrt{\frac{\sum n_i d_i^2}{\sum n_i}} \tag{2}$$

$$\overline{d_v} = \sqrt[3]{\frac{\sum n_i d_i^3}{\sum n_i}} \tag{3}$$

$$A_{interface} = \frac{6 \times V_o \times \overline{d_s}^2}{\overline{d_v}^3} \tag{4}$$

In the Fig. 3a, the comparative analysis demonstrated that the DAC corresponded to the smallest oil-water interface area, the DTAC corresponded to an increased oil-water interface area, and the DTEAC corresponded to the largest oil-water interface area within the emulsions attaining their respective *EIPC*, which was consistent with the *EIPC* and head group occupied area results. It can be considered that for a constant surfactant concentration, the surfactant with larger head group occupied area can achieve greater oil-water interface area within the emulsion, thus exhibiting a higher *EIPC*. Furthermore, in the Fig. 3b and Fig. 3c, it was demonstrated that the addition of NaCl and the mixture of DTAC/SDS led to the decrease of the oil-water interface area, which was also concordant with the *EIPC* and head group occupied area results. For a constant surfactant concentration, the smaller head group occupies area leads to the narrower oil-water interface area within the emulsion, thus performing a lower *EIPC*.

Indeed, there is deformation of spherical droplets in high internal phase emulsions (Fig. S4), which could result in an underestimation of the true oil-water interfacial area [27]. However, it is important to note that the appended interfacial area is proportional to the droplet deformation magnitude which is dependent on the internal phase content [28]. The appended interfacial area demonstrates a consistent growth trend in relation to the aforesaid calculated interfacial area. Consequently, it does not compromise the qualitative comprehension of the oil-water interfacial area in emulsion systems.

3.4. Strategies to enhance EIPC of low-concentration surfactant

It is widely acknowledged that the construction of HIPE typically necessitates the use of surfactant at a concentration ranging from 5 wt% to 50 wt% [14]. Given that the surfactant with a larger head group occupied area exhibited the greater capacity to emulsify the internal phase, it is feasible to construct the HIPE with low concentration of these surfactants. Nevertheless, the enlargement of the molecular head group through synthetic methods is costly, time-consuming and accompanied by pollution [29]. It is still recommended that low-cost, convenient, and non-polluting physicochemical methods be employed [30]. When some amphiphilic molecules are adopted to insert into the voids between surfactant molecules at the oil-water interface, which can be regarded as

