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pH-Responsive Viscoelastic Fluids of a C₂₂-Tailed Surfactant Induced by Trivalent Metal Ions

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Abstract: pH-responsive viscoelastic fluids are often achieved by adding hydrotropes into surfactant solutions. However, the use of metal salts to prepare pH-responsive viscoelastic fluids has been less documented. Herein, a pH-responsive viscoelastic fluid was developed by blending an ultra-long-chain tertiary amine, *N*-erucamidopropyl-*N*, *N*-dimethylamine (UC₂₂AMPM), with metal salts (i.e., AlCl₃, CrCl₃, and FeCl₃). The effects of the surfactant/metal salt mixing ratio and the type of metal ions on the viscoelasticity and phase behavior of fluids were systematically examined by appearance observation and rheometry. To elucidate the role of metal ions, the rheological properties between AlCl₃– and HCl–UC₂₂AMPM systems were compared. Results showed the above metal salt evoked the low-viscosity UC₂₂AMPM dispersions to form viscoelastic solutions. Similar to HCl, AlCl₃ could also protonate the UC₂₂AMPM into a cationic surfactant, forming wormlike micelles (WLMs). Notably, much stronger viscoelastic behavior was evidenced in the UC₂₂AMPM–AlCl₃ systems because the Al³⁺ as metal chelators coordinated with WLMs, promoting the increment of viscosity. By tuning the pH, the macroscopic appearance of the UC₂₂AMPM–AlCl₃ system switched between transparent solutions and milky dispersion, concomitant with a viscosity variation of one order of magnitude. Importantly, the UC₂₂AMPM–AlCl₃ systems showed a constant viscosity of 40 mPa·s at 80 °C and 170 s^{−1} for 120 min, indicative of good heat and shear resistances. The metal-containing viscoelastic fluids are expected to be good candidates for high-temperature reservoir hydraulic fracturing.

Keywords: viscoelastic fluids; wormlike micelles; ultra-long chain surfactants; metal-coordination; pH-responsiveness



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1. Introduction

Viscoelastic fluids, based on surfactants, are typically “living polymers”, with unique rheological properties, viz., viscoelasticity [1]. The peculiar viscoelasticity of the solution originates from the spontaneous assembly of the surfactants into wormlike micelles (WLMs) [1,2]. A striking advantage of viscoelastic surfactant fluids over regular water-soluble polymers is their reversibly shear-degradable characteristics because WLMs are connected by weak physical interactions that can continuously break and reform [3]. Among numerous viscoelastic fluids, viscoelastic fluids of C₂₂-tailed surfactants are arguably the most attractive for the following reasons. (i) The viscoelastic fluids made of C₂₂-tailed surfactants exhibit stronger viscoelasticity and better thermostability compared to their short-chain counterparts [4]. (ii) Unlike short-chain surfactants that are derived from crude oil-based products, C₂₂-tailed surfactants are environmentally benign and sustainable because their feedstocks are natural, renewable raw materials, such as vegetable oil [5–7]. Owing to their fascinating rheological behavior, C₂₂-tailed surfactant viscoelastic fluids

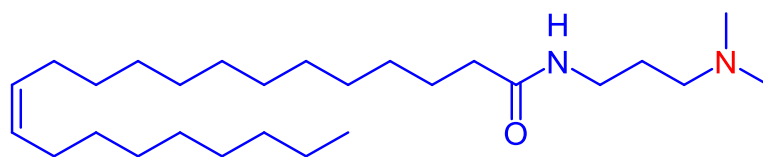
have shown great potential in a wide range of areas, such as clean fracturing fluids [8], drag reduction [9], and personal care products [10].

In some cases, the viscoelasticity of the fluid needs to be tailored to the demand [11]. Taking hydraulic fracturing as an example [12,13], the high viscosity of fracturing fluids is typically needed to transport sand particles in the construction process. After fracturing, fracturing fluids with low viscosity are preferably considered, as they can flow back smoothly, thus minimizing fracture blockage. The general strategy to achieve such a purpose is to use internal breakers to reduce the viscoelasticity of flow-back fracturing fluid [14]. Unfortunately, these external additives would not only change the composition of the viscoelastic fluids, but they would also prevent their recovery and reuse. Therefore, much attention has been shifted to constructing smart viscoelastic fluids, which can be switched reversibly between water-like and viscoelastic states [15]. Of these stimulus-responsive systems, pH-responsive viscoelastic solutions possess the advantages of simple preparation, controllability, easy operation, and being cost-effective [16]. A classical methodology for fabricating pH-switchable viscoelastic solutions is to introduce organic acid to the surfactant system [17]. For instance, Huang and co-workers [18] employed cetyltrimethylammonium bromide and potassium phthalic acid to prepare a pH-responsive viscoelastic solution that undergoes a fully reversible, repeatable “sol–gel” transition within a narrow pH region from 3.90 to 5.35. Likewise, our group [17] developed a pH-switchable viscoelastic solution by mixing a long-chain tertiary amine, *N*-erucamidopropyl-*N*, *N*-dimethylamine (UC₂₂AMPM), and maleic acid in a 2:1 molar ratio. It was found that the solution exhibited a reversible Newtonian-to-viscoelastic transition with an increase in zero-shear viscosity (η_0) by five orders of magnitude as the pH increased from 6.20 to 7.29. Correspondingly, the micellar aggregate showed a structural transformation from spheres to WLMs. Nevertheless, it has been recognized that these organic acids, such as maleic acid, experienced decomposition or polymerization [16] at elevated temperatures, impairing the pH responsiveness and viscoelasticity of fluids. Obviously, such systems are not available for high-temperature reservoirs. In this context, it is desirable and beneficial to develop novel pH-responsive viscoelastic fluids with good temperature-resistance properties.

