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Paper

Coacervation of Dynamic Covalent Surfactant with Polyacrylamide: Property and Application

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Dynamic covalent surfactants have been prepared from the mixture of 4-formyl-N, N, N-trimethylbenzenaminium iodide (FBA) with heptylamine (C_7A) or octylamine (C_8A) in alkaline aqueous solutions. The reversible pH-dependent nature of imine bond is characterized by ^1H NMR and fluorescence analysis. The dynamic covalent surfactants self-assemble into micelles in alkaline condition and form coacervation with 10% hydrolyzed polyacrylamide (PAM) over a wide concentration range. The coacervate phase with a net-work structure was found to effectively extract anionic dye Conge Red (CR). When the solution is adjusted to acidity, the imine bond is hydrolyzed, leading to the transition of coacervates into a homogeneous and clear solution, and the precipitation of CR into purple-black solids due to the protonation of sulfonic groups. Thus the extraction and release of CR molecules are realized with the dynamic covalent surfactant/PAM system. Moreover the initial components, FBA, amine, and PAM, can be easily regenerated with hydrochloric acid. This method shows potential applications in wastewater treatment.

Introduction

Coacervation, i.e. liquid-liquid phase separation, is a spontaneous formation of two immiscible liquid phases in a colloidal dispersion: a dense coacervate phase and a diluted phase.[1,2] Coacervation has attracted a growing interest because of its utility in protein purification,[3,4] water treatment,[5] drug encapsulation[6,7] and cosmetic formulation.[8] Separation and extraction via coacervation as a well-known approach, have been utilized for long years, because it has an array of superior properties, for instance, non-volatility and non-flammability, high preconcentration factors, and tunability of coacervate polarity for enriching both organic and inorganic compounds.[9-11] Many studies have reported the application of nonionic surfactant coacervation as a function of temperature in the extraction of hydrophobic organic compounds, i.e. cloud point extraction technique, and the main driving force of phase separation is hydrophobic interaction.[12-14] Recent years, ionic surfactant-mediated coacervation, enlarges the scope of coacervation in extraction applications[15-17] because of its more binding sites. In order to realize the release of extracted compounds from coacervation, stimulus-responsive coacervation is desired. Applying dynamic covalent surfactants[18] to construct coacervation is here expected to be one of the most effective approaches to extract and release organic compounds.

Dynamic covalent surfactants switch the structure and property of surfactants between amphiphilic and non-amphiphilic characteristics by utilizing dynamic covalent bonds, which convert between covalent bonds and non-covalent bonds under a certain stimulus.[19-23] Stimulus-responsive dynamic covalent bonds include hydrazones, imines (Schiff bases), disulfides, acetals, carboxylic and boronic esters.[24] Imine bonds display good product stability and fast kinetics under mild reaction conditions, forming in neutral or basic solutions but being hydrolyzed under weakly acidic condition. Thus imine bonds have been widely used as dynamic covalent bonds to constructing diverse functional surfactants. Nguyen et al.[25, 26] fabricated nonionic dynamic covalent surfactants by the condensation of a p-substituted benzyl aldehyde with a hydrophobic tail and aliphatic, benzylic, aromatic, and hydroxy amines, which show different equilibrium constants and self-assembled structures. The group of van Esch[27] reported a cationic dynamic covalent surfactant which utilizes an imine bond to link aromatic aldehyde and alkyl amine of different chain length, and found that the micellization of the surfactant is responsive to pH and temperature. The surfactant is stable under mild basic conditions, but dissociated into a non-aggregated and non-amphiphilic state under neutral or mild acidic conditions due to the imine hydrolysis. The group[28, 29] also fabricated gemini surfactant and the surfactant with one head and two hydrophobic tails by bis-aldehyde and alkyl amines, and the surfactants separately form worm-like micelles and vesicles and display responsive behaviors to the imine bonds between a non-aggregated state and an aggregated state. Zhang group[30, 31] employed pH-responsive imine bond to form bola-shaped and H-shaped surfactants

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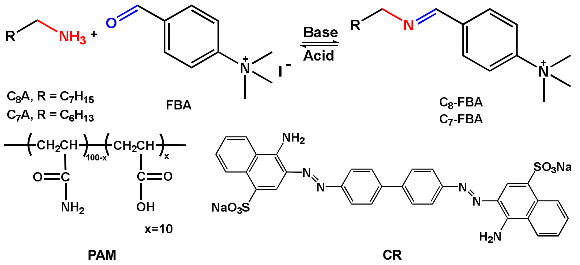
with both amino and benzyl aldehyde moieties. Compared with the surface-active building blocks, both the surfactants display stronger self-assembling ability, depending on critical hydrolysis pH values. In addition, this kind of pH-responsive dynamic imine surfactants was also exploited in building stimuli-responsive emulsion,[32] supramolecular gel,[33, 34] and selective sensors.[35] However, so far coacervation based on dynamic covalent surfactants has not yet been reported.

