

The pH-Dependent Surface Properties of Gelatin-Alkenylsuccinic Acid Anhydride Derived Surfactants

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ABSTRACT: The pH-dependent surface properties of a gelatin-alkenylsuccinic acid anhydride derived surfactants, containing an oligopeptide residue and alkenyl groups, were studied. The surface properties examined included surface tension, contact angle, emulsifying power, and fluorescence properties. The results showed that the surface activities of gelatin derivatives and their detergent properties for T/W fabrics

are improved at low pH. These improved features make gelatin-derived surfactants suitable for use as cleaning agents for lime-degradable substrates such as hair and wool. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3371–3377, 2007

Key words: surfactants; proteins; solution properties; fibers; fluorescence

INTRODUCTION

In many household and industrial detergents and cleaning agents, such as hair shampoo and textile scouring agents, the primary components include surfactants and pH modifiers. Accordingly, it is well-known that cleaning efficiency is highly dependent on the appropriate selection of surfactants and pH.^{1–3} A surfactant is a substance that has a characteristic molecular structure consisting of a hydrophobic portion and a polar or an ionic portion. When surfactant is added to a substrate at a low concentration, it adsorbs onto its surface or interface, thereby markedly altering the surface or interfacial properties of the substrate. Surface activities of surfactants include emulsification, dispersion, solubilization, wetting, and foaming; and these provide the characteristic cleaning actions of household and industrial cleaning agents.^{4–8} Moreover, the properties of these agents are enhanced by the addition of pH modifiers, such as caustic soda.⁹

In general, a high-pH cleaning bath is more efficient than a low-pH bath in removing oils and impurities from substrates. However, at high pH, many substrates, especially keratinous materials, such as hair, skin, and wool, are degraded by lime.¹⁰ Thus, to outperform traditional cleaning agents, new products must combine high cleaning efficiency but at a lower pH.

Gelatin-derived surfactants have been studied previously and were found to exhibit good surface activ-

ities;^{11,12} however, only limited information is available regarding the effect of pH on cleaning baths containing these compounds.

In this study, we examined the influence of pH on the surface activities of gelatin-derived surfactants. These pH-dependent surface properties included surface tension, contact angle, emulsifying power, foaming, and fluorescence. In addition, the scouring properties for T/W fabrics were studied by electron microscopy and by measuring the whiteness of cleaned fabrics.

EXPERIMENTAL

Materials

The gelatin-derived surfactants used in this study were prepared by reacting gelatin hydrolysate and alkenylsuccinic acid anhydride. The preparation and purification of these surfactants were described previously,¹² and their structures are shown in Figure 1(a). Reagent-grade sodium hydroxide, hydrochloric acid, liquid paraffin, and kerosene were purchased from Hayashi Pure Chemical Co. (Osaka, Japan) and used without further purification.

The fluorescence probe was tris(8-hydroxy-chinolinate) aluminum (Alq₃), supplied by SynTec GmbH Wolfen Co. (Wolfen, Germany). The structure of the fluorescence probe is shown in Figure 1(b).

Preparation and purification of gelatin-derived surfactants

Gelatin-derived surfactants were prepared from gelatin hydrolysate and alkenylsuccinic acid anhydride.

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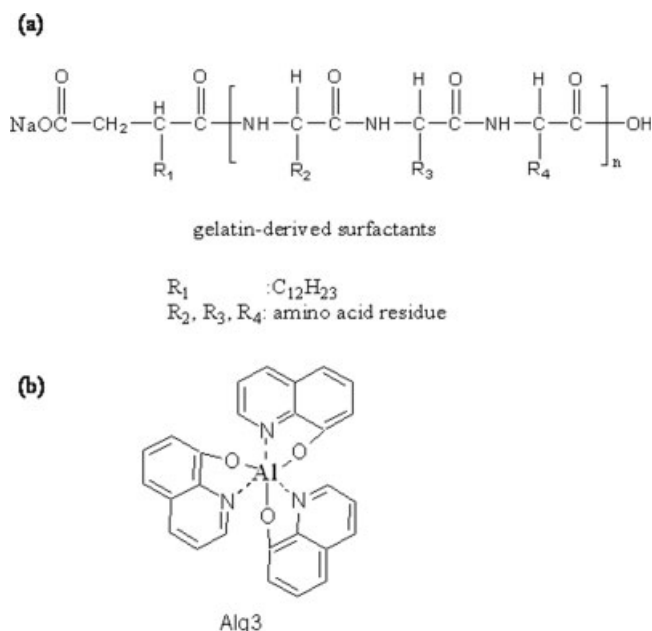


Figure 1 Structure of (a) gelatin-derived surfactants and (b) the fluorescence probe tris(8-hydroxy-chinolino) aluminum (Alq₃).

