

Electrostatic Complexes of Nano-Montmorillonite/Ethyl Lauroyl Arginate Stabilized Sunflower Oil Pickering Emulsions

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Abstract

Compared with traditional surfactant-stabilised emulsions, Pickering emulsions, stabilised by clay nanoparticles, have the advantages of strong interface stability, strong versatility, and low toxicity. Moreover, they have excellent application potential in the fields of food and medicine. In this study, a food-grade Pickering emulsion stabiliser was prepared by physically adsorbing the cationic surfactant ethyl lauroyl arginate (LAE) on the surface of nano-montmorillonite (NMMT). Different LAE/NMMT combinations were assessed for their capacity to stabilise an oil-in-water emulsion at a low solid concentration (0.5%, w/v). The controllability of the droplet diameter and stability of the Pickering emulsions can be realised by changing the content of LAE. Scanning electron microscopy (SEM), and laser confocal microscopy (CLSM) confirmed the successful preparation of sunflower oil Pickering emulsion droplets stabilised by LAE/NMMT (0.0075%/1%). Additionally, the LAE/NMMT studied in this work could be used as a highly effective antibacterial surfactant with inorganic nanoparticles to efficiently stabilise Pickering emulsions, thus expanding the potential of preparing edible Pickering emulsion formulae.

Keywords

Pickering Emulsion, Ethyl Lauroyl Arginate, Nano-Montmorillonite, Stabilisation, Edible Emulsifier

1. Introduction

The emulsion is thermodynamically unstable and requires particular strategies to ensure long-term stability [1]. Pickering emulsions stabilise emulsions uni-

quely, by virtue of forming a dense granular film at the oil/water interface to stabilise the droplets [2]. Compared with traditional emulsions stabilised by small molecular surfactants such as Tween and Span, the adsorption of particles in Pickering emulsions at the oil-water interface is irreversible, thus ensuring that Pickering emulsions have the advantages of strong stability, isothermal quenching resistance, and good safety. Therefore, Pickering particles exhibit good application potential for carrying and releasing active substances and improving nutritional quality [3] [4]. Moreover, Pickering emulsions are an ideal choice for food manufacturers because of their low particle concentration. Thus, research into Pickering emulsions is very dynamic within the food industry and is expected to provide a safe and green food-grade emulsion formula [5] [6].

Nano-montmorillonite (NMMT), a type of 2D inorganic nanoparticle, exhibits excellent adsorption capacity and expansibility and also exhibits the characteristics of flexibility, low density, high moldability, heat stability, good strength, and chemical stability, which ensure it is widely used [7] [8]. However, the property of two-dimensional platelet-like NMMT is severely hindered by its tendency to aggregate or stack. Methods to solve this problem have been proposed, including the creation of hierarchical structures, the generation of inter-layer spaces, and the assembly of 2D-material sheets into 3D macrostructures [9]. Moreover, the surface of NMMT contains many hydrophilic hydroxyl groups; thus, when preparing Pickering emulsions as solid-particle stabilisers, it is necessary to modify the nano-clay particles to adjust their surface potential and wettability [10] [11]. The amphipathic nano-sized clay particles that are hydrophobically modified are usually suitable for fabricating Pickering emulsions exhibiting excellent stability. Ethyl lauroyl arginate (LAE) is a cationic surfactant with broad-spectrum antibacterial function, and is widely used in the cosmetics and food industries in many countries worldwide. LAE has been approved by the Codex Alimentarius Commission as a food processing aid [12] [13]. As a surfactant, LAE has been successfully applied to many Pickering systems [14] [15]. The particles of the LAE/NMMT composite should be partially wetted by two phases of the Pickering emulsion; NMMT is too hydrophilic, therefore, its emulsifying ability is weak, and the hydrophobic tail of LAE improves the amphipathic property of the LAE/NMMT composite, thereby, enhancing the application potential of the Pickering emulsion system as a stabiliser in the food industry [16] [17].

Herein, we evaluate the microstructure and physicochemical properties of a sunflower oil Pickering emulsion stabilised by LAE/NMMT electrostatic complexes. The interaction mechanism between LAE and NMMT in aqueous solution and the properties of the Pickering emulsion system comprising different LAE contents were analysed and characterised. Ultra-high resolution confocal laser scanning microscopy (CLSM) was used to determine the particle distribution of the LAE/NMMT complex at the oil-water interface and the continuous phase, to study the general mechanism behind the stability of the Pickering emulsion. Routine experiments of stability analysis, rheological properties, in-

fluence of pH values, and long-term storage stability were performed to provide theoretical support and feasible preparation methods for the preparation of food-grade green Pickering emulsion systems. The introduction of functionalised nano-montmorillonite into food-grade emulsions to prepare stable and edible emulsions is a long-term project that will facilitate the colloid interface chemistry and enrich the application of clay materials in food science.

2. Materials and Methods

2.1. Materials

Nano-montmorillonite, a platelet-like particle with a thickness of 1 nm and a diameter of 20 to 25 nm, was purchased from Macklin (Shanghai, China) as a white powder; Ethyl-*N*α-lauroyl-L-arginate hydrochloride (≥98% purity, C₂₀H₄₁N₄O₃Cl, MW 421.02) was provided by Macklin (Shanghai, China); sunflower seed oil, corn oil, and docosahexaenoic acid were purchased from a supermarket and were not purified further before use; alkenyl succinic anhydride (ASA) was purchased from Kemira (Shanghai, China); liquid paraffin, hexane, dodecane, and *n*-heptane were purchased from Macklin (Shanghai, China). Nile blue and Nile red were provided by Aladdin (China). All chemical reagents were analytically pure and were used without further purification. Ultrapure water (18.2 M·Ω·cm) (Elga PURELAB flex 4, UK) was used to prepare all solutions.

