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Co-Stabilisation Mechanisms of Nanoparticles and Surfactants in Pickering Emulsions produced by Membrane Emulsification

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Abstract

Two different membrane emulsification methods were used to study mechanisms for co-stabilisation of emulsions, by either electrostatic or steric stabilised nanoparticles with anionic, cationic or non-ionic surfactants. The experimental results demonstrated the existence of two distinct co-stabilisation mechanisms that arise from interactions of the nanoparticles and of surfactant molecules. When significant interaction is not involved, independent competitive adsorption of nanoparticles and surfactant molecules occurs spontaneously to stabilise the droplets in formation. The adsorption/desorption equilibrium between surfactant molecules determines the longevity of the droplet stability. When the surfactant molecule reacts with the nanoparticle surface, the resultant surface modification appears to generate faster wetting kinetics for nanoparticles at the oil/water interface and yields enhanced stabilisation. The paper discusses the implications of controlling these interactions for emulsion production membrane systems.

Keywords: Pickering emulsion, co-stabilisation, stabilisation mechanism, membrane emulsification

Introduction

Emulsions are quasi-stable mixtures of an oily phase and an aqueous phase. The oily or aqueous phase disperses in the other as droplets sized micrometres to nanometres. The droplet phase is, therefore, called the dispersed phase and the other as the continuous phase. The dispersed droplets have a strong tendency to merge out from the continuous phase to form its own bulk layer due to the immiscibility of the two phases. Surface active agents as emulsifiers are normally added to adsorb onto the droplet surface, namely, the interface of the two phases. The adsorption decreases the interfacial tension existing between the two phases and stabilises the dispersion of droplets in the continuous phase as a quasi-stable system. Surfactants are the traditional type of emulsifiers and its molecules are composed of a hydrophilic and a hydrophobic section. At the interface, the hydrophilic section exists in the aqueous phase and the hydrophobic section in the oily phase. Small solid particles in the range of micron, submicron and nanometres represent another type of more recently developed emulsifiers, which are partially wettable in both the oil phase and aqueous phases. Solid particles play the stabilisation role in a similar way to that of surfactants through adsorption at the interface. However, the adsorption force of solid particles is in a different magnitude compared to that of surfactant molecules due to their size and mass. It is generally believed that the molecules establish a dynamic adsorption and desorption equilibrium at the interface while the solid particles stay more permanently on the interface once adsorbed\textsuperscript{1}.

Solid particle emulsifiers, especially nanoparticles, have been extensively studied. The study spans over the formation of Pickering emulsions using different types of nanoparticles\textsuperscript{1-12}, characterisation of particle surface wetting\textsuperscript{13}, more sustainable-release as drug delivery devices\textsuperscript{14}, as templates for the construction of multifunctional microstructures\textsuperscript{15-18}, and as microreactors for heterogeneous catalysis\textsuperscript{19-22}. The versatility stems from that of the particle resources that vary from metal oxides (SiO\textsubscript{2}\textsuperscript{12}, iron oxide\textsuperscript{3,17}, Al\textsubscript{2}O\textsubscript{3}\textsuperscript{11}, TiO\textsubscript{2}\textsuperscript{22}), responsive latex colloids\textsuperscript{20-24}, natural polymeric crystals (cellulose\textsuperscript{4,6}, starch\textsuperscript{5}), layered mineral crystal disc (graphene\textsuperscript{3}, clay\textsuperscript{25,26} and apatite\textsuperscript{27}), to more interestingly, nanoporous crystals such as metal organic framework\textsuperscript{12}. The fluids formulated with Pickering emulsions can also provide varied rheological 1.
properties\textsuperscript{11,28,29}. These desired functions benefit from the unique structure and the controllability of size and stability Pickering emulsions provide during manufacturing and processing.

Particles and surfactants need to be used together in one emulsion system in many cases. Food emulsions, such as typical examples reviewed in\textsuperscript{30}, are often designed and constructed as structured (texture modification) healthier foods for calorie reduction, bioactive compound encapsulation and delivery to meet requirements of different groups of people. Such co-stabilisation incorporates multiple active components to provide balanced nutrition and to obtain a more stable system, which is thermodynamically unstable, for better functional delivery and a longer shelf life\textsuperscript{31}. It has also been used in the emulsion formulation with an ultrahigh volume of internal phase (98.5%) to improve processing efficiency\textsuperscript{32}.

