Interfacial Dynamics of a Gelatin Solution with Surfactant

Shi-Yow Lin,† Tsuei-Fen Wu,† and Heng-Kwong Tsao*,‡

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan 106, R.O.C., and Department of Chemical and Materials Engineering, National Central University, Chung-li, Taiwan 320, R.O.C.

Received June 23, 2003

ABSTRACT: In terms of dynamic surface tension, the interfacial dynamics of gelation solutions with various surfactants are investigated by pendant bubble tensiometry. On the basis of local equilibrium assumption, the thermodynamics of dynamic surface tension is analyzed. The adsorption efficiency of gelatin is low compared to that of small surfactant. However, the surface activity of gelatin may be enhanced due to intrachain and interchain rearrangement at the interface, which results in long relaxation time signature. The interplay between adsorption efficiency and surface activity categorizes our experimental results into two types of dynamic behavior. For type I dynamics, the gelatin molecule is completely displaced from the interface, and the interfacial dynamics is dominated by that associated with surfactant. Nevertheless, the interaction of gelatin with surfactant in the bulk solution can alter the surfactant surface excess and hence the surface tension. For type II dynamics, the gelatin molecule is partially displaced from the surface, and the dynamics displays a long relaxation characteristic. The extent of surface tension decrement due to gelatin conformational change manifests the degree of gelatin displacement from the interface. Our conclusion is able to elucidate the peculiar dynamic surface tension of a solution of gelatin and PEG.

I. Introduction

Polymers at interfaces are important because of both their practical applications and fundamental properties. For example, the adsorption of polymers onto colloid surfaces plays an essential role in the stabilization of emulsions in photographic, food, and pharmaceutical industries.[1] In another example, biopolymers often contain a disorder hydrophobic and hydrophilic sequences. A protein molecule may therefore stabilize at an oil−water interface and reduce the interfacial tension.[2] From a fundamental point of view, it is interesting to explore how the conformation of a heteropolymer is adjusted at the air−water interface and the factors that influence the interfacial properties.

The adsorption of heteropolymers containing hydrophobic segments, such as protein, onto air−water interfaces is a very much slower process than the adsorption of simple amphiphiles owing to the much greater size and structural complexity. Although it takes merely a few seconds for adsorption of small molecules, the time scale for reaching equilibrium interfacial tension can be many hours for heteropolymer. As a consequence, the time-dependent interfacial property, such as dynamic surface tension, plays an important role in industrial processes. The gradual decrease in the surface tension generally involves three steps: (1) the diffusion of the macromolecules to the subsurface region, (2) interaction and adsorption of the heteropolymer with the interface, which may involve perturbations in heteropolymer structure, and (3) relaxation of the adsorbed polymer to its equilibrium conformations.[3] In the very early stage of adsorption at a clean interface, the variation of the surface tension γ with time t is controlled by molecular diffusion. According to the Ward−Tordai theory and the ideal gas surface equation of state, the dynamic surface tension is described by $\gamma_0 - \gamma(t) \propto \sqrt{t}$.[4] When the molecular concentration in the immediate subsurface region is not negligible, the local concentration gradient and hence the mass transfer rate are reduced. Beyond the initial diffusion-controlled stage, the adsorption−desorption kinetics must be specified to describe the change in surface tension.[4,5] For the heteropolymer such as gelatin, changes in surface tension arise not only from new macromolecules arriving at the interface but also from conformational changes in previously adsorbed polymers. Nevertheless, the quantitative description of the relaxation dynamics is still lacking in the literature.

The interfacial relaxation of a dilute heteropolymer solution can be investigated by measuring its dynamic surface tension. A simple yet well-known choice of the heteropolymer is the gelatin molecule, which is a very efficient stabilizer for colloid stability.[2] Gelatin is a cheap, readily available polypeptide obtained from denatured collagen. It is a linear polymer having a typical molecular weight of $(1-2) \times 10^5$ Da. When the concentration is below ∼1.0 wt %, the gelatin solution is in the sol state, and the gelatin molecule is characterized as a random coil with a radius ∼ 17.5−35 nm.[6−8] The chain contains ∼27% glycine and ∼27% proline and hydroxyproline. The monomeric representation of this biopolymer is -(Gly-X-Pro)$_n$-, where X denotes the amino acid residues, typically glutamic acid and aspartic acid (∼16%), lysine and arginine (∼13%), and leucine, isoleucine, and valine (∼7%). At neutral pH, about 16% of the gelatin molecule is negatively charged and about 13% positively charged. Approximately 7% residues of the chain are strongly hydrophobic in nature, leaving the rest of the chain to be neutral. When the concentration is beyond ∼2.0 wt % at 25 °C, gelation (gel phase) takes place, and the gelatin molecules are strongly interconnected in the form of a triple-helix conformation held by hydrogen bonds between adjacent peptides.

---

† National Taiwan University of Science and Technology.
‡ National Central University.
* Corresponding author: e-mail hktsao@cc.ncu.edu.tw.

10.1021/ma034853y CCC: $25.00

Polymer and surfactant mixtures in solutions are widely involved in industrial applications in cosmetic products, foods, pharmaceuticals, and other sectors. The bulk relaxation and dynamics of these systems have studied by dynamic light scattering.[7,8] The interaction between polymers and surfactants may lead to polymer/surfactant complexes and therefore alter the dynamics of polymers. On the surface, the dynamics of polymers not only depends on the competitive adsorption between polymers and surfactants[2] but also is closely related to the nature and strength of any polymer–surfactant interactions in bulk solution. The former effect is generally demonstrated by the dynamic surface tension because the small surface-active molecules compete with polymer segments for sites at the surface. In a system containing adsorbed polymer, addition of surfactant into the system can reduce the mean binding energy per polymer segment, and therefore the polymer is competitively displaced from the interface by surfactant. In this approach, the effects contributed by conformational changes cannot be observed. However, it is of great interest to understand the interfacial dynamics of solutions containing both polymer and surfactant and the role played by the conformational relaxation of heteropolymers. Useful information can be revealed from the dynamic surface tension, starting from the condition of zero surface excess.

In this paper we shall be concerned with the relaxation dynamics at the air–water interfaces of gelatin and gelatin–surfactant solutions because the gelatin molecule is a linear heteropolymer capable of forming network by hydrogen bonds. The interfacial dynamics is investigated on the basis of the dynamic surface tension determined by the shape analysis of a pendant bubble. On the basis of local equilibrium assumption, the thermodynamic principle for the interfacial dynamics is developed. The effect of surface-active solute on the interfacial dynamics of the gelatin solution is studied by the addition of normal alcohols with different alkyl chain lengths. Moreover, the influences of strong surface-active surfactants, which interact with gelatin molecules differently in the bulk solution, are also examined.

II. Experimental Section

Materials and Sample Preparation. Anionic surfactant CTAB (cetyltrimethylammonium bromide; purity > 99%) is purchased from ACROS. Cationic surfactant SDS (sodium dodecyl sulfate; purity > 99%) is from J.T. Baker. 1-Ethanol with purity >99% is from ACROS, 1-pentanol (purity >99.0%) and 1-octanol (purity >99.5%) are from Fluka, and 1-decanol (purity >99%) is from Aldrich. Sodium chloride with purity >99.5% is obtained from Merck. Poly(ethylene glycol), PEG 20K and PEG 4600, are from Fluka and Aldrich, respectively. PEG 20K has a molecular weight (M_n) ranging between 16 000 and 24 000 g/mol, and PEG 4600 has an average M_n of 4600 g/mol. Gelatin (type A, from porcine skin; $M_w = 50\,000-100\,000$ g/mol) is purchased from Sigma. All the compounds above were used without further modification.