2.2. Preparation and Characterisation of LAE/NMMT Complexes

Deionised water was used to prepare the NMMT powder in a 2 wt% suspension, stirred, and allowed to stand for one week to swell fully. Thereafter, a specific quantity of LAE (0 - 0.05 wt%) was added to the NMMT suspension, and the obtained mixture was shaken for 30 s, and treated with a KQ-700V ultrasonic cell disruptor (Kunshan, China) for 5 min to obtain a suspension of the LAE/NMMT complex. Photographs of the LAE/NMMT suspensions comprising the different LAE concentrations were taken and the suspensions were used immediately after preparation.

A Nano-ZS Zetasizer instrument (Malvern Instruments, UK) was used to measure the zeta potential and droplet size of the samples. Before measurement, the sample was diluted with deionised water to avoid multiple scattering effects. The interfacial tension was measured using the drape method using an OCA25 automatic video optical contact angle metre (Dataphysics, Germany). Sunflower oil was added to the cuvette, and the transmittance of sunflower oil was checked before measurement. In brief, solution suspension droplets (5 μL) containing pure NMMT or the LAE/NMMT complex formed at the end of the low retention pipette tip immersed in the oil phase. After balancing the formed droplets at ambient temperature (25°C) for 10 min, the interfacial tension was calculated according to the droplet shape that was recorded in the balancing process. The surface tension was measured using the same method but air was used as the

continuous phase. The optical turbidity (at 600 nm) of the LAE/NMMT complex suspension was measured using an ultraviolet-visible spectrophotometer (Agilent, China) operating at ambient temperature. The sample was contained in an optical element having an optical path length of 1.0 cm. All measurements were performed on freshly prepared duplicate samples within 2 h of preparation. The three-phase contact angles were measured using an OCA40 micro contact angle measuring tool (Dataphysics, Germany) and a traditional particle-platelet method [18]. Prior to measurement, an HY-12 tablet machine (Tianguang, China) was used to coat the solid particles onto 2 mm-thick circular pieces. The NMMT and LAE/NMMT samples were analysed using a Fourier transform infrared spectrometer (ALPHA Bruker, Germany) with a scanning range of 4000 - 400 cm^{-1} . The morphology was observed using a JEM 2100 tungsten filament 80 kV transmission electron microscope (Hitachi, Japan).

2.3. Preparation and Characterisation of LAE/NMMT-Pickering Emulsion

The ratio of sunflower oil to the LAE/NMMT complex suspension was 1:5, and the LAE/NMMT-Pickering emulsion was obtained using ultrasonic treatment (3 min) with an ultrasonic cell disruptor (KQ-700 V Kunshan, China). Before characterisation, photographs and micrographs of the emulsion were taken within 6 h of preparation.

Pickering emulsions obtained by emulsifying *n*-hexane with LAE/NMMT complexes were diluted 20 times and then dropped onto a single-layer mica sheet via a pipette. After the oil phase was completely volatilised by freeze drying, the morphology of the droplets of the LAE/NMMT-Pickering emulsion and the particle film of the LAE/NMMT complexes, coated on the surface of droplets, were observed by AFM (Multimode 8, Bruker, USA). All rheological measurements were performed using a strain-controlled rheometer (MCR 300, Anton Paar, Germany) using a cone and plate clamp. The cone had a diameter of 50 mm and a radius of 0.0398 rad. The gelation of the LAE/NMMT-Pickering emulsion was detected by frequency scanning (0.1 - 100 rad/s) and shear scanning (shear rate 0.01 - 100 s^{-1}), and the relationship between the elastic modulus, loss modulus, and frequency was recorded. During the measurements, the temperature was maintained at 25°C. The Pickering emulsion, obtained by emulsifying *n*-hexane with LAE/NMMT, was diluted 20 times and then dropped onto a conductive glass sheet. The oil phase of the emulsion was completely volatilised by freeze drying. The morphology of the droplets of the LAE/NMMT-Pickering emulsion and the particle film of the LAE/NMMT compound, coated on the surface of the droplets, were observed using AFM (Multimode 8, Bruker, USA). To observe the aggregation of NMMT in the emulsion system, the dyed LAE/NMMT-Pickering emulsion was observed using a laser confocal microscope (SP8-X, Leica, Germany). Before observation, oil droplets (2 mL, top layer) were stained with Nile Red solution (0.2 mL). After mixing evenly with a pipette and equilibrating at ambient temperature for 10 min, the stained sample (6 μL) was transferred to a

microscope slide and covered with a cover glass. The excitation and emission spectra of Nile Red were 488 and 539 nm, respectively. Optical microscopy (Leica, Germany) images of the LAE/NMMT complex and sunflower oil were taken simultaneously with a $63\times$ oil immersion objective lens. Before preparing the emulsion, sunflower oil was dyed with Nile Red, and NMMT was stained with Nile blue. The excitation and emission spectra of Nile blue were obtained at 633 and 672 nm, respectively. An SU3500 scanning electron microscope (Hitachi, Japan) equipped with a cryo-SEM preparation system was employed to examine the morphology of the droplets stabilised by LAE/NMMT.