During past decades, the development of metal ion–ligand coordination bonds has also been a common approach to constructing pH-responsive materials. The mechanism behind this is that such a bond would break under acidic conditions, causing changes in the macroscopic properties of the material as H⁺ replaces the metal ion bound to the ligand [19,20]. At alkaline conditions, the metal ion–ligand coordination bonds would reform [21]. For example, Che et al. [20] developed a novel pH-responsive mesoporous silica drug delivery system by incorporating drug molecules into the mesopores silica using coordination bonding in a “host–metal–guest” architecture. Under weakly acidic conditions (pH 5.0–6.0), the encapsulated drugs were readily released in response to a reduction in pH due to a breakdown of coordination bonds. Given the excellent thermal stability of metal ions, a promising way to build a novel pH-responsive viscoelastic fluid, tolerating high temperatures, is to introduce metal ions that can coordinate with surfactant ligands.

To realize the abovementioned idea, a pH-responsive viscoelastic fluid was proposed by simple complexation of the ultra-long-chain tertiary amines UC₂₂AMPM (Scheme 1) and AlCl₃. The chosen UC₂₂AMPM is capable of providing a pair of electrons that can be deemed a Lewis base. AlCl₃ was selected because it is a typical hard Lewis acid that coordinates hard basic centers, such as nitrogen atoms in amine groups, and then it forms coordination bonding. The phase behavior and rheological properties of the UC₂₂AMPM–AlCl₃ system were meticulously examined and compared with the UC₂₂AMPM–HCl system to shed light on the role of AlCl₃ in UC₂₂AMPM. Meanwhile, the pH-responsiveness of the UC₂₂AMPM–AlCl₃ system was illustrated by macroscopic appearance observation and rheological measurement at different pH values. Then, cryo-transmission electron microscopy (cryo-TEM) and proton nuclear magnetic resonance spectroscopy (¹H NMR) were employed to unravel the intrinsic mechanism involved in the pH-responsiveness of the UC₂₂AMPM–AlCl₃ mixed system. Finally, the properties of the UC₂₂AMPM–AlCl₃

viscoelastic solution as a fracturing fluid were evaluated in terms of temperature tolerance and shear tolerance.



Scheme 1. The chemical structure of *N*-erucamidopropyl-*N,N*-dimethylamine (UC₂₂AMPM).

2. Results and Discussion

2.1. Phase Behavior of UC₂₂AMPM–AlCl₃ System

The macroscopic appearance photos of the UC₂₂AMPM–AlCl₃ system at different α (molar ratio = UC₂₂AMPM:AlCl₃) under $C_{\text{UC22AMPM}} = 50$ mM are shown in Figure 1. One can find that, with increasing AlCl₃ concentration, the UC₂₂AMPM dispersion transformed from an opalescent dispersion to a transparent solution, indicative of the increment in water solubility of the UC₂₂AMPM molecules. Remarkably, at $\alpha = 1:9$, the mixed system exhibited phase separation.

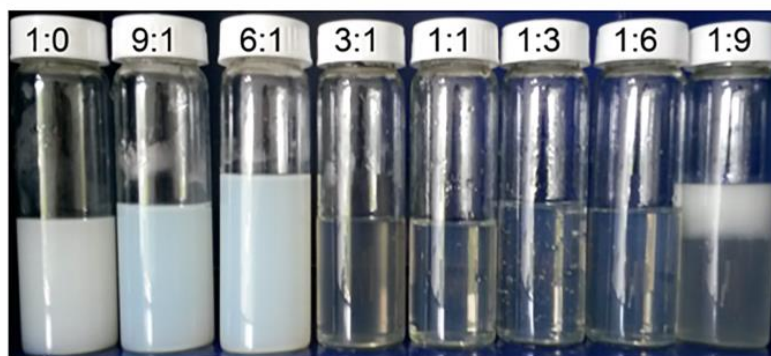


Figure 1. Snapshots of the UC₂₂AMPM–AlCl₃ mixed system with various molar ratios of UC₂₂AMPM to AlCl₃ (α). The number at the top of the bottle represents the α .

To unveil the underlying reasons for the phase behavior variation, pH and ¹H NMR measurements were carried out. It can be seen from Figure 2A that the pH of the sample dramatically decreased from 8.17 to 3.73 as the AlCl₃ concentration rose from 0 to 50 mM. The reducing pH was associated with the hydrolysis of AlCl₃ in water, yielding substantial amounts of H⁺ in the solution. There is also no appreciable change in the pH values with further increase in AlCl₃ concentration, indicating that the AlCl₃ hydrolysis has reached equilibrium. Figure 2B compares the ¹H NMR spectra of UC₂₂AMPM to those of a sample in which AlCl₃ ($\alpha = 1:3$) was added. In comparison to neat UC₂₂AMPM, the chemical shifts of protons neighboring amine groups (peaks a, b, and c) of UC₂₂AMPM molecules in the presence of 150 mM AlCl₃ were shifted from 1.74, 2.47, and 2.30 ppm to 1.96, 3.15, and 2.91 ppm, respectively, manifesting the protonation of the tertiary amine group. Combined with the results of pH and ¹H NMR, it was suggested that the hydrolysis of AlCl₃ in water yields substantial amounts of H⁺, leading to the protonation of UC₂₂AMPM. Consequently, UC₂₂AMPM behaves like a cationic surfactant, exhibiting good water solubility.