Aqueous surfactant solutions were prepared first with clean water purified using a Barnstead NANOpure water purification system, with the output water having a specific conductance of less than 0.057 $\mathrm{mW^{-1}/cm}$. Gelatin was then added into the surfactant solutions to make gelatin solutions. To make solutions uniform, the gelatin solutions were stirred using an ultrasonic cleaner for around 30 min at 50 °C. The solutions were then kept in 25 °C and used in 24 h.

Apparatus. Pendant bubble tensiometry[4,5,9] enhanced by video digitization was employed for the measurement of dynamic surface tension. The tensiometer creates a silhouette of a pendant bubble, video images the silhouette, and digitizes the image. A 17 gauge stainless steel inverted needle (1.07 mm i.d.; 1.47 mm o.d.), which was connected to the normally closed port of a three-way miniature solenoid valve, was used for the bubble generation. The common port of the valve, controlled by a computer, is connected to a gastight Hamilton syringe placed in a syringe pump. The pendant bubble was generated in a gelatin aqueous solution, which was put inside a quartz cell. The quartz cell was enclosed in a thermostatic air chamber, and the temperature variation of the gelatin solution is less than ±0.05 K. A parallel light of constant intensity passes through the pendant bubble and forms a silhouette of a bubble on a video camera. The silhouette image was digitized into 480 lines × 512 pixels with a level of gray of 8 bit resolution. The edge is defined as the x or z position where the intensity is 127.5.

Surface Tension. The theoretical shape of a pendant bubble is derived from the classical Laplace equation, which relates the pressure difference across the fluid interface ΔP to the curvatures of the surface by the surface tension, $\Delta P = \gamma[R_1^{-1} + R_2^{-1}]$, where R_1 and R_2 are the principal radii of curvature of surface. The Laplace equation is recast as a set of three first-order differential equations for the spatial positions x and z and turning angle θ of the interface as a function of arc length s and then integrated with boundary conditions $x(s = 0) = z(0) = \theta(0) = 0$. An objective function is defined as the sum of squares of the normal distance between the experimental edge points and the theoretical profile evaluated from the Laplace equation. The objective function depends on four unknown variables: the actual location of the apex (X_0 and Z_0), the radius of curvature at the apex (R_0), and the capillary constant ($B = \Delta\rho g R_0^2/\gamma$). The surface tension was determined from the best fit between the theoretical curve and the data points by minimizing the objective function. The accuracy and reproducibility of the dynamic surface tension measurement obtained by this procedure are ca. 0.1 mN/m.[4,5]

III. Results and Discussion

We have studied the interfacial dynamics of a gelatin solution with/without surfactant by measuring the dynamic surface tension. By comparing the dynamic surface tension of the three-component mixture (gelatin/surfactant/water) with those of the two-component mixtures (gelatin/water and surfactant/water), we observed that the relationship among them is absolutely not evident and straightforward. The intricate dynamic behavior may be attributed to the long relaxation behavior associated with gelatin molecules and the competitive adsorption between gelatin and surfactant. In this section, first, we present a thermodynamic framework for interfacial dynamics based on a local equilibrium assumption. Then, we analyze the interfacial dynamics of a gelatin solution qualitatively and infer the mechanism of its long relaxation time. Finally, a systematic variation of the surface activity of surfactant helps us to clarify the roles played by adsorption efficiency and surface activity. Our conclusion is able to shed some light on the peculiar interfacial dynamics of the solution of gelatin and PEG.

Local Equilibrium Analysis of Interfacial Dynamics. The heteropolymer containing hydrophobic segments is a surface-active macromolecule, and its dynamic surface tension often displays a long time varying behavior. An extreme example is the protein adsorption. The dynamic process of heteropolymer adsorption onto the air–water interface is very complicated because it involves several steps: polymer diffusion, adsorption, and conformational change which includes intrachain and interchain interactions. In fact, the determination of equilibrium surface tension of the heteropolymer solution is frequently hampered by the long relaxation time associated with the interfacial dynamics. As a consequence, the theoretical description of dynamic surface tension for polymer solutions is scarce in the literature.

The interfacial dynamics for heteropolymer with hydrophobic segments can be approximated as four consecutive steps. When a clean surface is created, i.e., zero surface excess of polymers $\Gamma_p = 0$, the diffusion of polymers to the subsurface layer takes place first. It is simply driven by the chemical potential gradient associated with the polymer.[10] The polymers at the subsurface layer will then adsorb onto the interface. A sorption kinetics such as the Langmuir formalism is required to depict the adsorption process.[4,9] These two steps are generally adopted to describe the kinetics of surfactant adsorption at fluid–fluid interfaces. When the equilibration process in the bulk solution is much slower than the one at the interface, it is diffusion-limited adsorption. On the contrary, kinetically limited adsorption occurs.

As a macromolecule reaches the interface, its conformation may change unlike simple surfactant molecule. For a surface-active polymer, the process is driven by hydrophobic energy gain at the expense of the conformational entropy loss. The conformational relaxation may takes much longer time than those associated with diffusion and adsorption. The linear heteropolymer, gelatin, is an example. An extreme case is the change in protein secondary and tertiary structure. When the polymers are gradually accumulated at the interface, the interactions between the adsorbed polymers become significant. The reassociation between polymers at the interface may also result in slow interfacial dynamics. In general, it is believed that the relaxations associated with intrachain and interchain interactions are responsible for the slow dynamics of surface tension for surface-active polymer solutions.

Because the dynamic surface tension does not represent the equilibrium surface tension except reaching its steady state, the process is certainly out of equilibrium. Nevertheless, one measures the time-varying value of surface tension by the same experimental techniques as equilibrium surface tension. The consequence indicates that the instantaneous shape associated with the interface can be well described by the Young–Laplace equation, which corresponds to the thermodynamic equilibrium condition at the interface. In other words, the surface tension during the dynamic process is at local equilibrium state and can still be defined as

$$\gamma(t) = [\partial F(t)/\partial A]_{T,V} \tag{1}$$

where F represents the Helmholtz free energy and A and V are respectively the interfacial area and the volume of the system. Since the evolution of the system is toward the minimization of the Helmholtz free energy, one must have

$$\frac{\mathrm{d}F}{\mathrm{d}t} \le 0 \tag{2}$$

at constant volume and temperature. The equal sign holds at thermodynamic equilibrium or metastable state.

On the basis of the assumption of local equilibrium, one is able to write the Gibbs–Duhem equation for the interfacial phase σ[1]

$$0 = S^{\sigma}\,\mathrm{d}T + A\,\mathrm{d}\gamma + \sum_i n_i^{\sigma}\,\mathrm{d}\mu_i^{\sigma} \tag{3}$$

where S denotes entropy and n_i^{σ} the total numbers of species i present at the interface. Note that the chemical potential μ_i^{σ} corresponds to the interface σ only. At constant temperature ($\mathrm{d}T = 0$), one arrives at the adsorption isotherm for the interface

$$\mathrm{d}\gamma = -\sum_i \Gamma_i\,\mathrm{d}\mu_i^{\sigma} \tag{4}$$

When the whole system reaches equilibrium, thermodynamics requests that the chemical potential is constant throughout the entire system, $\mu_i^{\sigma} = \mu_i$. Consequently, the chemical potential can be easily obtained from the bulk solution, and eq 4 becomes the well-known Gibbs adsorption isotherm. Note that there are at least two components (solvent and solute) at the interface. To avoid phase separation at the interface, the thermodynamic stability requires[11]

$$\frac{\mathrm{d}\mu_i^{\sigma}}{\mathrm{d}n_i^{\sigma}} \ge 0 \tag{5}$$

In accordance with the foregoing equation, one has $\mathrm{d}\mu_i^{\sigma}/\mathrm{d}t \ge 0$ if $\mathrm{d}n_i^{\sigma}/\mathrm{d}t \ge 0$. For surface-active solutes, the surface excess is positive $\Gamma_i > 0$ and eqs 4 and 5 yield

$$\frac{\mathrm{d}\gamma}{\mathrm{d}t} \le 0 \tag{6}$$

It is evident that most experimental findings for surface-active solutes satisfy the above statement.

