Preparation and Surface Activity of Gelatin-Derived Surfactants Modified with Polyoxyethylene Stearyl Ether Units

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ABSTRACT: We have prepared a series of novel gelatin derivatives through reactions of gelatin with alkyl succinic anhydride and polyoxyethylene stearyl ether. These derivatives contain gelatin units and polyoxyethylene chains as their hydrophilic moieties and alkyl succinic anhydrides and 18-carbon-atom alkyl chains as their hydrophobic moieties. Surface activities were evaluated in terms of the materials' surface tensions, wetting abilities, emulsifying powers, and foaming properties. The surface tensions were characterized with respect to the critical micelle concentration (cmc), the surface tension at the cmc, the maximum surface excess concentration, the standard free energy, and the surface area per molecule at the air-water interface. The modified gelatins were more surface-active relative to gelatin itself. Increasing the polyoxyethylene chain length led to a decrease in surface activity. The excellent foaming, wetting, and emulsifying behavior of the gelatin derivatives was a direct result of the presence of their multiple hydrophilic and hydrophobic units. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2993–3000, 2011

Key words: surfactants; synthesis; water-soluble polymers; gelatin

INTRODUCTION

Gelatin is a protein derived from collagen through either acidic or basic degradation processes. This hydrophilic protein has only limited function as a surface-active agent. Chemical modification can lead to changes in a protein's hydrophobicity, thereby changing its surface activity and functional properties. More specifically, covalent attachment of hydrophobic groups to a water-soluble protein can transform it into an amphiphilic protein. In addition, the changes in hydrophobicity of protein molecules can drastically affect their binding affinities and surface coverages when adsorbed at various interfaces. Such changes in surface activity can play significant roles in many practical applications.[1]

The hydrophobicity of a protein can be increased by changing its structure or molecular weight via the covalent attachment of hydrophobic groups. Controlling the site of modification can also contribute to the overall hydrophobicity of the protein. For example, acylation of the free lysine groups of a protein, using a fatty acid, reduces the number of positive charges in the structure. The combined effect of increasing the number of hydrophobic moieties and decreasing the hydrophilicity can significantly influence the surface activity of the protein.

All of these gelatin-derived surfactants were nonionic surfactants containing a nonionic hydrophilic polyoxyethylene moiety in structure. It is generally accepted, however, that the presence of polyoxyethylene chain structures improve the industrial applicability of nonionic surfactants. For example, when using surfactants as dyeing auxiliaries in the textile industry, polyoxyethylene nonionic surfactants provide excellent wetting, emulsifying, and dye dispersant ability and improved dyeing behavior.[2,3]

Magdassi and coworkers reported that covalent modification of human immunoglobulin G with alkyl chains results in considerable changes in its surface activity, with improved functional properties. The modified protein displayed higher affinity for hydrophobic surfaces and formed more compact surface layers relative to those of the unmodified protein.[4,5] They also found that the emulsifying activity of gelatin was enhanced after its hydrophobization via covalent attachment of fatty acids (C_4–C_{16}) to lysine groups using N-hydroxysuccinimide esters; these emulsions obtained were also more stable than those prepared using native gelatin.[6,7]

Haque and Kito reported the covalent attachment of hydrophobic ligands to the proteins soybean glycinin and casein via base-catalyzed ester exchange using the N-hydroxysuccinimide ester of palmitic acid as the lipophilic electrophile.[8–10] The foaming activity of the modified casein was dependent on the number of the hydrophobic groups attached; in addition, the foam stability increased upon increasing the number of attached hydrophobic groups.

Taken together, the studies mentioned above suggest that the presence of many hydrophilic and hydrophobic units results in polymeric surfactants exhibiting excellent surface-active properties. In this article, we prepared novel gelatin-derived surfactants through the reactions of modified gelatins with polyoxyethylene stearyl ether. These derivative surfactants contain gelatin molecules and polyoxyethylene chains as their hydrophilic segments and alkyl succinic anhydrides and 18-carbon-atoms glycidyl ethers as their hydrophobic segments. We determined the surface-active properties of these gelatin-derived surfactants in terms of their surface tensions, contact angles, and foaming and emulsification properties.