Herein we report a pH-responsive coacervation system formed by 10% hydrolyzed polyacrylamide (PAM) and cationic ammonium dynamic covalent surfactants (C_7-FBA, C_8-FBA) to realize the extraction and release of anionic dye Conge Red (CR) (Scheme 1). The dynamic covalent surfactants (DS) are formed by connecting 4-formyl-N, N, N-trimethylbenzenaminium iodide (FBA) with heptylamine (C_7A) or octylamine (C_8A) through a dynamic imine bond. In alkaline conditions, both C_7-FBA and C_8-FBA can self-assemble into small micelles. When PAM is added, coacervation takes place in the mixture due to the balance of hydrophobic, electrostatic, and solvent interactions. The coacervate phase with net-work structure is efficient in extracting CR. By changing the pH of the coacervate to acidic values, the imine bond is hydrolyzed and the composition in coacervates is transformed to non-aggregated state, leading to the release of CR.



Scheme 1 Molecular Structures of FBA, Dynamic Covalent surfactants (C_7-FBA and C_8-FBA), CR and PAM.

Experimental section

Materials

4-Dimethylamino benzaldehyde, heptylamine (C_7A), octylamine (C_8A), and nile red (NR) were purchased from Acros company with a purity higher than 99%. Iodomethane was purchased from Energy Chemical company. Polyacrylamide (PAM), 10% hydrolyzed, was purchased from Sigma and the average molecular weight is approximately 200000. The pK_a value of carboxylate groups of PAM is about 4.60. Congo Red (CR > 98%) was purchased from the TCI company. All organic solvents used in the experiments were purchased from Beijing Chemical Works and were dried and distilled before use. Deionized water (18.2 MΩ·cm) from Milli-Q equipment was used in all experiments. ^1H NMR and ^{13}C NMR of FBA were recorded on a Bruker Avance 400 MHz spectrometer. Mass spectra (ESI) were measured on a SHIMADZU LCMS-2010 spectrometer and elemental analysis measurement was recorded on Flash EA1112.

Synthesis of 4-Formyl-N, N, N-trimethylbenzenaminium Iodide (FBA)

Compound FBA was synthesized according to Figure S1 and characterized by ^1H NMR, ^{13}C NMR, mass spectra, and elemental analysis. Compound 4-dimethylamino benzaldehyde (4.47 g, 30.0 mmol) and iodomethane (9.34 mL, 150.0 mmol) were dissolved in 40 mL acetone. After being stirred and refluxed at 70 °C for 8 hours, the mixture was filtered to obtain the yellow precipitates. Crystallization from methanol gave pure FBA as white solid (40% yield). ^1H NMR (400 MHz, D_2O, ppm): δ 3.76 (s, 9H, CH_3), 8.12 (d, 2H, CH, J = 9.00 Hz), 8.24 (d, 2H, CH, J = 9.08 Hz), 10.09 (s, 1H, CHO). ^{13}C NMR (D_2O, ppm): 57.08, 121.07, 131.82, 136.80, 150.72, 194.34. MS-ESI (m/z, $[M + H]^+$): calcd, 164.1; found, 164.2.

Surface Tension Measurements

The surface tension measurements of the dynamic covalent surfactants at pH 12.2 and the protonated amines at pH 1.5 were conducted using a Pt/Ir plate method on a DCAT21 tensiometer (Dataphysics Co., Germany). The experiments were carried out at 25.00 ± 0.01 °C and the calibration of the tensiometer by measuring pure water before each set of measurements. Each surface tension curve was repeated at least twice. The critical micellar concentrations (CMC) of the dynamic covalent surfactants were determined from the surface tension curves.

Dynamic Light Scattering (DLS)

The size distribution of C_7-FBA and C_8-FBA aggregates at pH 12.2 was studied by Nano ZS (Malvern Instruments) at a scattering angle of 173° equipped with a 4 mW He−Ne laser ($\lambda = 632.8$ nm) and a thermostated chamber at 25.0 ± 0.1 °C.

Fluorescence Measurement

The fluorescence spectra of Nile red (NR) in the dynamic covalent surfactants were obtained at 25.0 ± 0.1 °C by a Hitachi F-7000 fluorescence spectrophotometer. NR, a hydrophobic molecule, was used to probe the polarity of the microenvironment in the aggregates. The concentration of NR was kept around 5 μM. The NR probe in the solution was excited at 565 nm, and the maximum emission wavelength (λ_{max}) of dynamic covalent surfactants at different concentrations was recorded by the fluorescence spectrophotometer.