3. Results and Discussion

3.1. Characterisation of LAE/NMMT

The possible electrostatic binding and interaction between NMMT and LAE is shown in **Figure 1(a)**. The combination of NMMT and LAE mainly depends on the surface property of NMMT and the characteristics of the tail and head groups of LAE, which follow the complex process of the oppositely charged polymer and/or surfactant system [19]. As expected, the zeta potential, turbidity, and interfacial behaviour of the LAE/NMMT complexes were affected by the

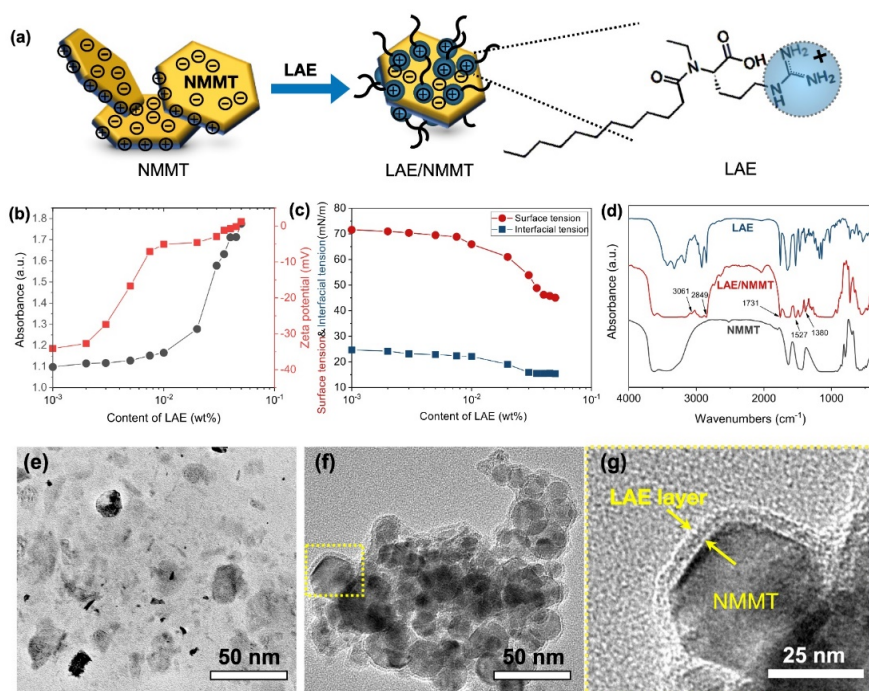


Figure 1. (a) Schematic drawing (not to scale) of electrostatic binding between the nano-montmorillonite and the guanidinium group of LAE. (b) Zeta potential of NMMT (2.0 wt%) dispersed in aqueous LAE solutions as a function of initial surfactant content. (c) Surface tension and interfacial tension of aqueous solutions containing LAE without and with nano-montmorillonite nanoparticles (2.0 wt%) as a function of initial surfactant concentration at 25°C. (d) FTIR spectra of original NMMT and modified NMMT with LAE. (e) TEM images of the prime NMMT platelets and ((e), (f)) LAE/NMMT complexes.

quantity of LAE added. As the LAE concentration increased (0 - 0.05 wt%), the suspension became increasingly turbid, but the obvious macroscopic phase separation did not occur (**Figure 1(a)**). It can be explained by the electrostatic stability caused by strong electrostatic repulsion between LAE/NMMT complexes at low LAE concentration [17]. The bonding between the LAE and NMMT surfaces is determined mainly by the long-range electrostatic attraction between the sulfuric acid group and the cationic head group of LAE. NMMT is covered by the surfactant, LAE, and its negative surface is neutralised, leading to a change in the zeta potential (**Figure 1(a)**).

The surface (air-water) and interface (sunflower oil-water) behaviours of the LAE/NMMT complexes were studied using a video contact angle measuring instrument with the hanging drop method (see **Figure 1(c)**). The surface tension of the LAE/NMMT suspension decreased from 72 to 42 mN/m, and the interfacial tension decreased from 25.5 to 15 mN/m, with the addition of LAE. At approximately 0.01 wt% LAE, interface tension and surface tension both decreased obviously, indicating the hydrophobic interactions between LAE tail groups. It was the result of the increase of LAE content and the basic polymer-induced micellization caused by negatively charged NMMT surface [14]. When the concentration of LAE (C_{LAE}) was 0.03 wt%, the surface and interfacial tension reached a plateau of 41 and 15 mN/m, respectively. This may be due to the dissociative LAE micelles in the continuous phase, indicating the saturation point where the LAE binds to NMMT through electrostatic interaction. The experimental results also indicate that the LAE/NMMT complex can significantly reduce the interfacial tension to sunflower oil, which could be explained by the hydrophobic modification of NMMT by LAE.

