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pH-Responsive Emulsions Stabilized by Rosin Gemini Surfactant: Construction, Stability, and Recyclability

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Abstract: A novel rosin-based Gemini pH-responsive surfactant DA-3-CYS with dual carboxyl groups was synthesized and utilized as a particulate emulsifier to construct pH-switchable Pickering oil-in-water (O/W) emulsions. The pH-regulated molecular conformation, interfacial adsorption behavior, and colloidal characteristics of DA-3-CYS were systematically explored. Two distinct pK_a values of 3.43 and 5.88 were identified, endowing the surfactant with reversible protonation–deprotonation structural transformation under pH stimulation. The formation and stability of the Pickering emulsions could be effectively modulated by environmental pH, surfactant dosage, and oil-water volume ratio. The optimal preparation conditions were determined as pH 4–6, DA-3-CYS concentration no less than 2 mM, and oil fraction of 50–70%, which afforded uniform Pickering emulsions with tiny droplet sizes (8–11 μm), narrow size distribution and outstanding long-term storage stability. The as-prepared Pickering emulsions possessed prominent thermal tolerance at 50–80 °C and excellent structural stability against moderate centrifugation below 2000 rpm. Alternating regulation of pH achieved reversible emulsification and demulsification behavior; moreover, the oil phase could be efficiently recycled after six cyclic operations without chemical structural degradation. This study develops a sustainable, green, and recyclable biomass-derived Pickering emulsion system, which displays great application potential in oil recovery, targeted substance delivery, and smart interfacial functional materials.

Keywords: pH-responsive emulsion; rosin; surfactant; emulsion stability; recyclability

1. INTRODUCTION

As a dispersion system comprising two immiscible phases, emulsions hold significant promise across diverse industrial sectors, including food, cosmetics, materials science, and energy[1-4]. Conventional emulsions typically rely on surfactants or polymeric emulsifiers to sustain kinetic stability[5]. However, many synthetic surfactants are petroleum-derived and pose issues regarding ecotoxicity, bioaccumulation, and non-renewability, thereby restricting their application in sustainable development and green chemistry[6].

Pickering emulsions utilize the irreversible adsorption of solid particles at the oil-water interface to form mechanical barriers, thereby significantly enhancing long-term stability and reducing or even circumventing reliance on traditional surfactants[7, 8]. Although inorganic nanoparticles (e.g., SiO_2 , TiO_2) can effectively stabilize emulsions, their poor biodegradability, potential ecological risks, and the complexity of required surface modifications have driven research toward natural, renewable, and biocompatible organic particles[9, 10]. Among these, rosin and its derivatives—derived from pine exudates—exhibit distinct advantages for green emulsifier development due to their renewability, excellent biocompatibility, degradability, and unique rigid tricyclic hydrophobic structure[11-13].

The rigid tricyclic phenanthrene skeleton at the core of the rosin molecule imparts strong hydrophobicity and high chemical modifiability. By introducing hydrophilic segments—such as carboxyl, ester, or polyether groups—a series of rosin-based surfactants with well-defined amphiphilic structures can be conveniently synthesized[14, 15]. These surfactants not only exhibit excellent emulsification efficiency, but their distinctive spatial configuration also promotes the formation of a dense and robust adsorption layer at the interface, or facilitates self-assembly into a three-dimensional network in the aqueous phase. As a result, they simultaneously enhance both the interfacial stability and the bulk viscoelasticity of emulsions, enabling the structural transition from a conventional fluid to a gel-like emulsion[16-20]. More importantly, the functionality of rosin-based surfactants can be reversibly switched between emulsification and demulsification in response to environmental stimuli—such as pH, CO_2 , or temperature—providing a foundation for developing intelligent, controllable emulsion delivery and separation systems[21-24].

In this work, a novel rosin-based Gemini surfactant DA-3-CYS was synthesized from renewable rosin and amino acids, and was used to construct pH-responsive switchable emulsions. DA-3-CYS self-assembles into stable Pickering emulsions at pH 4–6. The effects of pH, surfactant concentration, oil–water ratio and oil type on emulsion stability and droplet

size were systematically investigated. In addition, the stability of emulsions against high temperature, freeze–thaw and centrifugation was evaluated. Importantly, the emulsifier can be recovered after acidification and reused after alkalization, realizing a green and sustainable emulsion system with good recyclability.

2. MATERIALS AND METHODS

2.1 Materials

Dehydroabiatic acid (purity >85%) and dichloromethane (AR) were purchased from Titan Technology Co., Ltd., Shanghai, China. L-Cystine (99%) and β -Alanine (99%) were purchased from Meryer Chemical Technology Co., Ltd., Shanghai, China. Thionyl chloride (CP), anhydrous methanol (AR), ethyl alcohol anhydrous (AR), sodium sulfate (AR), triethylamine (AR), ethyl acetate (AR), petroleum ether (AR) ether (AR), sodium hydroxide (AR) and hydrochloric acid (HCl, 36~38%) were obtained from Sinopharm Chemical Reagent Company, Ltd., China. n-Octane, n-Hexadecane, n-Dodecane, olive oil and soybean oil were obtained from Sinopharm Chemical Reagent Company, Ltd., China. The water used in all experiments was ultrapure water with a resistance of 18.2 M Ω ·cm.

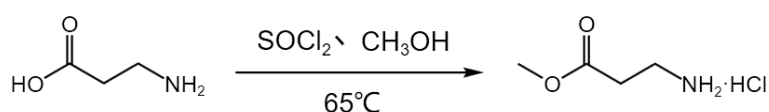
2.2 Methods

2.2.1. Beta-Alanine methyl ester hydrochloride (β -ADE) and L-Cystine Dimethyl Ester Dihydrochloride (CDE)

First, β -alanine (8.91 g, 100 mmol) and 100 mL of anhydrous methanol were placed in a 250-mL round-bottom flask. The mixture was cooled to 0–5 °C in an ice bath, and thionyl chloride (SOCl₂, 14.28 g, 120 mmol) was added dropwise. Upon completion of the addition, the mixture was heated to 65 °C and refluxed for 4 hours. After that, the excess solvent was removed by rotary evaporation, the residue was dissolved in methanol, followed by the addition of diethyl ether. After filtration and drying, β -ADE was obtained with a yield of 95.4%. The complete synthetic route of the product is shown in Scheme 1.

L-Cystine Dimethyl Ester Dihydrochloride (CDE) was synthesized according to ref.

¹H NMR (600 MHz, DMSO-d₆) δ 8.30-8.27 (s, 2H, N1-2H), 5.17-5.14 (s, 3H, C4-3H), 4.72-4.65 (t, J = 6.4 Hz, 2H, C2-2H), 4.29-4.24 (t, J = 6.4 Hz, 2H, C3-2H).



Scheme 1: synthesis of β -ADE

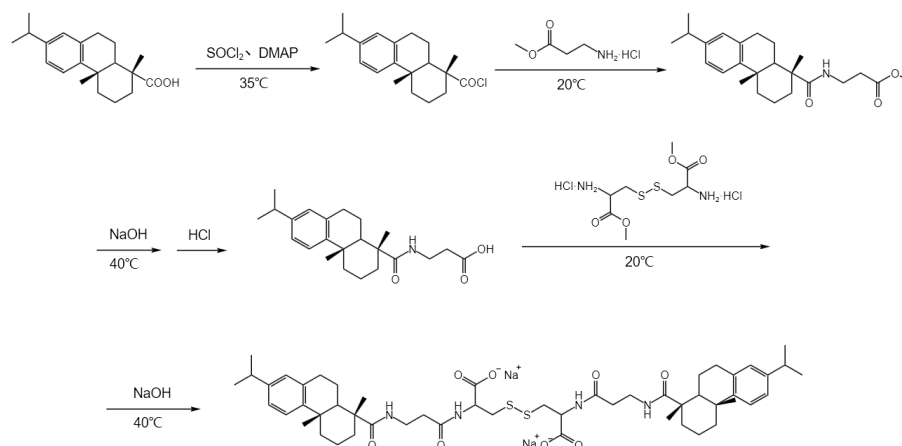
2.2.2. Synthesis of Rosin Amine Cystine (DA-3-CYS)

Dehydroabietic acid (30.00 g, 100 mmol) and a catalytic amount of 4-dimethylaminopyridine (DMAP) were dissolved in dichloromethane (DCM) in a 250-mL three-necked flask. The reaction system was heated to 35°C using a temperature-controlled oil bath, and thionyl chloride (17.85 g, 150 mmol) was added dropwise. The acidic gases evolved during the reaction (primarily HCl and SO₂) were effectively neutralized by passing them through a saturated aqueous sodium hydroxide scrubber. After completion, the solvent and excess thionyl chloride were removed under reduced pressure using a rotary evaporator, affording dehydroabietyl chloride as a golden-yellow viscous liquid with a purity suitable for subsequent reactions.