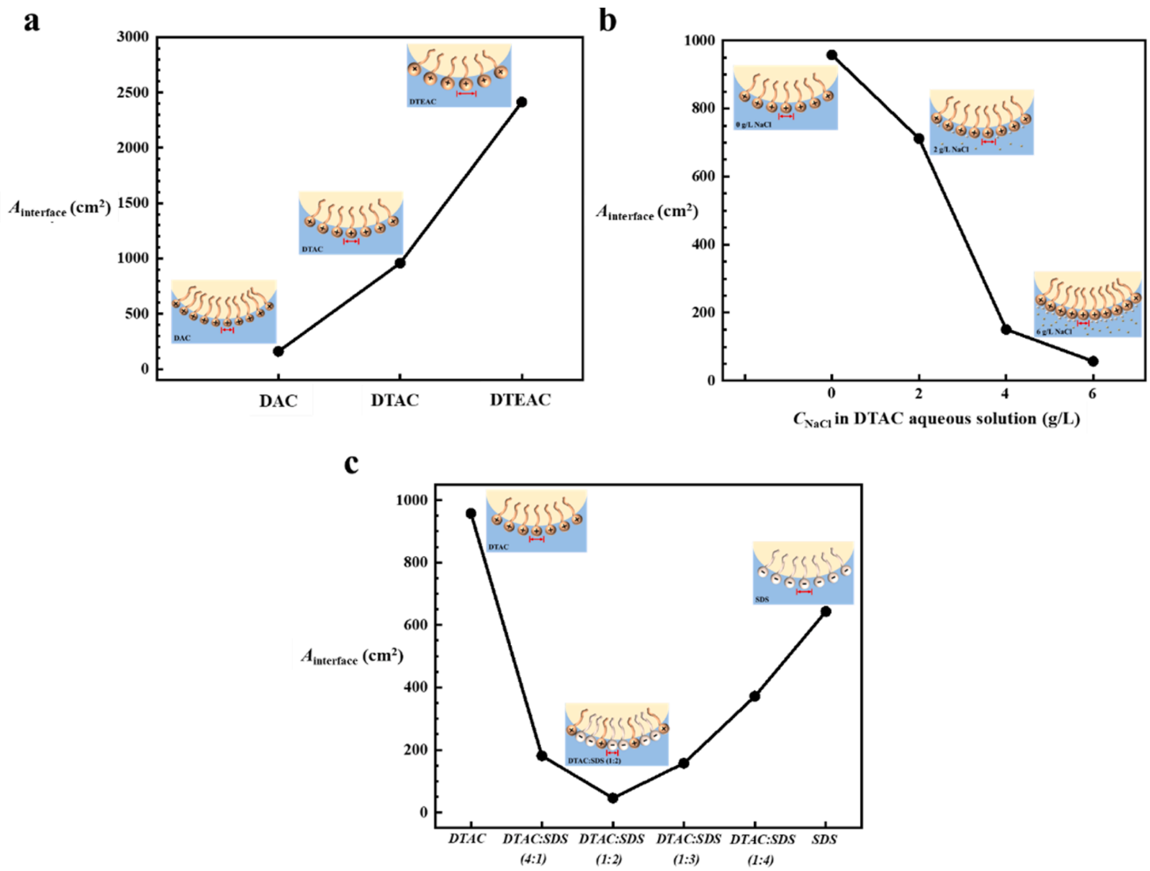

Fig. 3. (a) The $A_{interface}$ of emulsions attaining *EIPC* by DAC, DTAC, DTEAC and corresponding molecular arrangements at the oil-water interface. (b) The $A_{interface}$ of DTAC emulsions attaining *EIPC* under varied NaCl addition conditions and corresponding molecular arrangements at the oil-water interface. (c) The $A_{interface}$ of emulsions attaining *EIPC* by DTAC/SDS mixtures and corresponding molecular arrangements at the oil-water interface. (All of the emulsions are based on 1 mL of surfactant aqueous solutions at a concentration of 30 mmol/L).

an enlargement of the surfactant head group occupied area. To guarantee the maximum feasible increase of the interface area, it is recommended that the electrostatic repulsive amphiphilic molecules and the steric-hindrance amphiphilic molecules be employed as filler molecules.

Strategy 1: Surfactant molecules doped with electrostatic repulsive amphiphilic molecules. Compared with the same addition of surfactant molecules themselves and electrostatic attractive amphiphilic molecules, the adoption of electrostatic repulsive amphiphilic molecules significantly improved the *EIPC* of low-concentration surfactant, suggesting this strategy is effective (see Fig. 4a and Fig. 4b). In the Fig. 4a, the incorporation of electrostatic repulsive $C_6(NH_3)_2Cl_2$ molecules into the 0.5 wt% DTAC aqueous solution resulted in an enhancement of *EIPC*$_{(DTAC)}$. The incorporation of 0.2 wt% $C_6(NH_3)_2Cl_2$ (where the pH of the solution is 4.3 and $C_6(NH_3)_2Cl_2$ exists primarily in the $NH_3^+C_6NH_3^+$ form, as demonstrated in Tbl. S1b) resulted in the *EIPC*$_{(DTAC)}$ reaching a maximum value of 8. Similarly, the addition of electrostatic repulsive $C_4(COO)_2Na_2$ molecule to the 0.3 wt% SDS aqueous solution has been observed to enhance the *EIPC*$_{(SDS)}$, as shown in Fig. 4b. Upon the addition of 0.1 wt% $C_4(COO)_2Na_2$ (where the pH of the solution is 7.1 and $C_4(COO)_2Na_2$ exists primarily in the $COO^-C_4COO^-$ form, as demonstrated in Tbl. S1d), the *EIPC*$_{(SDS)}$ reached a maximum value of 9.

Strategy 2: Surfactant molecules doped with steric-hindrance amphiphilic molecules. Compared with the same addition of surfactant molecules themselves, the adoption of steric-hindrance amphiphilic molecules significantly improved the *EIPC* of low-concentration surfactant, suggesting this strategy is effective (see Fig. 4c and Fig. 4d). In the Fig. 4c, with the large spatial size SC molecules added to the 0.5 wt% DTAC aqueous solution, an increase of *EIPC*$_{(DTAC)}$ was observed. Upon