To a reaction mixture containing 40 g of gelatin in 60 g of water, 1.6 g of sodium hydroxide was added and the solution was heated for 16 h to 130°C. To 100 g of this solution, 4 g (0.04 mol) of alkenylsuccinic acid anhydride were added with stirring at 70°C. The pH value of the reaction mixture was maintained at 10 by the addition of dilute sodium hydroxide. After a reaction time of 5 h, the mixture was cooled to room temperature and the pH adjusted to 7 with dilute hydrochloric acid.

Water-insoluble products (mainly unreacted alkenylsuccinic acid) were removed from the reaction mixture by extraction with methyl *tert*-butylether (MTBE). Traces of MTBE were removed from the aqueous phase by heating to 40°C in a water-jet vacuum.

Measurements

The desired pH of the aqueous solutions was obtained using HCl and NaOH. The pH was measured using a pH meter (model SP-2200, Suntex, Tapei, Taiwan).

Surface tension was determined at room temperature with a Japan Kaimenkagaku CBVP-A3 surface tensiometer (Kyowa Interface Science Co., Tokyo, Japan). The tensiometer was calibrated with ultra pure water before use. The platinum plate was cleaned by flaming, while the glassware was rinsed with tap water and ultra pure water. A series of 0.5% (by weight) surfactant solutions at various pH values was prepared. Surface tension was measured three

times for each concentration and an average error less than 0.5 dyn/cm can be obtained routinely. The emission spectrum of the solutions was measured using a Aminco-Bowman Series 2 Luminescence Spectrometer (Rochester, NY). The excitation wavelength was 350 nm; emission was measured at wavelengths between 370 and 700 nm. The fluorescence probe (Alq₃) was dispersed in the presence of 20 g/L with a concentration of $6 \times 10^{-5}M$, and the solutions were then stirred at a rate of 150 rpm for 20 min to reach their steady states.

The contact angle, which describes the angle formed between the planes tangent to the surfaces of the solid and the liquid at the wetting perimeter, was measured with a FACE CA-5 contact-angle meter (Tokyo, Japan). Emulsifying power was determined according to the method described by Takeshita et al.¹³ Ten-milliliter of 0.1 g L/surfactant, at various pH values, and 10 mL of oily material were mixed in a test tube. After 20 vigorous shakes, the tube was allowed to stand undisturbed until the two phases had separated.

A laboratory dyeing machine was used to study the scouring of a T/W fabric by gelatin-derived surfactant solutions at various pH values. The T/W fabric was responsible for the content of blends at about 65% polyester and 35% wool (by weight). The scouring recipe consisted of 2 g/L auxiliaries and a liquor ratio of 30:1. Scouring was carried out at room temperature and at 40°C for 20 min. After scouring, the whiteness of the T/W fabrics was measured using an Applied Color System (ACS, Color Matching System, CS-5) spectrophotometer (Port Royal, NJ). The scoured fabrics were also used to evaluate the wetting ability of the surfactants, as measured by a contact-angle meter. The surface morphology of the scoured fabrics was analyzed by scanning electron microscopy (SEM, model S-3000N, Hitachi, Ibaraki, Japan). A zeta potential analyzer (Colloidal Dynamics, model Zeta-Probe, Warwick, RI) was used to measure the zeta potentials of the aqueous gelatin-derived surfactants at 25°C. The modified gelatin derivatives were diluted with deionized water to 0.5 wt % before measurement.