The interfacial dynamics of gelatin solutions can be qualitatively examined based on the framework of local thermodynamics, eqs 2 and 4–6. Although heteropolymers possess conformations much complicated than that of small surfactant, understanding the interfacial dynamics of small surfactants is helpful in elucidating the behavior of surface-active heteropolymers. Therefore, we will embark by analyzing the dynamic surface tension of surfactant solutions.[10] We adopt the commonly used model for surfactant adsorption, the Frumkin formulation. The free energy per unit area at the interface is given by[10]

$$\frac{F^{\sigma}}{A} = \frac{1}{a^2}\left\{k_B T[\phi \ln \phi + (1-\phi)\ln(1-\phi)] - \alpha\phi - \frac{\beta}{2}\phi^2\right\} \tag{7}$$

where k_B is the Boltzmann constant and a denotes the surfactant molecular dimension. The surface volume fraction of surfactant is $0 < \phi < 1$. The surface free energy comprises mixing entropy and interaction energy. The term in the square bracket is the entropy of mixing. The energy term α accounts for the energetic preference of the surfactants to lie at the interface. Because the molecule is surface-active, the interfacial energy α is positive by definition. The energy term β represents the lateral interaction between neighboring surfactants at the interface. The interaction energy β is usually positive, expressing an overall attractive interaction. Note that the well-known Langmuir adsorption isotherm is recovered when the interaction term is neglected ($\beta = 0$). The internal energy decreases with increasing the surface concentration while the entropy is minimal at $\phi = {}^1/_2$ and becomes zero at $\phi = 0$ and 1. In general, the internal energy gain compensates for the entropy loss at the interface.

The chemical potential at the interface $\mu_s{}^\sigma$ is then obtained from the variation of F^σ with respect to ϕ based on local equilibrium at the interface

$$\mu_s{}^\sigma = \frac{\delta(F^\sigma/A)}{\delta(\phi/a^2)} = k_BT \ln \frac{\phi}{1-\phi} - \alpha - \beta\phi \qquad (8)$$

The chemical potential associated with dilute, bulk solution $\mu_s{}^b$ can be assumed to be ideal

$$\mu_s{}^b = k_BT \ln \phi_b(\mathbf{x}) \qquad (9)$$

where the surfactant volume fraction is $\phi_b \ll 1$ and can varies with position **x**. Substituting eq 8 into the Gibbs equation at the interface, eq 4, and performing the integration gives the dynamic surface tension

$$\gamma(t) - \gamma_0 = \frac{1}{a^2}\left\{k_BT \ln[1-\phi(t)] + \frac{\beta}{2}\phi^2(t)\right\} \qquad (10)$$

Here the surface excess of surfactant $\Gamma_s = \phi/a^2$ is used. Equation 10 has exactly the same expression as the well-known equilibrium Frumkin equation of state, which relates the interfacial tension to the surface coverage. We have proved that eq 10 is still valid during the dynamic process and justified the assumption all previous works practically adopted. Note that eq 10 is derived without specifying whether the dynamics is diffusion-limited or kinetically limited adsorption. To predict the dynamic surface tension $\gamma(t)$, one has to know the variation of the surface fraction with time, $\phi(t)$. It can be calculated by solving the diffusion equation with the adsorption kinetics specified.

Now we can grasp the essential physics of the interfacial dynamics furthermore based on the thermodynamic framework. When the whole system reaches equilibrium, one must have $\mu_s{}^\sigma = \mu_s{}^b$ and thereby obtains the Frumkin adsorption isotherm

$$\phi^* = \frac{\phi_b{}^*}{\phi_b{}^* + e^{-(\alpha+\beta\phi^*)/k_BT}} \qquad (11)$$

where ϕ^* and $\phi_b{}^*$ are the equilibrium surface and bulk fraction, respectively. Four consequences are obtained by examining eqs 7−10 with eqs 2 and 4−6.

(i) When $\phi \le \phi^*$, the chemical potential at the interface is always smaller than that in the bulk solution during the process according to eqs 8 and 9. That is

$$\Delta\mu_s = \mu_s{}^\sigma - \mu_s{}^b \le 0 \qquad (12)$$

At the initial period of the process, the surfactant diffusion from the bulk solution toward the interface leads to an increase of the local concentration ϕ_b in the vicinity of the surface. Adsorption of surfactant onto the interface increases ϕ and in turn a rise of surface chemical potential $\mu_s{}^\sigma$. This process continues until $\mu_s{}^\sigma(\phi^*) = \mu_s{}^b(\phi_b{}^*)$. Obviously, this process satisfies eq 5.

(ii) The thermodynamic stability eq 5 requires $\beta < 4k_BT$. Otherwise, phase separation at the interface may take place due to strong attraction between surfactant molecules.

(iii) The free energy of the system at time t consists of the surface free energy F^σ and the free energy of the bulk solution with respect to the reservior of $\phi_b{}^*$, $\Delta F_b[\phi_b(\mathbf{x})]$. According to eq 7, the increment of ϕ lowers the surface free energy F^σ. Because $\mathrm{d}\phi/\mathrm{d}t \ge 0$, the process satisfies $\mathrm{d}F^\sigma/\mathrm{d}t \le 0$. For ideal, dilute solutions, the bulk free energy can be expressed as

$$\Delta F_b(t) = \frac{k_BT}{a^3}\int_V^Z[(\phi_b \ln \phi_b - \phi_b) - (\phi_b{}^* \ln \phi_b{}^* - \phi_b{}^*)]\,\mathrm{d}x$$

When $\phi_b < \phi_b{}^*$, $\Delta F_b(t) > 0$. The concentration gradient causes solute diffusion and hence $\mathrm{d}\phi_b/\mathrm{d}t \ge 0$. Thus, $\mathrm{d}F_b/\mathrm{d}t = \mathrm{d}\Delta F_b/\mathrm{d}t \sim (\mathrm{d}\phi_b/\mathrm{d}t) \ln \phi_b \le 0$ at constant volume and temperature. Equation 2 is thereby followed regardless of diffusion-limited or kinetically limited adsorption.

(iv) Equation 4 yields eq 10. The variation of surface tension with time in eq 10 is always less than zero if $\beta/k_BT < 4$. This result agrees with eq 6; the surface tension of the system declines during the dynamic process.

The interfacial dynamics of heteropolymer adsorption is expected to be much more complicated than that of surfactant because of the conformational change associated with the former. Nevertheless, the dynamic surface tension of the heteropolymer solution should satisfy the local equilibrium condition, and therefore we anticipate the thermodynamic framework to be valid, particularly for the long relaxation behavior. The polymers diffuse from the bulk solution onto the interface and leads to an increase of the chemical potential at the interface. However, it will be shown later that the characteristic time of diffusion is quite short, particularly for high bulk concentrations. As a result, the surface excess of polymers almost reaches its equilibrium amount in a relatively short time. The slow decay of the surface tension is not caused by adsorption of molecules onto the interface like surfactant but is due to the intrachain rearrangement and interchain interactions. In other words, different from surfactant adsorption, we encounter a special situation that as time passes, the surface free energy declines and the surface chemical potential rises, but the increment of surface excess of polymers is insignificant.