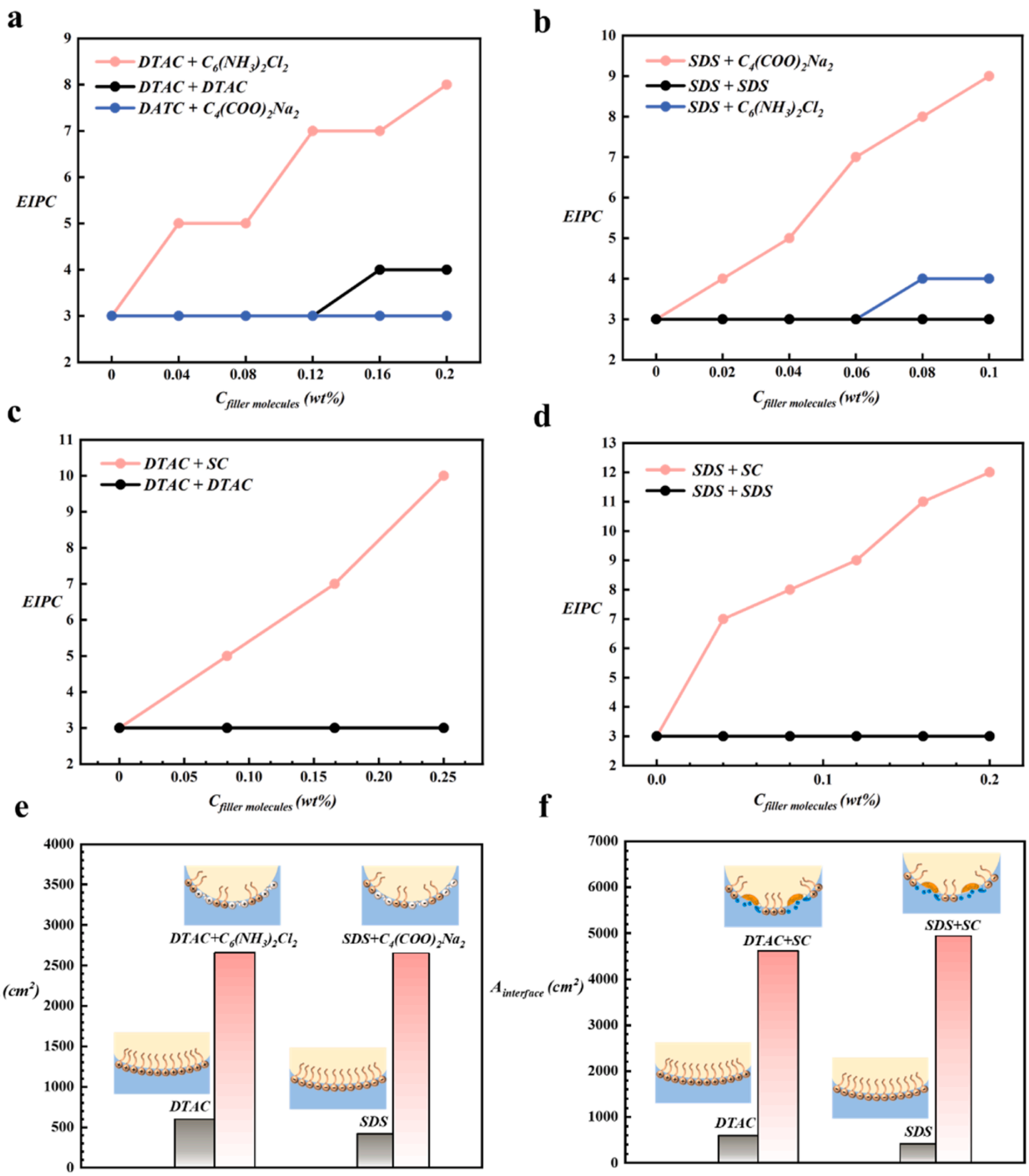

Fig. 4. (a) *EIPC* of 0.5 wt% DTAC aqueous solutions with varying addition of $C_6(NH_3)_2Cl_2$, DTAC, and $C_4(COO)_2Na_2$. (b) *EIPC* of 0.3 wt% SDS aqueous solutions with varying addition of $C_4(COO)_2Na_2$, SDS, and $C_6(NH_3)_2Cl_2$. (c) *EIPC* of 0.5 wt% DTAC aqueous solutions with varying addition of SC and DTAC. (d) *EIPC* of 0.3 wt% SDS aqueous solutions with varying addition of SC and SDS. (e) The $A_{interface}$ of emulsions attaining *EIPC* by 0.5 wt% DTAC, 0.5 wt% DTAC with addition of 0.2 wt% $C_6(NH_3)_2Cl_2$, 0.3 wt% SDS, and 0.3 wt% SDS with addition of 0.1 wt% $C_4(COO)_2Na_2$. (f) The $A_{interface}$ of emulsions attaining *EIPC* by 0.5 wt% DTAC, 0.5 wt% DTAC with addition of 0.25 wt% SC, 0.3 wt% SDS, and 0.3 wt% SDS with addition of 0.2 wt% SC.

the addition of 0.25 wt% (where the pH of the solution is 7.1 and the SC molecules exist primarily in the ionic form, see Tbl. S1c), the *EIPC*$_{(DTAC)}$ reached a maximum value of 10. Similarly, the addition of the SC molecules to the 0.3 wt% SDS aqueous solution has been observed to enhance the *EIPC*$_{(SDS)}$. Upon the addition of 0.2 wt% (where the pH of the solution is 7.9 and the SC molecules also exist primarily in the ionic form, see Tbl. S1e), the *EIPC*$_{(SDS)}$ reached a maximum value of 12 (Fig. 4d).