β-ADE (11.17 g, 80 mmol) and triethylamine (24.29 g, 240 mmol) were dissolved in dichloromethane. A dichloromethane solution of dehydroabietyl chloride was added dropwise at 0 °C. After the addition was complete, the reaction was allowed to proceed at room temperature for 5 hours. Upon completion, the organic phase was washed several times with sodium hydroxide solution (pH = 12), dewatering with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2:1, v/v) as the eluent. The combined fractions were concentrated in vacuo to give the intermediate, which was dissolved in absolute ethanol (100 mL). Sodium hydroxide (3.2 g, 80 mmol) was added, and the reaction system was reacted at 40 °C for 5 hours. After removal of the solvent under reduced pressure, the residue was taken up in water and acidified to pH 2–3, leading to precipitation of a solid. Ethyl acetate was added until the solid completely dissolved. The organic phase was separated, dried over anhydrous sodium sulfate, and concentrated. The residue was redissolved in dichloromethane, followed by addition of CDE (13.65 g, 40 mmol), triethylamine (24.29 g, 240 mmol), DMAP, and HATU (30.42 g, 80 mmol) were added. The reaction was stirred at 20 °C for 4 h, then washed, separated, and concentrated. The crude product was purified by column chromatography to afford a brownish-yellow viscous liquid. This liquid was treated with anhydrous ethanol and sodium hydroxide at 40 °C for 5 hours. After cooling to room temperature, ethyl acetate was added, affording a pale yellow solid. The solid was collected by filtration and dried to give DA-3-CYS in 61.5% yield. The complete synthetic route of the product is shown in Scheme 2.

¹H NMR (600 MHz, D₂O) δ 7.15–7.11(d, 1H, C5-1H), 6.89–6.86(d, 1H, C6-1H), 6.69–6.67(s, 1H, C4-1H), 3.78–4.74(s, 2H, N18-1H, N15-1H), 3.26–3.23(d, 2H, C16-2H), 3.19–3.17(d, 2H, C17-2H), 3.09–3.06(d, 1H, C19-1H), 2.86–2.82(m, 2H, C20-2H), 2.36–2.31(m, 2H,

C8-2H), 2.24-2.20(m, 1H, C3-1H), 2.16-2.14(m, 1H, C9-1H), 2.04-2.01(m, 2H, C7-2H), 1.85-1.77(m, 2H, C11-2H), 1.56-1.51(m, 2H, C12-2H), 1.44-1.40(m, 2H, C10-2H), 1.16-1.01(m, 12H, C14-3H, C1-3H, C13-3H, C2-3H).



Scheme 2: synthesis of DA-3-CYS

2.2.3. Characterization

Nuclear Magnetic Resonance (NMR) Spectroscopy: ^1H NMR spectra were recorded on a Bruker Avance III 600 MHz spectrometer at 25°C . Samples were dissolved in D_2O . Data processing was performed using MestReNova v12.0. Fourier-transform infrared (FT-IR) spectroscopy: DA-3-CYS was characterized using FTIR spectroscopy (NICOLET IS10, Thermo Scientific Company of the United States) with a scanning range of $4000\text{--}500\text{ cm}^{-1}$ and resolution of 4 cm^{-1} .

2.2.4. Surface tension

The equilibrium surface tension of DA-3-CYS aqueous solutions were measured by the Du Noüy method[25, 26]. The platinum ring had an outer diameter 19.8mm and a platinum wire diameter of 0.37 mm. Different concentrations of DA-3-CYS aqueous solutions were prepared using $18.2\text{ M}\Omega\cdot\text{cm}$ ultrapure water. The solutions were transferred into clean 100 mL beakers, sealed with plastic wrap, and equilibrated at $25 \pm 0.1^\circ\text{C}$ for 24 hours before testing. All measurements were conducted at a controlled temperature of $25 \pm 0.1^\circ\text{C}$. Each data set was measured in triplicate to ensure accuracy, and the average values were calculated. The equilibrium surface tension of DA-3-CYS was plotted as a function of the logarithmic concentration, resulting in the $\gamma\text{-log C}$ relationship curve.

2.2.5. pKa of DA-3-CYS solution

The titration endpoint of DA-3-CYS was determined using an acid–base titration method. A 1 g/L solution of DA-3-CYS was prepared in ultrapure water, and the pH was adjusted to 12 with 0.1 M NaOH. The solution was then titrated with 0.1 M hydrochloric acid in 0.05 mL

increments. The pH was monitored at 25 °C using a pH meter until a value of 2 was reached. Data were plotted as pH versus HCl volume (V), and the first derivative (dpH/dV) was calculated to identify the inflection points corresponding to the pKa values.

2.2.6. Transmittance of DA-3-CYS aqueous solution

The transmittance properties of DA-3-CYS aqueous solution were characterized using a Lambda950 UV-Vis spectrophotometer (PerkinElmer) with scanning parameters set at 200-800 nm wavelength range. For optical measurement, the sample solution was loaded into standard quartz cuvettes (1 cm path length) maintained at 25.0 ± 0.1 °C using a thermostated cell holder. Prior to measurement, baseline correction was performed with ultrapure water as reference solvent.

2.2.7. Characterization of DA-3-CYS particles

The particle size and zeta potential of the 0.1 wt% DA-3-CYS suspension was measured over a pH range of 3 to 9 using a Zetasizer instrument (Malvern, UK). All measurements were performed in triplicate at 25 °C, and the average values were reported. DA-3-CYS particles, obtained by centrifugation of suspensions at various pH values, were compressed into round disks using a tablet press. Contact angle measurements were performed using a contact angle meter (PT-602A), where 5 μ L droplets of deionized water were deposited onto the samples and the resulting contact angle was recorded.

2.2.8. Preparation of emulsions

Aqueous surfactant solutions of varying concentrations were prepared, and the pH of the DA-3-CYS solution was adjusted using HCl. An equal volume of the oil phase was then added, and the mixture was homogenized at 10,000 rpm for 3 min to form an emulsion. The morphology of the emulsions was subsequently characterized using confocal laser scanning microscopy (CLSM). The mean size and distribution of the emulsion droplets were determined using ImageJ software, where at least 200 droplets were analyzed per sample.

2.2.9. Rheology

Different concentrations of DA-3-CYS emulsions were incubated at 25°C for 24 hours, followed by frequency sweep testing from 0.1 to 100 rad/s using a Physica MCR301 rotary rheometer at 25°C.

3. RESULT AND DISCUSSION

3.1. Structure characterization of DA-3-CYS

The molecular structures of β -ADE and DA-3-CYS were characterized by FT-IR, the spectra of which are shown in Fig. 1. The β -ADE spectrum confirms the hydrochloride salt

form through a broad band at 2885 cm^{-1} , where the protonated -NH_3^+ stretching vibration overlaps with saturated C–H stretches[27]. It also displays characteristic ester peaks: 1725 cm^{-1} (C=O stretch), 1216 cm^{-1} (asymmetric C–O–C stretch), and 1123 cm^{-1} (C–N stretch). In contrast, the DA-3-CYS spectrum displays features consistent with an amide-containing, disulfide-linked molecule, including an S–S stretch at 539 cm^{-1} , saturated C–H stretches at 2917 and 2867 cm^{-1} , and amide I (1620 cm^{-1}), II (1582 cm^{-1}), and III (1484 cm^{-1}) bands that confirm peptide bond formation, alongside an additional amide carbonyl peak at 1708 cm^{-1} [28-30]. Combined with the ^1H NMR spectra (Fig. S1–S2, see Supporting Information), these results confirm that the target product DA-3-CYS was successfully synthesized.