RESULTS AND DISCUSSION

Surface tension

The surface tension of the unmodified gelatin solution at various pH values was about 61–64 dyn/cm, as shown in Figure 2(a). This was much higher than the surface tensions of the corresponding modified gelatin-derived solutions.

Figure 2(b) shows the surface tensions of the gelatin-derived surfactants as a function of pH. As the pH increased, so did the surface tension. Moreover, the surface tension remained at 33 dyn/cm in the range

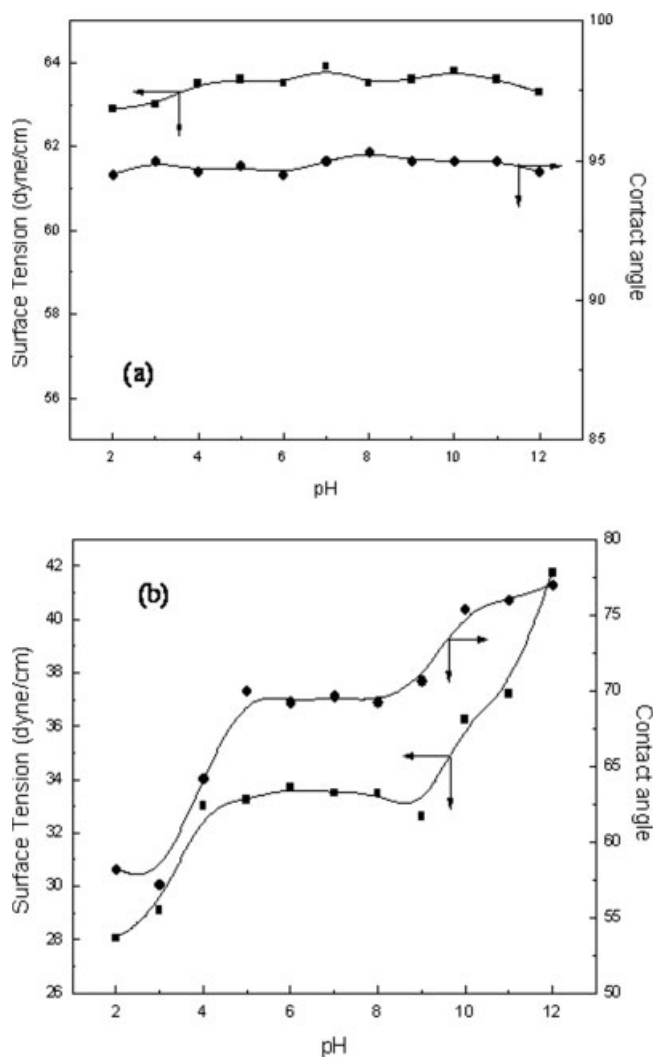


Figure 2 Plots of surface tension (■) and contact angle (●) against pH of (a) unmodified gelatin and (b) gelatin-derived surfactants.

of pH 5–9, and then increased gradually in the alkali range (pH 10–12). Thus, the gelatin-derived surfactants were more surface-active in the acidic range than under alkaline condition; that is, lowering the pH seems to lower surface-tension equilibrium. Changes in hydrophobicity and hence surface activity of gelatins can be obtained by chemical modification of gelatins. After covalent attachment of hydrophobic alkenylsuccinic acid anhydride chains to gelatin the surface tension was reduced faster. As more alkenylsuccinic acid anhydride were attached, the surface hydrophobicity was increased and net negative charge was decreased, which causes a reduction of surface tension. In addition, the carbohydrate groups restrict close molecular packing in the interfacial film and inhibit unfolding of the hydrophobic regions to the apolar phase. When the gelatin molecule was chemically modified by alkyl groups, this effect may be connected not only with the alteration of the gela-

tin hydrophobicity but also with the electrostatic repulsion of negatively charged molecules.¹⁴

Figure 3 shows the surface tension as a function of time for the gelatin-derived surfactants at various pH values. The surface tension of the surfactant solutions was not affected with time. Again, the surface activity was sensitive to pH, as a decrease in pH resulted in an increase in surface activity.