Coacervate Phase Extraction and Release

UV-vis absorption measurements were carried out on a Shimadau UV 2800 spectrometer to study the extraction and release efficiency of CR by coacervate phase. 2 mL mixed solution of dynamic covalent surfactant, PAM and CR was prepared in a centrifuge tube. The aqueous suspension was stand for 12 h and then centrifuged at 8000 rpm for 7 min to separate coacervate phase and dilute phase. The concentration of CR in the dilute phase, i.e., supernatant, was determined by the UV spectrometer and the amount of CR

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extracted by coacervate phase was calculated from the relationship, extraction efficiency (%) = $(C_0 - C_e)/C_0$, where C_0 is the initial concentration of dye and C_e is the equilibrium concentration of dye (mM) in the supernatant. After removing the dilute phase, the pH value of the coacervate phase was adjusted to 1.5 and CR was released as purple-black precipitate. The release amount of CR was calculated by the initial and final concentrations of CR in the solution. The experiments were performed at 25.0 °C.

Turbidity Measurement

The turbidity values of the aqueous solutions of dynamic covalent surfactants and PAM mixtures were measured against the surfactant concentration or pH at 670 nm using a Brinkman PC920 probe colorimeter or a Shimadzu UV–vis spectrophotometer (model UV-2800) thermostatted at 25.0 ± 0.01 °C. All the measured values were corrected by taking the turbidity of water at pH 12.2 as zero.

Scanning Electron Microscopy (SEM)

The morphology of the coacervate formed by the dynamic covalent surfactants and 0.50 wt % PAM was imaged with a field-emission scanning electron microscope (Hitachi S-4800). The samples were prepared by freezing a small drop of coacervate on a clean silica wafer with liquid nitrogen so that the microstructure of the coacervate phase was retained. Immediately afterward, the frozen sample was lyophilized under vacuum at about −55 °C. Finally, a 1–2 nm Pt coating completed the sample preparation.

Light microscopy

The image of the liquid-liquid phase separation was captured with 10 μL of the mixed solution of dynamic covalent surfactants and 0.50 wt % PAM by a light microscope (XSP-8C(8CA)) with a mounted digital camera.

^{1}H NMR Spectroscopy

^{1}H NMR measurements of the dynamic covalent surfactants were performed on a Bruker AV400 FT-NMR spectrometer operating at 25 ± 2 °C. Deuterium oxide (99.9%) was purchased from CIL (Cambridge Isotope Laboratories) and used to prepare the stock solutions of the dynamic covalent surfactants. The center of the HDO signal (4.790 ppm) was used as the reference in the D_2O solutions.

Results and discussion

Formation of Dynamic Covalent Surfactants

FBA forms dynamic covalent surfactants (C_7-FBA and C_8-FBA) with C_7A or C_8A through a pH-responsive imine bond. The formation of imine bond was confirmed by ^{1}H NMR. Herein, C_7-FBA is chosen as a representative with the results shown in Figure 1. Compared with the ^{1}H NMR spectrum of FBA, the spectrum of the equimolar mixture of FBA and C_7A at pH 12.2 is obvious different. The peak of aldehyde group (-CHO) at 10.06 ppm nearly cannot be found anymore, while a new peak around 8.45 ppm appears, indicating the formation of imine bond in the dynamic covalent surfactant C_7-FBA. Then, by adjusting the pH of the solution to acidic condition, the peak of imine bond at 8.45 ppm disappears, and meanwhile the peak of -CHO reappears, demonstrating the hydrolyzation of imine bond in C_7-FBA. In order to further confirm the formation of dynamic covalent surfactants, elemental analysis of C_7-FBA, C_8-FBA, and FBA solids are also performed as shown in Table S1 (Supporting Information). The experimental values are consistent with the theoretical values of C, H, and N compositions. The MS-ESI spectra of 20 mM C_7-FBA and 20 mM C_8-FBA at pH 12.2 (Figure S2) show the main peaks belonging to the formed C_7-FBA or C_8-FBA. All the above results confirm the formation of the dynamic covalent surfactants. Obviously the dynamic covalent surfactants can be formed or dissociated by conveniently controlling the pH-responsive imine bond.