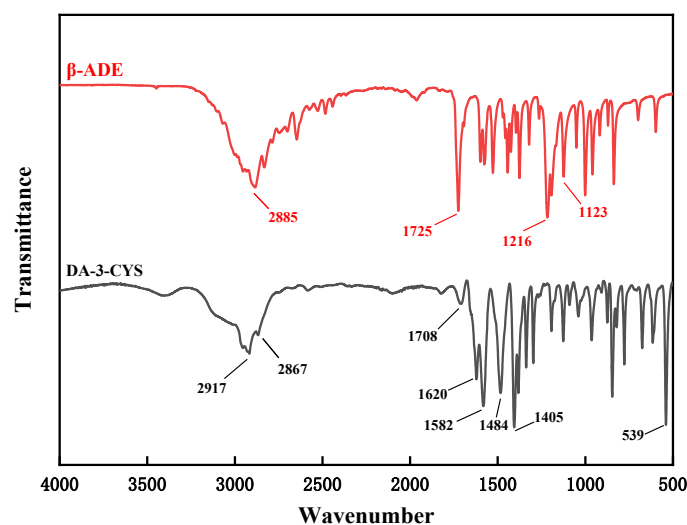


Fig. 1. FT-IR spectra of β -ADE and rosin Gemini surfactant DA-3-CYS

3.2. Surface activity of DA-3-CYS

Fig. 2 illustrates the surface tension of DA-3-CYS aqueous solutions as a function of concentration. As depicted, the surface tension decreases sharply with increasing concentration, indicating that DA-3-CYS molecules preferentially adsorb at the air-water interface, displacing water molecules and reducing the surface energy. Beyond a specific concentration, the surface tension stabilizes at a near-constant value, signifying the onset of micellization following saturated adsorption at the interface. The corresponding adsorption parameters, including the critical micelle concentration (cmc), surface tension at the cmc (γ_{cmc}), maximum surface excess (Γ^∞), and minimum surface area per molecule (A_{min}), are summarized in Table 1.

Table 1 Surface activity parameters of DA-3-CYS (25 °C)

Parameter	CMC /	γ_{CMC} /	Γ^∞ /	A^∞ /
Sample	($\text{mol}\cdot\text{L}^{-1}$)	($\text{mN}\cdot\text{m}^{-1}$)	($\mu\text{mol}\cdot\text{m}^{-2}$)	(nm^2)
DA-3-CYS	3.64×10^{-4}	34.82	2.07	0.80

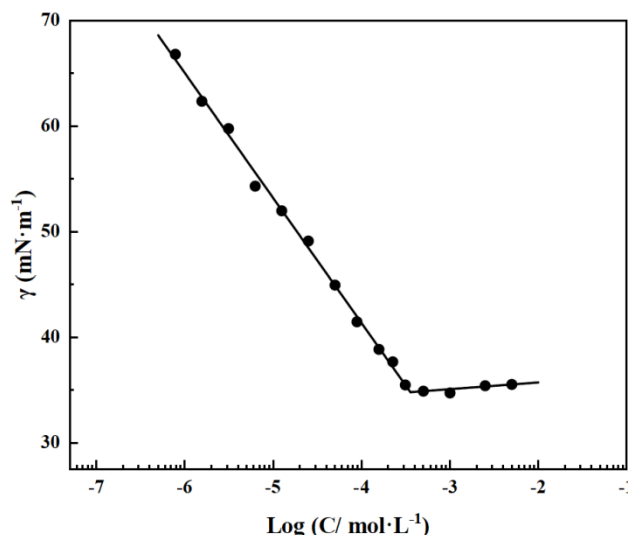


Fig. 2. Equilibrium surface tension of DA-3-CYS aqueous solutions as a function of logarithmic concentration at 25 °C

3.3. DA-3-CYS solution performance at different pH

The acid–base titration curve of DA-3-CYS (Fig. 3a) reveals two distinct inflection points, from which pKa values of 3.43 and 5.88 are determined. These two pKa values correspond to the sequential deprotonation of the two carboxyl groups. The pKa separation of 2.45 suggests limited electrostatic interaction between the two ionizable sites, likely due to the rigid spacer structure isolating the carboxyl groups. The species distribution (Fig. 3b) was calculated using the Henderson–Hasselbalch equation assuming non-interacting sites[31, 32]. The turbid solution at $\text{pH} \leq 3$ is attributed to the formation of large aggregates (confirmed by DLS, Fig. 4b) of the neutral DA-3-CYS species, which cause strong light scattering and obscure fine UV absorption features. In contrast, at $\text{pH} \geq 7$, the fully deprotonated species exists as small particles or unimers, resulting in a clear solution and distinct π – π^* absorption maxima[33]. Consistent with this speciation, the solution appearance changes markedly with pH (Fig. 3c). At pH 2–3, the dispersion is milky white and turbid; between pH 4 and 6, it becomes translucent; and above pH 7, it turns completely transparent. The UV–Vis absorption spectra (Fig. 3d) further support this pH-dependent transition. At low pH (2–3), a broad and intense background absorption appears across the entire 200–800 nm range, characteristic of strong light scattering by large aggregates, while the characteristic π – π^* absorption bands of the aromatic ring in the 200–240 nm region are heavily masked. As the pH increases, the scattering contribution diminishes, and the fine π – π^* absorption features become progressively resolved, especially at $\text{pH} \geq 7$, indicating the prevalence of molecularly dispersed or finely particulate species. These results demonstrate that the protonation state of DA-3-CYS can be precisely tuned by pH, switching the system between aggregated, partially dispersed, and fully dissolved states.

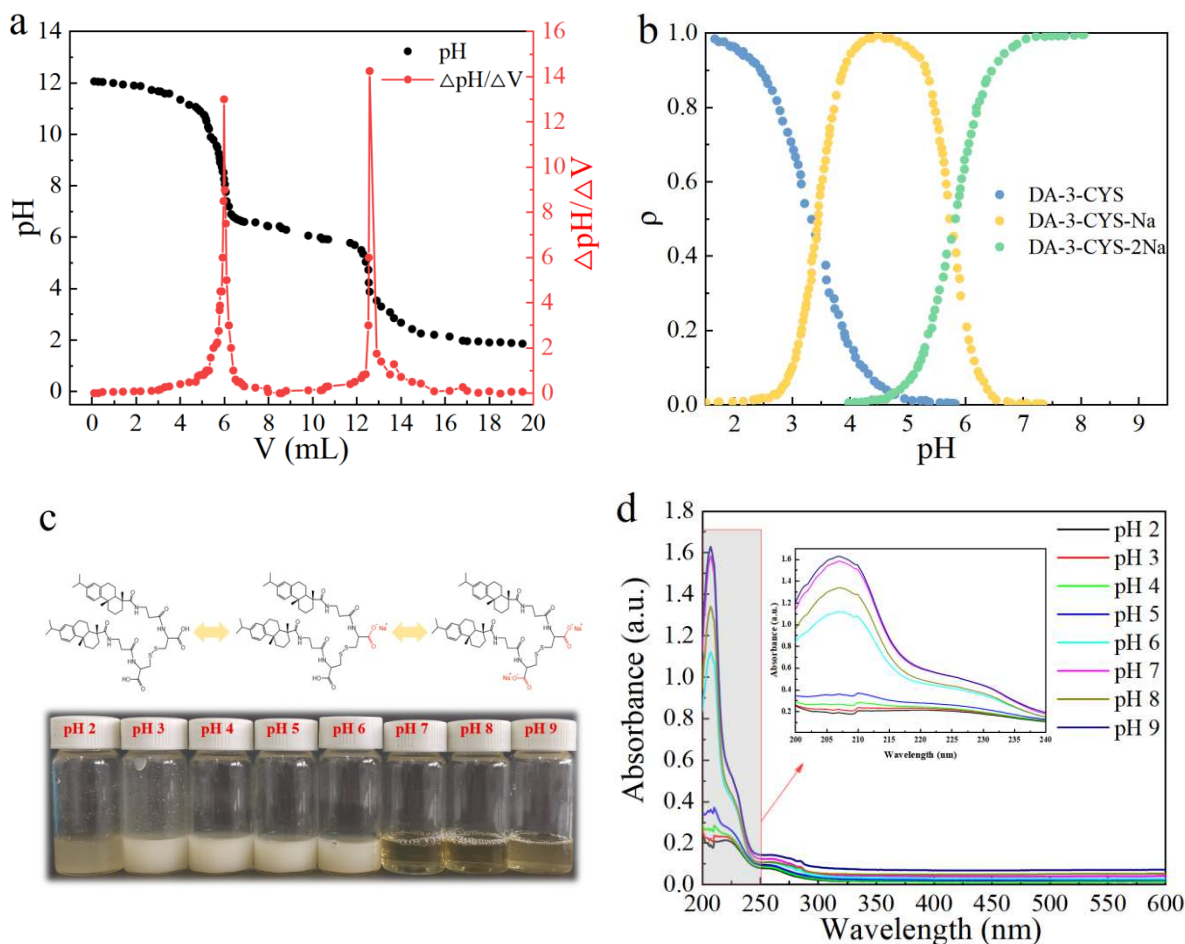


Fig. 3. (a) Acid–base titration curve of aqueous DA-3-CYS: pH and first derivative ($\Delta\text{pH}/\Delta V$) vs. titrant volume. (b) Species distribution (DA-3-CYS, DA-3-CYS-Na, DA-3-CYS-2Na) as a function of pH. (c) Schematic of pH-responsive structural transformation and corresponding solution appearance at pH 2–9. (d) UV–Vis absorption spectra of DA-3-CYS at pH 2–9; inset: magnified view of the 200–240 nm

