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pH-Responsive Surface Activity and Solubilization with Novel Pyrrolidone-Based Gemini Surfactants

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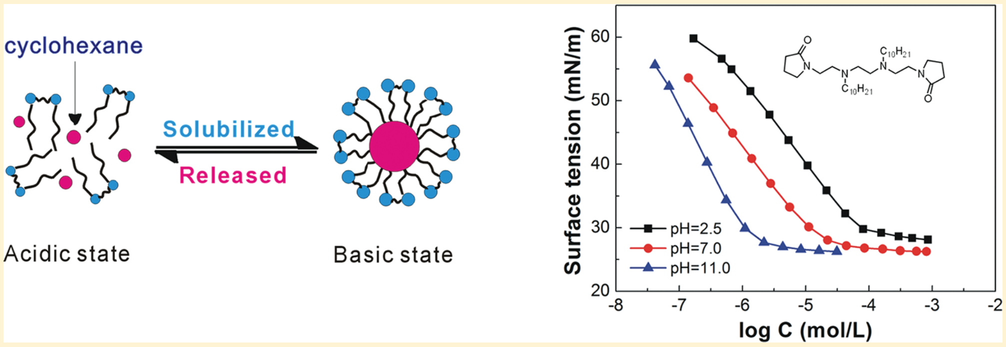
Ⓢ *Supporting Information*



ABSTRACT: A new series of pH-responsive Gemini surfactants with 2-pyrrolidone head groups, *N,N*′-dialkyl-*N,N*′-di(ethyl-2-pyrrolidone)ethylenediamine (Di-C$_n$P, where $n = 6$, 8 10, 12), were synthesized and characterized by ^{1}H NMR, ^{13}C NMR, ESI-MS, and elemental analysis. The surface activity and micellization behavior at acidic, neutral, and basic conditions were characterized by equilibrium surface tension and fluorescence techniques. It was found that the surface activity of Di-C$_n$P depends on the pH of aqueous solutions due to the protonation state of surfactant molecules when pH was varied. The new compounds have lower cmc and γ_{cmc} in comparison with that of *m*-2-*m* type conventional cationic Gemini surfactants and gluconamide-type nonionic Gemini surfactants. Fluorescence data confirm that micelles are formed when the concentration is above the cmc. Since micellization is of fundamental importance in surfactant applications such as solubilization, microemulsion, and related technologies, the significant difference in cmc at different pH of this new Gemini surfactant is employed to solubilize cyclohexane. The preliminary result indeed shows that the solubilization capacity of Di-C$_n$P can be tuned by pH.

1. INTRODUCTION

N-Alkyl 2-pyrrolidones (C$_n$P) are well-known solvents with low vapor pressure and toxicity. They have wide industrial applications such as flocculation of particles, skin permeation enhancers, shampoo and cosmetics.[1] It was established that when the alkyl chain length exceeded 6, C$_n$P could reduce the air−water surface tension, but the aqueous solution exhibited lower consolute temperatures and phase separation occurred even at ambient temperature.[2] Hence, C$_n$P is hard to form micelles in aqueous which limits their further applications. Gemini-type amphiphiles are known to possess more predominant surface active properties than corresponding traditional single-chain surfactants: a lower critical micelle concentration (cmc), a higher efficiency in reducing air/water and oil/water interfacial tensions, unusual aggregation morphologies, and very complex phase behavior.[3,4] Thus, developing pyrrolidone Gemini surfactants is exceedingly interesting. At the same time chemical combination of some stimuli-responsive groups in the new surfactant could enable its specific functionalities. Indeed, stimuli-responsive surfactants have attracted considerable attention in the fields of biotechnology and drug delivery systems.[5] Typically, the external stimulus is heat,[6] pH,[7] light,[8] or electrolyte.[9−11] Among them pH was the most used trigger to response a system. Some very rich phase behavior and aggregates morphologies were induced simply by the variation of solution pH.[12,13]

The motivation of this work is to generate a new type of pH-sensitive Gemini surfactants containing 2-pyrrolidone head groups and investigate their surface activities. The behavior of new structured surfactants is expected to illustrate the contribution of a heterocyclic headgroup to the surface activity by comparing with traditional analogues. This is of fundamental importance in understanding surfactant properties at the molecular level. Meanwhile, the surface activity and solubilization capacity of new surfactants are investigated at acidic, neutral and basic conditions aiming to provide a new type of pH-sensitive surfactants. The developed surfactants are expected to have some potential applications in enhance oil

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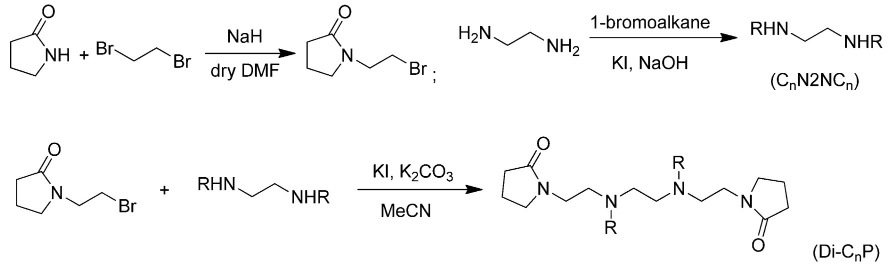
Scheme 1. Synthetic Route of Di-C_nP ($R = C_nH_{2n+1}$, n = 6, 8, 10, and 12)



recovery, demulsification, contaminants remediation, controlled drug release, and textile treatment.

