Effect of Added Tetraalkylammonium Counterions on the Dilational Rheological Behaviors of N-Cocoyl Glycinate

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Abstract: Ion specific effect, which is also known as Hofmeister effect, has been reported in numerous systems including ionic surfactant aggregates. Acyl amino acid surfactants have attracted growing attentions in the field of novel surfactants research due to their environmentally benign characteristics. The objective of this study was to investigate the effect of different salts containing NH_4^+ and tetraalkylammonium (TAA^+), where alkyl = methyl (TMA^+), ethyl (TEA^+), and propyl (TPA^+), cations on the dilational rheological properties of interfacial film are stabilized by potassium N-cocoyl glycinate (KCGI). The interfacial behaviors were studied using oscillating drop shape analysis method. The interfacial tensions (IFTs) and dilational rheological parameters results illustrate that KCGI in the presence of salts has better interfacial activity and stronger intermolecular interaction, indicating that added cations contribute to denser molecular packing at oil-water interface. Ion specific effects were observed in the system. Among the cations, KCGI shows highest dilational modulus in the presence of NH_4^+ . The overall interaction between cations and headgroups of KCGI decreases in the sequence $\text{NH}_4^+ > \text{TMA}^+ > \text{TEA}^+ \approx \text{TPA}^+$, which follows Hofmeister series. The increasing hydrophobicity of TAA^+ prevents the interaction between cations and KCGI's headgroup, and therefore prevent amphiphiles from packing closely at interface. The results present a theoretical origin for useful application of KCGI in cosmetics, petroleum and daily chemical industries.

Key words: tetraalkylammonium, amino acid-based surfactant, interfacial tension, interfacial dilational rheology, ion specific effects

1 Introduction

Ion specific effect, which was first reported by Hofmeister in 1888¹⁾, has been reported in tons of systems with charged interfaces or surfaces, including surfactant aggregates, supramolecular structures, enzymes, and polymers over the past several decades²⁻⁵⁾. Counterions in added salts are an important factor affecting the intermolecular interaction, surface activity, micellization, and aggregate morphological transition of ionic surfactants. Various organic and inorganic counterions are often used because they not only affect the interfacial behaviors of the surfactants, but also affect their self-aggregation structures⁶⁻¹¹⁾.

Added salts affect the interfacial behaviors of ionic surfactants in different ways such as, electrolytes increase their oil-soluble nature and enhance their diffusion to oil-water interface from bulk or stabilize oil-water interface by

increasing their adsorption through electrostatic interaction with counterions in added electrolytes¹²⁾. Tetraalkylammonium ions are a class of kosmotropic cations, and their effects on surfactants are even more pronounced¹²⁻¹⁷⁾. Interfacial tensions (IFT) can be reduced to an ultralow value with added tetrabutylammonium bromide¹³⁾. Yuan S. *et al.* have studied interfacial aggregations of different TAA^+ counterions with sodium dodecyl sulfate (SDS) and found that mixed interfacial layers are formed with methyl groups of TAA^+ penetrate into the monolayer¹⁷⁾. Therefore, it is of great importance to study the specific effect of different TAA^+ on the interfacial behaviors of ionic surfactants.

To study the adsorption progresses of surfactants, dynamic interfacial tensions are often used. Only the adsorption amounts cannot give a detail description about the interaction between the molecules at interface. Cur-

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rently, the adsorption of surfactants at interface is illustrated by their interfacial dilational rheology properties^{18–23}. Information of the molecular packing at interfacial absorption film is hidden in the interfacial properties, and can be decoded by studying the influence of many factors, i.e., disturbance frequency, time, concentration, interfacial pressure, on the interfacial rheology properties^{24–26}. Therefore, for the assessment of interfacial behaviors of amphiphile systems, like surfactants and proteins, interfacial dilational rheological experiments are used and have been widely studied in foam and emulsion stability^{27–30}.

Amino acids bearing both carboxyl and amine groups are excellent natural building blocks used for the preparation of surfactants³¹. Acyl amino acid surfactants are a class of environmentally friendly surfactants^{32–34}. They have been widely applied to various industry, including personal care, cosmetics, and pharmaceuticals^{32, 35–41}.