For small surfactants, the surface chemical potential rises due to the surface excess increment $\mu_s{}^\sigma(\phi)$. Equation 4 points out that at nearly constant surface excess the reduction of surface tension is due to the increase of surface chemical potential. The foregoing statement may be a little bit difficult to image at first sight. To clearly see the picture of eq 4 for heteropolymers, it would be easier to rewrite eq 4 in terms of polymer segments instead of macromolecules. We consider a heteropolymer as hydrophobic segments and hydrophilic segments. For simplicity, we assume hydrophilic segments and solvents as the same entity. On the other hand, the hydrophobic segment is regarded as surfactant-like entity (x). The dynamic Gibbs equation can then be expressed as

$$\mathrm{d}\gamma = -\Gamma_x(t)\,\mathrm{d}\mu_x{}^\sigma(t) \qquad (13)$$

where Γ_x is defined as the surface concentration of hydrophobic segments. The dividing surface is chosen to be at zero surface excess associated with solventlike entity. This approach is useful for semidilute solutions and crowded interfaces because it is difficult to distinguish which polymer the segment belongs to due to entanglement of polymers. Now it is straightforward to comprehend that the interfacial dynamics of the hydrophobic segment x is quite similar to that of surfactant with the interfacial energy of entity x (α) and the interaction energy between entity x (β). The surface chemical potential $\mu_x{}^\sigma$ is increased, owing to the rise of the surface excess Γ_x. On the basis of the aforementioned argument, the thermodynamic picture of intrachain and interchain interactions is analogous to that of surfactant. In this crude model, we have totally neglected the connectivity of polymer, which does not influence the thermodynamic explanation but poses a major energy barrier on the interfacial dynamics. As a matter of fact, we believe that the slow relaxation of gelatin solutions is primarily caused by the chain dynamics.

Interfacial Dynamics of Gelatin Solutions. Although macromolecules possess the degree of freedom associated with their conformations, it is generally found that the interfacial dynamics of water-soluble homopolymers is quite fast for concentrations about 0.1−1 wt %. On the other hand, the rearrangement of the hydrophobic segments of heteropolymers at the interface results in slow relaxation. For example, the surface activity of polyacryamide of molecular weight 5 $\times$ 10^6 in aqueous solutions (1 wt %) is very small, and the dynamic surface tension can become very close to its equilibrium value (~69.2 mJ/m^2 at 25 °C) within 1 s.[12] Similarly, poly(N-isopropylacrylamide) with molecular weight 1.31×10^5 or 5.47×10^5 is a quite surface-active, water-soluble polymer, and its aqueous solution (0.1 and 1 wt %) almost reaches equilibrium surface tension (~42 mJ/m^2 at 25 °C) within 1 s.[13] Similar experimental findings are observed for PEG. However, the hydrophobically modified polyacryamide demonstrates a much longer relaxation time to reach its equilibrium value.[3]

A gelatin molecule, similar to proteins, is a heteropolymer with hydrophobic and hydrophilic segments and therefore is expected to display a long relaxation time. Nevertheless, the gelatin molecule does not possess structural complexity like proteins because it is a linear polymer. As a result, the gelatin solution may reach its steady-state (equilibrium) value within several hours. Figure 1 demonstrates the dynamic surface tension of gelatin solutions from dilute regime (0.01 wt %) to semidilute regime (1.0 wt %). All bulk concentrations, below the gel point, exhibit very slow relaxation. It is clear that the gelatin solution takes at least $O(10^4)$ seconds to achieve its equilibrium surface tension. Since the dynamic process starts with gelatin diffusion due to the creation of fresh interfaces in the pedant bubble tensiometry, we have to examine the time period possibly taken by diffusion before dealing with slow relaxation.

The concentration at which the coils start to overlap (c^*) can be estimated by assuming that the chains occupy a spherical volume with radius R. For a polymer with a radius $R \sim 30$ nm, one has $c^* \sim 0.1$ wt % if the molecular weight is about 10^5. The diffusivity of the polymer in dilute solutions can be estimated as $D \sim 10^{-12}$ m^2/s according to the Stokes−Einstein relation. At the regime where chains are overlapped, the movement from the bulk to the interface needs to overcome additional frictional barrier between polymers. During the initial period of interfacial dynamics, the movement of polymers from the bulk solution onto the surface takes place, and the main mechanism responsible for surface tension reduction is the increase of surface excess due to diffusion and adsorption. The characteristic time scale of diffusion is given by $\tau_d \sim (\Gamma/c_b)^2/D$,[4] where c_b is the bulk concentration. The maximum surface coverage of the surface-active polymer poly(N-isopropylacrylamide) measured by ellipsometry[14] or neutron reflectivity[15] is about $\Gamma_\infty \sim 2$ mg/m^2 with a molecular weight about 5×10^5 and radius of gyration about 25 nm. This value could be a reasonable estimation for gelatin solutions if the molecules are considered as short rods with a diameter 10 nm. For dilute solutions, $c_b \ll c^*$, one has $\tau_d \sim (\Gamma_\infty e^{\alpha/k_BT}/c_b)^2/D$ according to the Frumkin isotherm. For a gelatin solution with 10^{-2} wt %, the diffusion time may take about $\tau_d \sim 400e^{2\alpha/k_BT}$ seconds. It will be explained later that the surface activity of gelatin in the bulk is quite weak, and hence one can assume $\alpha/k_BT \sim 1$. However, in the semidilute regime (c_b and c^*), $\tau_d \sim (\Gamma_\infty/c_b)^2/D$. As a consequence, it takes about $\tau_d \sim O(10)$ seconds for gelatin molecules to diffuse from the bulk to the sublayer. According to our foregoing estimation, one can safely conclude that in the dilute limit the diffusion of gelatin from the bulk to the subsurface takes less an hour for $c_b = 0.01$ wt %. On the other hand, gelatin diffusion probably accomplishes within a minute for semidilute concentrations.

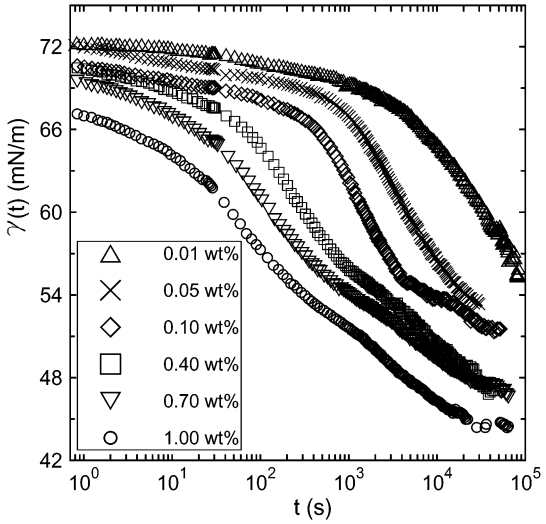

Figure 1. Dynamic surface tension for gelatin solutions at 25 °C. The polymer concentration varies from the dilute regime (0.01 wt %) to the semidilute regime (1.0 wt %).