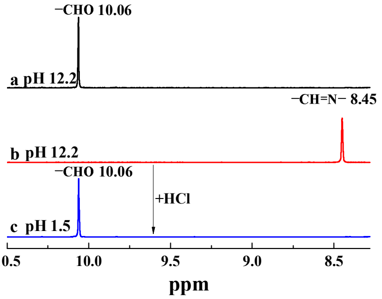

Figure 1 ^{1}H NMR spectra of (a) 20 mM FBA, (b) 20 mM C_7-FBA at pH 12.2, and (c) 20 mM C_7-FBA at pH 1.5.

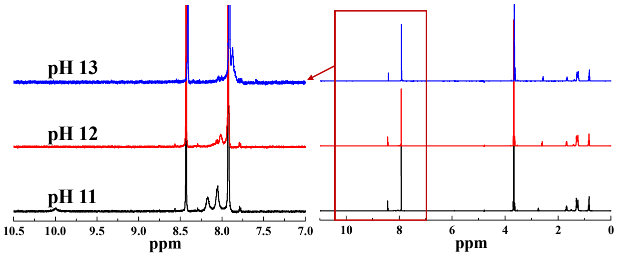

Figure 2 ^{1}H NMR spectra of 20 mM C_7-FBA at different pH values.

Figure 2 shows the ^{1}H NMR spectra of 20 mM C_7-FBA at different pH values. The peak around 8.4 ppm and 10.0 ppm are respectively assigned to the imine proton and aldehyde proton. As the pH increases，the peak for aldehyde proton weakens significantly, while the intensity of imine proton peak increases, indicating the higher imine bond conversion efficiency at high pH value. The imine bond conversion can be roughly estimated by the ratio of $A_1/(A_1 + A_0)$, where A_1 and A_0 are separately defined as the integral intensity values of the peaks of the imine proton and aldehyde proton. When pH increases to 12.2, most of FBA has been converted to C_7-FBA by the formation of the imine bond. Thus, pH 12.2 is chosen in all the following experiments. The imine conversion of C_7-FBA and C_8-FBA as a function of surfactant concentration is also

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measured by ^{1}H NMR at the pH 12.2 (Figure S3). The curves display similar increasing slope at low surfactant concentration and then remain at about 80%, which will be further discussed in the following text.

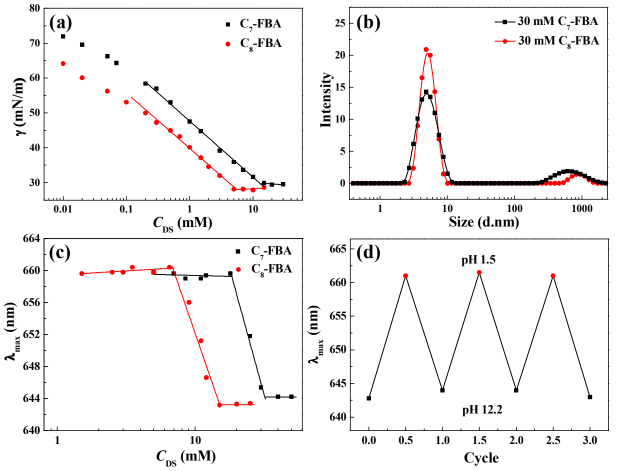

Figure 3 (a) Surface tension curves of C_7-FBA and C_8-FBA solutions against the total surfactant concentration at pH 12.2. (b) DLS results of the aggregates of 30 mM C_7-FBA and C_8-FBA at pH 12.2. (c) λ_{max} of Nile red as a function of the C_7-FBA or C_8-FBA concentration (C_{DS}) at pH 12.2. (d) λ_{max} of Nile red in 30 mM C_7-FBA aqueous solutions in response to the pH cycle process at emission wavelength of 565 nm (Black cube and red circle correspond to pH 12.2 and 1.5, respectively).

Self-assembly of Dynamic Covalent Surfactants

To investigate the aggregation of the dynamic covalent surfactants C_7-FBA and C_8-FBA, surface tension, fluorescence, and DLS measurements are performed at 25 °C with the results depicted in Figure 3 a-c.

The surface tension measurements indicate that neither benzene aldehyde FBA nor alkyl amine C_7A and C_8A are surface active under pH 12.2, but the formed dynamic covalent surfactants C_7-FBA and C_8-FBA are very surface active, with the surface tension at critical micellization concentration (CMC) close to 30 mN/m (Figure 3a). The turning points at the surface tension curves show that the CMC values, which is defined as the concentration of FBA needed for the aggregate formation when the mixing molar ratio of FBA with C_7A or C_8A is 1:1, are 12.78 and 5.54 mM for C_7-FBA and C_8-FBA, respectively. The DLS result (Figure 3b) confirms that the aggregates formed by C_7-FBA and C_8-FBA are small micelles with an average diameter of ~ 6 nm.