3.4. Structures, colloidal behavior, and interfacial properties of DA-3-CYS at different pH

Data from Figure 4 demonstrate how pH regulates the protonation state, colloidal behavior, and interfacial wettability of DA-3-CYS. FTIR spectra (Fig. 4a) confirm the conversion of protonated $-\text{COOH}$ (1691 cm^{-1}) to deprotonated $-\text{COO}^-$ (1559 cm^{-1}) under alkaline conditions[34]. Particle size distribution (Fig. 4b) decreases significantly with increasing pH: at low pH, weak charge and hydrophobic attraction induce aggregation (size $> 1000\text{ nm}$ at pH 3), whereas at high pH, enhanced electrostatic repulsion maintains fine dispersion (around 200 nm at pH 9). Zeta potential (Fig. 4c) becomes increasingly negative above pH 5.88, consistent with the second pK_a value, indicating improved colloidal stability. The water contact angle of compressed DA-3-CYS pellets (Fig. 4d) declines continuously from acidic to neutral conditions, reflecting enhanced surface hydrophilicity upon deprotonation. Although the water contact angle remains above 90° even at pH 6 (approximately 100°), the particles can still stabilize O/W

Pickering emulsions. This apparent discrepancy arises because the contact angle measured on a flat pellet may overestimate the intrinsic wettability of individual nanoparticles at the curved oil–water interface. Additionally, partial protonation at pH 4–6 renders the particles interfacially active, enabling irreversible adsorption and formation of a mechanically robust layer[35, 36]. Thus, the combination of pH-tunable aggregation, charge, and wettability allows DA-3-CYS to function as an effective Pickering emulsifier under mildly acidic conditions.

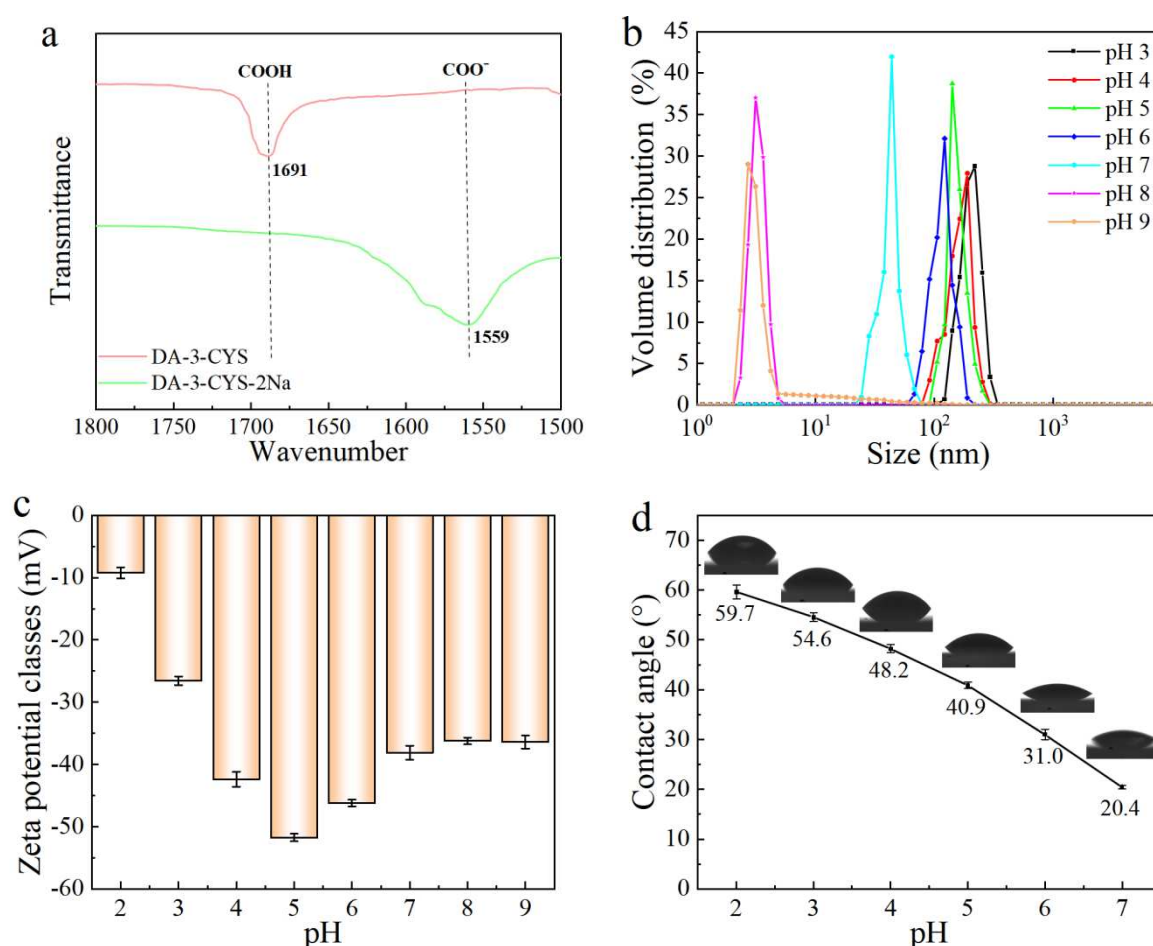


Fig. 4. (a) FT-IR spectra of DA-3-CYS at acidic and alkaline conditions; (b) Particle size distribution of DA-3-CYS suspensions at pH 3–9; (c) Zeta potential of DA-3-CYS particles as a function of pH; (d) Water contact angle of DA-3-CYS pellets at different pH values

3.5. pH-Dependent Emulsion Stability and Droplet Size

The long-term storage stability of n-dodecane/water emulsions stabilized by 4 mM DA-3-CYS is highly pH-dependent (Fig. 5). After 30 days, emulsions prepared at pH 2–6 remain homogeneous and stable without obvious phase separation. In contrast, those at pH 7–9 undergo severe oil–water demulsification, particularly at pH 9 where complete phase separation occurs. All emulsions are verified to be of the oil-in-water (O/W) type, indicating that acidic to near-neutral conditions favor sustained emulsion stability.