The FT-IR spectra of the original NMMT, LAE, and LAE/NMMT complex are shown in **Figure 1(d)**. The adsorption of LAE onto the NMMT surface was confirmed by multiple peaks. The two new bands at 2849 cm^{-1} and 3061 cm^{-1} are attributed to the symmetrical stretching and asymmetrical of CH_2 from the long alkyl chain of LAE [20]. In the FT-IR spectrum of the LAE/NMMT, the band at 1731 cm^{-1} corresponds to the carbonyl group of the side chain of LAE. Moreover, the signals at 1527 cm^{-1} and 1380 cm^{-1} are related to amide II (combined C-N stretching N-H deformation) and the deformation vibration of the saturated C-H on the methyl group, respectively. This result is consistent with those of previous reports [20] [21]. Transmission electron microscopy (TEM) was employed to further study the structure of the complexes (**Figures 1(e)-(g)**). The origin NMMT particles comprised stacked irregular clusters of nanoplatelets, which may be induced by the nanoscale structure and electrostatic attraction of the montmorillonite (**Figure 1(e)**). However, with the addition of LAE, the LAE/NMMT complexes became regularly stacked, exhibiting hexagonal 2D-platelet-like particles surrounded by a thin LAE layer (see **Figure 1(f)**). It is proved that the successful adsorption of LAE onto the surface of NMMT. As reported in our previous work [12], the improved emulsification and structural stability of the complexes can result from the adhesive action of LAE to bind the nano-clay particles.

In the higher-magnification TEM image (Figure 1(f)), it can be clearly seen that the single MMT platelet was rough and a substantial quantity of LAE molecules were regularly and closely stacked onto it, which resulting from the LAE attaching onto the NMMT surface.

3.2. Pickering Emulsion Stabilised by LAE/NMMT

An NMMT/LAE-stabilised oil-in-water Pickering emulsion was prepared using the LAE/NMMT suspension and sunflower oil comprising various LAE concentrations; the visual appearance and optical micrographs of the as-prepared Pickering emulsion are shown in Figure 2(a). All the emulsions exhibited uniform appearance without phase separation, but the microtopography of the droplets showed a huge difference with varying C_{LAE} . However, the emulsions containing unmodified NMMT showed instability and experience frequent and strong coalescence between oil droplets, resulting in a large average droplet size ($>100 \mu\text{m}$). A uniform emulsion stabilised by LAE/NMMT with a small droplet size of $\sim 1.0 \mu\text{m}$ can be obtained by using 0.0075 wt% LAE. Introducing LAE markedly reduced the average droplet size from 56.2 to $1.0 \mu\text{m}$. Further increasing the C_{LAE} from 0.02 wt% to 0.05 wt% led to an enlarged droplet size and coalescence, which could affect the centrifugal stability of the emulsions. After the concentration of LAE increased to 0.04 wt% (0.04 - 0.05 wt%), the appearance of the LAE/NMMT-Pickering emulsion did not exhibit obvious oil phase precipitation;

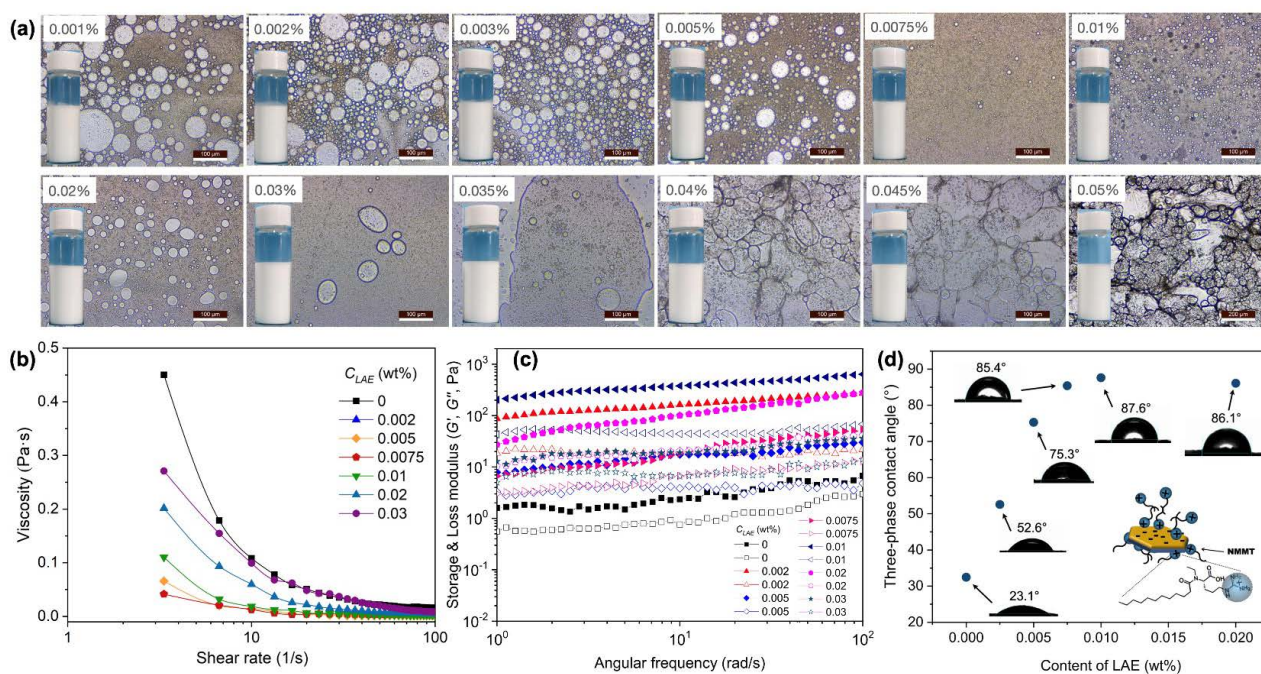


Figure 2. (a) Visual appearance and optical micrographs of NMMT/LAE-stabilised oil-in-water Pickering emulsions comprising different concentrations of LAE. The dosage of NMMT is fixed to 1.0 wt% (based on aqueous dispersion). (b) Relationship between apparent viscosity and shear rate of LAE/NMMT-Pickering emulsion stabilised using different concentrations of LAE. (c) Oscillation frequency scanning curve of LAE/NMMT-Pickering emulsion stabilised using different concentrations of LAE. (d) Three-phase contact angle of LAE/NMMT complexes. Inset is the schematic drawing (not to scale) of possible electrostatic binding between the laponite and the guanidinium group of LAE.