EXPERIMENTAL

Materials

Gelatin type B, Bloom 75 (M_w: 20,000–25,000), was obtained from Sigma; methyl tert-butyl ether (MTBE) was obtained from ACROS; polyoxyethylene stearyl ether was supplied by Sino-Japan Chemical Co. Reagent-grade succinic anhydride, epichlorohydrin, sodium hydroxide, and hydrochloric acid were purchased from Hayashi Pure Chemical Co. and used without further purification. Pyrene was obtained from Fluka Chemical Co.

Synthesis of gelatin-derived surfactants containing polyoxyethylene stearyl ether

A gelatin hydrolyzate containing 40 g of gelatin were taken up in 60 g of water and, after the addition of 1.6 g of sodium hydroxide, the solution was heated for 16 h to 130°C. Figure 1 displays the three-step procedure used to prepare the gelatin-derived surfactants containing polyoxyethylene stearyl ether units. In the first step, a mixture of gelatin hydrolyzate and alkenylsuccinic acid anhydride (0.04 mol) was stirred at 70°C for 5 h. In the second step, hydrophobic glycidyl ethers were obtained through the reactions of epichlorohydrin (0.3 mol) with polyoxyethylene stearyl ethers (0.5 mol) ($n = 7$, 20, and 30 stand for 1807, 1820, and 1830) at 60°C for 3 h. In the third step, the products from the first (0.3 mol) and second (0.2 mol) steps were mixed and stirred mechanically at 70–80°C for 5 h. The water-insoluble products were removed from the reaction mixture through extraction with MTBE. Traces of MTBE were removed from the aqueous phase by heating it at 40°C in a water jet vacuum.

Analysis

The structures of the final products were confirmed using Fourier transform infrared (FTIR) spectroscopy and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. FTIR spectra were recorded using a Japan Spectroscopic FT/IR-3 spectrophotometer, with the compounds was deposited on KBr discs; for each sample, 32 scans were collected at a resolution of 4 cm^{-1}. ^{1}H-NMR spectra were recorded using a Varian 360 L NMR spectrometer, with the samples dissolved in D$_2$O. The average molecular weight was determined using a potentiometric method. The gelatin hydrolyzate (1 g) was dissolved in glacial acetic acid (25 mL) and then titrated with 0.1N HCl standard solution in glacial acetic acid. The results are given as grams of gelatin hydrolyzate by equivalent of HCl standard solution used for the inflection during titration.

Measurements

Surface tensions were measured at room temperature using a Japan Kaimenkaguka CBVP-A3 surface tensiometer, which was calibrated with ultra-pure water prior use. The platinum plate was cleaned by flaming; the glassware was rinsed with tap water and ultra-pure water. The equilibrium surface tension was measured three times for each concentration, routinely providing an average error of less than 0.5 mN m^{-1}. The critical micelle concentration (cmc) and surface tension at the cmc (γ_{cmc}) were determined from the break point in the plot of the surface tension with respect to the logarithm of the concentration. The surface excess concentration of the surfactants at the air–water interface (Γ; mol m^{-2}) was calculated using the following Gibbs adsorption isotherm equation[11,12]:

$$\Gamma = -\left(\frac{1}{2.303RT}\right)\left(\frac{d\gamma}{d\log C}\right) \quad (1)$$

where γ represents the surface tension (mN m^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature, C is the surfactant concentration, and $\left(\frac{d\gamma}{d\log C}\right)$ is the slope below the cmc in the surface tension plots. The area occupied by the surfactant molecule at the air–water interface (A_{cmc}) was obtained from the saturated adsorption using the equation:

$$A_{cmc} = \frac{1}{N \cdot \Gamma_{cmc}} \quad (2)$$

where N is Avogadro's number (6.02×10^{23} molecules mol^{-1}) and Γ_{cmc} represents the surface excess
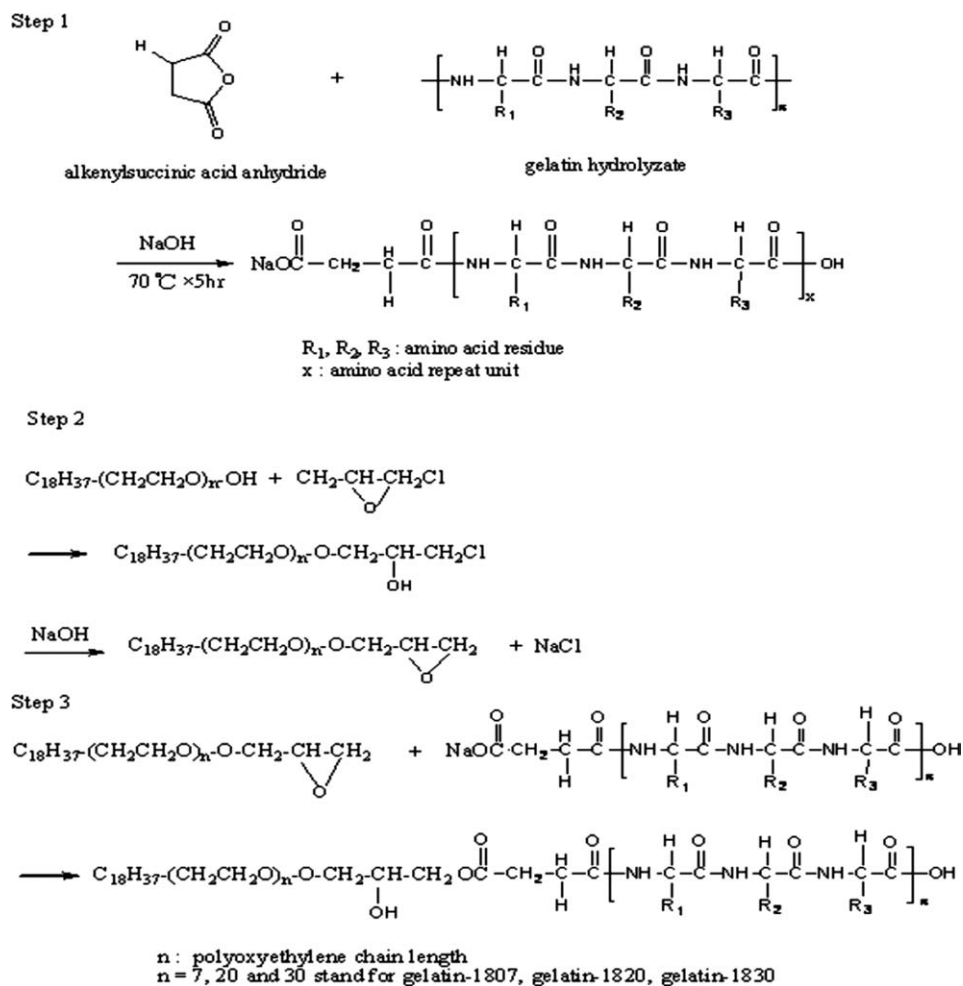
Figure 1 Synthesis of gelatin-derived surfactants.

concentration at the cmc. The standard free energy of micellization per mole of monomer units (ΔG_m°), with reference to the standard state of unit mole fraction for the nonionic surfactants, was calculated using the equation[13]

$$\Delta G_m^\circ = RT \ln \text{cmc} \qquad (3)$$

The emission spectra of the solutions were recorded using an Aminco-Bowman Series 2 luminescence spectrometer; the excitation wavelength was 335 nm and the emission was measured at wavelengths between 350 and 450 nm. Hydrophobicity was evaluated with respect to the emission spectrum of pyrene. The pyrene solutions were prepared by evaporating the solvent from a $1 \times 10^{-6} M$ pyrene solution (0.1 mL) in ethanol and then adding the gelatin-derived surfactant solutions (10 mL).

Contact angles (i.e., the angles formed between the planes tangent to the surfaces of solids and liquids at the wetting perimeter) were measured using a FACE CA-5 contact angle meter. An acrylic plastic sheet and unscoured cotton fabric were used as substrates. Foaming properties were determined using the Ross-Miles method. A 500 mL gelatin-derived surfactant solution is prepared and placed into a beaker. A dilute solution is dropped from a fixed height into a pool of the 1 g L^{-1} surfactant solution and the foam height is measurement. Foam production was measured in terms of the height of the foam initially produced; foam stability was measured in terms of the height after 3 min.