2. EXPERIMENTAL METHODS

2.1. Materials. 1-Bromohexane, 1-bromooctane, 1-bromodecane, 1-bromododecane, 2-pyrrolidone, and pyrene were obtained from TCI. Sodium hydride, dichloromethane, *N,N'*-dimethylformide, methanol, acetonitrile, ethyl acetate, NaOH, HCl, KI, K_2CO_3, anhydrous $MgSO_4$, and NaCl were analytical grade and purchased from Chinese Medical Co. (Shanghai). All reagents were used as received without further purification except 2-pyrrolidone and DMF, which were dried and distilled before use. The water used in the current study was of Millipore Milli-Q grade.

2.2. Synthesis. The Gemini surfactants Di-C_nP (n = 6, 8, 10, and 12) were made in-house. Although the structure of the compounds was patented earlier by our group,[14] the physical property has not been investigated due to its poor purity. Here a complete new route was designed to synthesize the compounds which are of high surface purity. The structure and synthetic route of these surfactants are shown in Scheme 1. Further details on the synthetic procedure and purification are provided in the Supporting Information. The products were characterized by employing elemental analysis (VarioEL III), ESI-MS (P/ACE MDQ), and ^1H and ^{13}C NMR spectra (Mercury VX-300) in $CDCl_3$. The results in the Supporting Information prove that they are all objective products, and the purity is higher than 99% as calculated from the elemental analysis and the data of HPLC (Figure S5 in Supporting Information).

2.3. pH Titration. The protonation constants (pK_a) of synthesized surfactants were measured using the Rex model PHSJ-5 digital pH meter (Leici, China). Generally, 0.1 mol/L hydrochloric acid aqueous solutions was added to 10 mL 0.002 mol/L Di-C_nP aqueous solution until pH was about 2 and then subsequently titrated with 0.1 mol/L sodium hydroxide aqueous solution until pH was 12. Each titration point was recorded as the potential drift was stable.

2.4. Surfactant Aqueous Preparation and Solubility. Di-C_nP aqueous solutions were prepared by dispersing samples in water (Millipore) by sonication. For those with required pH were prepared by titrating with hydrochloric acid or sodium hydroxide aqueous solution. The aqueous solutions were all homogeneous and clear throughout the test at 25 °C. The samples with required pD for ^{1}HNMR experiment were prepared in D_2O and titrated with DCl and NaOD. The solubilities of Di-C_nP and C_nN2NC_n were measured in water with required pH at 25 °C.

2.5. Equilibrium Surface Tension. The equilibrium surface tension was determined with Du Noüy ring method by using K100 (Krüss Co., Germany). The maximum uncertainty on γ values is ±0.2 mN/m. All the measurements were performed at 25.0 ± 0.1 °C and repeated at least twice. The pH of the samples for surface tension measurement was detected by pH meter before and after the experiments, and the results showed that the change in pH was less than 0.2.

2.6. Fluorescence. Intensities and spectra of fluorescence were carried out on a RF-5301(PC) fluorescence spectrophotometer using 1.0 cm quartz cell. Pyrene spectra were recorded with fixed excitation at 335 nm, and the slit widths of excitation and emission were all fixed at 3.0 nm. The concentration of pyrene was 1×10^{-6} mol/L for each solution.

2.7. Static Light Scattering. Static light scattering (SLS) measurements was performed on the Zetasizer instrument ZEN3600 (Malvern, YK) at 25.0 ± 0.1 °C. A solid-state He−Ne laser (λ = 633 nm) was used as a light source. Solutions at different pH were measured at a fixed back scattering angle of 173°. The pH-dependent intensities of static light scattering experiments were performed.

2.8. Solubilization of Cyclohexane. Cyclohexane (275 μL) were added to 0.1 mM Di-$C_{10}P$ aqueous solutions (9 mL) and stirred at 25 °C for solubilization at different pH. The light scattering intensities of the solution before and after solubilization were measured by SLS, and the difference in turbidity caused by adding cyclohexane was obtained.