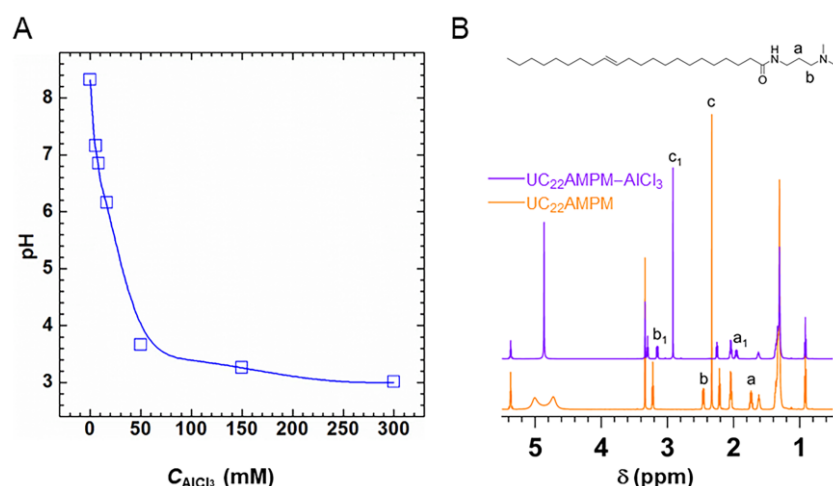


Figure 2. (A) Evolution of the pH of an AlCl_3 solution with increasing concentration. (B) ^1H NMR spectra ($\text{CD}_3\text{OD}-\text{D}_2\text{O}$, $V/V = 5:1$) of neat $\text{UC}_{22}\text{AMPM}$ and $\text{UC}_{22}\text{AMPM}-\text{AlCl}_3$ mixed systems.

As for phase separation, it may be due to the fact that the excessive AlCl_3 salted the $\text{UC}_{22}\text{AMPM}$ compounds out by dehydration, lowering their water solubility.

2.2. Rheological Properties of the $\text{UC}_{22}\text{AMPM}-\text{AlCl}_3$ Mixed System

To further shed light on the effect of AlCl_3 on the $\text{UC}_{22}\text{AMPM}$ solution, the rheological properties of $\text{UC}_{22}\text{AMPM}-\text{AlCl}_3$ with different α were studied. As depicted in Figure 3A, in the cases of $\alpha = 1:0$, 9:1, and 6:1, the viscosities (η) of the solutions were close to that of water, and they were independent of shear rate. That proved that these fluids were typical Newtonian fluids, implying the existence of only spherical micelles in the above solutions. Meanwhile, the $\text{UC}_{22}\text{AMPM}-\text{AlCl}_3$ samples at $\alpha = 3:1$, 1:1, 1:3, and 1:6 presented a Newtonian plateau and shear-thinning behavior at low- and high-shear rate regions, respectively, reflecting the formation of WLMs. To gain insight into the rheological properties of the $\text{UC}_{22}\text{AMPM}-\text{AlCl}_3$ solution, we performed dynamic rheological scans at 25 °C on the $\text{UC}_{22}\text{AMPM}-\text{AlCl}_3$ sample at $\alpha = 1:3$. As indicated in Figure 3B, it can be seen that the sample showed a gel-like response, i.e., the G' exceeds G'' over the frequency range. Similar rheology behavior has been extensively observed in the WLMs of C_{22} -tailed surfactants by both Raghavan [22,23] and Feng [22], mirroring the extremely long relaxation times of WLMs of $\text{UC}_{22}\text{AMPM}-\text{AlCl}_3$ complexes.

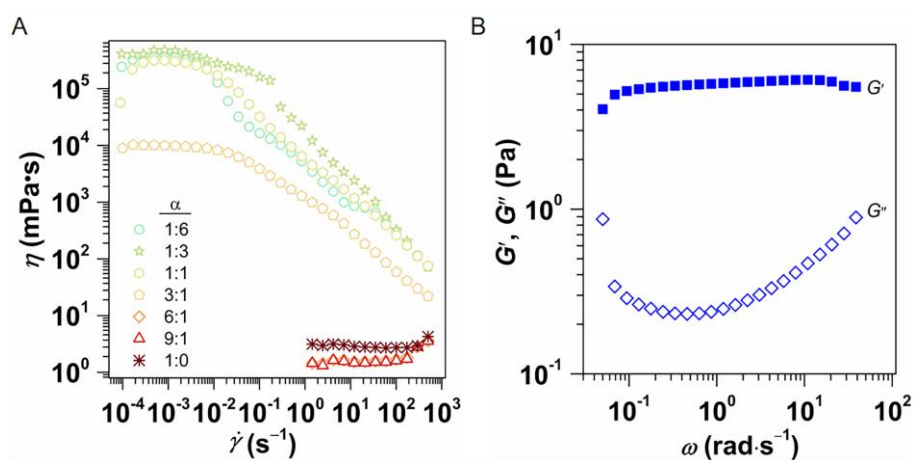


Figure 3. (A) Steady rheology of the $\text{UC}_{22}\text{AMPM}-\text{AlCl}_3$ mixed system with different molar ratios. (B) Dynamic rheology of the $\text{UC}_{22}\text{AMPM}-\text{AlCl}_3$ mixed system with $\alpha = 1:3$.

For comparison, we also investigated the steady rheology of the UC₂₂AMPM systems in the presence of HCl. As is exhibited in Figure 4A, at pHs of 7.14 and 6.88, the UC₂₂AMPM–HCl mixtures behaved as water-like Newtonian fluids with a constant η of ~ 3 mPa·s. At pH below 6.88, the mixtures displayed Newtonian plateau and shear-thinning behavior. The similarity in rheological behavior of the above two systems signified that AlCl₃ plays a comparable role to HCl in UC₂₂AMPM. That is, UC₂₂AMPM can be protonated by adding either HCl or AlCl₃, converting the cationic state and self-assembling into WLMs.