Contact angle

The contact angle of unmodified gelatin as a function of pH is plotted in Figure 2(a). The contact angle is about 93–95 at various pH values and is larger than that of the modified gelatin derivative, as shown in Figure 2(b). The gelatin-derived surfactants have a minor value contact angle at pH 2–4, which indicated that their wetting ability is better in the acid range than under alkaline conditions. This phenomenon is similar to surface tension, in that low pH also produces excellent surface activity.

Emulsifying power

In many textile processes, such as scouring and dyeing, it is necessary to introduce surfactants into the bath to remove oily impurities from the fibers. In these removal processes, the ability of the surfactant to emulsify impurities is important. The emulsifying ability of gelatin-derived surfactants at different pH values was estimated (Table I). In an acid aqueous solution (pH 4), the surfactants had a longer separation time than under neutral or alkaline conditions.

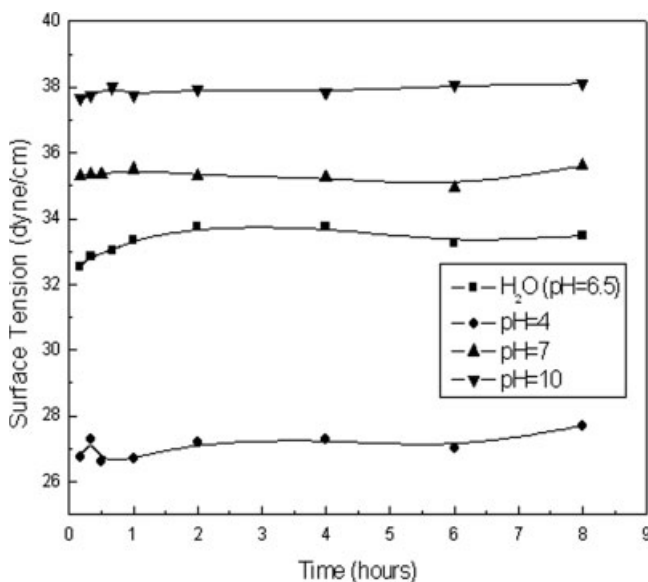


Figure 3 Time dependence of the surface tension for gelatin-12C at different pH values.

TABLE I
Emulsifying Power of Gelatin-12C at pH = 4, 7, 10

Condition	Separation time (min)	
	Liquid paraffin	Kerosene
H ₂ O	22.10	1.26
pH = 4	33.63	41.22
pH = 7	15.63	12.28
pH = 10	11.34	10.51

pH adjusted with HCl or NaOH; H₂O indicates that the pH was not adjusted.

Fluorescence properties

Tris (8-hydroxyquinoline) aluminum (Alq₃) is a molecular compound in which the Al³⁺ ion bonds to three bidentate 8-hydroxyquinolate ligands with oxygen and nitrogen binding sites. In Alq₃ molecule, the electron structure of Al³⁺ is 1s²2s²2p⁶, a metal ion structure similar to inert gas atom, so Alq₃ has good stability in dry atmosphere. Alq₃ is a representative fluorescent material in the research field of organic light-emitting devices (OLEDs), and has been widely used as the emitting layer or the electron-transporting layer since it was discovered to produce efficient electroluminescence.

The fluorescent probe Alq₃ has excellent photoluminescence. It emits bright fluorescence in response to ultraviolet radiation, with peaks at 510 nm (green range).¹⁵ Figure 4 shows the fluorescence emission spectra of the gelatin-derived surfactants at various pH values. Blanks means a solution of Alq₃ in pure water in the absence of the surfactant, H₂O means a solution of the gelatin-based surfactant in the presence of the Alq₃. Emission maximum shifted in the direction of shorter wavelengths by the addition of gelatin-12C (attachment of 2-dodecen-1-yl succinic anhydride to gelatin hydrolysate). In addition, as the