The core of co-stabilisation lies in the interaction at the nanoparticle surface with surfactant molecules and their adsorption at the oil/water interface. When the molecules and the nanoparticle interact strongly by forces such as electrostatic interaction\textsuperscript{33}, the nanoparticle surface becomes significantly modified. The modified surface shows different wettability at the oil/water interface for stabilisation.

In the other case, if the nanoparticle and surfactant molecules do not interact significantly with each other, they will largely exist independently in the same dispersion phase. During the emulsification process, they will compete to adsorb on the interface. The effect of competitive adsorption on the droplet formation and stability in a well-controlled condition is yet to be studied in detail. The adsorption kinetics of both species is related, and is likely to be carried out at varying speeds due to their difference in mobility. The adsorption speed of surfactants can be measured by dynamic interfacial tension, while for nanoparticles there are no existing method of measurement. This explains the ongoing research into the relationship between surface properties of nanoparticles and, emulsion size and stability. Such research is generally carried out using the final sizes of droplets formed under a random turbulent force, which expose limited information on competitive adsorption at the interface. Membrane emulsification technologies provide a new platform for the research and also a new vehicle to explore the interfacial mechanism in a dynamic environment.

Direct extrusion of liquid through a microporous membrane into another liquid, sometime referred to as direct membrane emulsification, exploits the uniformity of the pores to produce a population of droplets (an emulsion) essentially in a in a drop-by-drop manner\textsuperscript{34}. The dispersed phase is directed into one side of the membrane and forced to permeate through the micropores during the process. Individual droplets form on the other side of the membrane surface in the continuous phase, and are then detached as single entities by a combined force of inherent (interfacial tension, gravity, buoyancy) and external forces (relative motion of the membrane to the continuous phase), as explained in more detail in\textsuperscript{35}. The duration of droplet formation varies from a few seconds to milliseconds as the external force increases\textsuperscript{36, 37}. The detached individual droplets will remain as they are, if they are well stabilised at the time of detachment\textsuperscript{38}. In this case, the droplet sizes produced image that of the micropores in the membrane. Thus for a well manufactured membrane, the size and size distribution of the droplet produced reflect the adsorption kinetics of the emulsifiers during droplet formation.

This paper reports our recent work in the study of co-stabilisation of nanoparticle and surfactant in membrane emulsification. The formation of stable droplets, droplet size and size distribution are used to reflect the kinetic adsorption of surfactant molecules and nanoparticles on the surface of droplets. Both electrostatic and steric stabilised nanoparticle systems have been included for their reactions to anionic, cationic and non-ionic surfactants, as well as their effects on the stabilisation of oil in water emulsions. The knowledge obtained provides new formulation criteria for functional structural complexes.

2. Experimental

2.1 Materials

Silica nanoparticles of Nalco 1060 (containing 15 wt% silica nanoparticles) and responsive PS latex nanoparticles were employed as electrostatic and steric stabilised nanoparticles in an aqueous continuous phase, respectively. The silica suspension was formulated to have 3 wt% of silica nanoparticles with the addition of 1 wt% potassium hydrogen phthalate (KHP, >99.95%, Sigma-Aldrich) to give a well-controlled
pH environment at pH=4 for the co-stabilisation study. The latex nanoparticles were formulated to contain 2
wt% of latex particles and have a pH value higher than 8. This pH value ensures the solubility of the poly[2-(dimethylamino)ethyl methacrylate]-b-poly[methyl methacrylate] (PDMA-b-PMMA) chains and their
compatibility to the oil phase.

Sodium dodecyl sulphate (SDS, >90%, Fluka), hexadecyl trimethyl ammonium bromide (>99%, Acros
Organic) and Tween 20 (Fisher Scientific, UK) were used as representative anionic, cationic and non-ionic
surfactants, respectively, to study the surface interaction of the nanoparticles with different types of
surfactants and the effect of the interactions on the co-stabilisation in membrane emulsification process.

Four different oily systems were used as the dispersed phase in the preparation of oil-in-water emulsions
by a membrane. These were a low-viscosity paraffin oil (24 mPa·s at 25 °C, Fluka Ltd., UK), an ethyl
acetate solution of a polymeric resin (20 wt% Kao C binder) with a viscosity at 12 mPa·s (20 °C) and a
specific density at 0.95, and Tesco sunflower oil (UK).