3. RESULTS AND DISCUSSION

3.1. Solubility in Water. In order to understand the direct influence of 2-pyrrolidone group on the aqueous solubility of Di-C_nP, the solubilities of Di-C_nP and their intermediates, *N,N'*-dialkylethylenediamine (C_nN2NC_n, where n = 6, 8, 10, 12), were compared. Figure 1 shows the solubility of Di-C_nP and C_nN2NC_n at different pH at 25 °C. Clearly, the solubility of the heterocyclic surfactants Di-C_nP exceeded those of acyclic series C_nN2NC_n. For example, at pH 2.5, the solubility of Di-C_nP in water is nearly 40−130 times that of C_nN2NC_n as n varies. Hence, 2-pyrrolidone plays a critical role in the hydrophilicity of Di-C_nP, which improves the solubility of *N,N'*-dialkylethy-

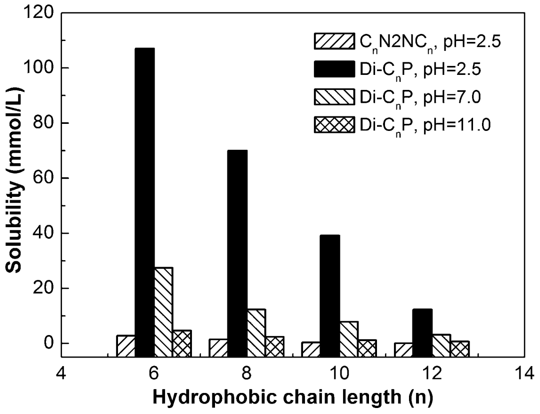


Figure 1. Solubility of C_nN2NC_n and Di-C_nP (n = 6, 8, 10, 12) at different pH at 25 °C.

Table 1. pK_a Values of Di-C_nP (n = 6, 8, 10, 12) at 25 °C

surfactants	pK_{a1}	pK_{a2}
Di-C_6P	5.22	8.65
Di-C_8P	5.02	8.65
Di-$C_{10}P$	4.61	8.62
Di-$C_{12}P$	4.38	8.57

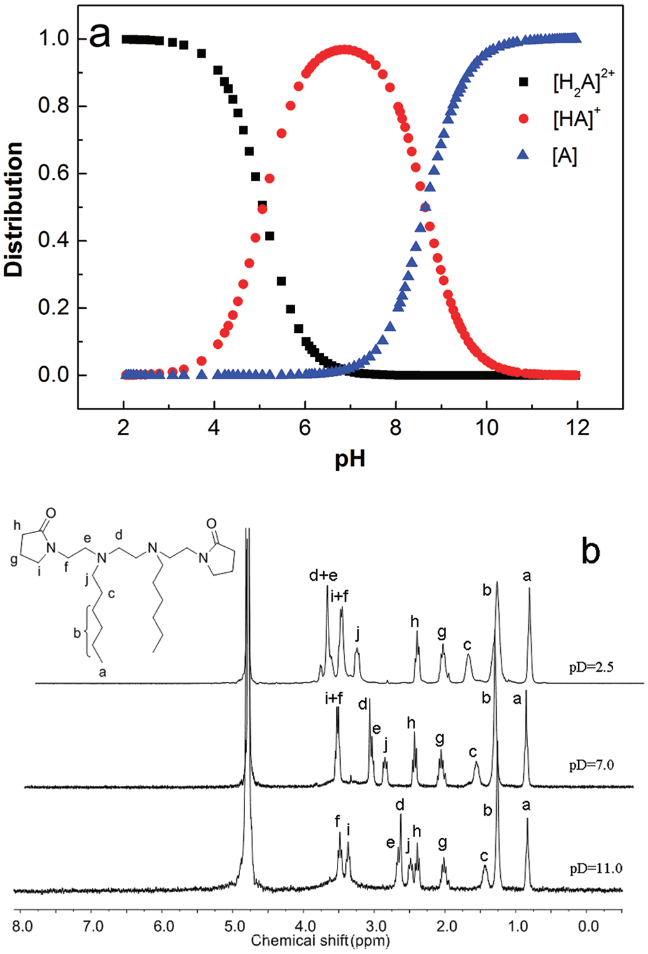


Figure 2. (a) Distribution of Di-C_6P species at different pH at 25 °C. (b) ^{1}HNMR of Di-C_6P at pD 2.5, 7.0, and 11.0 in D_2O aqueous solution at 25 °C (b).

lenediamine in water remarkably. A similar result was reported by Menger et al.[15] when other heterocyclic groups were introduced to surfactant molecules. Indeed, Login[1] reported that pyrrolidone is a versatile substituent, capable of enhancing the performance of a variety of surfactant structures by improving solubility, compatibility, and solvency in a compact headgroup.

3.2. pH-Dependent Protonation States of Di-C_nP.

There are two pH-sensitive tertiary nitrogens in the present surfactant molecules, which can be protonated under acidic conditions. The surfactant molecules can be in double cationic, single cationic, or nonionic state with the variation of the solution pH. It is very important to identity the composition at different pH conditions to understand the surface activity. From the curves of pH titration (Figure S6), there exists two distinguish pK_a values for all four amphiphiles investigated,