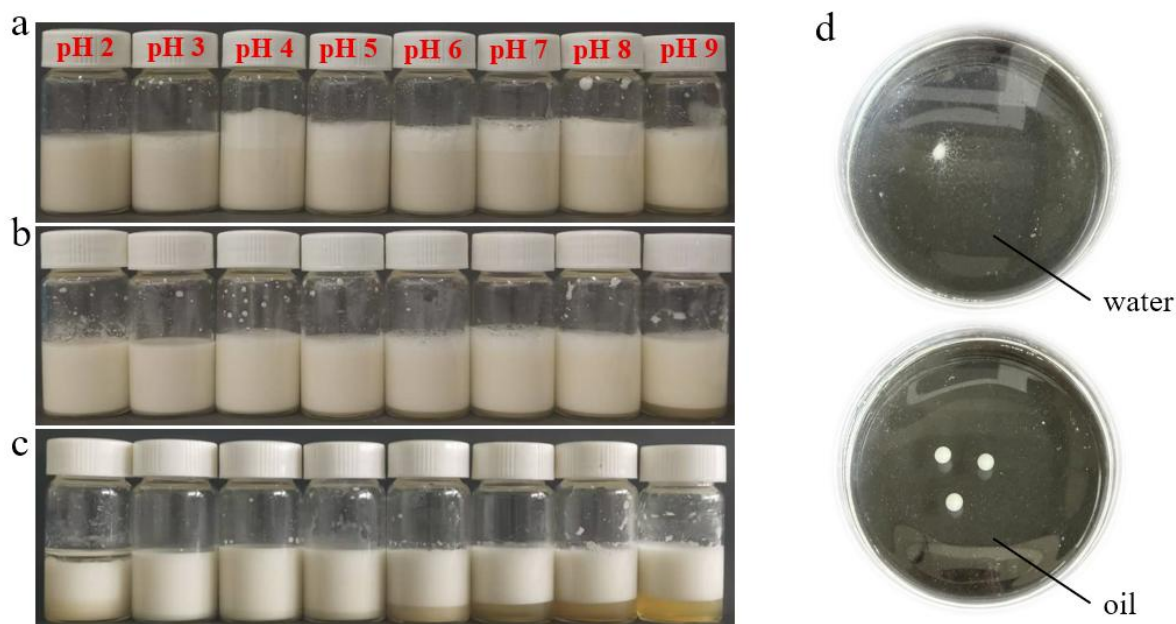


Fig. 5. Stability of DA-3-CYS-stabilized emulsions at pH 2–9: (a–c) Visual appearance after 1 day, 7 days, and 30 days of storage; (d) Emulsion type identification

At pH 2–3, DA-3-CYS exists as large aggregates ($>1\ \mu\text{m}$) with low charge, yet the emulsions remain stable for 30 days. This suggests a Pickering-type stabilization, where solid particles mechanically block droplet coalescence regardless of their size, provided they are sufficiently surface-active[37]. In contrast, at $\text{pH} \geq 7$, the fully deprotonated species are either molecularly dissolved or form very small aggregates ($<200\ \text{nm}$) with high negative charge, preventing effective adsorption at the oil–water interface, thus leading to rapid demulsification.

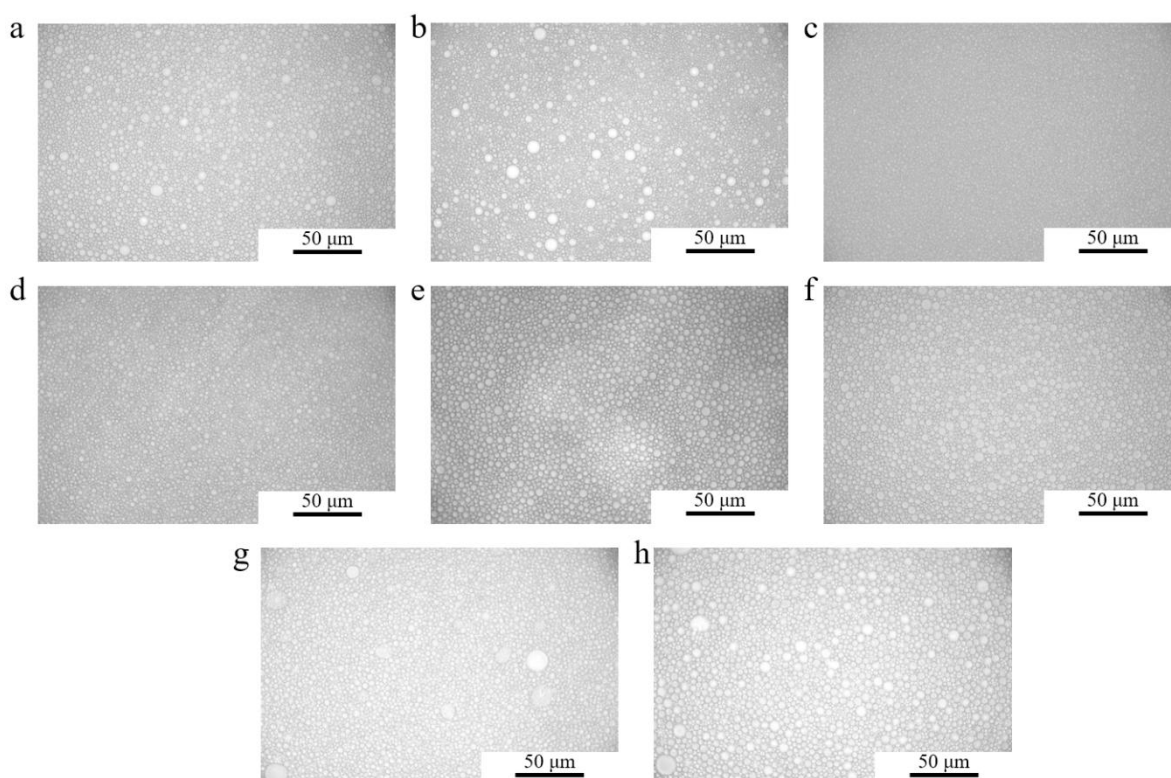


Fig. 6. CLSM images of n-dodecane/water emulsions stabilized by DA-3-CYS at (a) pH 2, (b) pH 3, (c) pH 4, (d) pH 5, (e) pH 6, (f) pH 7, (g) pH 8, (h) pH 9. Scale bar: 50 μm

The influence of pH on droplet size and distribution is presented in Figures 6 and 7. Emulsions at pH 2–6 exhibit small, narrowly distributed droplets with average diameters of 8–12.5 μm , attributed to the compact and stable interfacial film formed by moderately hydrophobic DA-3-CYS aggregates (at low pH) or partially deprotonated species (at pH 4–6)[38]. When the pH increases to 7–9, the average droplet size rises sharply to approximately 20 μm with a broadened distribution. This is because excessive deprotonation of the carboxyl groups above pH 5.88 enhances molecular hydrophilicity excessively and weakens interfacial adsorption, thereby accelerating droplet coalescence and emulsion destabilization.