2.2 Membrane emulsification

Cross flow and rotating membrane emulsification methods were employed in the preparation of emulsions
as reported in [34-36] at room temperatures. A ceramic membrane with an average pore size of 1.2 μm
was used for the cross flow membrane emulsification. The experiment was carried out at a constant
transmembrane pressure of 0.05 MPa and varied crossflow velocity.

The rotating membrane emulsification was carried out using a laser drilled stainless tubular membrane. The
membrane tube had a diameter of 7mm, thickness of 0.5 mm and 5 mm effective length of pore region. The
pores in the membrane are square 80x80 μm. The membrane was vertically connected with a hollow shaft
to rotate at a given speed in the continuous phase. More in details see [39]. For all the experiments in this
paper, the membrane was rotated at 1000 rpm. Cylindrical containers with a diameter of 30 mm were used
to hold the continuous phase of 30 ml. The oil of 7.5 ml was charged in the shaft connected with the
membrane. The hydraulic pressure was used as the driving force to pressurise the oil going through the
membrane. The emulsion prepared contained approximately 5 ml oil. The droplet was carefully sampled on
glass slides for the observation and measurement of droplet sizes using optical microscopes.

2.3 Examination of particle dispersions and emulsions

A Krüss DSA 100M was used to measure surface tension by the pending drop method. The pending droplet
was generated and held by blunt stainless steel needles with an inner diameter of 0.17 mm. The system was
characterised by measuring the surface tension of MiniQ water before the measurement. Droplet image
videos were recorded and analysed using commercial software.

Viscosity of both the oils and the continuous phase were measured using a Bolin rheometer (C-VOR). The
measurement was carried out at controlled shear stress ranging from 0.01 to 75 Pa at 20 °C.

Nanoparticle imaging was carried out using scanning electron microscopy (LEO 1530 FEGSEM). A drop
of diluted samples was spread on an aluminium stub and coated with platinum after it has dried to reduce
sample charging. The stage distance and the accelerating voltage used were ~3 mm and 3 kV, respectively.

A stereomicroscope (Nikon Ltd, model SMZ800) and an inverted confocal microscope (Nikon Ltd., Eclipse
TE 2000-U) were used to observe the emulsion droplet. The image was respectively recorded by digital
cameras of Spot Insight QE Model 4.2 and Digital Sight DS-U1 (Nikon) and through SPOT Advanced
software and NIS freeware 2.10. The droplet diameter was measured after calibrating the magnification
using a microbar (1 mm in 100 units). The reported data were calculated from more than 500 measurements.
The size distribution is expressed by the parameter of coefficient of variation (CV), calculated by:

\[ CV,\% = \frac{\sigma}{d_{av}} \times 100 \]
\[ \sigma = \sqrt{\frac{\sum (d_i - d_{av})^2}{N - 1}} \]

where \(d_i\) and \(d_{av}\) are the \(i^{th}\) droplet diameter and number average diameter, \(\sigma\) is the standard deviation of the
droplet diameters and \(N\) is the total number of droplets analysed.
3. Results and discussion

3.1 Nanoparticles as a single emulsifier in membrane emulsification

Experimental studies from crossflow and rotating membrane emulsifications have shown that the adsorption speed of surfactants on the droplet surface has a significant influence on the dynamic interfacial tension and droplet size \(^{38,40}\); the faster the adsorption, the smaller the droplets when other conditions are under strict control including the membrane pore size, transmembrane pressure, crossflow velocity and viscosities of the both phases. To examine the adsorption behaviour of the nanoparticles studied, the aqueous suspensions of the silica and the responsive latex nanoparticles were used as the continuous phase for the emulsification of different disperse phases.

![Figure 1: Silica nanoparticle stabilised emulsions of the polymer solution (viscosity 12 mPas) by (a) rotating membrane emulsification, and (b) crossflow membrane emulsification. For comparison, emulsions of paraffin oil with a viscosity at 11 mPas stabilised by 0.5% SDS are included.](image)

The emulsions shown in Fig. 1 a and b are formed from the silica suspension as the continuous phase and the polymer solution as the dispersed phase by rotating and cross flow membrane emulsification, respectively. The results from rotating emulsification shows that the droplets produced have an average diameter at 186 μm and a CV value of 14.3%. The CV value is comparable to that obtained from paraffin oil (viscosity 28 mPas at 25°C), stabilised by 2 wt% Tween 20 as an affinitive emulsifier and 0.1 wt% Carbomer as a thickener for the enhancement of droplet stabilisation at the same operational conditions \(^{39}\) (average diameter of ~200 μm and CV ~10%).