10 wt % Oil-in-water emulsions were prepared by adding soybean oil (10 g) to the gelatin-derived surfactant solutions (90 g) and homogenizing the mixtures (11,000 rpm; 5 min) with an IKA Labortechnik Ultra-Turrax T25 homogenizer. The average diameter (by volume) and size distribution of the emulsion droplets were measured using a Microtrac S3000 apparatus.

RESULTS AND DISCUSSION

Characterization of structure and molar mass

We determined the number average molar mass of the gelatin hydrolyzate through potentiometric
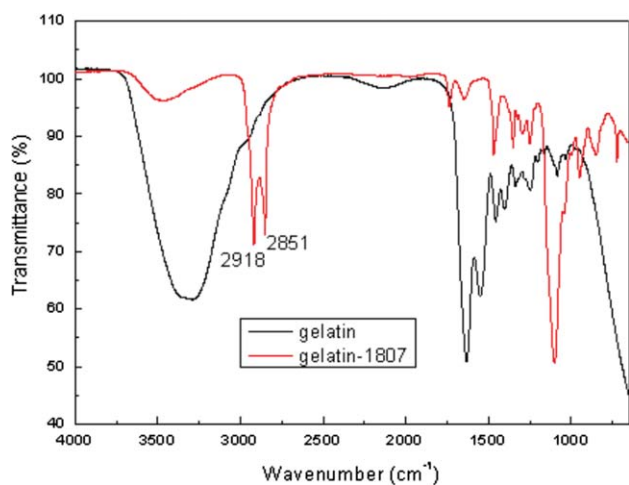
Figure 2 FTIR spectra (650–4000 cm^{-1}) of (1) unmodified gelatin and (2) the modified gelatin-1807. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

titration,[14–16] calculated in accordance with the equation,

$$\frac{w}{E} = N \times \frac{V}{1000}$$

where w is the weight of gelatin hydrolyzate, E is the equivalent, N the concentration (L) of the equivalent of HCl used during titration, and V is the volume of the HCl used for the inflection (= 9.486). The number average molar mass (M_n) was 1796. Similar results were obtained from mass spectrometric measurement, which provided a molecular weight of $\sim$ 1944.

Figure 2 presents a typical FTIR spectrum of one of the gelatin-derived surfactants and unmodified gelatin; we observe bands at 3200–3550 (O—H stretching), 3100–3500 (N—H stretching), 2918 (CH$_2$, asymmetric), 2851 (CH$_2$, symmetric), 1640–1700 (C=O stretching), 1515–1650 (N—H bending), 1425 (C—N stretching), and 1040–1110 (C—O stretching) cm^{-1}. The modified gelatin-derived surfactant showed that attachment of 18-carbon-atom alkyl hydrophobic chains to the gelatin hydrolyzate caused an increase 2918 cm^{-1} (—CH$_2$, asymmetric), 2851 cm^{-1} (—CH$_2$, symmetric), these bands were characteristics of the desired compounds. The structures of the compounds were further supported by their ^{1}H-NMR spectra, which revealed signals at δ 0.9 (CH$_3$), 1.3 [(CH$_2$)$_n$], 5.0–5.5 (CONH), 3.5–3.7 (CH$_2$CH$_2$O), and 3.3–4.0 (CHOH) ppm. The modified gelatin-derived surfactant showed that attachment of polyoxyethylene chains to the gelatin hydrolyzate caused appeared signals at 3.5–3.7 (CH$_2$CH$_2$O), and 3.3–4.0 (CHOH) ppm.

