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Dilational rheology of different globular protein with imidazolium-based ionic liquid surfactant adsorption layer at the decane/water interface

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ABSTRACT

This contribution is concerned with the imidazolium-based ionic liquid surfactant being considered potential amphiphilic molecules. The interfacial dilational rheology of solutions of globular proteins (lysozyme and bovine serum albumin (BSA)) with imidazolium-based ionic liquid surfactant (1-dodecyl-3-methyl imidazolium bromide ([C_{12}mim]Br)) have been measured as a function of the surfactant concentration, interface lifetime and interfacial pressure. The dynamic interfacial dilational modulus of lysozyme/[C_{12}mim]Br solutions are always monotonous, but that of the BSA/[C_{12}mim]Br solutions become nonmonotonous indicating the destruction of the protein structure. One can assume that some lysozyme molecules desorb from interface due to competitive of free [C_{12}mim]Br molecules for lysozyme/[C_{12}mim]Br solution with [C_{12}mim]Br concentration increasing, however, BSA molecules unfolding of compact globule have been subject to conformational changes so that it can give space for more [C_{12}mim]Br molecules to co-adsorb. This aimed to provide more theoretical information for practical applications of imidazolium-based ionic liquid surfactant.

1. Introduction

Room temperature ionic liquids (RTILs), an interesting class of tunable and designer solvents, have been extensively used as a "green" replacement for toxic, hazardous, flammable and highly volatile organic solvents [1,2]. Owning to their unique chemical and physical properties, RTILs are chosen instead of many traditional volatile organic solvents in many applications, such as synthetic food colourants in soft drinks and confectioneries, and for the food separation science [3–5]. In the case of an increasing awareness of environmental protection, the ionic liquids are considered to be promising alternatives to traditional solvents, and are widely used [6]. However, a number of non surface-active RTILs having high viscosity and potential toxicity possess limited uses in some fields, such as food and cosmetic industry, in deed, the surface active ionic liquids (SAILs) are known to exhibit low toxicity and have tuneable physicochemical properties [2,7] and are being considered potential amphiphilic molecule in some applications. In the present work, we have chosen the imidazolium-based ionic liquid surfactant because they have been demonstrated excellent antimicrobial activity against a wide variety of microorganisms and the critical micelle concentration (CMC) in an aqueous solution was proven to be lower than that of typical cationic surfactants [8]. Compared with conventional ammonium surfactants, imidazolium-based SAILs display some advantages due to the existence of cationic imidazolium head groups [8]. Owning to the delocalized positive charge on the imidazolium ring and the ubiquitous hydrogen bonds among the imidazolium cations, the imidazolium-based SAILs are somewhat better than that of conventional ionic surfactants, and they would exhibit significantly stronger tendency for self-aggregation [9].

The protein/surfactant system is very important in the formation and stabilization of foams and emulsions in many fields, such as in the cosmetic and pharmaceutical industry, and in the manufacture of the processing. The main role of surfactant and proteins in foamed and emulsive products is to stabilise the liquid/liquid of air/liquid interface through their capacity to lower the interfacial tension [10–12]. Imidazolium surfactants can interact with a variety of protein molecules and are able to influence the film forming, gelation, viscosity, and emulsification properties of protein by forming surfactant/protein complexes [2,8]. These surfactants are able to influence the behavior of the proteins and its stability by combination of both physical and chemical interaction [13]. Information of the protein/surfactant interactions in the bulk phase have been studied by an abundance of ways, such as optical spectroscopy, fluorescence probe techniques, circular dichroism, neutron and X-ray small-angle scattering and dynamic light scattering. It is thought that the surfactant can bind to the special sites of the protein at lower surfactant concentration, and at high surfactant concentration, the surfactant can destroy the tertiary structure of protein. Although the

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interfacial properties of the protein/surfactant mixed system is very important in the formation and stabilization of foams and emulsions, the interfacial properties have been studied mainly by the interfacial tension measurement. The interfacial tension and adsorbed amount usually change monotonously as a function of the interfacial formation life, and it obtained limited information and cannot extract the information of the changes of the protein conformation from the change of interfacial tension. Recently, the interfacial dilational rheology properties have been proved to measure the protein/surfactant interfacial adsorption layer structure, and the interest in interfacial dilational rheology has increased in recent years. The interfacial rheological property is based on the thermodynamics and kinetics of the respective adsorption layers, which plays a significant role in acquiring the information of the adsorption layer structure, like molecule orientation, molecule interaction and characteristics of mixed macromolecule/surfactant at the liquid/liquid interfacial films. Also, the dilational rheology property turns out to be more sensitive to the conformation of macromolecules at the liquid interfacial than interfacial tension. It has been shown recently that most of the interfacial dilational rheology studies on protein and surfactant mixtures are mainly on conventional ionic and non-ionic surfactants, such as β-lactoglobulin (BLG) with dodecyl trimethyl ammonium bromide (DTAB) complexes [14], Mixed β-Casein/DTAB solution [15], bovine serum albumin (BSA) with sodium dodecyl sulfate (SDS) mixed solution [16] and β-casein (BCS) with triblock copolymer(C_{12}DMPO) [17]. To the best of our knowledge, the information of the structure of adsorption layers of protein/ionic liquid-type imidazolium surfactant has been scarce [18–21]. Compared with conventional surfactant, ionic liquid-type imidazolium surfactant system can bring some advantages such as stronger tendency to self-aggregation, and stronger attraction with aromatic rings through π-π interaction because of the existence of imidazolium head group [22,23].