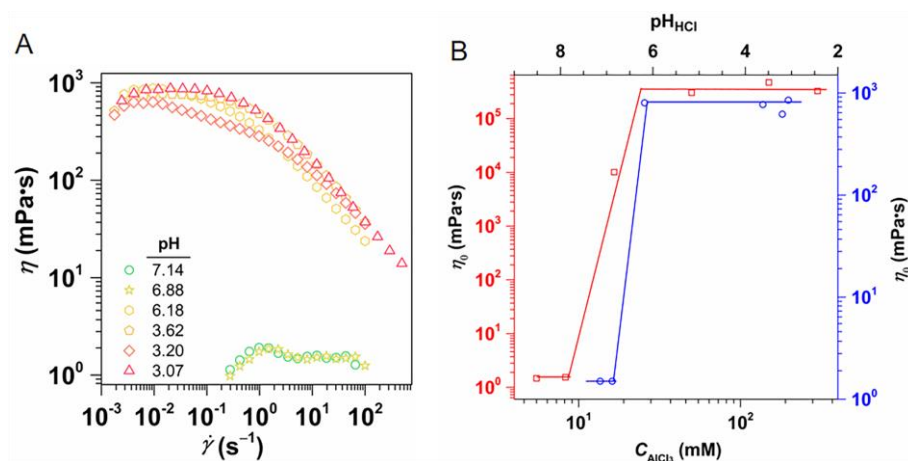


Figure 4. (A) Steady rheology of UC₂₂AMPM–HCl mixed systems at different pHs. (B) Zero-shear viscosity (η_0) of the UC₂₂AMPM solution plotted as a function of AlCl₃ concentration or pH values at 25 °C.

To further compare the effects of AlCl₃ and HCl on the rheological properties of UC₂₂AMPM solution, the zero-shear viscosity (η_0) of the UC₂₂AMPM solution was plotted as a function of AlCl₃ concentration or pH (Figure 4B). It was found that η_0 increased by five orders of magnitude when the AlCl₃ concentration increased from 15 to 30 mM. Following an increase in AlCl₃ concentration above 30 mM, the η_0 almost remained unchanged at 10^5 mPa·s. In contrast, the η_0 of UC₂₂AMPM solution increased by three orders of magnitude as HCl increased. Apparently, AlCl₃ is more efficient in thickening the UC₂₂AMPM dispersion as compared to HCl. A plausible explanation could be that the tertiary amine of UC₂₂AMPM can coordinate with trivalent metal ions, i.e., Al³⁺, leading to cross-linking of the wormlike micellar chains, enhancing the solution viscosity [24–26]. Similar results were reported by Hao et al. [25], who found the presence of trivalent metal ions (Fe³⁺ and Al³⁺) increased the viscosity of WLMs of tetradecyldimethylamine oxide and amphiphilic short peptides by 10- and 25-fold, respectively.

2.3. Effect of Other Trivalent Metal Salts on UC₂₂AMPM

It is well known that properties of the coordinated ion, such as ionic radius and crystal field stabilization energy, profoundly affect the strength of ion–ligand coordination bonds and the solution viscoelasticity [24,27]. To clarify the influence of these different trivalent metal ions on the rheological behavior of UC₂₂AMPM, two trivalent metal salts (FeCl₃ and CrCl₃) were separately added to 50 mM UC₂₂AMPM dispersion, and the resulting mixed samples were examined by a combination of rheometer and visual observations.

As depicted in Figure 5A,B, both mixtures underwent a transformation from orange or white dispersions to red or black translucent solutions as the metal salt concentration (C_{MCl_3}) increased. The different solution colors originated from the nature of Fe³⁺ or Cr³⁺ ions [28]. Steady rheology spectra of the UC₂₂AMPM–FeCl₃ and UC₂₂AMPM–CrCl₃ systems are shown in Figure 5C,D, and it was demonstrated that both systems also exhibited similar transitions from a water-like, low-viscosity fluid to a translucent viscoelastic fluid with increasing β (molar ratio = UC₂₂AMPM:FeCl₃) and χ (molar ratio = UC₂₂AMPM:CrCl₃). This

finding demonstrated that the trivalent metal ions could induce UC₂₂AMPM dispersion to form viscoelasticity fluid, regardless of the type of trivalent metal ions.

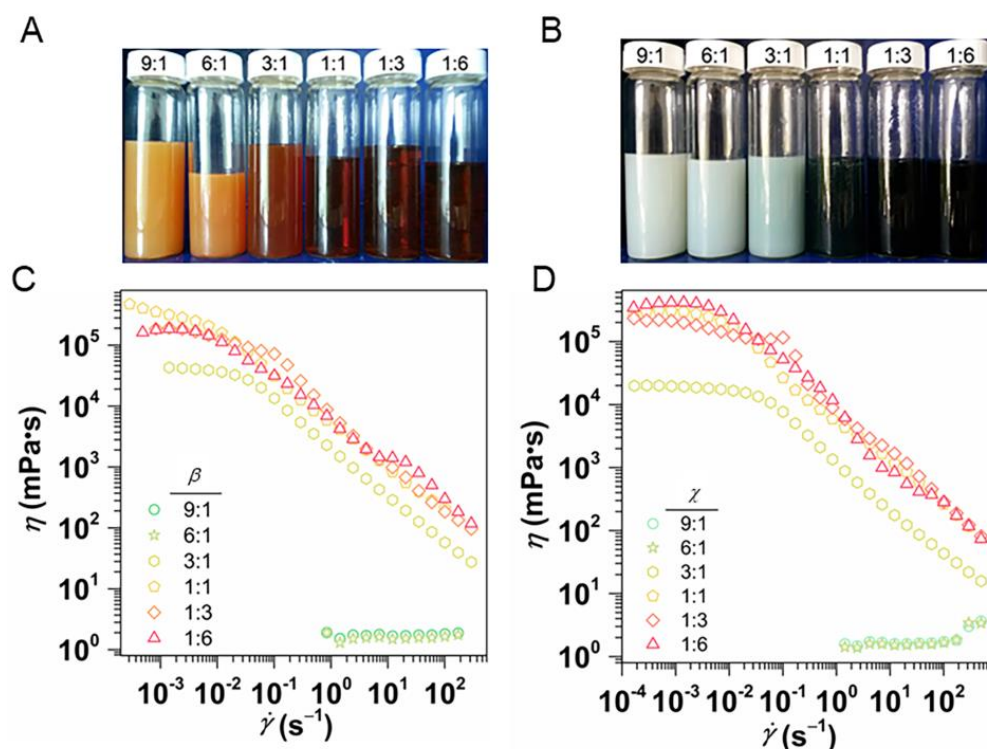


Figure 5. Macroscopic appearance of (A) UC₂₂AMPM-FeCl₃ and (B) UC₂₂AMPM-CrCl₃ mixed systems at different molar ratios at 25 °C, respectively. The number at the top of the bottle represents the molar ratio of UC₂₂AMPM to FeCl₃ or CrCl₃. Steady rheology for (C) UC₂₂AMPM-FeCl₃ and (D) UC₂₂AMPM-CrCl₃ mixed systems at a different molar ratio at 25 °C, respectively.