The Ward−Tordai theory indicates that the plot of $(\gamma_0 - \gamma)$ vs $t^{1/2}$ is linear and passes through the origin for purely diffusion-controlled dynamics.[2] Typically, this condition corresponds to the surface pressure $\pi = \gamma_0 - \gamma < 0.1$ mN/m and is not observed in Figure 1. When the surface pressure exceeds about 1 mN/m, the buildup of gelatin concentration in the neighborhood of the interface reduces the local concentration gradient and hence the mass transfer rate. Beyond the initial diffusion-limited stage, the change in surface pressure arises not only from new molecules arriving at the interface but also from conformational changes in previously adsorbed molecules.[2] Evidently, in comparison with the fast interfacial dynamics of surface-active homopolymers poly(N -isopropylacrylamide) with similar molecular weight,[13] the surface activity of gelatin molecules in the bulk solution is very weak (hydrophilic), and the surface pressure may be less than ca. 2 mN/m for $c_b \sim$ 0.1 wt % if gelatin at the interface does not undergo the conformational change. Nonetheless, the significant intramolecular and intermolecular rearrangement of gelatin at the interface leads to the gradual increase of the interfacial tension (surface activity). The interfacial dynamics of gelatin may be closely related to surface gelation, i.e., adsorbed layers showing a gradual thickening and strengthening, which is analogous to network formation (gelation) of gelatin in bulk solution above a certain critical concentration.

Figure 1 reveals that the gelatin solution always exhibits a long relaxation behavior, more than 3 h, regardless of the bulk concentration. This cannot be simply explained by diffusion and adsorption and is most probably caused by rearrangement of polymers. As a result, the equilibrium surface tension is not the only indicator of surface activity. For example, the gelatin solution with 0.1 wt % concentration displays surface activity greater than that of ethanol with 0.1 wt % after a few seconds, and the surface activity becomes greater than that of pentanol with 0.1 wt % after 10 min. When gelatin molecules compete with surface-active solutes for adsorption, the slowly changing nature in surface activity can significantly affect its efficiency of adsorption. Thus, we study the interfacial dynamics of a gelatin solution with various surfactants. By varying the surface activity associated with surfactant, the adsorption efficiency of gelatin is manifested through the dynamic surface tension.

Weak Surface Activity of Surfactant: Partial Displacement. When the relaxation time for reaching equilibrium surface tension is very short, e.g., less than a second, the equilibrium surface activity is able to indicate the adsorption efficiency in the experiments. When a solute displays long relaxation time, its surface activity varies with time substantially, and therefore its adsorption efficiency cannot be correctly represented by its equilibrium surface tension. In this paper, we scrutinize the efficiency of gelatin adsorption based on competitive adsorption between gelatin and surfactant. The latter includes 1-ethanol, 1-pentanol, 1-octanol, and 1-decanol. That is, the surface activity of surfactant is increased by increasing the chain length of normal alcohol. Note that the comparison is made among the gelatin solution of concentration c_g, the surfactant solution of concentration c_s, and the gelatin−surfactant solution of c_g and c_s. Long relaxation time behavior can be regarded as the signature of the presence of gelatin molecules at the interface.

Figure 2 illustrates the dynamic surface tension for solutions of gelatin, ethanol, and their mixture. The equilibrium surface tension of ethanol solution with 0.046 or 0.138 wt % is obtained in less than 1 s. This is consistent with the typical results for small molecules. Moreover, its value is close to $\gamma_s \approx 72$ mN/m, and hence the surface activity is very weak. In contrast, the gelatin−ethanol solution exhibits the time-varying surface tension (γ_{g+s}), which is between those of ethanol (γ_s) and gelatin (γ_g), i.e.

$$\gamma_s > \gamma_{g+s}(t) > \gamma_g(t)$$

Two features are revealed in this result. First, like gelatin solutions, the mixture also displays long relaxation behavior. It indicates gelatin molecules are present at the interface. Second, the fact that the surface tension of the mixture is always in between points out that the surface excess of gelatin is reduced by the presence of ethanol at the interface. As a result, despite low surface activity associated with ethanol, its adsorption efficiency is higher than that of gelatin and hence reduces the surface tension decrement due to gelatin.

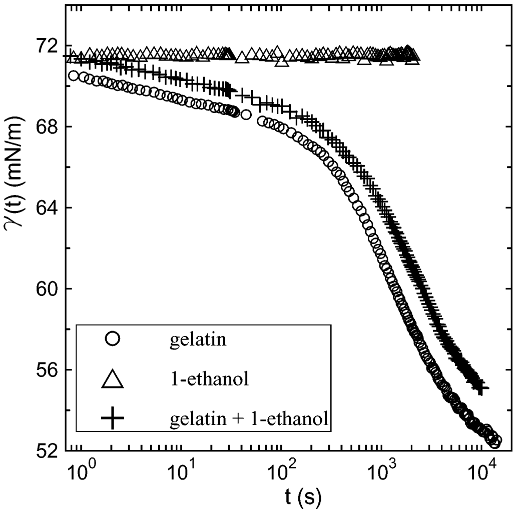

Figure 2. Dynamic surface tension for 1-ethanol solution (0.138 wt %) and gelatin−ethanol solution (0.1 wt % + 0.1 wt %). The long relaxation behavior is observed for the latter.

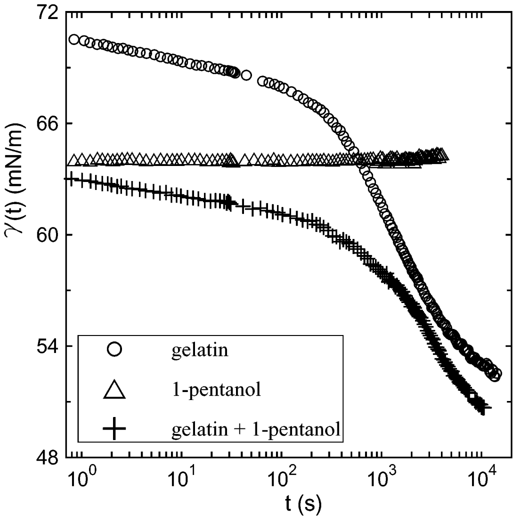

Figure 3. Dynamic surface tension for 1-pentanol solution (0.1 wt %) and gelatin−pentanol solution (0.1 wt % + 0.1 wt %). The long relaxation behavior is observed for the latter.

Figure 3 shows the dynamic surface tension for solutions of gelatin, 1-pentanol, and their mixture. Obviously, the surface activity of pentanol is greater than that of ethanol, and its relaxation time is less than 1 s. That is, the adsorption efficiency of pentanol is better than ethanol and gelatin. Nevertheless, the surface activity of gelatin may be greater than that of pentanol after 10^3 s. The comparison of dynamic surface tension of those solutions yields

$$\gamma_s > \gamma_{g+s}(t) \quad \text{and} \quad \gamma_g(t) > \gamma_{g+s}(t)$$

Two characteristics are illustrated in this result. The long relaxation behavior is observed and indicates the presence of gelatin molecules on the surface. Moreover, the fact that the surface tension of the mixture is always less than that of surfactant solution shows that the

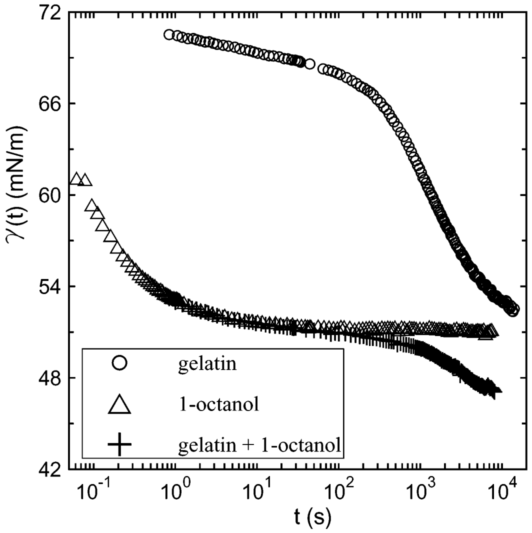

Figure 4. Dynamic surface tension for 1-octanol solution (8.0 × 10^{-4} M) and gelatin–octanol solution (0.1 wt % + 8 × 10^{-4} M). The long relaxation time signature is still observed.

gelatin molecule replaces the pentanol molecules and is adsorbed onto the interface. Since the process has to be proceeding by satisfying eqs 2, 5, and 6, one expects that the increment of gelatin surface excess $\Gamma_g\, d\mu_g^{\sigma}/dt$ must be able to compensate the loss of surfactant $\Gamma_s\, d\mu_s^{\sigma}/dt$.