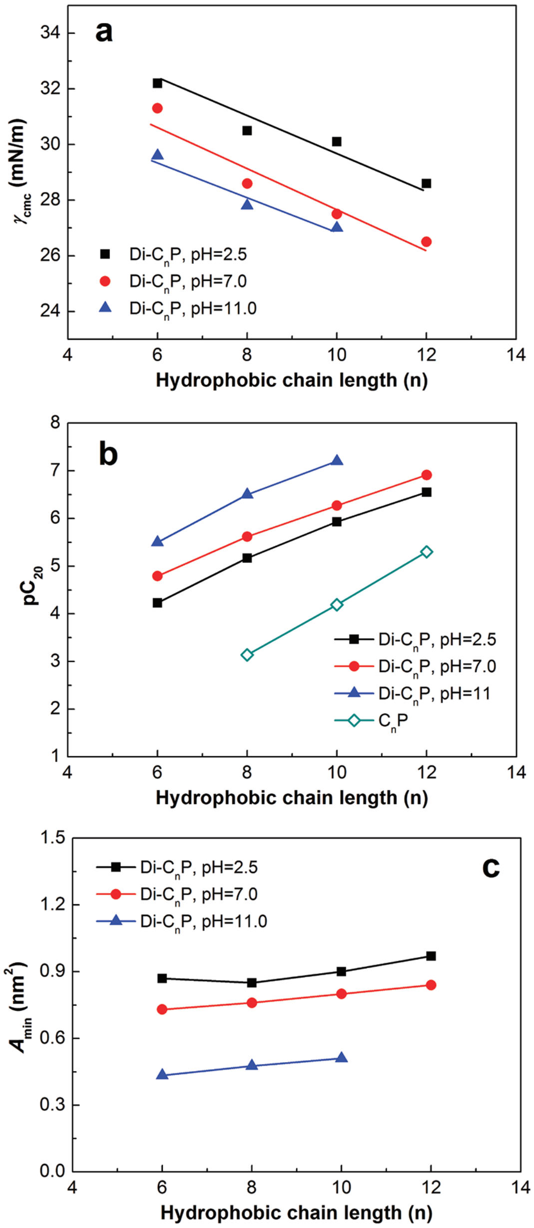


Figure 4. Effect of carbon number in the surfactant hydrophobic chains on γ_{cmc} (a), pC_{20} (b), and A_{min} (c) for Di-C_nP at pH 2.5, 7.0, and 11.0.

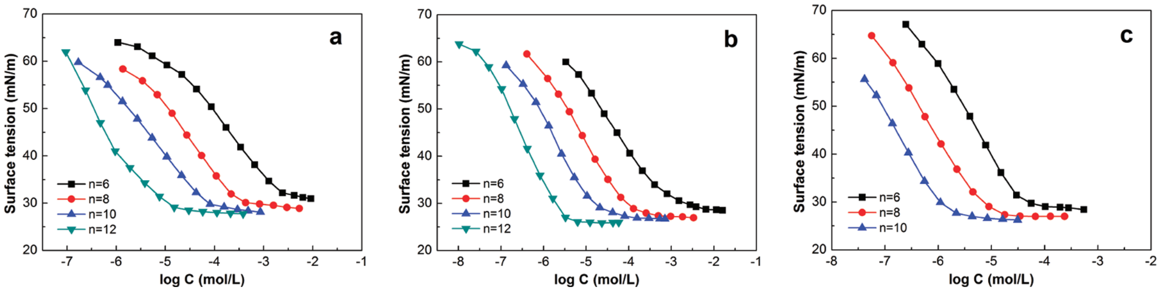


Figure 3. The γ−log c plots of Di-C_nP (n = 6, 8, 10, 12) aqueous solutions in the absence of salt at pH 2.5 (a), 7.0 (b), and 11.0 (c) at 25 °C.

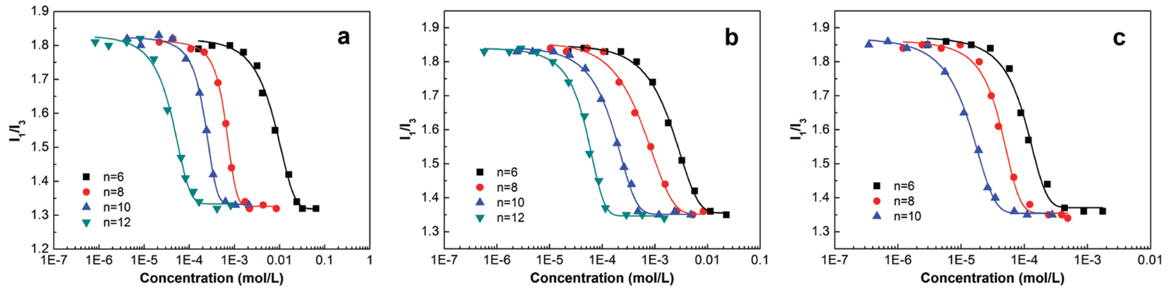


Figure 5. Relationship between I_1/I_3 values of pyrene and the concentration for Di-C_nP at pH 2.5 (a), 7.0 (b), and 11.0 (c).