To explore the efficiency of viscosity enhancement, the effect of the above two cases of C_{MCl_3} on η_0 of the UC₂₂AMPM solution was further investigated. From the results shown in Figure 6A, it was clear that the η_0 of both cases first remained constant when the C_{MCl_3} was lower than 10 mM, and then it sharply rose in the C_{MCl_3} range of 10–25 mM, and, finally, it reached a viscosity plateau once the C_{MCl_3} exceeded 25 mM. Note that the above two solutions achieved a η_0 of 10⁵ mPa·s within the studied salinity scope, suggesting the identical thickening capability of both metal salts (i.e., FeCl₃ and CrCl₃). Interestingly, a relatively lower amount of FeCl₃ (20 mM) was required to reach such a high η_0 compared to CrCl₃ (24 mM), meaning that the efficiency of viscosity enhancement of Fe³⁺ is superior to that of Cr³⁺. In Figure 6B, the pH for the above two cases is compared as a function of C_{MCl_3} . Overall, the pH of the UC₂₂AMPM-metal salt mixtures showed a decreasing trend within the studied salinity scope, which can also be interpreted in relation to the hydrolysis of metal salts. It is noteworthy that the pH of the UC₂₂AMPM-CrCl₃ sample was higher than that of the UC₂₂AMPM-FeCl₃ sample under identical C_{MCl_3} , signifying that FeCl₃ is more adequately hydrolyzed than CrCl₃. Therefore, we attributed the preferable viscosity-enhancing efficiency of Fe³⁺ to the more adequate hydrolysis of FeCl₃.

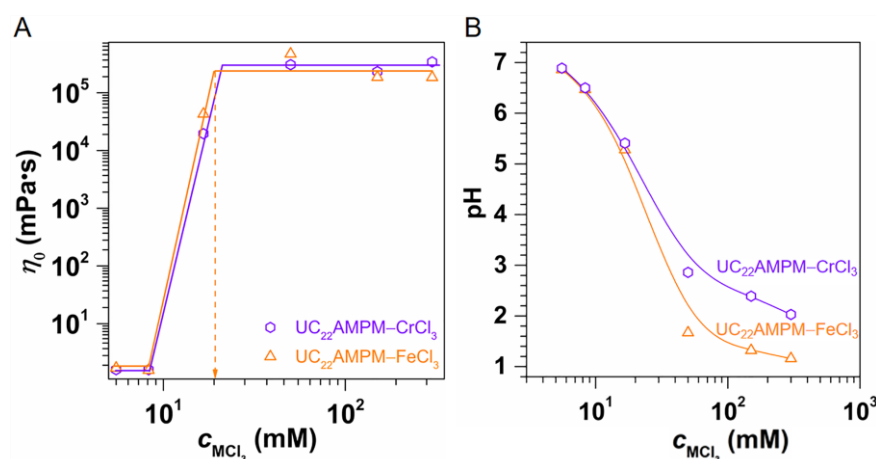


Figure 6. (A) The η_0 of UC₂₂AMPM solution plotted as a function of FeCl₃ or CrCl₃ concentration. (B) The pH for the UC₂₂AMPM–CrCl₃ and UC₂₂AMPM–FeCl₃ solutions plotted as a function of concentration at 25 °C.

2.4. pH Responsiveness of the UC₂₂AMPM–AlCl₃ Mixed System

As stated, the metal ion–ligand coordination bonds are sensitive to external pH variations because both metal ions and H⁺ ions compete to combine with the ligand. Therefore, it is expected that the UC₂₂AMPM–AlCl₃ blends would exhibit tunable viscoelasticity by altering the pH of the solution. To prove this concept, the UC₂₂AMPM–AlCl₃ mixed system at $\alpha = 1:3$ was chosen as a representative sample and characterized concerning its rheological behavior at different pH values. As observed in Figure 7A, the η_0 of the UC₂₂AMPM–AlCl₃ mixed system increased slightly, then rapidly reduced, and finally remained intact as pH increased. From the insets of Figure 7A, the sample was the bluish transparent solution and milky turbid fluid at the examined pH levels (pH 3.75 and 7.05), respectively, which were related to the protonation and deprotonation of UC₂₂AMPM. To be specific, the UC₂₂AMPM was protonated and thus it easily dissolved in water in acidic conditions. Under alkaline conditions, UC₂₂AMPM preferred non-ionic species and showed poor solubility due to its extremely long hydrophobic tail, resulting in the formation of turbid solutions. Impressively, unlike regular pH-responsive systems, which switch between gel-like and water-like states [29,30], the η_0 of UC₂₂AMPM–AlCl₃ varied by merely one order of magnitude at the examined pH scope (1.30–8.78). According to our previous studies [29], it was demonstrated that the nonionic UC₂₂AMPM would self-assemble vesicles in basic conditions. Here, we proposed that the vesicles could also coordinate with Al³⁺ ions to form metal ions–vesicle complexes, blocking a substantial solution viscosity reduction.

Figure 7B describes the curve of pH-stimulated reversibility for the UC₂₂AMPM–AlCl₃ mixed system. As the cycle number increased, the η_0 of the blends diminished slightly at both pH 7.05 and 3.75, reflecting their poor switchability. We attributed this to the formation of by-products during the repeated addition of acids and bases, which would deteriorate the viscoelasticity of fluids.