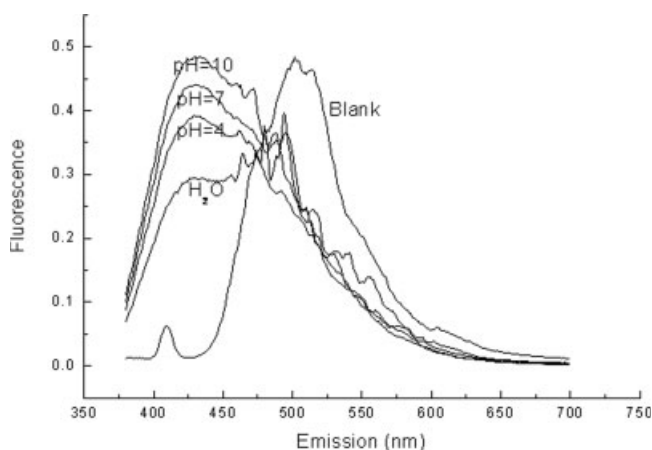


Figure 4 Fluorescence spectra of Alq₃ in the presence of 20 g/L gelatin derivative surfactants under different pH conditions. The excitation wavelength was 350 nm and the emission was measured between 370 and 700 nm.

pH of the surfactant solutions increased, the fluorescence intensity of Alq₃ increased gradually, indicating the increased polarity of the surfactants. The polarity at pH 10 was higher than that at pH 4 and pH 7. Hence, electrostatic repulsion of the charged COO⁻ groups may be important in decreasing water permeability under the hydrophilic charged conditions present at this region. In addition, the resulting COO⁻ possesses strong polarizing and covalent characteristics, since their polarity at alkaline pH is greater than at acidic pH.^{16,17}

This phenomenon, which is consistent with the results regarding surface tension, can be attributed to the enlargement of the hydrophilic portion of the surfactant molecule, resulting in an increase in the concentration of surfactant at the liquid surface.

Scouring properties for T/W fabrics

T/W contaminants are typically grouped into three main classes: solvent-soluble substances (usually referred to as grease), water-soluble substances (suint), and insoluble material (mineral dirt). All three types of contaminants must be removed before the fabric can be mechanically processed. Commercially, the removal process (scouring) is carried out in a series of aqueous solutions containing detergent and builder, followed by rinsing with water.¹⁸ Of the many parameters analyzed, pH has been shown to significantly affect the efficiency of contaminant removal from fabric surfaces in the presence of surfactant solutions.¹⁹

The ability of gelatin-derived surfactants to improve the whiteness of T/W fabrics at different pH values is shown in Table II. "Blank" indicates that no surfactant was added. Ethyl ether removed contaminants completely, resulting in a whiteness of 48.07. However, the gelatin-derived surfactant at acidic pH resulted in whiteness even greater than that obtained with ethyl ether. This finding demonstrates that the presence of gelatin-derived surfactant increases

TABLE II
Whiteness of Gelatin-12C and Polyoxyethylene Nonyl Phenyl Ether (NP-9) at pH = 4, 7, 10

Condition	Whiteness (WI)			
	Gelatin-12C		NP-9	
	Room temperature	40	Room temperature	40
Blank	46.92	47.84	46.92	47.84
H ₂ O	46.68	48.71	47.45	47.92
pH = 4	48.23	48.90	46.22	46.59
pH = 7	46.64	46.69	47.41	46.41
pH = 10	47.48	48.00	47.61	47.85

The concentration of the gelatin-12C and NP-9 is 2 g/L.
*The whiteness of the ethyl ether is 48.07.

the removal of contaminants in acidic scouring baths. The increased whiteness is because of the greater efficiency of the rinse process in removing contaminants, which increases the brightness and decreases the yellowness of the product.²⁰ The scouring properties of gelatin-derived surfactants were also compared with that of polyoxyethylene nonyl phenyl ether (NP-9). The whiteness of NP-9 increased slightly as the pH of scouring increased. The increase in whiteness was