Surface tension

Gelatin is a hydrophilic compound that exhibits little surface activity because no hydrophobic groups are present in the molecules. After modification with hydrophobic groups (alkyl succinic anhydride and 18-carbon-atom glycidyl ether units), the resulting amphiphilic derivatives assembled at the water surface with their hydrophobic chains pointing to the air and their hydrophilic backbones laying on the surface to reduce surface tension. When the concentration was sufficiently high, the surface adsorption was completed and the surface tension no longer decreased. Figure 3 displays a plot of the surface tension with respect to the concentration of the gelatin-derived surfactants. We found that the gelatin-derived surfactants containing polyoxyethylene stearyl ether units were more surface active than the unmodified gelatin at all concentration; in addition, increasing the length of the polyoxyethylene chain decreased the surface activity, presumably because fewer amphiphilic molecules reached the surface of the solution, decreasing their ability to influence the surface tension. This phenomenon was due to the increased hydrophilicity of the surfactants that occurred upon decreasing the concentration of surfactants at the surface. We observe, however, a deviation in the curve for the surfactant lacking oxyethylene chains in its structure. We attribute this phenomenon to the low solubility of the unmodified gelatin providing a less homogeneous environment for surface tension measurement. The surface tensions of solutions of the gelatin-derived surfactants decreased upon increasing the concentration, and then reached constant values within narrow
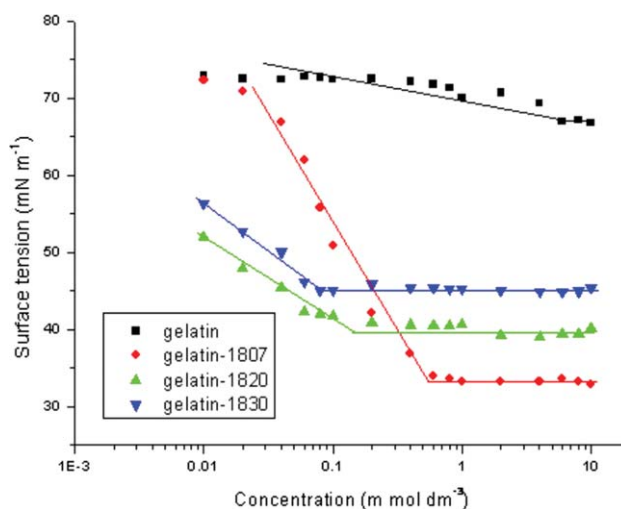

Figure 3 Plots of surface tension against the concentration of the gelatin-derived surfactants. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Surface Activity Properties of Gelatin-Derived Surfactants

Cpd.	cmc (mmol dm^{-3})	γ_{cmc} (mN m^{-1})	Γ_{cmc} ($\times 10^{-6}$ mol m^{-2})	A_{cmc} (nm^2 molecule^{-1})	ΔG_m° (kJ mol^{-1})
Gelatin-1807	0.541	33.2	4.32	0.385	−18.64
Gelatin-1820	0.142	39.7	1.87	0.886	−21.95
Gelatin-1830	0.0815	44.9	2.20	0.755	−23.33

concentration ranges. The break points were taken to be the values of the cmc. Table I lists the values of cmc, γ_{cmc}, Γ_{cmc}, A_{cmc}, and ΔG_m° obtained from the surface tension measurements. The values of cmc and γ_{cmc} of the modified gelatins were lower than those for unmodified gelatin. The value of γ_{cmc} for the surfactant featuring a polyoxyethylene chain having a value of n of 7 was 33.2 mN m^{-1}, indicating that this surfactant was particularly efficient at lowering the surface tension; i.e., when adsorbed at the air–water interface, this surfactant oriented itself to improve the surface activity. The area (A_{cmc}) occupied by the surfactant molecule provides information regarding the packing the adsorbed molecules at the air-water interface. The modified gelatins containing polyoxyethylene chains had smaller occupied areas in comparison with that of the unmodified gelatin, indicating that the time required for the surface tension to reach equilibrium at concentrations below the cmc was much longer for the unmodified gelatin than for the modified gelatin. The negative values of ΔG_m° imply that the gelatin-derived surfactants had great abilities to form micelles in solution and to adsorb at the air–water interface. The absolute values of ΔG_m° increased upon increasing the polyoxyethylene chain length of the gelatin-derived surfactant, presumably because interactions between the hydrophilic chains were a driving force for micellization or adsorption.

The modified gelatin surfactants exhibited lower values of cmc and γ_{cmc} than did the unmodified gelatin. The value of cmc decreased upon increasing the polyoxyethylene chain length; i.e., the gelatin-derived surfactants displayed excellent micelle forming ability at low concentrations. The longer the polyoxyethylene chain of the modified gelatin the higher its value of γ_{cmc}. It showed that the hydrophobic groups were attached to gelatin, achieving increased surface activity of the gelatins.