To reveal the underlying reasons for the variation of macroscopic properties, the morphology of the UC₂₂AMPM–AlCl₃ mixed system with $\alpha = 1:3$ at different pH values was directly visualized by cryo-TEM. As shown in Figure 7C, high-density, long, and flexible WLMs were observed in the UC₂₂AMPM–AlCl₃ mixed system at pH 3.75, and it is difficult to identify where they begin and end. These WLMs overlapped and entangled with each other into three-dimensional network structures, accounting for the gel-like response and high η_0 of this sample. On the contrary, when increasing pH to 7.05, only spherical vesicles are observed (Figure 7D), consistent with our previous inference (Figures 3A and 7A).

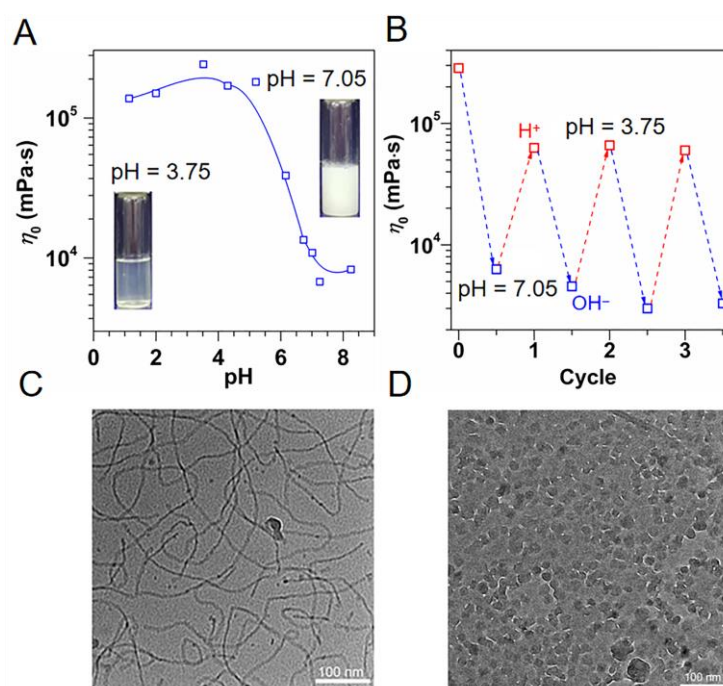
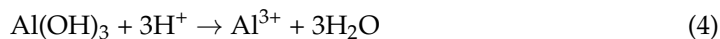


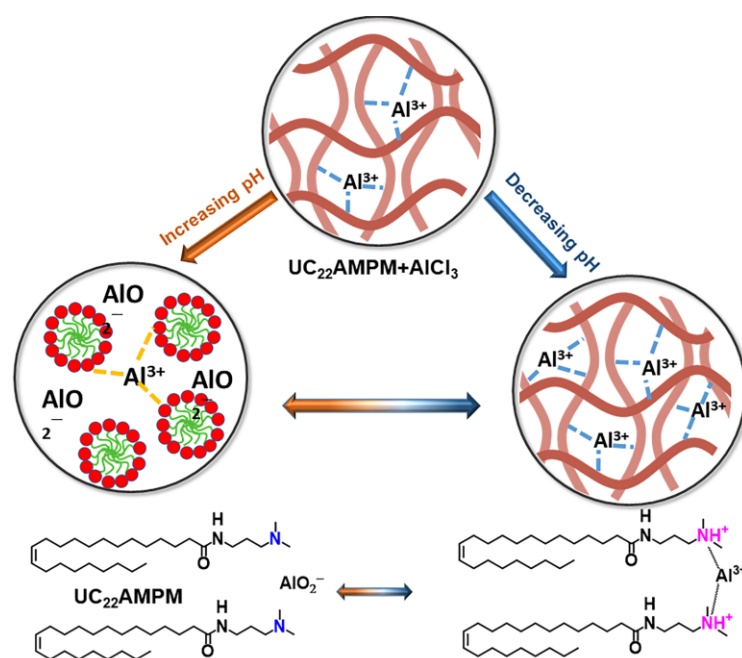
Figure 7. (A) η_0 variations of UC₂₂AMPM–AlCl₃ mixed system at $\alpha = 1:3$ by tuning pH. The inserts show macroscopic appearances of UC₂₂AMPM–AlCl₃ mixed system at pH 7.05 and 3.75, respectively. (B) η_0 of the UC₂₂AMPM–AlCl₃ mixed system at $\alpha = 1:3$ against pH cycles between 3.75 and 7.05. Cryo-TEM images of the UC₂₂AMPM–AlCl₃ blends $\alpha = 1:3$ at pHs of (C) 3.75 and (D) 7.05.

Based on the above results, we proposed the following mechanism to account for the effect of metal salts on the UC₂₂AMPM (Scheme 2). The addition of metal salts (AlCl₃) was first hydrolyzed to generate abundant trivalent metal ions (Al³⁺) and H⁺ (Equations (1) and (2)). In this scenario, the resulting H⁺ first protonated the UC₂₂AMPM molecules to their cationic form (Equation (3)), inducing the formation of WLMs. Entanglement of these WLMs into a transient network imparts high η to solutions. More importantly, Al³⁺ was tightly associated with the headgroups of UC₂₂AMPM to form metal–WLM ligand-coordinated systems by coordinating interaction, further enhancing the η of the solution [31]. These reactions could be expressed as follows:



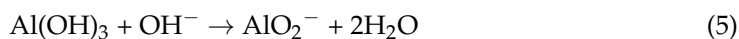
Upon decreasing pHs (by adding HCl solution), the UC₂₂AMPM molecules still maintained protonation states, and thus the corresponding wormlike micellar structure remained unchanged. Meanwhile, the reaction of H⁺ with Al(OH)₃ yields a larger amount of Al³⁺ (Equation (4)). There is no doubt that the increment in the amount of Al³⁺ further boosted the formation of metal–WLM ligand coordination, enhancing the entanglement density of the WLMs network and, thereby, leading to a remarkable enhancement of the solution η .