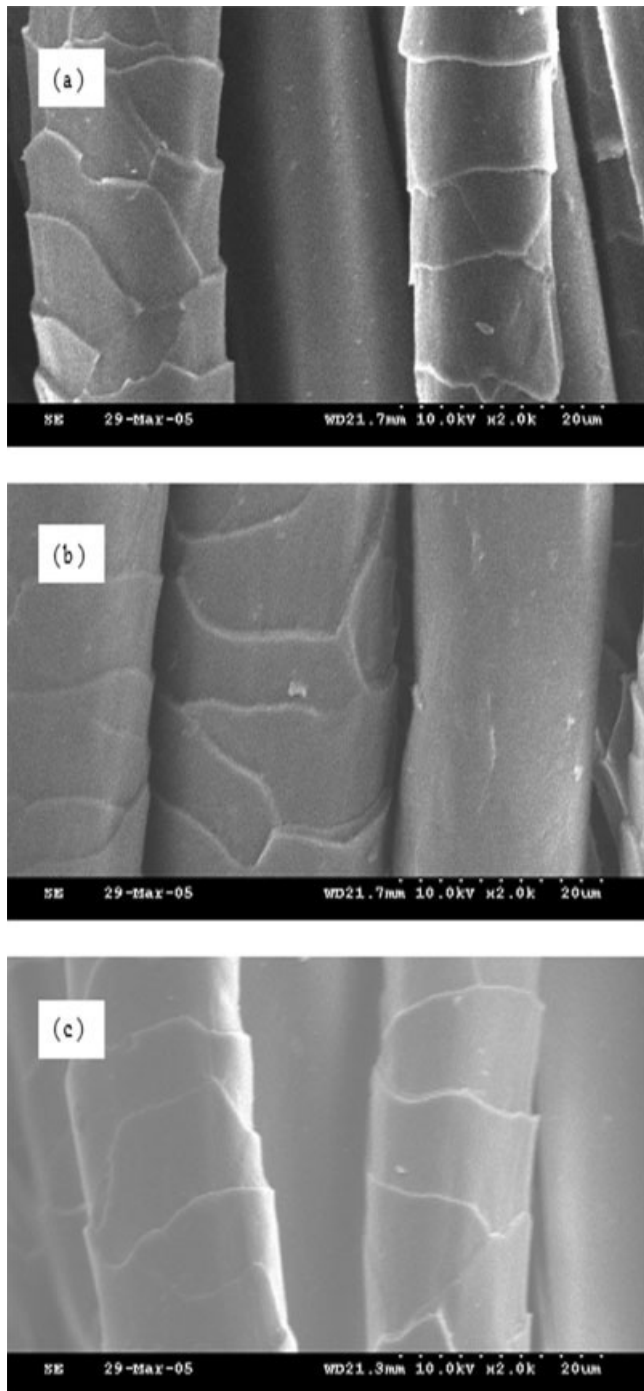


Figure 5 Scanning electron microscopy images of T/W fabrics following treatment with gelatin-12C at (a) pH = 4, (b) pH = 7, (c) pH = 10.

TABLE III
Water Droplet Formed on the Surface of T/W Fabrics by Treatment with Gelatin-12C or Polyoxyethylene Nonyl Phenyl Ether (NP-9) at pH = 4, 7, 10

Condition	Contact angle (degree)	
	Gelatin-12C	NP-9
Blank	125.0	125.0
H ₂ O	128.0	120.3
pH = 4	130.7	118.0
pH = 7	127.3	117.7
pH = 10	126.3	122.7

likely a result of the efficient removal of contaminants and possibly led to a decrease in the yellowness of the fabric in the alkaline rinse liquor.

Scanning electron microscopy analysis

Figure 5 shows the SEM images of T/W fabrics treated with gelatin-derived surfactant at pH 4, 7, and 10. These micrographs reveal the surface morphology of the T/W fabrics at different pH values. It can be seen that, in high-pH cleaning baths, scouring destroys the scales of T/W fabrics, whereas in low-pH baths the scales remained integrated and were not affected by the acidic conditions. The values of the contact angles of the water droplets formed on the surface of T/W fabrics by treating them with gelatin-derived surfactants or NP-9 at different pH values are shown in Table III. Alkaline scouring of the gelatin-12C surfactant increased its wetting ability, as by destroying the scales the contact angle between the cleaned fibers is reduced. In addition, as the pH of NP-9 increased the contact angle increased, that is, NP-9 possessed the minimum value contact angle at acidic condition, indicates that it is a better wetting agent under acidic condition for wool than gelatin-12C, however, the scale is easier to be destroyed.