Octanol possesses an even stronger surface activity which is comparable to the equilibrium surface tension of gelatin. The equilibrium surface tension of the octanol solution is obtained at about 10 s. Note that the bulk concentration of octanol is only 8 × 10^{-4} M, about 0.01 wt %, and the solubility of octanol is 3 × 10^{-3} M. In other words, this dynamic relaxation is primarily attributed to the diffusion processes. As shown in Figure 4 for the dynamic surface tension associated with a gelatin solution with octanol, the long relaxation time signature is still observed. However, the dynamic surface tension of the mixture is essentially the same as that of octanol for $t \sim 10^2$ s. This consequence reveals that the gelatin molecule is slowly substituted for octanol at the interface. The decrement of surface tension from the equilibrium surface tension of 1-octanol due to long relaxation behavior of gelatin is about 5 mN/m, which is significantly smaller than those of 1-ethanol (17 mN/m) and 1-pentanol (14 mN/m). This extent of surface tension decrement can be considered as the degree of gelatin displacement from the interface by surfactant in comparison of pure gelatin solution. Apparently, the normal alcohol with longer chain length is able to displace more gelatin on the surface.

When the chain length of normal alcohol is further increased to be decanol, the surface activity becomes so strong that its solubility is very low, 2 × 10^{-4} M. Figure 5 depicts the dynamic surface tension of the decanol solution. The relaxation time is about 10^3 s. Since the bulk concentration is only 1.34 × 10^{-4} M, about 2.1 × 10^{-3} wt %, the mixed diffusion-adsorption process is mainly responsible for the relatively long relaxation. As illustrated in Figure 5 for the gelatin and decanol mixture, its dynamic surface tension is essentially the same as that of pure decanol solution except at the time period before $t = 2$ s. Two features are revealed by the comparison of the interfacial dynamics between the surfactant solution and the surfactant–gelatin solution.

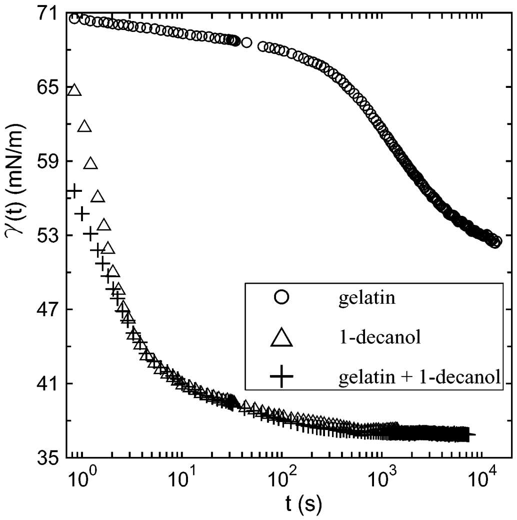

Figure 5. Dynamic surface tension for 1-decanol solution (1.34 × 10^{-4} M) and gelatin–decanol (0.1 wt % + 1.34 × 10^{-4} M). The long relaxation behavior due to gelatin rearrangement at the interface disappears.

First, the long relaxation behavior due to gelatin rearrangement at the interface disappears. This consequence points out that gelatin molecules are completed removed from the interface eventually. Second, at the earlier stage of the dynamic process, the dynamic surface tension of the decanol–gelatin solution is substantially lower than that of the decanol solution, about 8 mN/m difference. The additional increase in the surface pressure is unlikely to come from gelatin molecules directly. A possible explanation is that the interface, which is nearly saturated with small decanol molecules in pure surfactant solution, becomes much more compact due to the presence of large gelatin molecules. Note that gelatin is already present when the fresh surface is created since zero surface excess $\Gamma_g = 0$ means the local concentration in the vicinity of the interface is the same as that of the bulk. Nevertheless, gelatin is practically displaced from the interface by decanol after about 2 s.

Small surfactant is a more efficient adsorber than large gelatin because its adsorption rate, i.e., the characteristic time to reach equilibrium surface tension, is much faster than that of gelatin. On the other hand, the surface activity of gelatin is altered with time, and the surface activity of surfactant can be tuned by alkyl chain length and bulk concentration. The interplay between adsorption efficiency and surface activity lead to interesting dynamic behavior of surfactant–gelatin solutions compared to the interfacial dynamics of pure surfactant solutions. As shown in Figures 2–5, the consequence $\gamma_{g+s}(t) \le \gamma_s(t)$ indicates that the interface is essentially covered with small surfactant at the early stage. When the surface activity of gelatin becomes lower than that of surfactant, the latter will be partially replaced by the former. As a result, long relaxation behavior appears and designates the presence of gelatin at the interface. On the contrary, when the surface activity of gelatin is always lower than that of surfactant, gelatin is completely removed from the interface, and the dynamic surface tension of the gelatin–surfactant solution displays only part of the surfactant.

Strong Surface Activity of Surfactant: Complete Displacement. We have already shown that as the hydrocarbon chain length is greater than 10 methylene

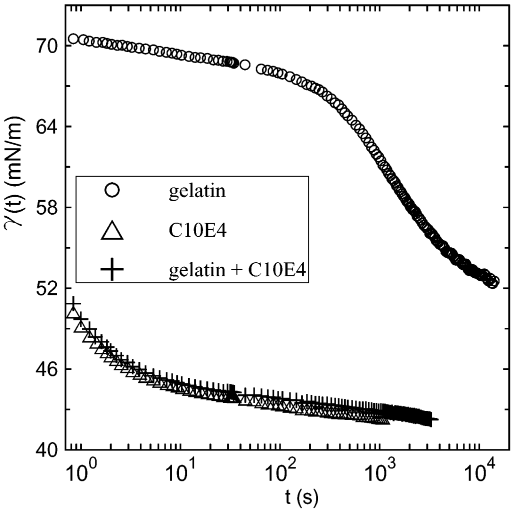

Figure 6. Dynamic surface tension for nonionic surfactant $C_{10}E_4$ solution (1.2×10^{-4} M) and gelatin−$C_{10}E_4$ solution (0.1 wt % + 1.2×10^{-4} M). The long relaxation behavior due to gelatin rearrangement is absent for the latter.

groups, the surface activity of normal alcohol is so strong that the effect of gelatin cannot be seen in the interfacial dynamics. In other words, surfactant displaces gelatin completely on the surface. Long-chain alcohol possesses high free energy if it is in the bulk instead of at the interface. In fact, phase separation takes place to reduce the free energy of the system if a sufficient amount of long-chain alcohol is added into an aqueous solution. However, if the hydroxyl head is replaced by other larger hydrophilic groups, such as polyoxyethylene, sulfate, and quaternary ammonium halides, then micellization (microphase) occurs instead of macrophase separation. In this paper we also study the interfacial property of a gelatin solution with a strong surface-active surfactant, which includes $C_{10}E_4$, SDS, and CTAB.