Similarly, the silica nanoparticles play an effective role in stabilisation in the crossflow membrane emulsification, Fig. 1b. The emulsion droplets formed are smaller and more uniform (lower CV values) than that of a complex alkane oil stabilised by SDS (0.5%) \(^{38}\), a good affinitive fast mobile surfactant. The complex alkane oil has very much the same viscosity as the polymer solution of 11 mPas at 20°C. The uniformity does not significantly change when the crossflow velocity varies from ~0.75 m/s to ~1.75 m/s. The SDS stabilised droplets show a bimodal size distribution at the crossflow velocity 0.95 m/s. The results from both the rotating and crossflow emulsification suggest that the silica nanoparticles at the concentration used can effectively diffuse and adsorb onto the droplet surface for the stabilisation. Its stabilisation can be more effective than that of SDS.

However, the silica or latex nanoparticle did not perform as positively in the sunflower oil emulsification using the rotating method. The emulsion sample using the silica suspension showed a floating layer of sunflower oil droplets at the top when freshly prepared. The droplets were large in size and identifiable by the naked eye. These large droplets were not stable and gradually separated out to a clear oil layer within one or two hours after standing, as shown in Fig. 2 a. Fig. 2b shows the emulsion droplets stabilised by the latex nanoparticle. The droplets were in the range of ~400 μm and broke in a very short time while being spread out for imaging.
It should be noted that the polymer solution used ethyl acetate as the solvent, which has a significant solubility of 8.3 g/100 mL (20 °C) in water. The dissolving action provides an opportunity for the nanoparticles to interact more strongly with the polar polymer molecules, when the droplet is subjected to the aqueous suspension and rapidly generate a more stable interface. The fast wetting of the droplet surface leaves the transport to the interface controls the stabilisation. The experimental results show that the nanoparticle concentrations applied is able to transfer sufficient particles to the interface. In the following section, the nanoparticle concentrations will be kept constant at the values used, as well as the rotating emulsification settings and operational conditions. In this case, the size and stability of droplets formed will be used to judge the wetting and co-stabilisation of surfactants and the nanoparticles.

### 3.2 Nanoparticles as co-stabiliser in the rotating membrane emulsification

SDS, HDTMABr and Tween 20 as representative anionic, cationic and non-ionic surfactants were added into the suspensions of the silica and latex nanoparticles at 0.5 wt% respectively. Table 1 tabulates their appearances and surface tensions.

The latex suspension did not change its visual appearance with the addition of the three types of surfactants. They also showed very similar surface tensions to that of the corresponding aqueous surfactant solutions at a concentration of 0.5 wt%. This phenomena suggest that the steric stabilised latex surface undergoes limited interactions with the surfactant molecules.

In contrast, the silica nanoparticle suspension behaved differently. The addition of anionic SDS did not change the visual appearance of the silica suspension however a small amount of needle-like deposits were formed. The deposit could be related to the impurities in the SDS (impurity up to 10%). The surface tension lowered from 41.6 mN/m of the SDS solution of 0.5 wt% to 37.6 mN/m.

**Table 1:** Appearance and surface tension of the Latex (2.0 wt%) and silica (3.0 wt%) nanoparticle suspensions with 0.5 wt% surfactant.

<table>
<thead>
<tr>
<th>Surfactants added</th>
<th>Latex nanoparticles</th>
<th>Silica nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dispersion appearance</td>
<td>Surface tension, mN/m</td>
</tr>
<tr>
<td>None</td>
<td>Uniform stable</td>
<td>72.8</td>
</tr>
<tr>
<td>SDS</td>
<td>Uniform stable</td>
<td>41.6</td>
</tr>
<tr>
<td>HDTMABr</td>
<td>Uniform stable</td>
<td>41.2</td>
</tr>
<tr>
<td>Tween 20</td>
<td>Uniform stable</td>
<td>49.6</td>
</tr>
</tbody>
</table>

The silica nanoparticle suspension was formulated from Nalco 1060, which has a pH value larger than 7. Such condition facilitates a surface zeta potential no less than ~45 mV for effective electrostatic stabilisation of the colloidal system. The addition of 1 wt% of potassium hydrogen phthalate (KHP), an acidic salt,
lowers the pH value of the suspension to 4 and concomitantly increases its ionic strength. A higher ionic strength normally lowers the critical micelle concentration, so that the interfacial tension decreases faster with more surfactant molecules in micelles and less free surfactant molecules in the system. This possibly explains the lower surface tension compared to the solution of 0.5% SDS.