Fluorescence properties

We studied the hydrophobicities of the modified gelatin-derived surfactants using fluorescence spectroscopy with pyrene as a probe. The emission intensities of the first (I_1, 374 nm) and third (I_3, 394 nm) peaks were sensitive to the microenvironment. The intensity ratio I_1/I_3 has been used to monitor the so-lution behavior of surfactants and polymers. A higher value of I_1/I_3 suggests a greater polarity of the solution surrounding the pyrene units. The formation of aggregates possessing hydrophobic inner cores can be determined by plotting the values of I_1/I_3 against the surfactant concentration; if aggregates are formed, the value of I_1/I_3 will decrease. Figure 4 presents the values of I_1/I_3 for pyrene in solution as a function of the concentration of the gelatin-derived surfactants. For gelatin, the value of I_1/I_3 was 1.051 at 0.1 mmol dm^{-3}. When the concentrations of gelatin-1820 and gelatin-1830 were greater than 0.1 mmol dm^{-3}, their values of I_1/I_3 gradually decreased, indicating that the microenvironments around the pyrene units became increasingly hydrophobic.[17–21] This behavior suggests the formation of aggregates possessing increasingly compact hydrophobic cores. Notably, the value of I_1/I_3 of the unmodified gelatin remained nearly unchanged upon increasing the concentration, consistent with the notion that unmodified gelatin barely form aggregates because it lacks hydrophobic groups. After modification with alkyl succinic anhydride and 18-carbon-atom glycidyl ethers, the gelatin-1820, and gelatin-1830 samples readily formed aggregates through interactions of their hydrophobic chains in solution. The surface tension and fluorescence
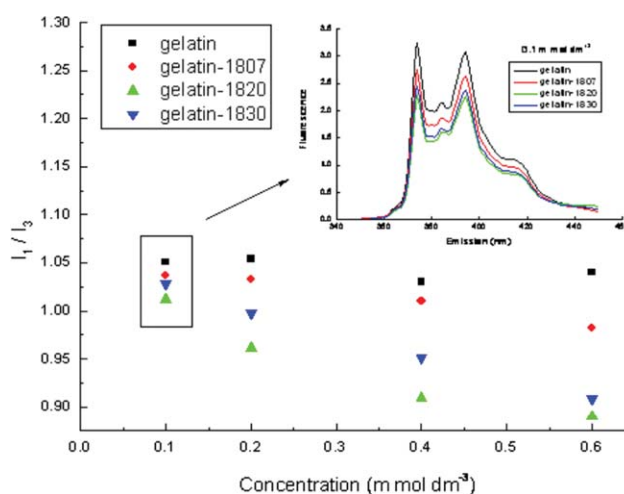

Figure 4 Plots of the pyrene intensity ratio I_1/I_3 against the concentration of the gelatin-derived surfactants. Inset: Fluorescence spectra of (1) gelatin, (2) gelatin-1807, (3) gelatin-1820, and (4) gelatin-1830. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

possessed similar results, indicating that smaller cmc and excellent surface activity properties can be achieved after appropriate modification. Our longest oxyethylene chain length of 30 units, however, exhibited a poorer surface activity, probably because the considerably decreased surface activity of this modified gelatin produced a less cohesive force on the surface.

Wetting power

The surface wettability of a solid plays very important roles in many processes, such as flotation, detergency, dying, painting, coating, and lubrication. Because water has a high surface tension (72.8 mN m^{-1} at 25°C), it does not spontaneously spread over solids having a surface free energy less than 72.8 mN m^{-1}. Addition of surfactants to water is a well-established means of enhancing the ability of aqueous solutions to wet and spread over solid surfaces. Adsorption of surfactants at solid–water and water–air interfaces leads to changes in interfacial tension and contact angles in solid–liquid–air systems; these parameters are, therefore, a measure of the wettability of solids.