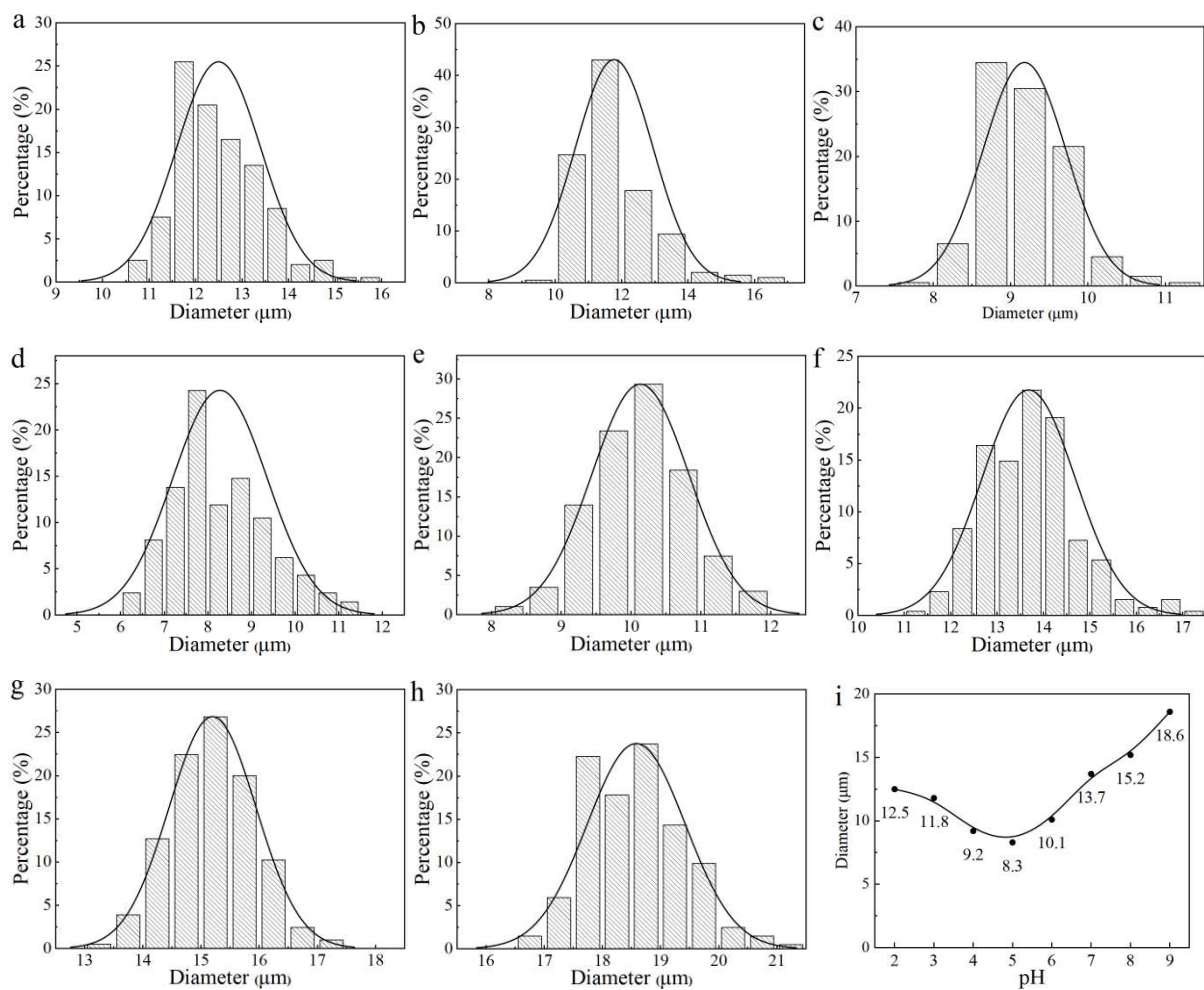


Fig. 7. Droplet size distribution of DA-3-CYS stabilized emulsions at (a) pH 2, (b) pH 3, (c) pH 4, (d) pH 5, (e) pH 6, (f) pH 7, (g) pH 8, (h) pH 9, (i) pH dependence of the average droplet size of DA-3-CYS-stabilized emulsions (n-dodecane/water)

3.6. Effect of DA-3-CYS Concentration on Emulsion Properties

The relationship between DA-3-CYS concentration and droplet size at different pH values is illustrated in Figures 8 and 9. At pH 4, 5, and 6, the droplet size decreases monotonically with increasing surfactant concentration. For a given pH, higher DA-3-CYS loading generates a

denser and stronger interfacial film, effectively suppressing droplet coalescence. At identical concentrations, emulsions at pH 6 exhibit slightly larger droplets than those at pH 4 and 5, especially below 2 mM, because the elevated pH promotes deprotonation and weakens interfacial adsorption. This difference diminishes at concentrations above 2 mM, where sufficient DA-3-CYS compensates for the reduced interfacial affinity, resulting in similarly small and stable droplets around 10 μm . These results identify pH 4–5 and concentrations ≥ 2 mM as the optimal conditions for preparing stable emulsions with fine droplet size.

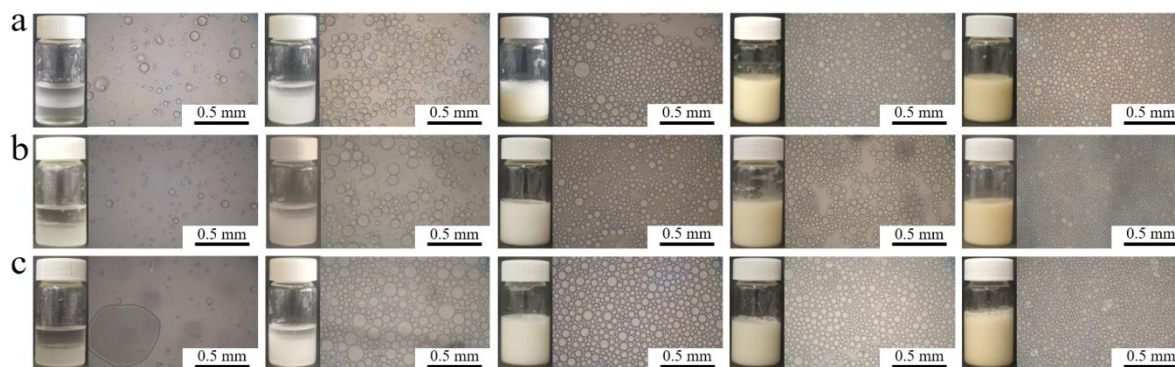


Fig. 8. CLSM images of n-dodecane/water emulsions stabilized by DA-3-CYS at pH 4 (a), pH 5 (b), and pH 6 (c), with concentrations varying from 0.1 to 5 mM (left to right: 0.1, 1, 2, 4, 5 mM). Scale bar: 50 μm

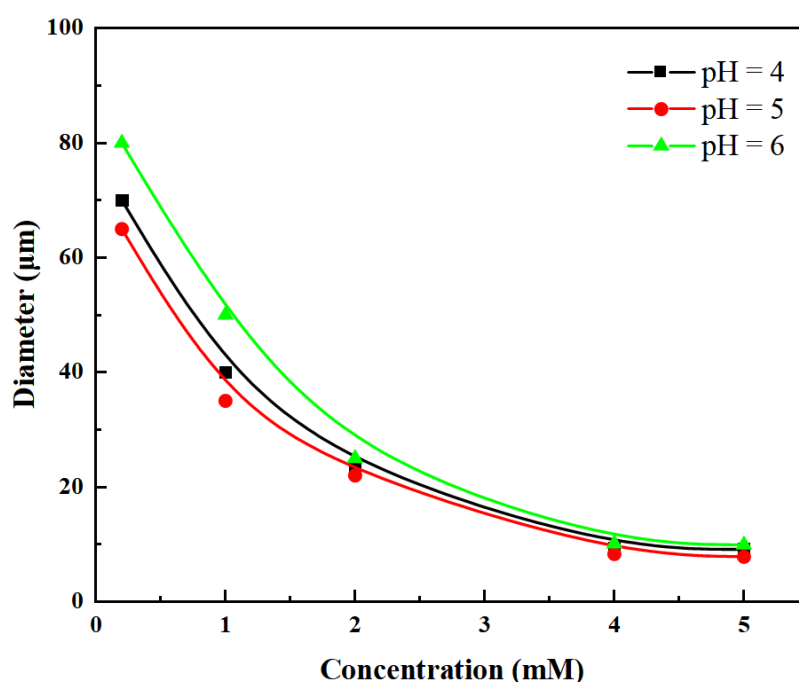


Fig. 9. Average droplet diameter of emulsions as a function of DA-3-CYS concentration at pH 4, 5 and 6

3.7. Effects of Different Oil/Water Ratios on Emulsion Properties

The effect of the oil-to-water ratio on droplet size and morphology is shown in Figure 10. The average droplet diameter decreases gradually as the oil fraction increases from 30% to 70%,

accompanied by a narrower size distribution. A low oil fraction of 30% leads to relatively large and inhomogeneous droplets, whereas oil fractions of 50%–70% produce smaller and more uniform droplets due to enhanced spatial hindrance between emulsion droplets[39].