however, a high degree of flocculation occurred in the emulsion system as evident through micrographs. The increased flocculation indicated that the emulsifying ability of the LAE/NMMT complex to sunflower oil decreased further with the continuous increase in the LAE concentration.

The rheological properties of food-grade Pickering emulsions have a major influence on their application and processing [22]. The effect of the LAE concentration on the rheological properties of the LAE/NMMT-Pickering emulsion is shown in **Figure 2(b)** and **Figure 2(c)**. All the samples showed shear thinning behaviour, which is related to the deformation and destruction of aggregation between droplets when the shear rate increased (**Figure 3(a)**). The viscosity of the emulsion maintained a high value with high concentration of LAE, which may be related to the flocculation of the emulsion under high concentrations of LAE. The measurement results of the oscillation frequency also supported the viscosity (**Figure 2(c)**). At low LAE concentrations; the G' value of the LAE/NMMT-Pickering emulsion was higher than that of G'' , suggesting that the emulsion showing significant gel-like properties and good elastic behaviour [23]. With the increase in frequency, both G' and G'' increased slightly, indicating that the physical interaction aided the formation of Pickering emulsions.

Figure 2(d) shows the three-phase contact angle of the LAE/NMMT composite. With increasing LAE concentrations, the hydrophobic tail of LAE enhanced the hydrophobicity of the LAE/NMMT complex and reached its highest value (87.6°) when the LAE concentration was 0.01%. As the increasing LAE concentration, the three-phase contact angle showed a downward trend. When the concentration of LAE was between 0.0075% and 0.02%, the three-phase contact angle of the LAE/NMMT complex was approximately 90° , which indicated that the LAE/NMMT complex had stronger amphiphilic property and better emulsifying ability. It was consistent with the microscopic observation [24]. The oil-water contact angle, measured through water in the oil phase having strong polarity, was larger, and the particles combined more easily at the oil-water interface, which was beneficial to the formation and stability of oil-in-water Pickering emulsions [25].

3.3. Stabilisation Mechanism

The morphology of the oil-water interface was further investigated by SEM to clarify the dispersive behaviour of LAE/NMMT at the interface. The oil-water interface effectively adsorbed the LAE/NMMT complex, and a dense granular film formed on the surface of the Pickering emulsion droplets (**Figure 3(a)**). The LAE/NMMT complexes effectively formed matrix at the oil-water interface, where the matrix with a specific strength was present between adjacent emulsion droplets (yellow dot box) [26]. The existence of LAE/NMMT matrix with a gel network structure was further corroborated by cryo-SEM (**Figure 3(b)**). The interaction between the LAE/NMMT complexes formed a three-dimensional network structure, which led to an increase in the viscosity of the continuous phase and reduced the migration speed of emulsion droplets, thereby, preventing the

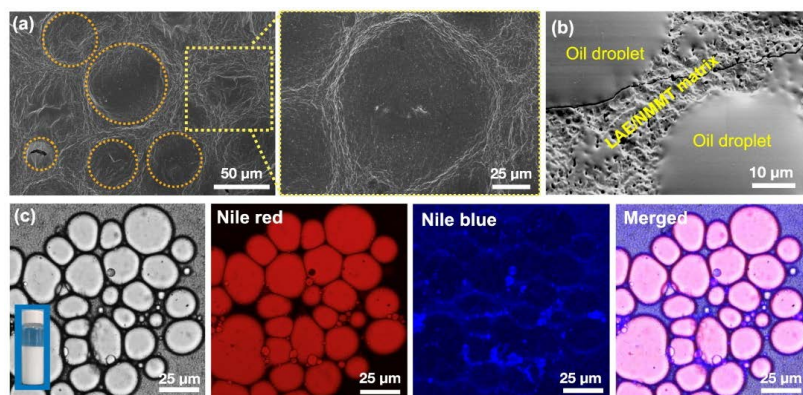


Figure 3. (a) SEM images of the n-hexane Pickering emulsion stabilised by LAE/NMMT. (b) Cryo-SEM and (c) CLSM images of the sunflower oil Pickering emulsion stabilised by LAE/NMMT after 1 d storage time. Inset is the appearance of the as-prepared Pickering emulsion. The sunflower oil was stained with Nile red before emulsion preparation, and LAE/NMMT complexes were dyed with Nile blue prior to observation.

coalescence of emulsion droplets, and improving the stability of the emulsion [27]. CLSM images of the sunflower oil Pickering emulsion stabilised by LAE/NMMT after 1 d storage time are shown in **Figure 3(c)**. The location of the LAE/NMMT complexes was traced to further probe the stabilisation mechanism of sunflower Pickering emulsion. NMMT/LAE complexes were stained with Nile blue, showing blue in the CLSM images, and the sunflower oil was stained with Nile red (red). **Figure 3(c)** presents the distribution of the LAE/NMMT matrix building up in the aqueous phase and the particle film coating on the surface of the oil droplet. The LAE/NMMT complexes were clearly visible on the o/w interface of emulsions. Emulsion showed homogenous droplets without demulsification and coalescence after 1 week storage time. Honeycomb-like structure played a role of barrier in the aqueous phase; that means the permeation of oil molecules among droplets were strengthened for acrossing the LAE/NMMT matrix which stood between adjacent drops in direct contact.