The addition of the cationic (HDTMABr) and non-ionic surfactants (Tween 20) resulted in precipitation of the silica nanoparticles, and the suspension separated into two layers: a clear top layer and a white bottom layer of flocs. The precipitated flocs are re-dispersible. The cationic head reacts with the negative charge on the silica surface, which lead to rapid precipitation and formation of structural aggregates. The silica nanoparticles took a longer time to precipitate in the non-ionic surfactant. This may be the result of domination by the weaker adsorption of hydrogen bonding along the EO chains of Tween 20 in the interaction. Adsorption significantly decreases the free molecular concentration in the aqueous phase due to the nanoparticles’ large specific surface area, thus the surface tensions were considerably higher than its counterpart of 0.5 wt% surfactant solution, respectively. These phenomena are summarised in Table 1.

The six aqueous suspensions were used as the continuous phase for the respective emulsification of sunflower oil using the rotating method. The droplets produced were examined using optical microscopes. The results are listed in Table 2. The sunflower oil emulsification results in each surfactant solution (0.5 wt%) are also presented for comparison.

Table 2: Co-stabilisation of sunflower oil emulsions by nanoparticles and 0.5 wt% surfactants, prepared by rotating membrane emulsification.

<table>
<thead>
<tr>
<th>Surfactant added</th>
<th>Surfactant only</th>
<th>PS + Surfactant</th>
<th>Silica + Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial tension, mN/m</td>
<td>D&lt;sub&gt;av&lt;/sub&gt;, μm</td>
<td>CV, %</td>
<td>Interfacial tension, mN/m</td>
</tr>
<tr>
<td>Anionic</td>
<td>5.0</td>
<td>245/11.4</td>
<td></td>
</tr>
<tr>
<td>Cationic</td>
<td>4.6</td>
<td>-</td>
<td>Bimodal</td>
</tr>
<tr>
<td>Nonionic</td>
<td>13.0</td>
<td>270/10.2</td>
<td></td>
</tr>
</tbody>
</table>

3.2.1 Steric stabilised latex nanoparticle

With anionic surfactant: Droplet appearance of the emulsion stabilised by the latex nanoparticle with 0.5 wt% of SDS are shown in Fig. 3a and the inset shows its size distribution. The droplets have an average diameter of 217 μm and a CV of 16.4%. The average size is smaller than droplets stabilised by 0.5 % SDS (D<sub>av</sub>=245 μm, CV=11.4 %), and the CV value is slightly larger. The smaller size can be resulted from the co-stabilisation or from the viscosity change due to the addition of nanoparticles, which increased by 7% based on the calculation using a modified Einstein’s equation for viscosity ratio \( \mu_r \):  

\[
\mu_r = 1 + 2.5 \phi + 14.1 \phi^2
\]

Equation 2

where \( \phi \) is the volume fraction of the nanoparticle in the suspension.

Fig. 3b shows an image of the droplet residues after the water evaporated in the continuous phase. It can be seen that the latex nanoparticles have remained around the “droplets”, which suggests a significant amount of the latex nanoparticles were adsorbed on the oil droplet (with SDS) surface and formed smaller stable droplets.
Figure 3: Sunflower oil droplets stabilised by 2.0 wt% latex nanoparticle and a given concentration of SDS, prepared by rotating membrane emulsification. (a, b) 0.5 wt% SDS with inset showing the droplet size distribution compared to that of the emulsion stabilised solely by 0.5 wt% SDS (the dash line). (c, d) 0.2 wt% with (b) show the sunflower oil droplets releasing from the emulsion. (e, f) Possible competitive adsorption mechanisms of nanoparticles and surfactant molecules for co-stabilisation of emulsions when they have limited/weak interaction: (e) adsorption and desorption equilibrium of the surfactant molecules are not sustainable; (f) sustainable adsorption and desorption equilibrium of the surfactant molecules formed for effective co-stabilisation.

Fig. 3b shows an image of the droplet residues after the water evaporated in the continuous phase. It can be seen that the latex nanoparticles have remained around the “droplets”, which suggests a significant amount of the latex nanoparticles were adsorbed on the oil droplet (with SDS) surface and formed smaller stable droplets.