All theories consider homopolymer adsorption as a first-order phase transition and predict that long flexible chains do not adsorb unless their segmental adsorption energy $\alpha_s k_B T$ exceeds some critical value $\alpha_s^c k_B T$.[2,16] Here $\alpha_s k_B T$ represents the interaction energy difference between segment−surface and solvent−surface contacts, where a site on the surface is occupied by either a solvent or a segment of the chain. The requirement for the existence of α_s^c arises because the loss in conformation entropy associated with adsorbed polymers must be outweighed by the decrease of internal energy due to polymer−surface contacts. It is reasonable to anticipate that heteropolymer adsorption follows a similar scenario, and α_s denotes the mean segmental adsorption energy. Introducing surfactant into the system decreases the α_s value and causes the heteropolymer to be partially displaced from the interface. When $\alpha_s < \alpha_s^c$, the polymer is completely removed from the surface. Our experimental results have confirmed this picture. This consequence also leads to the assertion that the interfacial property of gelatin−surfactant solution is the same as that of strong surface-active surfactant solution because both solutions have the same surfactant surface excess. However, the above statement is not entirely true according to our experimental findings.

Figure 6 illustrates the variation of the surface tension with time for nonionic surfactant $C_{10}E_4$. The bulk surfactant concentration is 1.2×10^{-4} M, which is less than the cmc, 7.7×10^{-4} M. The dynamic process of $C_{10}E_4$ takes about $O(10^3)$ seconds and is mainly caused by the free energy barrier associated with adsorption. The effect of $C_{10}E_4$ on the interfacial dynamics is quite similar to that of 1-decanol, and the dynamic surface tension of the gelatin−$C_{10}E_4$ solution approximately coincides with that of the $C_{10}E_4$ solution after t = 0.1 s. This result points out that the adsorption efficiency of $C_{10}E_4$ is better than that of 1-decanol so that gelatin molecules have been displaced completely by $C_{10}E_4$ before t = 0.1 s. A careful examination of Figure 6 also reveals that the dynamic surface tension of the gelatin−$C_{10}E_4$ solution is in fact slightly larger than that of the $C_{10}E_4$ solution, about 1 mN/m difference. One may suspect that this small difference is owing to experimental uncertainty. However, the difference becomes substantial if one studies the solution of gelatin and ionic surfactant.

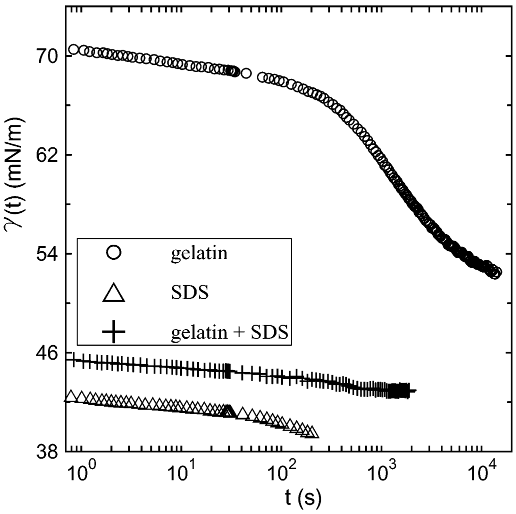

Figure 7. Dynamic surface tension for anionic surfactant SDS solution (7.0×10^{-3} M) and gelatin−SDS solution (0.1 wt % + 7.0×10^{-3} M). The long relaxation behavior due to gelatin rearrangement is absent for the latter.

Figure 7 shows the dynamic surface tension for anionic surfactant SDS. The bulk surfactant concentration is 7×10^{-3} M, which is less than the cmc, 8×10^{-3} M. The dynamic processes of SDS and gelatin−SDS solutions are relatively short, $O(10^2)$ seconds. However, the dynamic surface tension of the gelatin−SDS solution is about 8 mN/m higher than that of the SDS solution. That is to say

$$\gamma_{g+s}(t) > \gamma_s(t)$$

Since the long relaxation signature is not observed, one concludes that gelatin molecules have been completely replaced by SDS molecules. As a result, the explanation based on the interaction between gelatin and SDS on the surface is basically not rational. A contrast phenomenon is observed for cationic surfactant CTAB. As illustrated in Figure 8, the dynamic surface tension of the gelatin−CTAB solution is always less than that of pure CTAB solution. Namely, $\gamma_s(t) > \gamma_{g+s}(t)$. The bulk surfactant concentration is 7×10^{-4} M, which is less than the cmc, 10^{-3} M. The long relaxation dynamics due to gelatin rearrangement is not shown, and hence gelatin molecules are absent at the interface. The surface pressure comes only from the contribution associated with strong surface-active surfactant. The

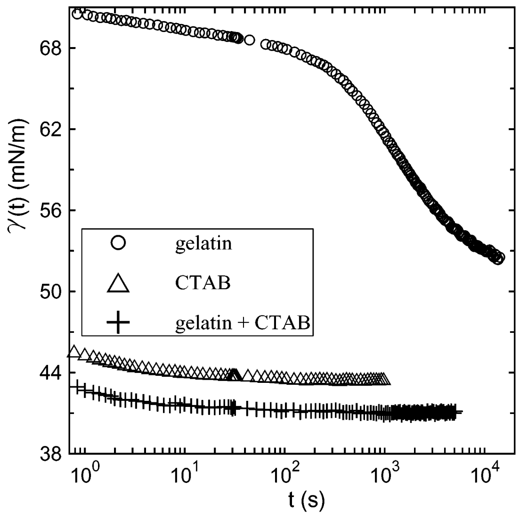

Figure 8. Dynamic surface tension for cationic surfactant CTAB solution (7.0×10^{-4} M) and gelatin−SDS solution (0.1 wt % + 7.0×10^{-4} M). The long relaxation behavior due to gelatin rearrangement is not observed for the latter.

most likely explanation for the difference between γ_{g+s} and γ_s arises from the interaction between gelatin and surfactant in the bulk solution.

The gelatin−surfactant interactions in the bulk solution have been investigated by dynamic light scattering.[7] Considerable reduction in the hydrodynamic radius of gelatin is observed for anionic SDS. It is conjectured that SDS binds electrostatically with the oppositely charged site of the polypeptide chain. This reduces the electrostatic repulsion within the polymer and hence the chain coils. The opposite is observed in the case of CTAB. The gelatin chain shows small increase in size. It is speculated that the expansion is due to electrostatic repulsion between the positive sites of chain and bulky cationic headgroups. For nonionic TX-100, of which the hydrophilic group is made of polyoxyethylene just like $C_{10}E_4$, little hydrophobic binding to gelatin is exhibited, and no observable change in gelatin size is seen due to the absence of electrostatic interactions. Although the above reasoning for the origin of the interaction may be rather speculative, the experimental findings demonstrate the interaction between gelatin and strong surface-active surfactant undoubtedly.