The possible mechanism of the binding interaction between NMMT and LAE is shown in **Figure 4**. The combination of NMMT and LAE depends mainly on the surface chemical properties of NMMT and the head-tail characteristics of LAE, and their interaction follows the complex process of the polymer/surfactant system comprising opposite charges. At low LAE concentrations (0.001% - 0.002%) (**Figure 4(a)**), the bonding between LAE and the surface of NMMT was caused predominantly by the long-distance electrostatic attraction between the cationic head group of the LAE and the surface negative charge of NMMT. The LAE monomer was bound to the negatively charged surface of NMMT and existed freely at the oil/water interface or in solution [19], which may have a distinct dynamic equilibrium. The ζ potential results showed that a few LAE/NMMT complexes were attached to the oil-water interface, the ζ potential didn't change significantly (-38.1 - -32.7 mV) and the emulsion didn't show obvious improvement. As the LAE concentration increased (0.002% - 0.0075%) (**Figure 4(b)**), the ζ potential showed a significant change (-32.7 -

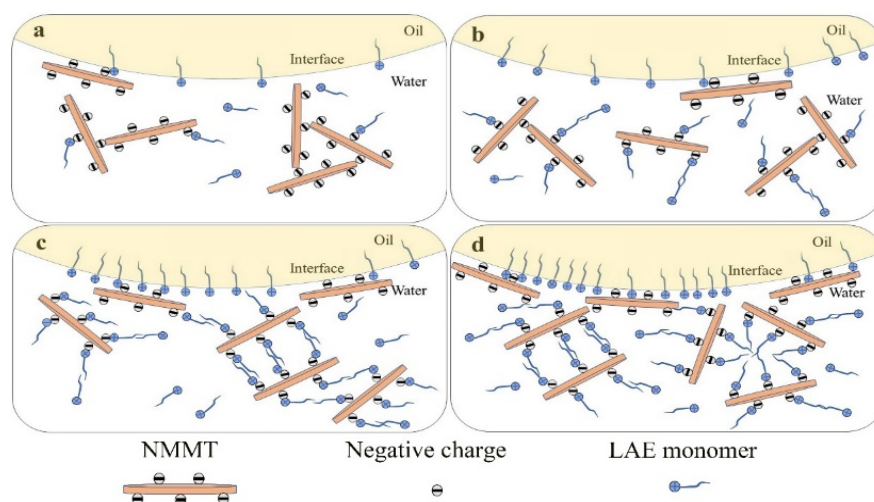


Figure 4. Schematic representation (not drawn to scale) of the interaction mechanism between LAE and NMMT as a function of surfactant concentration at (a) 0.001%, (b) 0.0075%, (c) 0.02% and 0.1%. The concentration of NMMT is fixed at 2.0% before the titration of LAE stock solution.

−7.1 mV), indicating the negative electrode surface of NMMT was neutralised and covered by the surfactant LAE monolayer. In addition, it changed the hydrophobicity and aggregation state of NMMT; thus, the aggregated LAE/NMMT complexes were dispersed. As expected, the increased LAE addition produced complexes with less-negative ζ -potential. Hydrophobic interactions started to dominate the persistent adsorption of NMMT by LAE, the LAE bound on the surface of NMMT could be hydrophobically associated with the free LAE in solution or the other LAE bound on adjacent NMMT, resulting in larger charge reversal and cross-linked aggregates on the surface of NMMT (**Figure 4(c)**). At this concentration range of LAE (0.0075% - 0.02%), more LAE/NMMT complexes with less-negative ζ -potential (−7.1 - −4.6 mV) were attached to the oil-water interface, forming a granular layer with barrier function. This “barrier” layer played a significant role in the stability of emulsion. Nonetheless, the transition point for charge compensation or balance occurred and strong hydrophobic association led to the agglomeration of the LAE/NMMT complexes when the concentration of LAE exceeds a certain range (0.03% - 0.05%) (**Figure 4(d)**) [28]. It engendered a negative effect on the stability of emulsion.

3.4. Effect of Oil Type on the Stability of LAE/NMMT-Based Pickering Emulsion

Eight oil phases with different polarities, including sunflower oil, ASA, corn oil, DHA, *n*-hexane, liquid paraffin, dodecane, and *n*-heptane were selected to prepare the Pickering emulsion for observing the emulsifying ability of the LAE/NMMT complex in different oil phases. The LAE/NMMT complex had a better emulsifying and stabilisation performance for the non-polar oil phase compared with that for the polar oil phase (**Figure 5**). The Pickering emulsions prepared using the four selected polar oil phases exhibited long-term stability