Interestingly, when 0.2 wt% SDS was incorporated in the latex suspension, sunflower oil formed uniform droplets of ~295 μm, which is smaller than that without SDS (~400 μm), Fig. 3c. However, the droplets released the oil while the image was taken, Fig. 3d. Comparing Fig. 3c and d, it can be seen that the released transparent oil droplets are of similar sizes to when they are covered by the latex particles, which are opaque. This droplet size is significantly smaller than that produced in the aqueous solution with 0.2 wt% SDS at 521 μm average diameter. The resulting smaller size and uniformity of the emulsion suggest the addition of 0.2 % SDS generate significant synergistic effect in droplet formation, but the smaller droplet formed is not as stable as the larger one with 0.2 % SDS solely.

It is known that surfactants and particles stabilise emulsion droplets in different mechanisms: Gibbs Marangoni and Pickering emulsion, respectively. The former involves an adsorption-desorption equilibrium. During membrane emulsification, only when the coverage reaches a critical level to avoid any coalescence and support further adsorption to reach the equilibrium after detachment, the droplet formed will have the ability to keep its size. Otherwise, the droplet will break up and/or agglomerate, losing its size-stability. The above experimental phenomena at 0.2 wt% and 0.5 wt% SDS suggest that the SDS and the latex nanoparticles experienced a competitive adsorption at the oil/water interface. At concentration of 0.2 wt%
SDS, a smaller population of SDS molecules adsorb at the interface along with the latex nanoparticles, as demonstrated in Fig. 3e. The small continuous areas adsorbed by the SDS limits the establishment of the adsorption and desorption equilibrium, a naked hole occurs that results to the oil release. When the concentration of SDS increases to 0.5 wt%, the continuous area adsorbed by SDS increases to above a critical value so that the adsorption-desorption equilibrium can be maintained, Fig. 3f. This ensures the size maintenance.

**With non-ionic surfactant:** The mechanism described in Fig. 3e and f can be applied to the system of the latex nanoparticle with Tween 20 as well, where the surfactant molecules and the nanoparticles do not have strong interactions. The rotating emulsification produced uniform droplets, but the droplet gradually aggregated and formed a clear layer of oil after standing overnight. The larger molecular weight of Tween 20 ($M_w=1227$ for Tween 20 comparing to 288 for SDS) gives a smaller population of Tween 20 molecules in suspension (0.5 wt%), and the larger molecules correspond to slower mobility to achieve equilibrium of desorption and adsorption. These, therefore, generate the delayed aggregation.

**With cationic surfactant:** The cationic surfactant has a positive charged hydrophilic head, which reacts with the negative charge on the surface of the stainless steel membrane. Such interactions change the hydrophilic membrane surface to hydrophobic, so that the oily dispersed phase wets the membrane surface easily. The oil wetted surface does not support the formation of oil droplets in water. The consequence is that the membrane emulsification of the system leads to a highly poly-dispersed emulsion.

### 3.2.2 Electrostatically stabilised silica nanoparticles

**With anionic surfactant:** The electrostatically stabilised silica nanoparticles do not interact strongly with SDS molecules. Their co-stabilisation is expected to follow the competitive adsorption mechanism. The sunflower oil droplets and their size distribution are shown in Fig. 4. The droplets in Fig. 4a clearly show two size groups approximately at 130 and 330 μm, which can also be seen in Fig. 4b. The smaller sizes account for approximately ~20%, and the larger sizes dominate at 80%.

As discussed above, in the presence of KHP the dissolved SDS molecules tend to stay in surfactant micelles and a smaller population remain as free individual molecules in the continuous aqueous phase, which determines the SDS adsorption rate on the oil droplets. This influence is further examined by varying the concentrations of SDS and KHP, as shown in Fig. 5. The emulsions were prepared by keeping the KHP concentration at 0 and 1 wt%, respectively, and the SDS concentration varied from 0.05, 0.1, 0.25, 0.5 to 0.75 wt%. In the absence of KHP, the stabilisation was achieved at the SDS concentration of as low as 0.05 wt%, while in the presence of 1 wt% KHP, stable droplets only achieved at a SDS concentration above 0.5 wt%. The SDS concentration requirement becomes higher with the addition of KHP for maintaining a higher percentage of free SDS molecules to compete with the silica nanoparticles for a minimum effective coverage of SDS, similar to the combination of the latex nanoparticle with SDS shown in Fig. 3e and f.