Table 2. Cmc and γ_{cmc} of Di-C_nP in Absence of Salt at Different pH at 25 °C

surfactants	pH	cmc[a] (mol/L)	cmc[b] (mol/L)	γ_{cmc} (mN/m)
Di-C_6P	2.5 ± 0.2	3.91×10^{-3}	2.21×10^{-3}	32.2
	7.0 ± 0.2	1.09×10^{-3}	6.35×10^{-4}	31.3
	11.0 ± 0.2	3.82×10^{-5}	3.11×10^{-5}	29.6
Di-C_8P	2.5 ± 0.2	4.66×10^{-4}	3.33×10^{-4}	30.5
	7.0 ± 0.2	2.42×10^{-4}	1.12×10^{-4}	28.6
	11.0 ± 0.2	1.50×10^{-5}	5.00×10^{-6}	27.8
Di-C_{10}P	2.5 ± 0.2	1.06×10^{-4}	6.79×10^{-5}	30.1
	7.0 ± 0.2	5.01×10^{-5}	2.33×10^{-5}	27.5
	11.0 ± 0.2	4.01×10^{-6}	1.44×10^{-6}	27.0
Di-C_{12}P	2.5 ± 0.2	2.22×10^{-5}	1.54×10^{-5}	28.6
	7.0 ± 0.2	1.19×10^{-5}	3.20×10^{-6}	26.5
	11.0 ± 0.2			

[a]Measured by fluorescence. [b]Measured by surface tension.

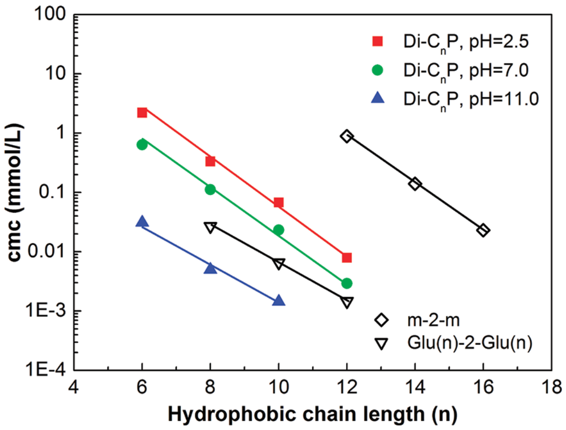


Figure 6. Effect of hydrophobic chains length of surfactants on cmc (mmol/L) for Di-C_nP at pH 2.5, 7.0, and 11.0 in comparison with that of *m*-2-*m* and Glu(*n*)-2-Glu(*n*) surfactants.

Table 3. *A* and *B* values for Di-C_nP, Glu(*n*)-2-Glu(*n*), and *m*-2-*m* Surfactants at 25 °C[a]

surfactants	pH	*A*	*B*
Di-C_nP	2.5 ± 0.2	2.76	0.40
Di-C_nP	7.0 ± 0.2	2.13	0.39
Di-C_nP	11.0 ± 0.2	0.45	0.33
Glu(*n*)-2-Glu(*n*)[b]		0.96	0.32
m-2-*m*[c]		4.71	0.40

[a]The data for Glu(*n*)-2-Glu(*n*) and *m*-2-*m* were taken from refs 32 and 33. [b]Reported in ref 32. [c]Reported in ref 33.

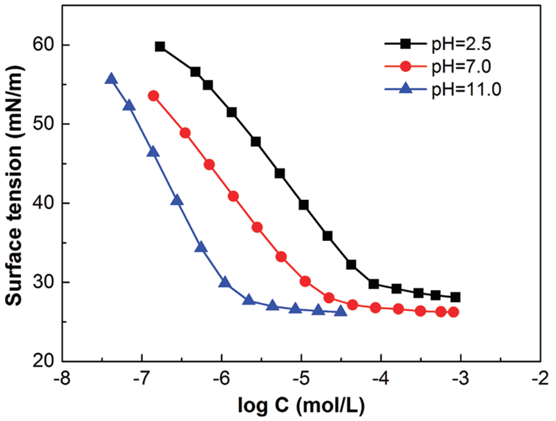


Figure 7. Variation of the surface tension versus logarithm concentration of Di-C_{10}P at different pH at 25 °C.

which are shown in Table 1. It is worth to point out that pK_a values are independent of salt concentration in the range investigated (Figure S7).

Based on the calculation from pK_a values, the species distributions in aqueous solution of Di-C_6P are shown in Figure 2a. The results for other chain length surfactants are shown in Figure S8. It demonstrates that Di-C_nP mainly appears to be 1:2 type cationic surfactant ($[H_2A]^{2+}$), 1:1 type cationic surfactant ($[HA]^{+}$), and nonionic surfactant ([A]) at acidic, neutral, and basic conditions, respectively, which was further confirmed by ^{1}HNMR technology (Figure 2b).

In Figure 2b, the spectra of Di-C_6P at pD 2.5, 7.0, and 11.0 are exhibited by fixing H−O−D as the reference.[16] The variation in chemical shift of H−O−D with pH is confirmed to be ignorable in the current system as shown in Figure S9. The spectra in D_2O at pD 11.0 consist with that in $CDCl_3$ (Figure S10), indicating that Di-C_6P in aqueous solution at pD 11.0 is nonionic type. The chemical shift of proton, next to the double nitrogen atoms of alkylamine (marked by d, e, and j in Figure 2b), changed remarkably when the solution pD changing from 11.0 to 2.5, whereas the other protons (marked by a, b, c, f, g, h, and i in Figure 2b) changed little. This is attributed to the state of nitrogen atoms in the molecule changes from amine to quaternary ammonium salt.