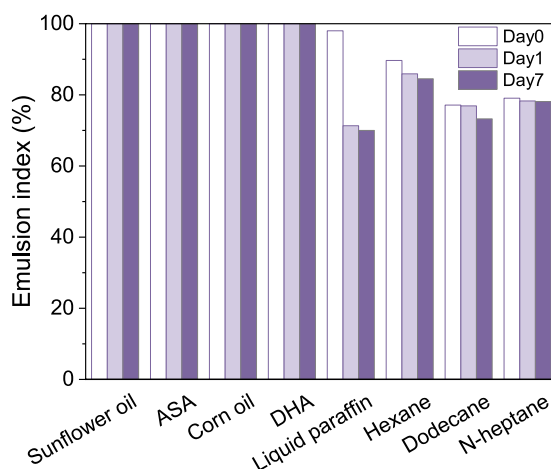


Figure 5. Emulsion index of the Pickering emulsion showing different oil phases stabilised by LAE/NMMT after 0, 1, and 7 d of storage time.

after standing for 7 d. Long-term storage (≥ 30 d) of sunflower oil emulsions stabilised by LAE/NMMT were also feasible. In contrast, the Pickering emulsions that contained a non-polar oil phase showed poor stabilisation but still have an EI of 70% after standing for 7 d. These results suggested that the LAE/NMMT complexes have positive effects on both the stability and the formation of the Pickering emulsions, especially for polar oil emulsions with strong polarity containing more hydroxyl and carboxyl groups, which could facilitate the adsorption of LAE/NMMT onto the oil/water interfaces.

4. Conclusion

By combining NMMT with the food-grade cationic surfactant LAE, sunflower oil was successfully emulsified to prepare a stable Pickering emulsion. The surface coverage of LAE/NMMT-Pickering emulsion droplets reached 70.9%, and the average droplet size was reduced from 56.2 to 1.0 μm when the optimal quantity of LAE was used. The LAE/NMMT complex comprising 0.01 wt% NMMT and 0.0075 wt% LAE had the best emulsifying properties. The wettability of LAE/NMMT composites is affected by the concentration of hydroxyl groups, which may disrupt the strength of network structure in the emulsion system. The LAE/NMMT-Pickering emulsion system based on a polar oil phase exhibits good emulsification and long-term stability in alkaline environments with $\text{pH} = 7.0 - 10.0$. These findings are of significance for pharmaceutical preparations and real food products. It would be prudent to consider surface-active electrostatic complexes based on clay nanoparticles and the effect of pH on the stability of Pickering emulsion formulations.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Bai, L., Huan, S., Gu, J., McClements, D.J. (2016) Fabrication of oil-in-water nanoemulsions by dual-channel microfluidization using natural emulsifiers: Saponins, phospholipids, proteins, and polysaccharides. *Food Hydrocolloids*, 61, 703-711. <https://doi.org/10.1016/j.foodhyd.2016.06.035>
- [2] Ramsden, W. (1904) Separation of solids in the surface-layers of solutions and 'suspensions'(observations on surface-membranes, bubbles, emulsions, and mechanical coagulation)—Preliminary account. *Proceedings of the royal Society of London*, 72, 156-164. <https://doi.org/10.1098/rspl.1903.0034>
- [3] Aveyard, R., Binks, B.P., Clint, J.H. (2003) Emulsions stabilised solely by colloidal particles. *Advances in Colloid and Interface Science*, 100, 503-546. [https://doi.org/10.1016/S0001-8686\(02\)00069-6](https://doi.org/10.1016/S0001-8686(02)00069-6)
- [4] Burgos-Díaz, C., Opazo-Navarrete, M., Soto-Añual, M., Leal-Calderón, F., Bustamante, M. (2020) Food-grade Pickering emulsion as a novel astaxanthin encapsulation system for making powder-based products: Evaluation of astaxanthin stability during processing, storage, and its bioaccessibility. *Food Research International*, 134, Article ID: 109244. <https://doi.org/10.1016/j.foodres.2020.109244>
- [5] Berton-Carabin, C.C., Schroën, K. (2015) Pickering emulsions for food applications: background, trends, and challenges. *Annual review of food science and technology*, 6, 263-297. <https://doi.org/10.1146/annurev-food-081114-110822>
- [6] Tavernier, I., Wijaya, W., Van der Meeren, P., Dewettinck, K., Patel, A. R. (2016) Food-grade particles for emulsion stabilization. *Trends in Food Science & Technology*, 50, 159-174. <https://doi.org/10.1016/j.tifs.2016.01.023>
- [7] Li, Y., *et al.* (2018) Research progress on the raw and modified montmorillonites as adsorbents for mycotoxins: A review. *Applied clay science*, 163, 299-311. <https://doi.org/10.1016/j.clay.2018.07.032>
- [8] Zhu, T.T., *et al.* (2019) Exfoliation of montmorillonite and related properties of clay/polymer nanocomposites. *Applied clay science*, 169, 48-66. <https://doi.org/10.1016/j.clay.2018.12.006>
- [9] Shang, T., *et al.* (2019) 3D macroscopic architectures from self - assembled MXene hydrogels. *Advanced Functional Materials*, 29, Article ID: 1903960. <https://doi.org/10.1002/adfm.201903960>
- [10] Wang, F., *et al.* (2021) Pickering medium internal phase emulsions based on natural clay particles: Route to a macroporous adsorbent. *Journal of Molecular Liquids*, 322, Article ID: 114995. <https://doi.org/10.1016/j.molliq.2020.114995>
- [11] Yan, H., Zhang, Z. (2020) Effect and mechanism of cation species on the gel properties of montmorillonite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 611, Article ID: 125824. <https://doi.org/10.1016/j.colsurfa.2020.125824>
- [12] Li, Y., *et al.* (2021) Laponite/lauric arginate stabilized AKD Pickering emulsions with shell-tunable hydrolytic resistance for use in sizing paper. *Applied Clay Science*, 206, Article ID: 106085. <https://doi.org/10.1016/j.clay.2021.106085>
- [13] Ziani, K., Chang, Y., McLandsborough, L., McClements, D.J. (2011) Influence of surfactant charge on antimicrobial efficacy of surfactant-stabilized thyme oil nanoemulsions. *Journal of agricultural and food chemistry*, 59, 6247-6255.