The influence of the gelatin−surfactant interaction in the bulk solution on the interfacial properties can be qualitatively described by modifying the Frumkin formulation. Although the solution of gelatin and surfactant is a three-component mixture, for simplicity, we can regard gelatin and water as an effective solvent and surfactant as a solute. It is justified in the present case because the gelatin concentration is about the overlap concentration. Therefore, the polymer−surfactant interaction in the bulk is manifested through the effective solvent−solute interaction. Note that if the solvent−solute interaction is neglected, the chemical potential of the surfactant in the bulk is assumed ideal as expressed in eq 9. However, the interaction between solute (1) and solvent (2) must be taken into account when it becomes important. On the basis of the lattice model, one has

$$\mu_s^{\ b} = k_B T \ln \phi_b + w(1 - \phi_b)^2 \qquad (14)$$

where the interaction parameter is defined as $w = z[\epsilon_{12} - (\epsilon_{11} + \epsilon_{22})/2]$. z is the coordination number, and ϵ_{ij} denotes the interaction energy of an $i-j$ pair. At thermodynamic equilibrium, since $\phi_b \ll 1$, one has

$$\phi^* = \frac{\phi_b^*}{\phi_b^* + e^{-(w+\alpha+\beta\phi^*)/k_B T}} \qquad (15)$$

The revised Frumkin equation indicates that the interaction parameter w plays a role similar to the interfacial energy α. Note that the conditions $w < 0$ and $\alpha > 0$ correspond to attraction. According to eq 15, one can clearly see that, for the repulsive gelatin−surfactant interaction such as CTAB ($w > 0$), the surfactant adsorption is enhanced, and thereby a lower surface tension is obtained. On the contrary, an attractive gelatin−surfactant interaction such as SDS ($w < 0$) leads to a decrease of surface excess and an increase of surface tension. When $w \simeq 0$ such as $C_{10}E_4$, the surface excess is maintained the same for the surfactant solution without gelatin. In summary, eq 15 is able to depict the effect of polymer−surfactant interaction in the bulk on the interfacial property, and its net result is equivalent to interfacial energy alteration.

In this paper we have explored the interfacial dynamics of the gelatin solution and the influence of surfactant on the dynamic surface tension. The gelatin solution always exhibits a long relaxation time due to gradual rearrangement of chain conformations. This characteristic can be regarded as signature of the presence of gelatin on the surface. Various dynamic behavior has been observed for gelatin−surfactant solutions. On the basis of the interplay between adsorption efficiency and surface activity, we are able to categorize our experimental findings into two types of dynamics. For type I dynamics, the surface activity of surfactant is so strong that gelatin molecules are completely displaced from the interface. Although the interfacial dynamic is dominated by surfactant, the interaction between gelatin and surfactant in the bulk solution can change the surface excess of surfactant and therefore the dynamic surface tension. For type II dynamics, the surface activity of surfactant is small or comparable to that of gelatin. As a result, the gelatin molecule is partially displaced from the surface and the dynamics displays a long relaxation characteristic.

To examine our deduction, we perform dynamic surface tension measurement for the gelatin−PEG solution. PEG is a neutral homopolymer, and its surface tension is insensitive to its bulk concentration and molecular weight. For PEG with molecular weight 2×10^4 and bulk concentration 0.1 wt %, the surface tension is about 62 mN/m, which is slightly less than that of 1-pentanol. The adsorption efficiency of PEG is very high, and its equilibrium surface tension can be reached in less than 0.1 s. Naturally, one anticipates that the dynamic behavior of the gelatin−PEG solution may be quite similar to that of the gelatin−pentanol solution. Nonetheless, we obtain a peculiar interfacial dynamics as shown in Figure 9. The dynamic surface tension of the gelatin−PEG solution maintains a constant value, essentially the same as that of pure PEG solution, for more than 30 min. One might easily mistake this value for the equilibrium surface tension while conducting experiments. According to thermodynamic principle, however, this state is only metastable because lower free energy state is possible if the conformation of gelatin is allowed to be altered. After about half an hour, the

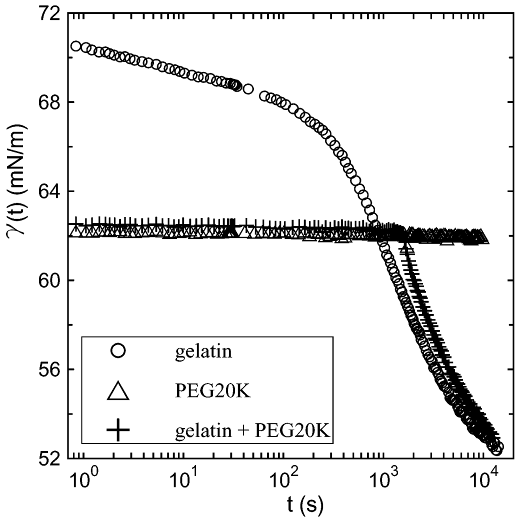

Figure 9. Dynamic surface tension for neutral homopolymer PEG solution (0.1 wt %) and gelatin−PEG solution (0.1 wt % + 0.1 wt %). The molecular weight of PEG is 2 × 10^4. The long relaxation behavior is observed for the latter.

dynamic surface tension suddenly drops and displays a long relaxation behavior just like pure gelatin solution. This consequence indicates that PEG is a very efficient adsorber and covers the surface immediately after the fresh surface is created. For the early period, gelatin molecules without significant conformational rearrangement are unable to lower the free energy and replace PEG at the interface. We speculate that gelatin molecules in the vicinity of the interface are still able to change their conformations by gradually protruding their hydrophobic segments into the surface. Nevertheless, the process is progressing under quasi-equilibrium condition with $dF/dt = d\gamma/dt = 0$ and $\Gamma_x \, d\mu_x^\sigma + \Gamma_s \, d\mu_s^\sigma = 0$. That is, the surface tension decrement due to the presence of hydrophobic segments is canceled out by the increase associated with the absence of PEG segments. At any rate, this interesting result is worth further investigation.

Acknowledgment. S.-Y.L. and H.-K.T. thank National Council of Science of Taiwan for financial support under Grants NSC 91-2214-E-011-001 and NSC 91-2214-E-008-002, respectively.

References and Notes

(1) Hunter, R. J. *Foundations of Colloid Science*; Oxford University Press: New York, 1992.
(2) Dickinson, E. *An Introduction to Food Colloids*; Oxford University Press: New York, 1992.
(3) Kopperud, H. B. M.; Hansen, F. K. *Macromolecules* **2001**, *34*, 5635.
(4) Lin, S. Y.; McKeigue, K.; Maldarelli, C. *AIChE J.* **1990**, *36*, 1785.
(5) Lin, S. Y.; Wang, W. J.; Hsu, C. T. *Langmuir* **1997**, *13*, 6211.
(6) Ren, S. Z.; Shi, W. F.; Zhang, W. B.; Sorensen, C. M. *Phys. Rev. A* **1992**, *45*, 2416.
(7) Saxena, A.; Antony, T.; Bohidar, H. B. *J. Phys. Chem. B* **1998**, *102*, 5063.
(8) Maity, S.; Bohidar, H. B. *Phys. Rev. E* **1998**, *58*, 729.
(9) Lin, S. Y.; McKeigue, K.; Maldarelli, C. *Langmuir* **1991**, *7*, 1055.
(10) Diamant, H.; Andelman, D. *J. Phys. Chem.* **1996**, *100*, 13732.
(11) Van Ness, H. C.; Abbott, M. M. *Classical Thermodynamics of Nonelectrolyte Solutions*; McGraw-Hill: Auckland, 1982.
(12) Zhang, J.; Pelton, R. *Colloids Surf. A* **1999**, *156*, 111.
(13) Zhang, J.; Pelton, R. *J. Polym. Sci., Part A: Polym Chem.* **1999**, *37*, 2137.
(14) Kawaguchi, M.; Saito, W.; Kato, T. *Macromolecules* **1994**, *27*, 5882.
(15) Richardson, R. M.; Pelton, R.; Cosgrove, T.; Zhang, J. *Macromolecules* **2000**, *33*, 6239.
(16) Cohen Stuart, M. A.; Fleer, G. J.; Scheutjens, J. M. H. M. *J. Colloid Interface Sci.* **1984**, *97*, 515.

MA034853Y