The fluorescence emission spectra of NR in the presence of the dynamic covalent surfactants strongly depend on the formation of micelles. Taking C_8-FBA as an example, the maximum emission wavelength (λ_{max}) of NR is about 659 nm when the concentration is below the CMC, and undergoes a blue shift with the micellization process, indicating that the NR molecules are solubilized in less-polar microdomain of the micelles. In addition, the imine conversion of C_7-FBA and C_8-FBA measured by ^{1}H NMR at pH 12.2 (Figure S3) indicates that the imine conversion quickly increases as the surfactant concentration increases and then remains at 80% beyond CMC. That is to say, the formation of micelles favours the stabilization of imine bond, which was also found in other similar systems.[25]

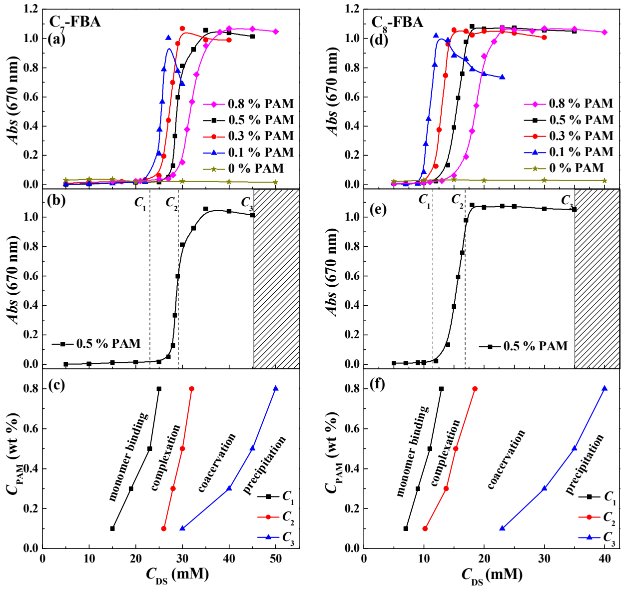

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Figure 4 (a, d) Turbidity for the mixed solutions of C_7-FBA or C_8-FBA with PAM of 0.1, 0.3, 0.5 and 0.8 wt % at 25 °C and pH 12.2, expressed by the absorbance at 670 nm and plotted against the surfactant concentration (C_{DS}). (b, e) Representative turbidity curves of C_7-FBA and C_8-FBA at 0.50 wt % PAM for the determination of critical concentrations. (c, f) Phase boundaries of C_7-FBA or C_8-FBA at 25 °C and pH 12.2.

Because the fluorescence emission spectra of NR are closely related to the micelle formation, the pH-controlled micelle formation and dissociation of the dynamic covalent surfactants C_7-FBA and C_8-FBA were examined by the NR fluorescence emission spectra. As shown in Figure 3d, at pH 12.2, 30 mM C_7-FBA exist as micelles, and the NR emissions are observed at λ_{max} of 643 ± 2 nm. By modulating the pH to 1.5, λ_{max} shifts to 660 ± 2 nm due to the dissociation of micelles and the release of NR from the hydrophobic environment of micelles. The λ_{max} transition of NR in the surfactant solution is reversible when the pH is switched between acidic and alkaline conditions for more than 3 cycles. Therefore, the micelle formation and dissociation of C_7-FBA and C_8-FBA can be effectively controlled by tuning the pH of the solution.

Phase Behavior of Dynamic Covalent Surfactant/PAM Mixture

Previously, we found that the mixture of cationic ammonium gemini surfactant (12-6-12) and PAM experiences coacervation over a wide concentration range and the coacervate phase shows great efficiency in concentrating anionic dyes.[36, 37] Herein, the pH-responsive single-chain dynamic covalent surfactants are used to form complexes and coacervate with PAM. At pH 12.2, all the carboxylate groups of PAM are deprotonated and can bind with the cationic headgroups of C_7-FBA and C_8-FBA through electrostatic interaction. The phase

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behavior of C_7-FBA and C_8-FBA with PAM was monitored by turbidity measurement as a function of the dynamic covalent surfactant concentration (C_{DS}) at constant PAM concentration (C_{PAM}). All the result are shown in Figure 4. The turbidity curves of C_7-FBA/PAM (Figure 4a) and C_8-FBA/PAM (Figure 4d) show similar variation tendency and can be divided into four regions by three critical surfactant concentrations C_1, C_2, and C_3 (Figure 4b and 4e), and thus the obtained phase boundaries are derived (Figure 4c and 4f).