Figure 5 presents the measured contact angles for aqueous solutions of gelatin-derived surfactants containing polyoxyethylene stearyl ether units. It reveals that they were more surface-active than the unmodified gelatin at all concentrations. The contact angles of the aqueous solutions decreased upon increasing the concentration of the gelatin-derived surfactant. In addition, the surface activity was sensitive to the length of the polyoxyethylene chain in these gelatin-derived surfactants; i.e., gelatin-1807 possessed that the lowest contact angle, suggesting that it is a superior wetting agent relative to the other products.
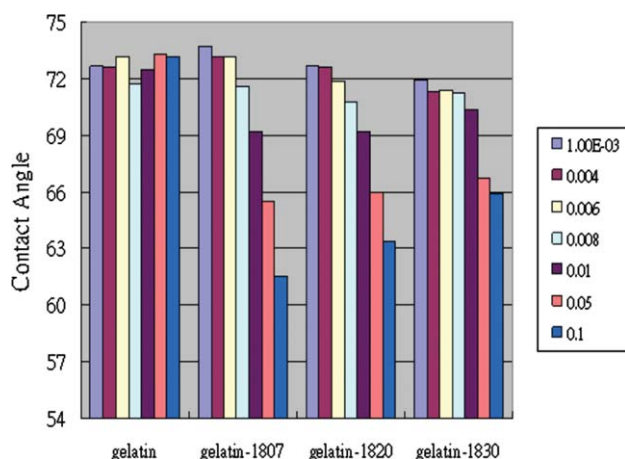

Figure 5 Plots of contact angle against the concentration of the gelatin-derived surfactants. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Foaming Properties of Gelatin-Derived Surfactants

	Foam height (cm)	
Compound	Initial	After 3 min
Gelatin	1.0	0.1
Gelatin-1807	1.4	0.9
Gelatin-1820	16.5	16.0
Gelatin-1830	18.5	17.1
SDBS	15.0	6.0
Triton-X 100	5.0	3.5

Similar to the surface tension behavior, this phenomenon was due to the decrease in concentration of surfactant at the liquid surface upon enlargement of the hydrophilic portion of the surfactant.

Foaming properties

Another aspect of surface activity is the ability of the modified gelatins to form stable foams. Table II lists the foam heights and foam stabilities of the gelatin-derived surfactants containing polyoxyethylene stearyl ether units. Gelatin is a poor foaming agent relative to the modified gelatin-derived surfactants. Increasing the length of the polyoxyethylene chain resulted in increased foam production and foam stability. The stability of a foam depends on several parameters, including the rate of attaining equilibrium surface tension, the bulk and surface viscosities, and the degrees of steric stabilization and electrical repulsion between the two sides of the foam lamella. In general, nonionic surfactants, such as octyl phenol ethoxylates (Triton-X 100) are low or moderate foamers, relative to anionic surfactants such as sodium dodecylbenzene sulfonate (SDBS), because of their lower solubilities in water; enhancing the hydrophilicity of surfactants (e.g., by increasing the oxyethylene chain length) usually leads to an increase in the foaming properties. It was, therefore, expected that the foams formed by the modified gelatins would be stable above a certain hydrophobicity of the anchoring groups at the air–water interface. This behavior can be explained by considering the combined effect of cohesive forces between the molecules in the foam lamella, due to the presence of the hydrophobic groups, and the prevention of drainage in the lamella, which could be achieved only by the gelatin molecules present in the lamella and anchored at the interface by the 18-carbon-atom alkyl hydrophobic chains.[4] It may be assumed that the other effect is more significant in stabilizing the foam. Once the air/water interface is covered by the gelatin molecules which are anchored by the 18-carbon-atom alky chains, it is expected that the foam

stability will not be changed while increasing the alkyl chain length.