3.3. Adsorption at Air−Water Surfaces. The surface activity and adsorption behavior of Gemini surfactants Di-C_nP in aqueous solutions were investigated by drawing the equilibrium surface tension and surfactant concentration relationship at different pH which is shown in Figure 3. The absence of a minimum around the breakpoint confirms that there are no substances with impurities. To minimize the influence of salt effect, the solution pH was controlled by hydrochloric acid or sodium hydroxide aqueous solution rather

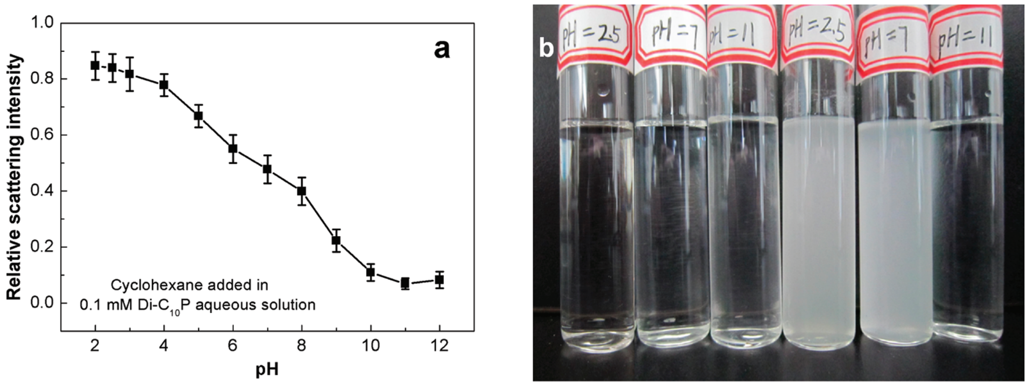


Figure 8. (a) pH effected variation in scattered light intensity at $\theta = 173°$ after cyclohexane added in 0.1 mM Di-C$_{10}$P at 25 °C. (b) Image taken from the samples before (in the left three tubes) and after (in the right three tubes) adding cyclohexane showing solubilization was happed at pH 11.0 whereas coarse emulsion were formed at others.

than buffer solution.[17] The change in pH was less than 0.2 in the whole measurement, indicating the state of surfactant molecules kept the same in the range of pH investigated. Clearly, all novel compounds exhibit the classical surface tension−concentration relationship when n is from 6 to 10. For $n = 12$, the surfactant has poor solubility in aqueous solution at pH 11.0, which inhibits the surface tension measurement by adsorption. The surface tension decreases with the increase of surfactant concentration and then reaches a clear breakpoint, indicating the onset of micellization. The surface tension for precmc decrease normally, which is manner matched with a typical γ−log c plots for a dilute solution of surfactant. For concentrations below but near the cmc, the slope of the curve is essentially constant, indicating that the surface concentration has reached a constant maximum value. In this range the interface is considered to be saturated with surfactant molecules and the continued reduction in the surface tension is mainly due to the increased activity of the surfactant in the bulk phase rather than at the interface.[18] This classic analysis was recently questioned by Menger et al. where new evidence show that surfactant molecules are cooperatively adsorbed rather than saturated in this region.[19,20] This view also caused a discussion by Laven[21] and Menger.[22] However, it is not possible to get a constant data for surfactant molecules according to the new theory. The purpose of this article is to report a new family of Gemini surfactants and compare their surface activity with some known Gemini surfactants. Hence, the Gibbs analysis is still employed to explain the results.

The saturation adsorption values $\Gamma_{\max}$ at the air/aqueous interface are calculated using the Gibbs adsorption isotherm equation[3]

$$\Gamma_{\max} = -\frac{1}{2.303nRT}\frac{\mathrm{d}\gamma}{\mathrm{d}\log c} \tag{1}$$

where γ is the surface tension in mN/m, $\Gamma_{\max}$ is the saturation adsorption amount in μmol/m^2, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature, c is the surfactant concentration, and (dγ/d log c) is the slope in the linear region. Normally the value of n is taken as 2 for the 1:1 ionic surfactant and 3 for gemini surfactants (1:2 ratio).[23] For nonionic surfactant and ionic surfactant in the presence of a swamping, constant amount of electrolyte containing a common non-surfactant counterion, $n = 1$ has been used.[18] However, this study employs HCl and NaOH to control the aqueous pH and the impact of salt cannot be ignored. The value of n is calculated by the following equation according to Rosen et al.[18]

$$n = 1 + C_s/(C_s + C_{\mathrm{Cl}^-}) \tag{2}$$

where C_s is the cmc of Di-C$_n$P and C_{Cl^-} is the concentration of chloride ion in the solution. Then the minimum surface area of surfactant molecule $A_{\min}$ can be obtained from the saturated equation

$$A_{\min} = (N_A\Gamma_{\max})^{-1} \times 10^{24} \tag{3}$$

in which N_A is Avogadro's number and $A_{\min}$ is in nm^2. The efficiency of surfactant adsorption at the air−water interface is characterized by pC$_{20}$, which is related to the surfactant concentration required for lowering the surface tension of water by 20 mN/m by pC$_{20}$ = −log C$_{20}$. Generally, the larger the pC$_{20}$, the higher adsorption efficiency of the surfactant is. The variation of surface tension at cmc, pC$_{20}$ and $A_{\min}$ of Di-C$_n$P with n at different pH is shown in Figures 4a, 4b, and 4c separately. Together shown is that of C$_n$P, a series of corresponding single-chain pyrrolidone based surfactants.[24]