Here, we study the interfacial dilational rheological properties of acyl amino acid surfactant in the presence of various ammonium and tetraalkylammonium salts. The interfacial dilational rheological behaviors of a representative acyl amino acid surfactant potassium N-cocoyl glycinate (KCGI) in the presence of different salts, namely ammonium chloride (NH_4Cl), tetramethylammonium bromide, where alkyl = methyl (TMAB), ethyl (TEAB), and propyl (TPABr), are investigated respectively by the oscillating drop method. By analyzing the results of the above salts, the influences of ammonium and tetraalkylammonium ion on the interfacial behaviors of KCGI are revealed.

2 Experimental

Table 1 lists the chemicals used in the experiments. The chemicals are used as received without further purification. The potassium N-cocoyl glycinate (average molecular weight = 522.82 g/mol) is bought as a 30 wt% surfactant solution. Water used in these experiments was ultrapure water (resistivity = 18.2 M Ω .cm). *n*-Decane with purity of 99.0% was used as oil phase.

A response in interfacial tension (IFT) is observed when the interfacial area is disturbed by a periodic compression and expansion. Gibbs has defined the interfacial dilational modulus, ε , to depict the IFT response with the changes of area, which can be expressed by Equation 1:

$$\varepsilon = \frac{d\gamma}{d\ln A} \quad (1)$$

Where γ represents IFT, and A denotes the interfacial area. Dilational modulus, ε , reveals the capability to oppose the deformation of the interface.

The IFT and interfacial dilational rheology data are all measured by the oscillating drop shape analysis method, with ODG-20 from Data Physics Instruments GmbH, as we described elsewhere⁴². An oil drop injected from a syringe into an optical glass cuvette containing surfactant aqueous solution was captured by a CCD camera and digitized by Fourier transform analysis. The glass cuvette was always thermo stated at $25 \pm 0.1^\circ\text{C}$. The profile of the oil droplet was fitted to the Laplace equation to determine the IFT. The accessible frequencies between 0.005 and 0.1 Hz for the drop oscillations were carried out in sinusoidal mode and the oscillations amplitude was 10% ($\Delta A/A$).

3 Results and Discussion

3.1 Dynamic IFT and dilational moduli of KCGI in the presence of different salts containing tetraalkylammonium cations (MR_4^+ , R=1-3) and NH_4^+

Figure 1 shows the results of dynamic IFTs and dilational moduli of KCGI with added 5×10^{-2} mol/L NH_4Cl , or tetraalkylammonium bromide (TAABr), where alkyl denotes methyl (TMABr), ethyl (TEABr), and propyl (TPABr). The concentration of KCGI varies from 10^{-7} – 10^{-3} mol/L. The interfacial adsorption of KCGI molecules increases over time as soon as an oil-water interface was created, resulting in the gradual decrease in the values of IFT. The intermolecular interactions become stronger with the enhanced interfacial coverage and cause higher IFT gradient when the interface deforms. Therefore, the interfacial dilational

Table 1 Purities and suppliers of chemicals.

Chemical	CAS registry number	Grade (purity)	Supplier
<i>n</i> -Decane	124-18-5	99.0%	Sigma Chemical Company (Germany)
N-cocoyl glycinate (KCGI)	301341-58-2	30% aqueous solution	Ajinomoto Company (Japan)
Ammonium Chloride (NH_4Cl)	26650328	98.0%	Hushi Company (Shanghai, China)
Tetramethylammonium ($\text{C}_4\text{H}_{12}\text{NBr}$)	71-91-0	99.0%	Shanghai Macklin Biochemical Company (China)
Tetraethylammonium ($\text{C}_8\text{H}_{20}\text{NBr}$)	64-20-0	98.0%	Shanghai Macklin Biochemical Company (China)
Tetrapropylammonium ($\text{C}_{12}\text{H}_{24}\text{NBr}$)	1941-30-6	98.0%	Shanghai Macklin Biochemical Company (China)

Fig. 1 Dynamic IFT (A, C, E, G) and dilational modulus (B, D, F, H) of KCGI in the presence of 5×10^{-2} mol/L NH_4Cl (A, B), TMABr (C, D), TEABr (E, F) and TPABr (G, H) salts.

modulus increases correspondingly. When the interface achieves equilibrium adsorption, both IFT and dilational modulus finally reach constant values. This is consistent with the general characteristics of surfactants⁴³⁾.