Figure 4: (a) Sunflower oil droplets stabilised by 3.0 wt% Silica nanoparticle and 0.5 wt% SDS (b) the droplet size distribution of the emulsion, comparing with that of the emulsion stabilised solely with 0.5wt% SDS. Prepared by the rotating membrane emulsification.
Figure 5: Sunflower oil emulsions stabilised by 3.0 wt% silica nanoparticles and SDS in the absence of KHP (a,b) and in the presence of 1 wt% KHP. SDS concentration: (A, A2) 0.05 wt%, (B, B2) 0.1 wt%, (C, C2) 0.25 wt%, (D, D2) 0.5 wt% and (E, E2) 0.75 wt%. The circled point in (b) shows the average size of emulsions stabilised solely by 0.5 wt% SDS.

Size analysis of the emulsions show that the average droplet sizes gradually decrease from ~425 μm to 350 μm as SDS concentration increases in the absence of KHP, Fig. 5b. However the sizes are much larger than that stabilised solely by SDS: 295 μm at 0.2 wt% and 245 μm at 0.5 wt%. More interestingly, the average sizes decreased with the increase of KHP concentration, as shown in Table 3. In the presence of 1 wt% KHP and 0.5 wt% SDS, the very low dynamic interfacial tension (at ~1 mN/m) may have caused the bimodal size distribution in the emulsion as the surface tension of sunflower oil is 36.6 mN/s.

<table>
<thead>
<tr>
<th>Continuous phase</th>
<th>Emulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica, %</td>
<td>SDS, %</td>
</tr>
<tr>
<td>3.0</td>
<td>0.5</td>
</tr>
<tr>
<td>3.0</td>
<td>0.5</td>
</tr>
<tr>
<td>3.0</td>
<td>0.5</td>
</tr>
<tr>
<td>0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

In summary, the silica nanoparticles do not have significant interaction with SDS molecules. Their co-stabilisation follows the competitive adsorption mechanism described above. The addition of KHP changes not only the pH but also the ionic strength of the aqueous phase, and further the micellisation and the concentration of free individual surfactant molecules. Only free individual surfactant molecules in the continuous phase compete with the nanoparticle for adsorption at the droplet surface which influences the droplet formation and stability.

Adsorption of the silica nanoparticle to the sunflower oil droplet could be faster than that of the Latex nanoparticle, and consequently the sunflower oil droplet produced from silica and SDS is significantly larger than that stabilised solely by SDS, and the droplet stabilised by the Latex combination have a size close to that stabilised solely by SDS. Both the small size of silica nanoparticles and its wetting kinetics can contribute to this outcome, hence the silica nanoparticles contribute more than the Latex nanoparticles in the co-stabilisation.
**With cationic surfactant:** The cationic surfactant adsorbed strongly on the silica nanoparticle surface by electrostatic interaction. The strong adsorption resulted in an increased surface tension from 41.2 up to 55.0 mN/m. This indicates the concentration of free individual HDTMABr molecules below the critical micelle concentration. The adsorption enables the nanoparticle to have a more hydrophobic surface, and in turn it promotes wetting at the oil droplet surface. The consequence is that the modified nanoparticles can provide enhanced stability to the oil droplets. Fig. 6 a and b presents droplets stabilised by the modified nanoparticles with some pale and darker droplets.

Figure 6: (a) Microscopic image of the sunflower oil droplets stabilised by 3.0 wt% silica nanoparticles and 0.5 wt.% of the cationic surfactant, (b,c) appearance of the emulsions, (d) mechanism of the cationic surfactant molecule-modified nanoparticles forming single layer and multiple layer adsorbed barriers at the droplet surface.

The hydrophobic surface also enabled the interaction among the nanoparticles forming multilayer coverage to the oil droplets and gradually formed into a large lump as shown in Fig. 6 c and d. The pale and darker droplets in Fig. 6a may have single and multiple layers of adsorption, respectively. The droplets produced have an average diameter of 397 μm and a CV value of 25.2 %, which is smaller and more uniform than its counterpart shown in Fig. 2a. It needs to be pointed out that the slurry suspension has an increased viscosity. It contributes to the detachment force to generate smaller droplets compared to that stabilised solely by the nanoparticles.