Furthermore, the oil-water interface area in emulsions attaining *EIPC* by surfactants before and after doping with filler molecules was calculated (Tbl. S3). It was observed that the oil-water interface area in DTAC emulsions was increased for addition of the 0.2 wt% $C_6(NH_3)_2Cl_2$ (Fig. 4e) or the 0.25 wt% SC (Fig. 4f). Similarly, the 0.1 wt% $C_4(COO)_2Na_2$ (Fig. 4e) and 0.2 wt% SC (Fig. 4f) were observed to enhance the oil-water interfacial area of the SDS emulsion. With the constant surfactant concentration, the filling of electrostatic repulsive amphiphilic molecules or the steric-hindrance amphiphilic molecules takes effects of enlarging surfactant head group occupied area, thereby the oil-water interface area in the emulsion is increased (Fig. 4e and Fig. 4f), corresponding to the improved *EIPC*.

In order to clarify the effects of addition of electrostatic repulsive amphiphilic molecules or steric-hindrance amphiphilic molecules on the stability of emulsions, an investigation was conducted into the stability of emulsions before and after incorporation of amphiphilic molecules (see Fig. S5 - Fig. S8), with each emulsion attaining its *EIPC*. For the emulsion systems in Fig. 4, it was found that the incorporation of amphiphilic molecules at low concentrations exerted no significant influence on emulsion stability. The emulsions demonstrated prolonged storage stability and outstanding centrifugation-resistant stability.

However, since the addition of amphiphilic molecules has effects on increasing oil-water interfacial tension (see Fig. S9), an excess addition of amphiphilic molecules would lead to the instability of emulsion and the decrease of *EIPC* (see Fig. S10). As more amphiphilic molecules with enlarging head group occupied area effects are co-arranged with surfactant molecules at the oil-water interface, the molecular arrangements at the interface will be too sparse. Consequently, the interfacial tension will be excessively high, thereby compromising the stability of the oil-water interface [31]. As a result, the emulsion will not be stabilized, which leads to the decline in *EIPC*.

4. Conclusion

In conclusion, the surfactant with larger head group occupied area exhibits a heightened capacity to emulsify the internal phase. The oil-water interface area within the emulsion by surfactant with larger head group occupied area is observed to be greater, which permits the emulsification of a greater number of oil droplets. Aimed at increasing *EIPC* of low-concentration surfactants, the electrostatic repulsive amphiphilic molecules or the steric-hindrance amphiphilic molecules are employed to insert into the interstitial voids between the surfactant molecules at the oil-water interface to enlarge the head group occupied area. The incorporation of 0.1–0.2 wt% amphiphilic molecules into the 0.3–0.5 wt% surfactants result in a maximum *EIPC* of 12, signifying an internal phase content of 92 %.

This study proposes the definitive guidelines for the surfactant molecular design to achieve the construction of high internal phase emulsion by low-concentration surfactants, which facilitates a more profound comprehension of the microscopic mechanisms underpinning emulsion macroscopic behaviors. Nevertheless, the focus of this study is on the emulsifying internal phase capacity of the single surfactant, and the combinatorial principles for mixed surfactant systems remains a topic for further investigation. The related research findings will be presented in subsequent publications. Moreover, the findings of this study have the potential to provide theoretical guidance for a wide range of emulsion application fields. In this regard, the n-hexadecane used in this study will be extended to edible oils and petroleum which possess practical value, and the correspondingly optimal principles will be explored in depth.

CRediT authorship contribution statement

Wang Fang: Writing – original draft, Visualization, Resources, Methodology, Investigation, Formal analysis, Data curation. **Chen Xingyue:** Resources, Methodology, Formal analysis, Conceptualization. **Chen Chen:** Methodology. **Qiu Jiaxian:** Methodology. **Zhao Hongxin:** Methodology. **Ma Cheng:** Writing – review & editing, Supervision. **Huang Jianbin:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2025.137068.

Data availability

Data will be made available on request.

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