In the present work, the dilational rheology properties are applied to mixed solutions of ionic liquid type imidazolium surfactant (1-dodecyl-3-methylimidazolium bromide ([C_{12}mim]Br)) with globular proteins (lysozyme and bovine serum albumin(BSA)), which have different charged at neutral solution and different tertiary and secondary structures, with the aim to investigate the interaction of globule protein and the imidazolium surfactant in the interfacial adsorption layer.

2. Experimental

2.1. Materials

The protein studied were hen egg-white lysozyme and Bovine Serum Albumin (BSA), with the molecular weight of 14.3 kD in the former case and 66 kDa in the latter, both proteins were purchased from Sigma Aldrich Co. (Germany) used as received. Ionic liquid–type imidazolium surfactant [C_{12}mim]Br was obtained from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. The purity of the surfactant [C_{12}mim]Br was checked by ^{1}HNMR spectroscopy, and the structure is displayed in Fig. 1. Decane was also obtained from Sigma Chemical Co. (Germany) used without further purification. All experiment solutions were prepared in sodium phosphate buffer (Sinopharm Chemical Reagent Beijing Co., Ltd) using in appropriate amounts. The pH values of the solutions before and after the experiments were controlled in the range of 6.8–7.0. The mixed protein/[C_{12}mim]Br solutions were prepared at constant protein concentrations(hen egg-white lysozyme at 7×10^{-7} mol/L and Bovine Serum Albumin at 1.5×10^{-8} mol/L) and varying [C_{12}mim]Br concentrations from 5×10^{-8} mol/L to 5×10^{-5} mol/L.

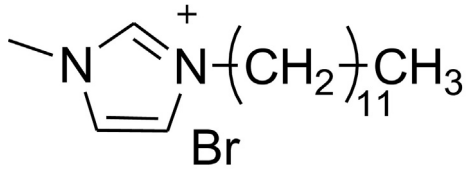

Fig. 1. The chemical structures of imidazolium-based ionic liquid surfactant [C_{12}mim]Br.

2.2. Methods

Interfacial tension and interfacial dilational rheological properties were measured by oscillating drop accessory ODG-20 from Data Physics Instruments GmbH, Germany. When we measure the interfacial dilational rheology of the adsorption film at the decane/water interface, the water phase is syringed into a thermostated optical glass cuvette containing decane. The image of the water drop in the decane was capture by a CCD camera and transferred to the data acquisition computer, where it was determined by digitizing and analyzing the profile of the droplet fitted to the Laplace equation. At the end of the experiment, the software retrieves the images and calculates using a Fourier transform analysis and the interfacial rheological parameters were determined.

For the experiments portrayed in this article, the drop oscillations were carried out at a fixed oscillations frequency 0.1 Hz during the adsorption reached to the equilibrium. Then the oscillations frequencies were varied between 0.005 and 0.1 Hz and the oscillations amplitude was 10% ($\Delta A/A$) in sine mode. In the interfacial tension relaxation measurement, the film was expanded about 15% in area by a sudden expand in 1 s. All experiments were carried out at 25 ± 0.1 °C. All experiments were repeated three times, and the error was within 3%.

3. Theoretical background

In sinusoidal interfacial compression and expansion experiment, the interfacial dilational modulus ε which gives a measurement of the interfacial resistance to changes in area, is defined as the change in interfacial tension γ for a small relative change of interfacial area A [24].

$$\varepsilon = d\gamma/dA \quad \text{(Eq. 1)}$$

The dilational modulus can also be defined as:

$$\varepsilon = \varepsilon' + \varepsilon'' \quad \text{(Eq. 2)}$$

The real part ε' is called the storage modulus, representing the elastic energy stored in the interface and is known as dilational elasticity, and the imaginary part (loss modulus) $\varepsilon'' = i\omega\eta_d$ accounting for the energy dissipated in the relaxation process is expressed in terms of the interfacial dilational viscosity modulus.

The phase angle θ difference between the strain and the response stress, resulting from the change in the dynamic interfacial tension γ, is derived from a small change in the interfacial area A, therefore

$$\varepsilon' = |\varepsilon| \cos\theta \quad (3)$$

$$\varepsilon'' = (|\varepsilon|/\omega) \sin\theta \quad (4)$$

Interfacial tension relaxation experiments are a reliable way to obtain interfacial dilational parameters. To determine the dilatational relaxation modulus, $E(t)$, we measure the stress relaxation after a sudden strain displacement. In these experiments, the interface is instantaneously deformed and then held constant while the interfacial stress is measured. The dilatational relaxation modulus is calculated as a function of time from the following expression:

$$E(t) = \Delta\gamma(t)^{A_0} \Big/ _{\Delta A} \quad (5)$$

Where $\Delta\gamma$ is the difference between the static interfacial tension prior to interfacial deformation and the measured isotropic interfacial