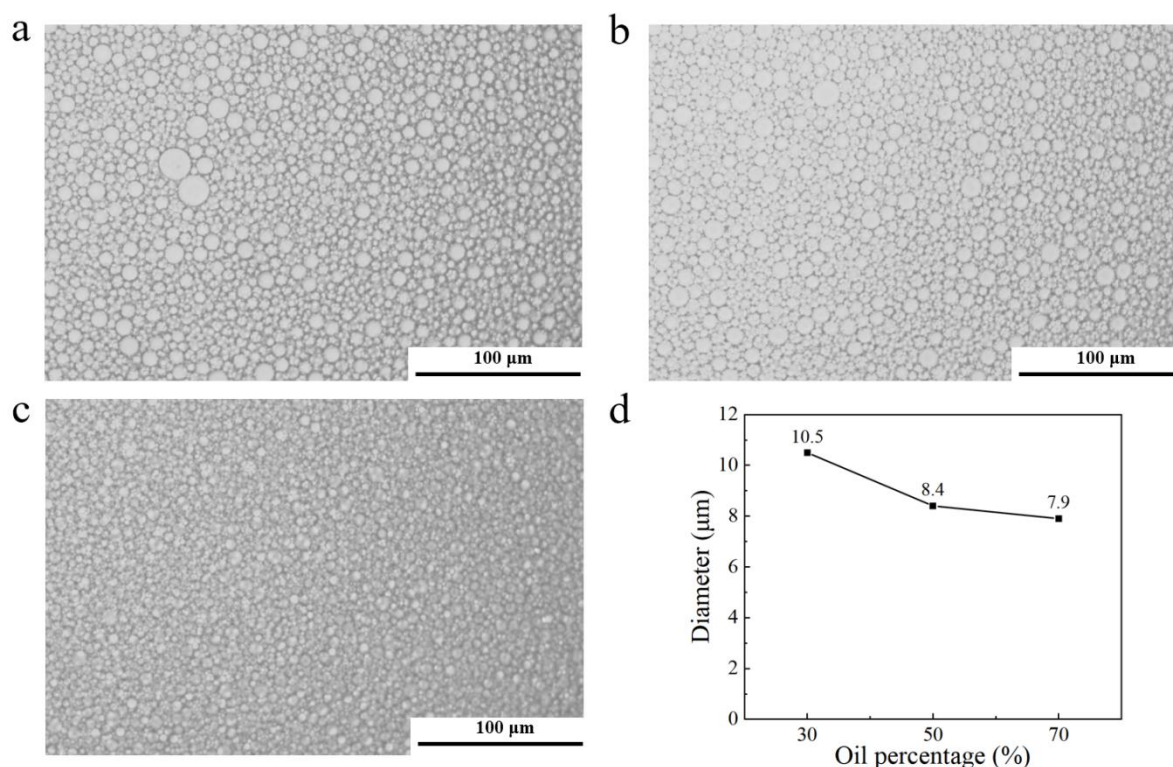


Fig. 10. (a–c) CLSM images and (d) average droplet diameter of emulsions with different oil volume fractions (30%, 50%, 70%). Scale bar: 100 μm.

Rheological measurements further elucidate the impact of the oil phase fraction (Figure 11). Both the storage modulus (G') and loss modulus (G'') increase significantly with rising oil fraction. Across the entire frequency range, G' remains consistently higher than G'' , and both moduli exhibit weak frequency dependence, especially at a 70% oil fraction. At 70% oil fraction, the emulsion exhibits a high G' that remains nearly frequency-independent, indicating a strong, solid-like gel network. This behavior is attributed to the combination of a dense interfacial film and high droplet packing fraction, which restricts droplet mobility and suppresses coalescence[40, 41]. The lower G' and stronger frequency dependence at 30% oil fraction reflect a less constrained droplet arrangement. This rheological behavior confirms the formation of a gel-like network structure with solid-like characteristics, which greatly enhances the structural stability and shear resistance of DA-3-CYS-based emulsions.

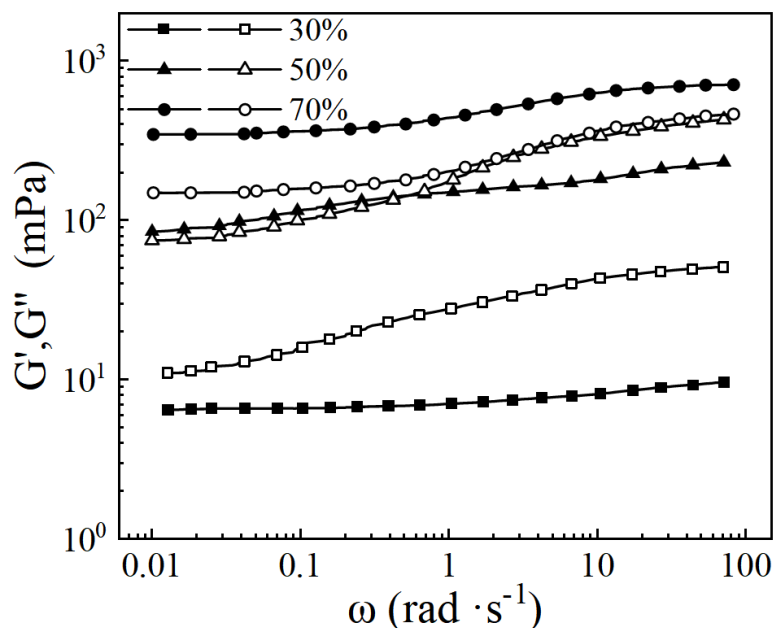


Fig. 11. Storage modulus (G') and loss modulus (G'') of emulsions with 30% and 70% oil fractions as a function of angular frequency.

3.8. Stability of DA-3-CYS Emulsion Properties

As evidenced by Figure 12, the n-dodecane/water emulsions stabilized by DA-3-CYS exhibit favorable stability against elevated temperature and centrifugation. After heating at 50–80 °C for 1 h, no obvious demulsification or phase separation occurs, and only a modest increase in droplet diameter is observed, confirming robust interfacial stability at high temperatures. Under centrifugation, the emulsions remain homogeneous below 2000 rpm, with only slight phase separation appearing at higher speeds. This phase separation likely arises from sedimentation of larger droplets rather than coalescence, as no significant increase in average droplet size is detected in the sedimented phase[42]. Nevertheless, the interfacial film retains sufficient mechanical strength to preserve droplet integrity under strong external forces.

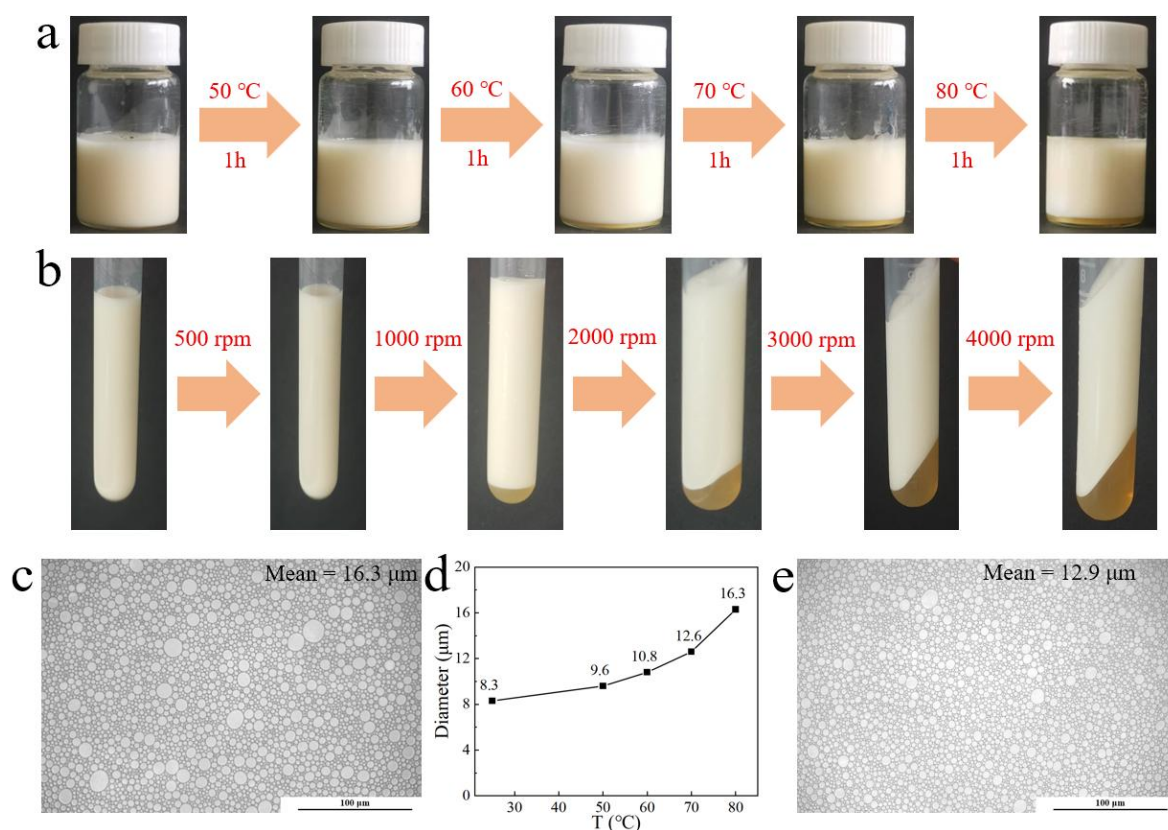


Fig. 12. Stability of DA-3-CYS-stabilized emulsions under different conditions: (a, c, d) Visual appearance and droplet size evolution after thermal treatment (50–80 °C); (b, e) Visual appearance and droplet size after centrifugation (500–4000 rpm)

3.9. DA-3-CYS Emulsion Circulation and Oil Phase Recovery

The excellent pH-responsive reversibility and recyclability of the DA-3-CYS-stabilized emulsion are summarized in Figure 13. Alternating addition of HCl and NaOH enables complete switching between emulsification and demulsification. After six cycles, the average droplet diameter remains stable at approximately 9–10 μm without obvious coalescence. Furthermore, ¹H NMR spectra confirm that the chemical structure of the recovered oil phase remains intact, showing no degradation[43]. These results demonstrate efficient oil recovery and good reusability of this pH-responsive emulsion system.