3.2 Concentration dependence of IFT and interfacial dilational properties of KCGI in the present of different salts containing tetraalkylammonium cations (MR_4^+ , $\text{R}=1-3$) and NH_4^+

The equilibrium IFTs at different concentrations of KCGI in the presence of different salts (NH_4Cl , TMABr , TEABr and TPABr) are summarized in Fig. 2. As expected, IFTs decrease gradually with the increase of surfactant concentration. The oil-water IFT versus KCGI concentration curve in pure water is presented as a dotted line. Interestingly, the IFTs for KCGI in electrolyte solutions are clearly lower than that in pure water, demonstrating that salts have improved the interfacial activity of KCGI and contribute to denser molecular packing at oil-water interface. As reported in previous researches, this may be attributed to the screening electrostatic repulsion between anionic headgroups of KCGI molecules by the counterions, which increases the interfacial concentration of the surfactants^{13, 44–46)}.

However, as shown in Fig. 2, the ability of KCGI to reduce IFT varies significantly in the presence of different salts, suggesting the hydrophobicity and size of the cations may have significant influence on the interfacial behaviors of KCGI. Ammonium ion, NH_4^+ , as the most hydrophilic cation, performs differently at low and high KCGI concentration. At low KCGI concentrations, the effect of NH_4^+ on the IFT is less obvious than other cations because it has less tendency to adsorb to the interface compared to other hydrophobic cations bearing methyl and methylene groups. Above 5×10^{-6} mol/L KCGI concentrations, where the interfacial KCGI concentrations are also enhanced, NH_4^+ is mixed adsorbed with anionic headgroups of KCGI at interface. The electrostatic repulsion between headgroups of surfactant is screened by NH_4^+ , which contributes to a denser adsorption of the KCGI molecules at interface. The IFT values for KCGI in the presence of TMA^+ and TEA^+

Fig. 2 Equilibrium IFTs as a function of concentration for KCGI with added NH_4Cl , TMABr , TEABr , and TPABr .

are higher than these in the presence of NH_4^+ . Although this can be explained by the increasing of cation size, to some extent, prevent surfactant molecules from packing closely, there are other possibilities, Scheme 1. First, based on Collins' concept^{47, 48)}, the strongly hydrated carboxylate headgroup tends to interact strongly, and form possibly ion-pairs, with strongly hydrated cations, than weakly hydrated cations. Therefore, the interaction between KCGI headgroup and NH_4^+ is stronger than other hydrophobic cations. Second, possible hydrogen bonding⁴⁹⁾ between NH_4^+ and amino acid headgroups may also contribute to the packing between amphiphiles with added NH_4^+ . Thus, the IFT at high surfactant concentration is lower for ammonium ions compared to TMA^+ and TEA^+ . However, TPA^+ , with longer alkyls, itself has certain interfacial activity. To some extent, TPA^+ behaves as co-surfactant and mixed adsorb together with KCGI. Therefore, TPA^+ also decreases the IFT to a very low value.

Even though very low IFT was observed for KCGI in the

Scheme 1 Cartoon of the adsorbed layers of KCGI in the presence of NH_4^+ , TMA^+ and TEA^+ at the oil-water interface.

Fig. 3 KCGI concentration dependence of dilational moduli with added NH_4Cl , TMABr , TEABr , and TPABr .

presence of either NH_4^+ or TPA^+ , the interfacial arrangement of KCGI is essentially different, which can be further demonstrated by the interfacial dilational moduli. Figure 3 shows the changes of the equilibrium dilational moduli with increasing KCGI concentration. Usually, with increasing surfactant concentration, the interfacial dilational modulus increases to a maximum followed by decreases. The initial increase of interfacial surfactant concentration results in the deformation of interface and stronger interactions between molecules at interfaces, thus the IFT values increase at first. However, the diffusion exchange of surfactant molecules between interfacial region and bulk region also increases with increasing bulk surfactant molarities. As a result, the rapid diffusion of surfactant molecules to the interface can reduce the IFT gradient and leads to a decrease of the dilational modulus at high surfactant concentrations. Thus, as surfactant concentration increases, the modulus runs through a maximum^{42, 50}.

Hydration shells are formed around the headgroups of KCGI that adsorbs at interface. Consequently, the molecules organize with long distance and the intermolecular interaction of the surfactant molecules is not significant. In the absence of salts, the maximum dilational modulus of pure KCGI determined by us is only 18.5 mN/m. Prominent maximum increase in dilational modulus is observed in the presence of NH_4^+ and TMA^+ with KCGI. As discuss above, the cations that have smaller size and less hydrophobicity have stronger interaction with the KCGI and cause surfactant molecules to pack tightly at interface by screening the electrostatic repulsion between the headgroups. As a result, the interactions of the molecules at interface, namely the Van der Waals interaction between hydrophobic tails and hydrogen bonds between amidos, are enhanced,

which results in higher dilational modulus. However, as for TEA^+ and TPA^+ , the interactions between added cations and headgroups are weak. Hence, the relaxation processes, such as diffusion exchange, play more significant roles in determining the interfacial properties and dilational modulus begins to decrease. Therefore, KCGI with added TEA^+ and TPA^+ shows lower dilational modulus than other counterions which can be further proved from the viscoelasticity of the adsorption films.