Scheme 2. Schematic illustration of the pH-responsive mechanism of the UC₂₂AMPM–AlCl₃ mixed system.

Conversely, the UC₂₂AMPM molecules converted into nonionized forms upon increasing pH (addition of NaOH into the aqueous solution), leading to a transformation of the aggregate structure from wormlike to the vesicle. More importantly, the OH[−] induced Al(OH)₃ to produce a larger amount of AlO₂[−] (Equation (5)), reducing the amount of Al³⁺. As a result, the metal–WLM ligand–coordinated and entangled WLM networks were broken, rendering a decrease in viscosity.



It is worth noting that the η_0 of UC₂₂AMPM–AlCl₃ mixtures was reduced by only one order of magnitude as pH increased from 3.75 to 7.05, which was due to the presence of metal–vesicle coordinated complexes.

2.5. Temperature Tolerance and Shear Tolerance of the UC₂₂AMPM–AlCl₃ Mixed System

At present, viscosity loss is the most prominent defect in clean fracturing fluids at high temperatures and high shear rates. Therefore, temperature- and shear-resistant properties have been considered the major criteria for evaluating the applicability of viscoelastic fluids in hydraulic fracturing [15].

To evaluate the potential of UC₂₂AMPM–AlCl₃ mixed systems as clean fracturing fluids, high temperature and high shear measurements were performed under simulated fracturing conditions. As shown in Figure 8A, the η at 170 s^{−1} of UC₂₂AMPM–AlCl₃ mixed system at $\alpha = 1:1$ gradually decreased and then maintained a constant viscosity of ~60 mPa·s with increasing temperature from 25 to 65 °C. Over the temperature range from 65 to 95 °C, the UC₂₂AMPM–AlCl₃ mixed system further declined to ~40 mPa·s, reflecting its good heat tolerance. Again, this can be interpreted by the fact that Al³⁺ ions are very tightly bound to the UC₂₂AMPM by coordination interaction, which greatly promotes the thermal stability of WLMs.

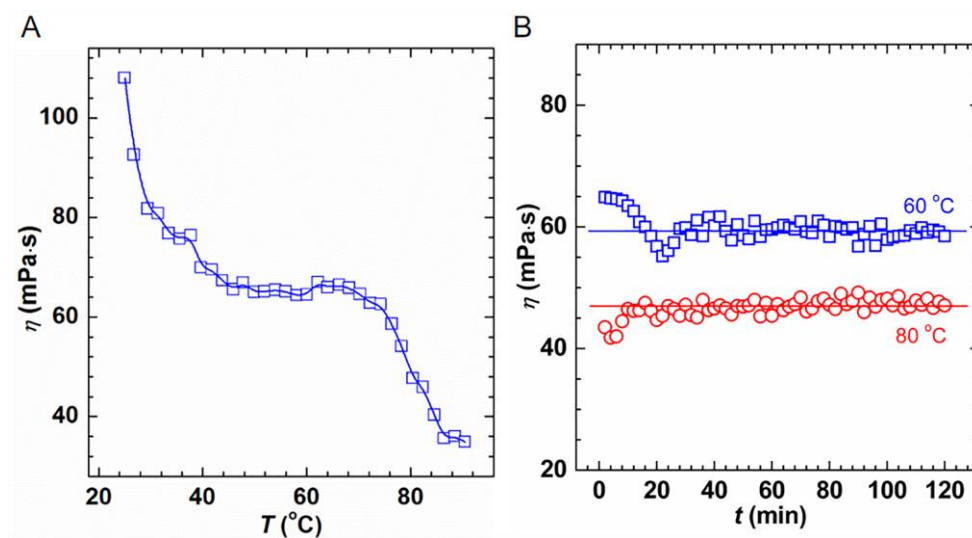


Figure 8. (A) Temperature dependence of the apparent viscosity of the UC₂₂AMPM–AlCl₃ mixed system at $\alpha = 1:1$. (B) Shear time dependence of η for the UC₂₂AMPM–AlCl₃ mixed system at 60 °C and 80 °C, respectively. The shear rate for all measurements is fixed at 170 s^{−1}.

Moreover, at temperatures of 80 and 60 °C, the UC₂₂AMPM–AlCl₃ mixed system can keep a stable viscosity around 40 mPa s and 60 mPa s for 120 min (Figure 8B), respectively, indicating the good shear tolerance of the UC₂₂AMPM–AlCl₃ mixed system. More importantly, it is also higher than the viscosity requirements (>25 mPa s) for clean fracturing fluid [32]. Therefore, it was believed that the UC₂₂AMPM–AlCl₃ mixed system can satisfy the demand for clean hydraulic fracturing in the vast majority of oil fields, from middle-low-temperature reservoirs to high-temperature reservoirs.

3. Materials and Methods

3.1. Materials

UC₂₂AMPM was synthesized, according to our previously-reported procedure [33], and confirmed by proton nuclear magnetic resonance spectroscopy (¹H NMR, Figure 2B). Hydrogen chloride (HCl, 34 vol.%), sodium chloride (NaCl, 99%, GC), aluminium chloride (AlCl₃, 99%, GC), ferric chloride (FeCl₃, 99%, GC), and chromium trichloride (CrCl₃, 99%, GC) were purchased from Chengdu Kelong Chemical Factory Co., Ltd. (Chengdu, China) and were used as received. CD₃OD and D₂O (both with 98% deuterium content) used for NMR analysis were obtained from Sigma-Aldrich (Shanghai, China). Deionized water with a resistivity of 18.25 MΩ·cm used throughout this study was prepared from a quartz water purification system (UPH-I-10T, Chengdu Ultra-pure Technology Co., Ltd., Chengdu, China).