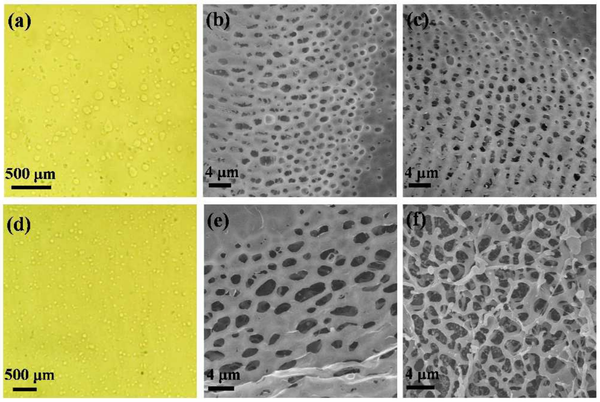

Figure 5 Coacervate droplets imaged with (a) 30.0 mM C_7-FBA and 0.5 wt % PAM, (d) 20.0 mM C_8-FBA and 0.5 wt % PAM by light microscopy at pH 12.2. The SEM image of the coacervate formed by 30.0 mM C_7-FBA and 0.5 wt % PAM (b), 40.0 mM C_7-FBA and 0.5 wt % PAM (c), 20.0 mM C_8-FBA and 0.5 wt % PAM (e), and 30.0 mM C_8-FBA and 0.5 wt % PAM (f) at pH 12.2.

In the following text, the phase behavior will be discussed by taking the mixture of C_7-FBA and PAM as a representative. Below C_1, which is close to the CMC of C_7-FBA, the mixed solution is transparent and the turbidity is close to zero, indicating that no aggregate is formed in this region. The increase of turbidity beyond C_1 suggests the complexation of C_7-FBA and PAM. Then, the turbidity starts to increase abruptly at C_2 and oil droplets appear under light microscopy (Figure 5a, d). Upon further addition of C_7-FBA, the turbidity continues to increase and reaches a maximum. The SEM images in Figure 5 show that the coacervate phase exhibits large network structures. Beyond C_3, the dynamic covalent surfactant C_7-FBA starts to precipitate out due to the limitation in solubility. So C_2 and C_3 are defined as the starting and ending point of coacervation. The interaction process resembles those observed in our previous work[36, 37]: below C_1, the surfactant monomers bind onto the oppositely charged chain of PAM through electrostatic interaction; beyond C_1, the surfactant micelles start to form complexes with polyelectrolyte as indicated by the increase of turbidity; the association of the surfactant/polyelectrolyte complexes lead to coacervation between C_2 and C_3; and the region beyond C_3 is the precipitation region. According to the phase boundaries (Figure 4c and 4f), by increasing the PAM concentration, all the critical concentrations C_1, C_2, and C_3 shift to larger values and the coacervation range expands greatly. Compared to C_7-FBA, C_8-FBA is more easily to form coacervates and the coacervation covers a larger concentration range, which should be attributed to the stronger self-assembly abilities and lower CMC values of C_8-FBA.

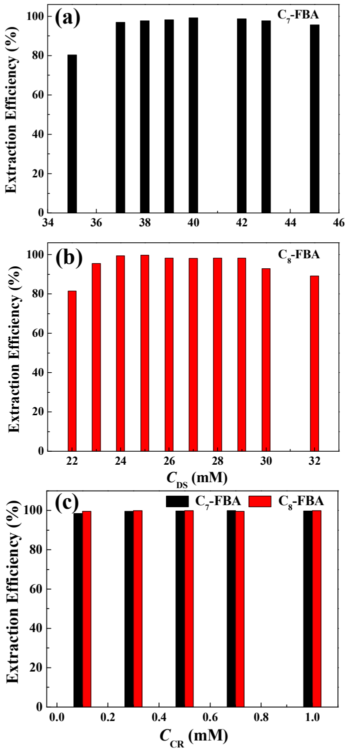

Figure 6 Extraction efficiency of 0.03 mM CR by the dynamic covalent surfactant/0.5 wt % PAM coacervate plotted against the concentration of C_7-FBA (a) and C_8-FBA (b). (c) Extraction efficiency of CR by the dynamic covalent surfactant/PAM coacervate as a function of the CR concentration (C_{CR}).