3.3 Frequency dependence of the interfacial dilational properties for KCGI in the presence of added salts

The interfacial dilational moduli versus oscillation frequency for KCGI with NH_4^+ , TMA^+ , TEA^+ and TPA^+ are characterized in Fig. 4, because the changes of dilational moduli with oscillating frequency further characterize the viscoelasticity of interfacial film²⁰. The experiments were carried out by varying the frequency in the range of 0.005 - 0.1 Hz. The salt concentration was fixed at 5×10^{-2} mol/L, and the KCGI concentration varies from 10^{-6} to 10^{-3} mol/L.

As increasing frequency, the dilational moduli of all systems increase as shown in Fig. 4. At low frequencies, the dilational modulus is small, indicating the time for surfactants to eliminate the IFT gradient caused by the deformation in area is sufficient. But at higher frequencies, the dilational modulus is also higher. The interfacial deformation is much faster and there is no enough time for the recovery of interfacial film. As oscillating frequency increases at moderate rate, change in interfacial area becomes faster than the relaxation progresses, making the IFT gradient become increasingly difficult to eliminate.

3.4 Interfacial dilational modulus as a function of interfacial pressure for KCGI in the presence of added salts

To determine the interfacial behaviors of amphiphiles, the changes of interfacial dilational modulus with interfacial pressure are usually evaluated^{28, 42, 51}. Therefore, the interfacial dilational moduli versus interfacial pressure for the KCGI/salts systems have been illustrated in Fig. 5.

Usually, under fixed interfacial pressure, the interfacial dilational moduli of amphiphiles decrease as their concentrations increase. At high surfactant concentration, the strong diffusion exchange between interfacial region and bulk region decreases the dilational modulus value. In the presence of salts, the characteristics of KCGI's dilational modulus versus interfacial pressure profiles are divided into two notable regions. At low KCGI concentrations, dilational modulus vs. interfacial pressure coincide on a single curve, representing the interfacial properties are primarily decided by the interactions between molecules, but not the diffusion-exchange process. As increasing surfactant concentration, the diffusion exchanges of surfactant molecules between interfacial region and bulk region becomes more and more significant. Thus, the dilational modulus versus

Fig. 4 Oscillation frequency dependence of dilational moduli of KCGI in the presence of 5×10^{-2} mol/L NH_4Cl (A), TMABr (B), TEABr (C), and TPABr (D).

Fig. 5 Interfacial dilational modulus as a function of interfacial pressure for the mixtures of KCGI and added NH_4Cl (A), TMABr (B), TEABr (C), and TPABr (D).

interfacial pressure curves starts to disperse from the main branch at higher concentrations. For KCGI in the presence of different counterions, the dispersion degree of the curves increases with the length of the alkyl/hydrogen arms on the counterions, suggesting the diffusion of surfactant monomers between interfacial region and bulk region becomes more significant, and the interfacial film becomes more viscoelastic.

4 Conclusions

In the current work, effects of different salts (NH_4Cl , TMABr , TEABr and TPABr) on the interfacial dilational rheological properties of KCGI have been investigated. The results demonstrate that the participations of salts in KCGI solutions have strongly decreased the IFTs and increased the dilational moduli of the system, due to the interaction between the added cations and surfactant headgroups. Interestingly, various cations bearing various sizes and hydrophilicities behave differently. In case of relatively small and hydrophilic cations, e.g., NH_4^+ , KCGI packs closer at interface, and decreases the diffusion between interfacial region and bulk region. However, those relatively large and hydrophobic cations, such as, TEA^+ and TPA^+ , interact weakly with surfactant headgroups and fail to induce a closer arrangement of molecules at interface. Relaxation processes are easy to take places and thus play an important role in determine interfacial properties. Therefore, viscoelastic films are formed in the presence of TEABr and TPABr . The experimental data of KCGI with salts may provide a hypothetical basis for its useful application in detergents, pharmaceutical, cosmetic, petroleum and daily chemical industries.

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