- <https://doi.org/10.1021/jf200450m>
- [14] Hu, Z., Ballinger, S., Pelton, R., Cranston, E.D. (2015) Surfactant-enhanced cellulose nanocrystal Pickering emulsions. *Journal of colloid and interface science*, 439, 139-148. <https://doi.org/10.1016/j.jcis.2014.10.034>
- [15] Kedzior, S.A., Marway, H.S., Cranston, E.D. (2017) Tailoring cellulose nanocrystal and surfactant behavior in miniemulsion polymerization. *Macromolecules*, 50, 2645-2655. <https://doi.org/10.1021/acs.macromol.7b00516>
- [16] Asker, D., Weiss, J., McClements, D. (2009) Analysis of the interactions of a cationic surfactant (lauric arginate) with an anionic biopolymer (pectin): isothermal titration calorimetry, light scattering, and microelectrophoresis. *Langmuir*, 25, 116-122. <https://doi.org/10.1021/la803038w>
- [17] Bai, L., Xiang, W., Huan, S., Rojas, O.J. (2018) Formulation and Stabilization of Concentrated Edible Oil-in-Water Emulsions Based on Electrostatic Complexes of a Food-Grade Cationic Surfactant (Ethyl Lauroyl Arginate) and Cellulose Nanocrystals. *Biomacromolecules*, 19, 1674-1685. <https://doi.org/10.1021/acs.biomac.8b00233>
- [18] Li, Z., Giese, R., Van Oss, C., Yvon, J., Cases, J. (1993) The surface thermodynamic properties of talc treated with octadecylamine. *Journal of colloid and interface science*, 156, 279-284. <https://doi.org/10.1006/jcis.1993.1112>
- [19] Brinatti, C., Huang, J., Berry, R.M., Tam, K.C., Loh, W. (2016) Structural and energetic studies on the interaction of cationic surfactants and cellulose nanocrystals. *Langmuir*, 32, 689-698. <https://doi.org/10.1021/acs.langmuir.5b03893>
- [20] Chi, K., Catchmark, J.M. (2017) Crystalline nanocellulose/lauric arginate complexes. *Carbohydrate Polymers*, 175, 320-329. <https://doi.org/10.1016/j.carbpol.2017.08.005>
- [21] Johnson, R.K., Zink-Sharp, A., Glasser, W.G. (2011) Preparation and characterization of hydrophobic derivatives of TEMPO-oxidized nanocelluloses. *Cellulose*, 18, 1599-1609. <https://doi.org/10.1007/s10570-011-9579-y>
- [22] Xia, T., Xue, C., Wei, Z. (2021) Physicochemical characteristics, applications and research trends of edible Pickering emulsions. *Trends in Food Science & Technology*, 107, 1-15. <https://doi.org/10.1016/j.tifs.2020.11.019>
- [23] Lin, D., Kelly, A.L., Miao, S. (2020) Preparation, structure-property relationships and applications of different emulsion gels: Bulk emulsion gels, emulsion gel particles, and fluid emulsion gels. *Trends in Food Science & Technology*, 102, 123-137. <https://doi.org/10.1016/j.tifs.2020.05.024>
- [24] Li, Q., *et al.* (2020) Food-grade emulsions and emulsion gels prepared by soy protein-pectin complex nanoparticles and glycyrrhizic acid nanofibrils. *Journal of agricultural and food chemistry*, 68, 1051-1063. <https://doi.org/10.1021/acs.jafc.9b04957>
- [25] Binks, B.P., Clint, J.H.J.L. (2002) Solid wettability from surface energy components: relevance to Pickering emulsions. *Langmuir*, 18, 1270-1273. <https://doi.org/10.1021/la011420k>
- [26] Wei, Z., Cheng, J., Huang, Q. (2019) Food-grade Pickering emulsions stabilized by ovotransferrin fibrils. *Food Hydrocolloids*, 94, 592-602. <https://doi.org/10.1016/j.foodhyd.2019.04.005>
- [27] Lagaly, G., Reese, M., Abend, S. (1999) Smectites as colloidal stabilizers of emulsions: I. Preparation and properties of emulsions with smectites and nonionic surfactants. *Applied Clay Science*, 14, 83-103. [https://doi.org/10.1016/S0169-1317\(98\)00051-9](https://doi.org/10.1016/S0169-1317(98)00051-9)

- [28] Bonnaud, M., Weiss, J., McClements, D.J. (2010) Interaction of a food-grade cationic surfactant (lauric arginate) with food-grade biopolymers (pectin, carrageenan, xanthan, alginate, dextran, and chitosan). *Journal of Agricultural and Food Chemistry*, 58, 9770-9777. <https://doi.org/10.1021/jf101309h>