Extraction and Release Process of CR

On the basis of the above studies, the dynamic covalent surfactant/PAM cocervate is utilized to extract anionic dye CR from the aqueous solution. The extraction efficiency of CR by the dynamic covalent surfactant/PAM coacervate as a function of the surfactant concentration (C_{DS}) or the CR concentration (C_{CR}) is shown in Figure 6. Figure 6a and b show that the extraction efficiency of C_7-FBA with 0.5 % PAM or C_8-FBA with 0.5 % PAM slightly increases in lower surfactant concentration region and then reaches the maximum close to 98% due to the increase of the coacervate amount. Further increasing the surfactant concentration, the extraction efficiency decreases owing to the partially dissolution of the coacervate phase. All the extraction efficiency values are higher than 80% in the investigated concentration regions, implying that the coacervate phase shows great efficiency in extracting CR from water. Then, 40 mM C_7-FBA with 0.5 % PAM and 25 mM C_8-FBA with 0.5 % PAM are chosen to study the extraction efficiency to CR of different concentrations (Figure 6c). In the CR concentration range from 0.1 to 1.0 mM, the extraction efficiency keeps at 98%. The preconcentration of CR by the coacervate phase from aqueous phase should be mainly driven by the electrostatic interaction between CR and the cationic

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head groups of dynamic covalent surfactants, the π−π stacking between the benzene rings, and the hydrophobic interaction between the benzene ring and the hydrophobic tails of surfactant.

Subsequently, the extraction and release process of CR by the coacervate of 0.5 % PAM with 40.0 mM C_7-FBA or 25.0 mM C_8-FBA is investigated by changing pH. Figure 7a shows the typical experiment process by taking C_7-FBA and PAM as a representative. The concentrated CR solution is added into 10 mL C_7-FBA/PAM coacervate solution and the mixture is blended. Then, the coacervate phase coalesces into the bottom with the dye molecules extracted in it. After the supernatant phase is removed, the pH value of the coacervate phase is tuned to 1.5 by adding HCl. After centrifugation, CR precipitates out as purple-black solid. The turbidity curves of the dynamic covalent surfactant/PAM mixed solutions in Figure 7b show that decreasing the pH from 12.2 to 1.5 makes the cloud coacervate change into a homogeneous and clear solution, and thus the dye is released. In the above steps, the supernatant phases are used to determine the respective CR concentration by UV-vis absorption spectroscopy. The extraction and release efficiency of CR are calculated by the difference of the initial and final concentration of CR in the solution, indicating with the extraction and release efficiency values are all above 98% for either C_7-FBA/PAM or C_8-FBA/PAM (Figure 7c). Thus, the CR can be effectively extracted and released by simply switching the pH of the coacervate.

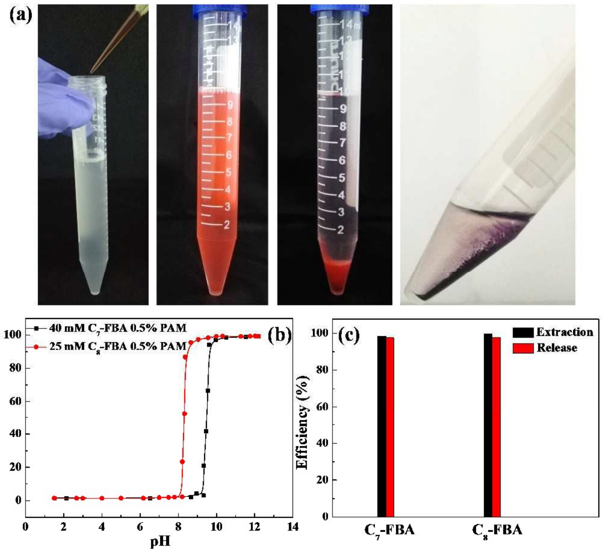

Figure 7. (a) Photos of extraction and release of CR by the coacervate formed with C_7-FBA and PAM at pH 12.2, and the subsequent release process by changing the pH to 1.5. (b) Turbidity curves of the mixed solution of 40.0 mM C_7-FBA with 0.5 wt % PAM or 25.0 mM C_8-FBA with 0.5 wt % PAM as a function of pH at 25.0 °C. (c) Extraction and efficiency of 0.03 mM CR by the coacervate of 40.0 mM C_7-FBA with 0.5 wt % PAM or 25.0 mM C_8-FBA with 0.5 wt % PAM by changing pH (extraction at pH 12.2; release at pH 1.5).

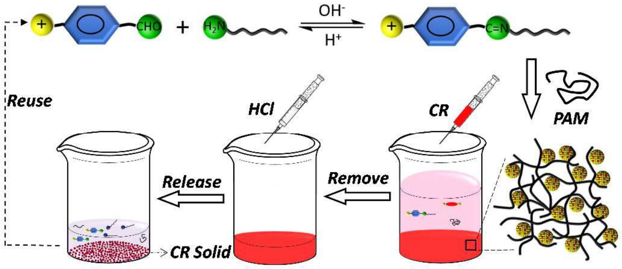

Figure 8 Possible mechanism of the extraction and release of CR in dynamic covalent surfactant/PAM mixture.