The γ_{cmc} decreases and pC$_{20}$ increases when the hydrophobic chain length increases, following the general rule of surfactants. This is because surfactants with longer alkyl chain adsorb more strongly at the air/water interface than shorter ones. The pC$_{20}$ of Di-C$_n$P is higher than that of C$_n$P, demonstrating that the surface activity of Di-C$_n$P Gemini surfactants is superior to that of single chain pyrrolidone-based surfactant as expected. Since C$_n$P cannot from aggregates in the investigated concentration range,[24] it is not possible to have further comparison. The minimum surface area $A_{\min}$ of Di-C$_n$P becomes larger as the increase of the hydrophobic chain length, which consists well with that of conventional m-s-m cationic gemini surfactants.[25] For single chained surfactants, $A_{\min}$ decreases slightly when the alkyl chain carbon number increases due to the hydrophobic effect. This is not always the case with Gemini surfactants; many researchers got the reverse tendency of $A_{\min}$[26,27] and attributed the $A_{\min}$ increase with hydrophobic chain length to more easily bending of longer chain.[28] $A_{\min}$ also has a reasonable increase as the decrease in pH, which could mostly attribute to different effect of electrostatic repulsion among hydrophilic head groups.[29] For pH at 2.5, there exists strong electrostatic repulsion in two ways: one is intramolecular repulsion between two tertiary nitrogen protonated completely in the same surfactant molecule, and the other is the intermolecular repulsion among different surfactant molecules.

As a result, the A_{min} has the highest value at this pH. For pH at 7.0, the electrostatic repulsion represents as only one type, that is, the intermolecular interaction, since only one tertiary amine is protonated in each surfactant molecule and the A_{min} is smaller than that of doubly charged type. As for pH at 11.0, there is no electrostatic repulsion due to the nonionic type Di-C_nP molecule so that the A_{min} is the smallest.

For $n = 12$, the synthesized surfactant has poor solubility in aqueous at pH 11.0. The ability of reducing the air−water surface tension was carried out by the formation of insoluble monolayer method. The π−A isotherm was determined to classify the surface pressure and the area per molecule packing at the air/water interface, which is then used to compare with the A_{min} and γ_{cmc} values of water-soluble Di-C_nP. Detailed π−A isotherm measurement and result are shown in Figure S12. The isotherm showed that the monolayer had a pronounced phase transition region and eventually collapsed at 46.1 mN/m surface pressure. The area per molecule obtained is ~82 Å^2, which is larger than that of soluble shorter chain Di-C_nP at the same pH condition but slightly smaller than that of Di-C_{12}P at pH 2.5 and 7.0 obtained by Gibbs analysis.

3.5. Micelle Formation of Gemini Surfactants Di-C_nP.

The fluorescence technique was used to study the micropolarity and the cmc of Di-C_nP at pH 2.5, 7.0, and 11.0 at 25 °C. Pyrene was solubilized in surfactant micelles. After excitated at 335 nm the fluorescence emission spectra of pyrene in aqueous solutions have 5 electronic vibration peaks. The intensity ratio of (I_1/I_3) in the first vibronic peak (373 nm) and the third vibronic peak (384 nm) is strongly dependent on the polarity of the environment of the pyrene molecules.[30] Figure 5 shows the relationship between I_1/I_3 ratio and the concentration of the surfactants Di-C_nP at pH 2.5, 7.0, and 11.0.

When surfactant concentrations is lower than the cmc I_1/I_3 value can be kept very close to that of water (1.87),[31] indicating that surfactant molecules exist as monomers in aqueous solutions. When the surfactant concentration is above the cmc, there is a sharp drop in I_1/I_3 for all the surfactant solutions, demonstrating that the microenvironment has changed to more hydrophobic due to the formation of aggregates. When surfactant molecules started to form micelles, the extreme hydrophobic pyrene molecules were transferred from the water environment to the hydrophobic core. The cmc determined by both surface tension and fluoresce are shown in Table 2. The difference in cmc obtained by two methods can be appreciated by the methodology; for surface tension it is adsorption, whereas for fluoresce it is solubilization. With the increase of concentration, surfactant molecules adsorbed first on the air/aqueous interface due to strong hydrophobic interaction. Then surfactant molecules aggregated gradually in bulk phase when the surface is saturated with surfactant molecules. That is why the cmc detected by fluoresce is higher than that by surface tension.[31] For all four Di-C_nP surfactants at the same pH, the minimum I_1/I_3 values are almost the same, indicating hydrophobic tail length has little effect on the aggregates environment. This is similar to that of the conventional surfactants and gluconamide-type Gemini surfactants.[32]

Figure 6 shows the logarithm of cmc as a function of the number of carbon atoms in the hydrocarbon chain of Di-C_nP at pH 2.5, 7.0 and 11.0, together shown are that of *m*-2-*m*[33] and Glu(*n*)-2-Glu(*n*) Gemini surfactants.[32]