3.2. Preparation of UC₂₂AMPM–Metal Salts Mixtures

A stock dispersion with 50 mM UC₂₂AMPM was prepared by adding designed amounts of power-like samples and deionized water to a sealed Schott-Duran bottle equipped with a magnetic bar inside, followed by gentle agitation at 60 °C, yielding a low-viscosity emulsion-like dispersion. Then, the desired amount of inorganic metal salts was added into a 50 mM UC₂₂AMPM dispersion, followed by mechanical agitation for 12 h. The samples were left at 25 °C for at least 24 h prior to measurements. The dilute NaOH and HCl solutions were employed to adjust the pH of the UC₂₂AMPM–metal salt mixtures; the pH was determined by a Sartorius basic pH meter PB-10 (±0.01).

3.3. Rheology Measurement

Rheological properties of mixture solutions were performed on a Physica MCR 302 (Anton Paar, Graz, Austria) rotational rheometer equipped with a concentric cylinder

geometry CC27 (ISO3219). Samples were equilibrated at the testing temperature for no less than 20 min prior to the experiments. During steady-shear tests, the $\dot{\gamma}$ and test time (t) parameters were varied logarithmically from 1×10^{-4} to $1.5 \times 10^3 \text{ s}^{-1}$ and 1×10^4 to 1 s , respectively, according to the relationship $\dot{\gamma} \times t \geq 1$. The extrapolation of η to zero-shear rate in the steady-shear measurement yields the zero-shear viscosity, η_0 .

For temperature sweep measurements, solution viscosity was recorded at a shear rate of 170 s^{-1} at various temperatures, ranging from 25 to 95 °C. The heating rate was fixed at 1 °C/min to ensure that the sample was equilibrated. Sufficient time was allowed before data collection at each temperature to ensure the viscosities reached their steady values.

The oscillatory measurements were conducted in the fixed stress (linear viscoelastic region), as determined from prior dynamic stress sweep measurements. The frequency varied from 0.01–100 $\text{rad} \cdot \text{s}^{-1}$. All measurements were carried out in stress-controlled mode, and Canon standard oil was used to calibrate the instrument before measurements. The temperature was controlled at 25 ± 0.1 °C using a Peltier device, and a solvent trap was used to minimize water evaporation during the measurements. For all experiments, flow curves were registered in a stress-controlled mode, and the data were acquired by the software Rheoplus™.

3.4. Micellar Structure Observation

The specimens of the UC₂₂AMPM–AlCl₃ mixed solution were prepared in a controlled environment vitrification system. The temperature of the chamber was maintained at about 25 °C, and the relative humidity was maintained close to saturation to prevent evaporation during preparation. Typically, 5 μL of sample solution was deposited on a copper grid and gently blotted with a piece of filter paper to obtain a thin liquid film (20–400 nm) on the grid. Next, the grid was plunged rapidly into liquid ethane (−183 °C) and transferred into liquid nitrogen (<−160 °C) for storage. Finally, the vitrified specimen was transferred into a FEI Talos F200C using a Gatan 626 cryo-holder and observed at an acceleration voltage of 200 KV and a temperature of −170 °C. The images were recorded digitally with a charge-coupled device camera under low-dose conditions with an under-focus of approximately 3 mm.

3.5. Phase Behavior Observation

Different amounts of melt salts were added to aliquots of UC₂₂AMPM solution (50 mM) to give a range of final melt salt concentrations ($C_s = 5.5 - 450 \text{ mM}$). The resulting colloidal dispersions were kept in a sealed glass vial at 25 °C for equilibration. Phase behavior was recorded by visual observation, following the previously reported procedure [34].

3.6. ¹H NMR Experiments

An amount of 4.0 mg of sample, including the neat UC₂₂AMPM and the mixtures of UC₂₂AMPM and AlCl₃, was dissolved in 0.6 mL of CD₃OD and D₂O ($V/V = 5:1$) mixed solvent. ¹H NMR spectra were registered in a Bruker AC 400 spectrometer (Bruker Instruments, Mannheim, Germany) at a proton resonance frequency of 400 MHz. Chemical shifts were reported on the δ (ppm) scale. The accuracy of the chemical shift reading was ± 0.01 ppm.

4. Conclusions

In this work, we developed a pH-responsive viscoelastic fluid by complexing a C₂₂-tailed surfactant, UC₂₂AMPM, with AlCl₃. For molar ratios of UC₂₂AMPM to AlCl₃ = 3:1, 1:1, 1:3, and 1:6, the UC₂₂AMPM dispersion could form a transparent viscoelastic fluid, similar to that of the UC₂₂AMPM–HCl mixed system. Due to the metal–ligand coordination between the Al³⁺ and N atoms of UC₂₂AMPM, the viscosity of the UC₂₂AMPM–AlCl₃ mixed system was higher than that of the UC₂₂AMPM–HCl system under identical pH values. By tuning the pH of the solution, the macroscopic behavior of the UC₂₂AMPM–AlCl₃ mixed system switched between milky dispersion and a clear viscoelastic solution,

accompanied by changes in viscosity. The pH responsiveness was caused by the morphology transition between WLMs and spherical vesicles at different pHs. The temperature and shear resistance test revealed the UC₂₂AMPM–AlCl₃ system attained a viscosity of 40 mPa·s at 80 °C and 170 s^{−1} for 120 min, featuring good thermal and shear resistance. These benefits indicated that such viscoelastic fluids can be a promising clean fracturing fluid for the exploration of high-temperature reservoirs. In summary, this study successfully constructed a pH-responsive viscoelastic fluid by introducing trivalent metal ions in a C₂₂-tailed surfactant and revealed the role of trivalent metal ions in viscoelastic fluids, enriching the methodology for the preparation of pH-responsive viscoelastic fluids.

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Sample Availability: The UC₂₂AMPM is available from the authors.

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