A possible mechanism of the pH-triggered extraction and release process is summarized in Figure 8. At pH 12.2, C_7-FBA or C_8-FBA forms coacervate with PAM in a wide concentration region. The coacervate phase with a net-work structure can efficiently solubilize anionic dye CR through electrostatic interaction, hydrophobic interaction and π-π interaction, while the supernatant phase contains less surfactant, PAM and CR molecules. Through this step, the dye is enriched in the coacervate phase. Then, the upper phase is removed for the subsequent release step. By decreasing the pH of coacervate from 12.2 to 1.5, C_7-FBA and C_8-FBA are dissociated into non-amphiphilic FBA and protonated amines due to the hydrolysis of imine bond in the surfactants, resulting that CR separates out as purple-black solid with the protonation of sulfonic groups in CR. The surface tension curves of C_7A and C_8A at pH 1.5 show that the surface tension is still decreasing at the experimental concentrations without the appearance of critical points, demonstrating the protonated amines exist as monomers (Figure S4). Without the complexation and association between PAM and micelles, the systems cannot form coacervate at acidic conditions. Owing to the fact that FBA, protonated amines, and PAM are all hydrophilic, the mixed solutions are homogeneous and clear, and can be recycled. Therefore, the recovery and reuse of dynamic covalent surfactants, polyelectrolytes, and dyes are realized by tuning the pH.

Conclusions

In this work, dynamic covalent surfactants have been constructed via the formation of imine bonds between aldehyde moiety and amines. The mixtures of aldehyde FBA with amines C_7A and C_8A form cationic single-chain surfactants (C_7-FBA and C_8-FBA) at alkaline condition and self-aggregate into micelles, but the surfactants and the micelles are dissociated at acidic condition due to the break of imine bonds in the dynamic covalent surfactants. At alkaline condition, the dynamic covalent surfactant/PAM mixtures in aqueous solution undergo several phase states as the surfactant concentration increases, including surfactant monomer-PAM complexes, micelle-PAM complexes, coacervate and precipitate. The area of coacervate region increases with the increase of the PAM concentration. The net-work structure of the coacervate phase promotes the preconcentration of

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anionic dye CR through electrostatic interaction, hydrophobic interaction and π-π interaction. The extraction efficiency keeps at 98% in the CR concentration range from 0.1 to 1.0 mM, which is much smaller than dye concentrations in normal wastewater of dyes. By changing the pH into acidic condition, the coacervate transits into a homogeneous and clear solution, while CR precipitates out as purple-black solid with the protonation of sulfonic groups. So the efficient extraction and release of the dye molecules are realized by tuning the pH. In this way, dyes as well as FBA, amine, and PAM can be recycled and reused. The results provide a novel and convenient route to fabricate functional dynamic covalent surfactants through dynamic covalent bonds, and set up a potential and efficient method to enrich and recycle dyes in wastewater through pH-triggered coacervation of dynamic covalent surfactants and polymer.

Conflicts of interest

There are no conflicts to declare.

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Table of Contents Graphic

Coacervation of Dynamic Covalent Surfactant with Polyacrylamide: Property and Application

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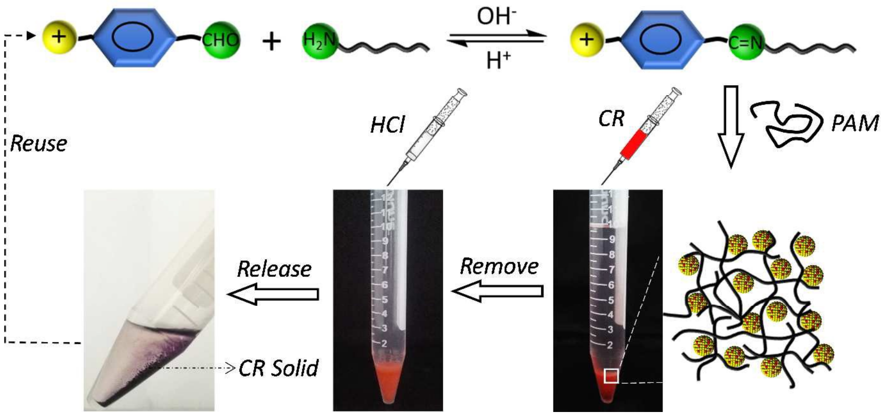

Coacervation of cationic dynamic covalent surfactant with polyacrylamide and its application in extracting and releasing anionic dye in water.