Emulsifying power

Figure 6 presents images of the emulsions prepared from gelatin and the modified gelatins at 1% (w/w) concentrations and their average diameters. As expected, the average droplet diameter increased upon increasing the preparation time for all types of gelatin. The emulsifying ability of the gelatin-derived surfactants was sensitive to the length of their polyoxyethylene chains. Each modified gelatin yielded a more stable emulsion relative to that of gelatin; in addition, the longer the polyoxyethylene chain, the smaller the droplet size, that is, gelatin-1830 possessed the minimum value droplet size, indicates that it is a better emulsifying agent than other products. The average size of the droplets changed slightly from 1 μm initially to 1.4 μm after 3.5 h for the gelatin derivative containing 30-unit oxyethylene chains; i.e., the good-quality of the stabilized droplets of gelatin-1830 suggests that it possesses adequate emulsifying power for oils. In this study, the average sizes of the droplet of the gelatin-derived surfactants containing polyoxyethylene chains were lower than those reported previously for gelatin derivatives covalently modified with hydrophobic chains.[6] Because the stability should correlate with the degree of coverage of the oil droplet by the gelatin molecule, the amount of gelatin adsorbed onto the oil droplets is dependent on the polyoxyethylene chain length; the longer the chain, the higher the surface concentration achieved
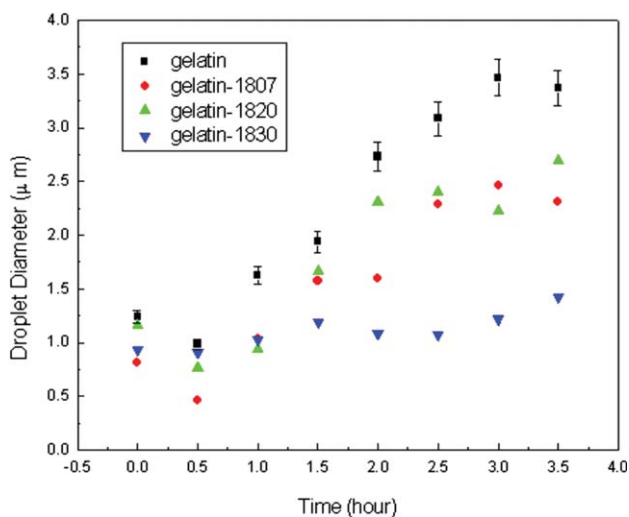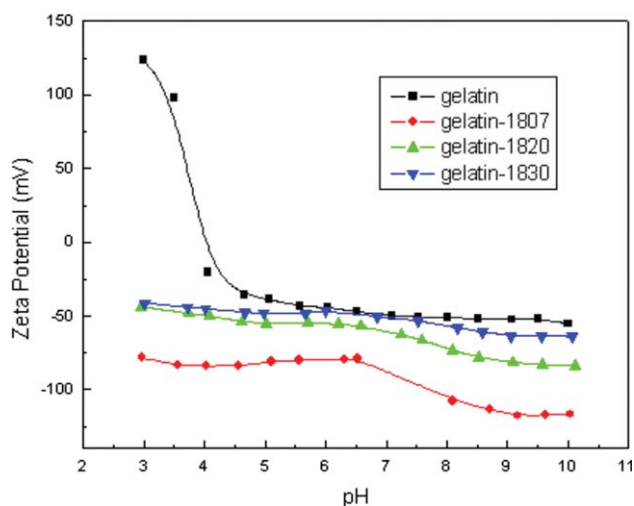

Figure 7 Zeta potentials of emulsions prepared at a gelatin-derived surfactant concentration of 1% w/w, plotted as a function of pH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for all gelatin molecules, leading to monolayer formation.[22,23]

Figure 7 displays the zeta potential of the emulsions prepared from gelatin and the modified gelatins at various values of pH. All of the modified gelatin emulsion droplets were negatively charged; the absolute value of the zeta potential increased upon decreasing the polyoxyethylene chain length. This result can be explained by considering that the surface concentration at the saturation level increased upon decreasing the polyoxyethylene chain length; i.e., it can be assumed that the stability of the emulsions results from electrical repulsion and steric stabilization. The isoelectric point (PI) for gelatin is 4.8 ± 0.1.[24,25] In this study, the isoelectric point of the emulsions prepared from gelatin was 4.03. Again, because the modified gelatin emulsion droplets are negatively charged, it appears that the presence of the polyoxyethylene chain segments led to decreases in their zeta potentials.

CONCLUSIONS

We have synthesized a series of gelatin-derived amphiphiles featuring polyoxyethylene stearyl ether units. These surfactants present polyoxyethylene chains as hydrophilic moieties and alkyl succinic anhydrides and 18-carbon-atom alkyl chains as hydrophobic moieties. We found that the surface activity was sensitive to the length of the polyoxyethylene chains. These novel compounds exhibit excellent surface activities, measured in terms of their surface tensions, wetting powers, and foaming and emulsifying abilities. We found that the gelatin-derived surfactants containing polyoxyethylene

Figure 6 Average droplet diameter (by volume) of emulsions prepared at a gelatin-derived surfactant concentration of 1% w/w, plotted as a function of time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stearyl ether units were more surface active than the unmodified gelatin at all concentration; presumably because fewer amphiphilic molecules reached the surface of the solution, decreasing their ability to influence the surface tension. We attribute this phenomenon to the low solubility of the unmodified gelatin providing a less homogeneous environment.

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