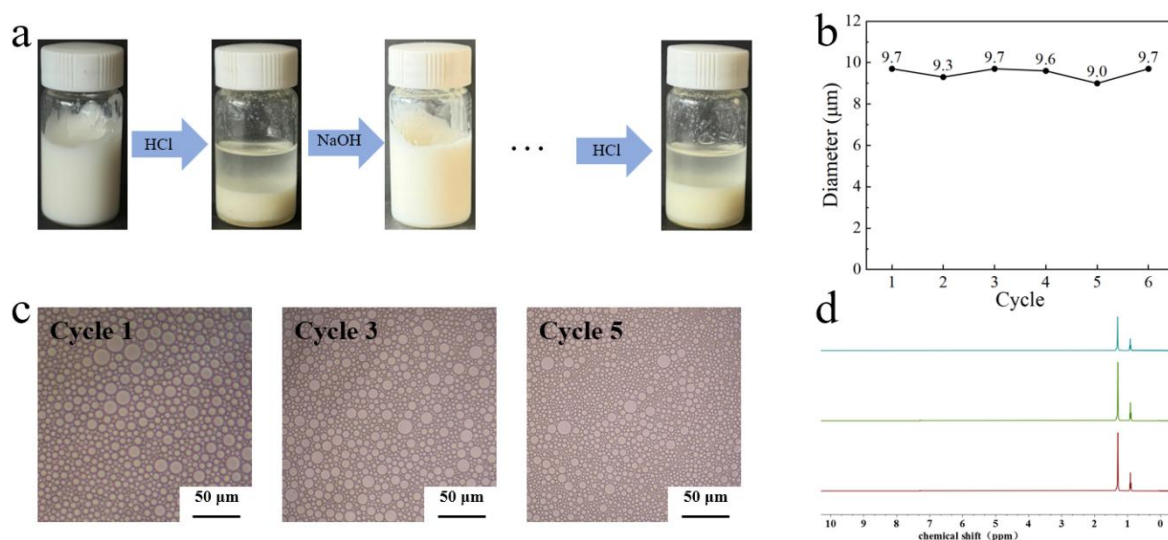


Fig. 13. pH-responsive reversible emulsification/demulsification cycles: (a) Schematic of the process; (b, c) Evolution of average droplet diameter and size distribution over six cycles; (d) ¹H NMR spectra of the recovered oil phases.

3.10. Emulsification performance of DA-3-CYS in different oil phases

The emulsifying performance of DA-3-CYS varies strongly with the oil type (Figure 14). Linear alkanes, including n-octane, n-decane, and n-dodecane, produce smaller and more uniform emulsion droplets, whereas vegetable oils such as soybean oil and olive oil result in larger droplets with a broader size distribution. The average droplet diameters follow the order: olive oil (16.7 μm) > soybean oil (12.4 μm) > n-octane (10.1 μm) > n-decane (9.8 μm) > n-dodecane (8.3 μm). These differences originate from variations in polarity, viscosity, and interfacial tension among the oil phases, indicating that DA-3-CYS is more efficient at emulsifying nonpolar alkane oils.

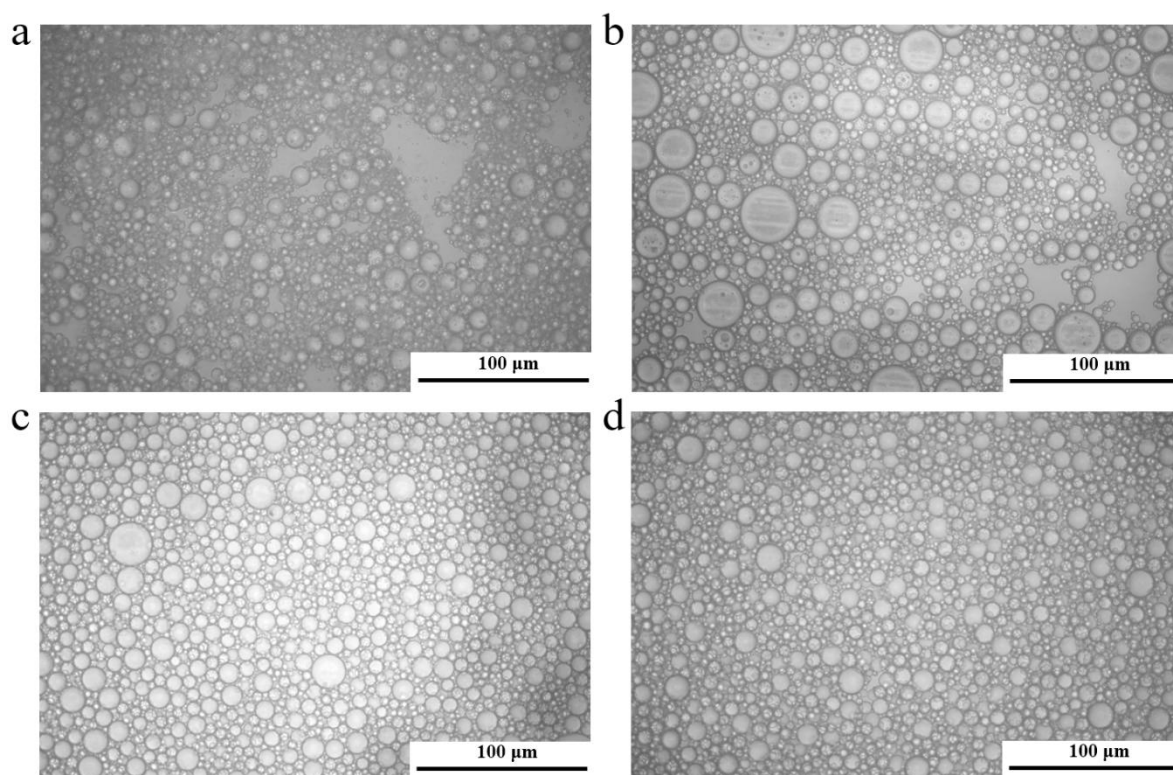


Fig. 14. CLSM images of emulsions stabilized by DA-3-CYS using different oil phases: (a) soybean oil, (b) olive oil, (c) n-octane, and (d) n-decane. Scale bar: 100 μm .

4. CONCLUSION

A novel rosin-based pH-responsive Gemini surfactant DA-3-CYS was successfully synthesized, and applied as a particulate stabilizer to construct pH-switchable Pickering oil-in-water emulsions. DA-3-CYS possesses two pK_a values of 3.43 and 5.88, and its reversible protonation–deprotonation transition can be precisely modulated by pH, thereby controllably regulating the formation and stabilization of Pickering emulsions. Well-stabilized Pickering emulsions with fine droplet size and superior long-term storage stability can be fabricated under the optimal conditions of pH 4–6, DA-3-CYS concentration ≥ 2 mM and oil fraction of 50–70%. The as-prepared Pickering emulsions display remarkable tolerance to high temperature and moderate centrifugal treatment. Furthermore, reversible emulsification–demulsification switching and efficient oil phase recovery can be readily achieved simply by pH regulation, and the recovered oil maintains intact chemical structure without degradation after multiple cycles. This study establishes a green, recyclable and pH-controllable Pickering emulsion platform based on renewable rosin biomass, which presents bright application prospects in the development of intelligent interfacial materials and oil separation and recycling fields.

5. AUTHOR CONTRIBUTIONS

Rong Li conceived and designed the study. Yin Luo wrote the first draft, carried out the research, and analyzed the data. All authors contributed to and approved the final draft of the manuscript.

6. CONFLICT OF INTEREST STATEMENT

The authors declare that they have no conflict of interest.

7. ETHICS STATEMENT

No human or animal subjects were used in this research.

8. DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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