**With non-ionic surfactant:** In the case of the silica nanoparticles combined with 0.5 wt% of Tween 20, the hydrophilic ethylene oxide (EO) chain in the Tween 20 molecules adsorbs onto the surface of the silica nanoparticles with the hydrophobic part dangled in the water phase, as shown in Fig.7a. In the emulsification, the dangled hydrophobic part could enhance the hydrophobicity and the wetting of the modified nanoparticles to the oil droplets. Very limited numbers of Tween 20 molecules remain free in the continuous phase as the surface tension is measured at 70.5 mN/m, which is very close to that of water at 72 mN/m. Fig. 7b shows the droplets produced in the rotating membrane emulsification.

The droplets produced have an average diameter of 222 μm and a CV value of 14.0 %, which is approximately 20% smaller than that stabilised only with 0.5% of Tween 20 (D_{av}=270 μm, CV=10.3%). The CV values are largely comparable as shown in the size distribution curves in Fig.7c. The addition of Tween 20 resulted in a dramatic increase in the continuous phase viscosity. This is the dominating factor that contributes to the size reduction. While the water evaporates, wrinkles on the droplets can be seen as in inset of Fig. 7b, this suggest the nanoparticles adsorption on the surface dominates.
More interestingly, the emulsion separated into three layers after standing overnight: a top layer consisting of oil droplets, a clear middle layer and a white bottom layer, as shown in Fig. 7d. Optical microscope observation shows that both the top and bottom layers contain droplets. The droplets in the top and bottom layers have very similar sizes, although the droplets in the top layer tend to merge up and do not maintain any individual characteristics unlike the droplets from the bottom layer as shown in Fig. 7e and f, respectively. This may suggest that the droplets from the top layer were largely stabilised by Tween 20, few nanoparticles exist on the droplet surface. In contrast, droplets from the bottom layer have sufficient population of nanoparticles on its surface so that the overall density of the stabilised droplets is greater than water, resulting in precipitation. Droplets such as these stabilised by nanoparticles form better physical barriers than that from surfactant molecules; their entities remain while under strong capillary forces during drying.

4. Conclusions

This research has demonstrated that nanoparticles can be used as a single effective emulsifier in membrane emulsification, for size-controlled emulsion production when their adsorption kinetics supports the formation of an effective barrier at the interface in time. In the case where an effective adsorption barrier does not form in time, molecular surfactants can enhance stabilisation of the nanoparticles by co-stabilisation. The co-stabilisation shows a complex scenario, and the behaviour can be classified into two groups:

- When there is limited interaction between the nanoparticle and surfactant molecules, the addition of surfactants does not significantly vary the interfacial tension. Competitive adsorption of the nanoparticles and surfactant molecules at interface occurs, which is controlled by their diffusion and the interaction at the interface. A larger continuity of surfactant adsorption areas is required to maintain the Gibbs Marangoni effect for effective stabilisation.

- When surfactant molecules adsorb on the nanoparticle surface, both the interfacial tension and nanoparticle surface are modified. Modified nanoparticles have similar surface chemistry to that of the surfactant, and their diffusion controls the adsorption.

These co-stabilisation mechanisms can be used to guide the formulation of complex particulates of multifunctional products. The co-existence of the nanoparticles and surfactants provide an extra design tool to construct microstructures for multifunctional delivery, or catalysed microreaction. Such structures have been conceptually used in the formulation and processing of multiple functional food emulsions through the use of surfactant, proteins and other edible particles such as fat crystal and cellulose nanoparticles. With the guidance of the mechanisms, more stable and better structured products can be formulated and manufactured. Using nanoparticle stabilised droplets as microreactor for catalytic reaction is emerging, and is seeing more demonstrative work to be published.

5. References (polished)


**Highlights**

- Emulsions formed by membrane emulsification are used for an experimental co-stabilisation study;
- Co-stabilisation arising from Interactions of both electrostatic and steric stabilised nanoparticles with different types of surfactant are reported;
- Two distinct co-stabilisation mechanisms of nanoparticles and surfactants are identified;
- Competitive adsorption kinetics or Gibbs Marangoni equilibrium play the key role in the co-stabilisation.
Competitive Adsorption vs Gibbs Marangoni Equilibrium

Emulsification

Unstable for Gibbs Marangoni equilibrium

Stable for Gibbs Marangoni equilibrium