The cmc varies linearly with the carbon number n in the hydrophobic alkyl chain, following the empirical Stauff−Klevens rule.[34]

$$\log \mathrm{cmc} = A - Bn \tag{4}$$

A and B are constants for a homologous series of surfactants. Usually, the constant A reflects the nature and numbers of the hydrophilic group, while B displays the effect of each additional methylene unit on the cmc. Table 3 shows A and B values for the new surfactants. Generally, the values of B are all around 0.43 ± 0.03 for the type of *m*-s-*m* cationic Gemini surfactants.[18] For ionic type Di-C_nP Gemini surfactants, these values are manner matched with the value of *m*-2-*m* type cationic Gemini surfactants. For nonionic type Di-C_nP Gemini surfactants, the value is also consistent with the value of nonionic type Glu(*n*)-2-Glu(*n*). This means that the contribution of hydrophobic chain to the micellization is not affected by the introduction of a heterocyclic in surfactant headgroup. While A is significantly lower than that of *m*-2-*m* and Glu(*n*)-2-Glu(*n*), indicating that the heterocyclic headgroup favors micellization. This is true since the less polar 2-pyrrolidone head groups make micelle formation energetically more favorable, which is in line with the earlier reports on imidazolium and pyridinium based surfactants.[35,36]

3.6. pH-Dependent Surface Activity and Solubilization Capacity of Di-C_nP.

One of the important properties of surfactant that directly related to micelle formation is solubilization. Solubilization may be defined as the spontaneous dissolving of a substance by reversible interaction with the micelles of a surfactant in a solvent to form thermodynamically stable isotropic solution with reduced thermodynamic activity of solubilized material.[18] As discussed above the surface activity of Di-C_nP at basic condition is superior to that at acidic condition. Taken the γ−log c plots of Di-C_{10}P at different pH (Figure 7), for example, the cmc at pH 11.0 is almost 2 orders of magnitude smaller than the cmc at pH 2.5, indicating that the solubilization ability of Di-C_{10}P can be varied by pH. Cyclohexane was employed to verify the solubilization capacity of Di-C_{10}P due to its widely reported applications in microemulsion technology. In order to show the influence of pH on the solubilization capacity, the amount of cyclohexane chosen was slightly smaller than the maximum amount at pH 11. Figure 8a shows the variations of scattering light intensity with the solution pH after the addition of cyclohexane. The relative scattering light intensity decreases gradually from 0.85 to 0.1 as the pH changes from 2 to 12, indicating the free cyclohexane was solubilized into surfactant micelles as the pH increased. Figure 8b shows the image of samples before and after the addition of cyclohexane. All the samples are clear before the addition of cyclohexane. With the addition of oil and gentle shaking the samples of pH 2.5 and 7.0 became turbid due to the formation of macroemulsions, whereas the sample of pH 11 keep clear due to the solubilization or the formation of a microemulsion. Thus, the exchange between stable microemulsions and unstable eumlsions could be achieved by simply varying the environmental pH in this case. In other words, most of the solubilized material can be released when the solution pH changes from basic to acidic conditions, which is useful in developing new materials for wide applications in demulsification, contaminants remediation, controlled release, and textile treatment.

4. CONCLUSIONS

In summary, a novel family of pH-sensitive Gemini surfactants containing 2-pyrrolidone head groups *N,N′*-dialkyl-*N,N′*-dipyrrolidone ethylenediamine (Di-C$_n$P, where $n = 6$, 8 10, 12) were successfully synthesized and characterized. Comparing with ionic type Gemini surfactants *m*-2-*m* and nonionic gluconamide-type Gemini surfactants Glu(*n*)-2-Glu(*n*), surfactants with pyrrolidone heterocyclic headgroup have slightly superior surface activity. It provides more evidence to understand the structure−property relationship of Gemini surfactant at the molecular level. As the pH changes from 2.5 to 11.0, the surface activity improves remarkably, which possess a nice potential application in the process of emulsion and demulsification by simply changing pH. Moreover, owing to the existence of 2-pyrrolidone heterocyclic in head groups, the new surfactants might find special applications in nanomaterial development and industrial technologies such as pesticide formulation, controlled release, and wastewater treatment. Further investigation on the aggregates morphology and applications of this novel family of Gemini surfactant is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details on the synthesis and characterizations of pH-sensitive Gemini surfactants containing 2-pyrrolidone head groups (Figures S1−S5), curves of pH titration experiments (Figures S6−S8), ^{1}H NMR spectrum of Di-C$_6$P in CDCl$_3$ and in D$_2$O at different pD (Figures S9 and S10), the $A_{\min}$ and pC$_{20}$ of Di-C$_n$P in absence of salt at pH 2.5, 7.0, and 11.0 (Table S1), the γ−log c plots of Di-C$_{10}$P aqueous solutions in presence of 0, 5, and 50 mM NaCl at pH 2.5 (Figure S11), pressure−area isotherms of spread Di-C$_{12}$P monolayer at pH 11.0 (Figure S12). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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