Mechanism of the pH-dependent properties

pH has an effect on the net charge of a protein depending on its isoelectric point (pI), which for gelatin is 4.8 ± 0.1 .^{21,22} In addition, the charge as well as its density and distribution in the protein molecule strongly influence surface activity. Experimentally, proteins have been found to exhibit greater surface activity near their pI, because electrostatic repulsion between identically charged adsorbed molecules is minimized.^{23,24}

The zeta-potentials of a modified gelatin-derived surfactant (gelatin-12C) were measured at various pH values, as shown in Figure 6. The modified gelatin derivative had a zeta-potential of -70.5 mV at pH = 4–5.5, about -108 mV at pH = 7, and about -130 mV at pH = 9–10; its isoelectric point is at about pH 2.4. At pH values less than pI, the zeta-potential is positive,

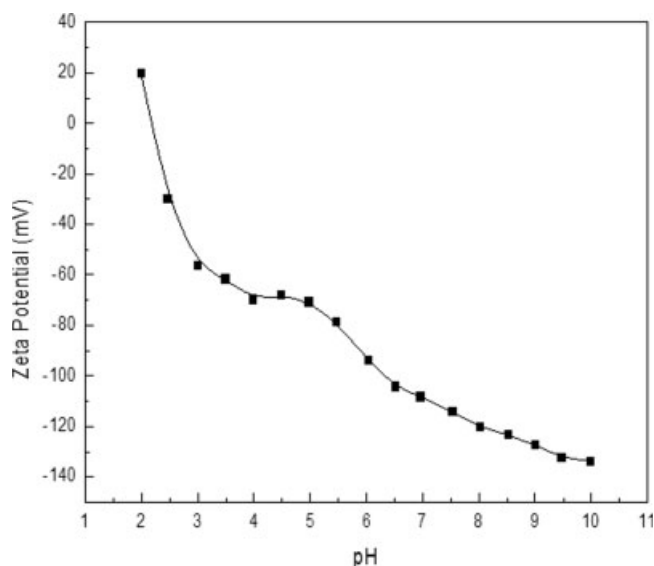


Figure 6 Dependence of zeta potential on pH for gelatin-12C.

whereas at pH values higher than pI, it is negative. Modification of gelatin leads to changes in its zeta potential, i.e., the more negatively charged the gelatin derivative, the lower its pI.

Figure 7 schematically shows ionized and un-ionized molecules of a gelatin-derived surfactant at pH values near its pI. At low pH values ($\text{pH} < 2$), the gelatin-derived surfactant is unionized and thus preferentially partitions in a lipophilic medium. The hydrogen bonds are particularly stable, when the carboxyl groups are attached to long alkyl chains. At isoelectric point hydrogen may bridge the carbonyl oxygen and the hydroxyl oxygen of two neighboring carboxyls. Water molecules could stabilize this bonding. Hydrogen bonds between the acid and the anion are known to be much stronger than those between the unionized molecules, so that the distance minimum is expected at ion-dipole interaction. At high pH values ($\text{pH} > 9$), the gelatin-derived surfactant is nearly ionized, leading to ionic repulsion between polar groups and greater solubility in water. One possible explanation of this behavior is that increased lateral electrostatic repulsion of the equally charged protein molecules prevents the formation of closely packed monolayers. Another explanation takes into account the structural stability of the protein molecule, which is maximal and the conformational rearrangements minimal when adsorption proceeds at a pH near the pI ($\text{pI} = 2.4$) of the protein.

CONCLUSIONS

This study investigated the effects of pH on the surface activity of gelatin-derived surfactants. These compounds exhibited good surface activity, including

surface tension, wetting ability, emulsifying power, and foaming, under acidic conditions. A decrease in pH induced a corresponding increase in surface activity. Moreover, the surface activity of the gelatin-derived surfactant was greatly enhanced under acidic conditions, which implies that the surface properties of the surfactant molecules were strongly influenced by acids. The scouring properties of the gelatin-derived surfactants for T/W fabrics, as determined by measuring whiteness, were also increased at low pH, most likely because of the increased removal of contaminants.

It was also found that, at decreasing pH, the gelatin hydrolysate chains were less concentrated at the interface and extended further from the surface. This was explained in terms of a reduction in the number of negative segments and an increase in the number of positive segments of the gelatin derivatives with

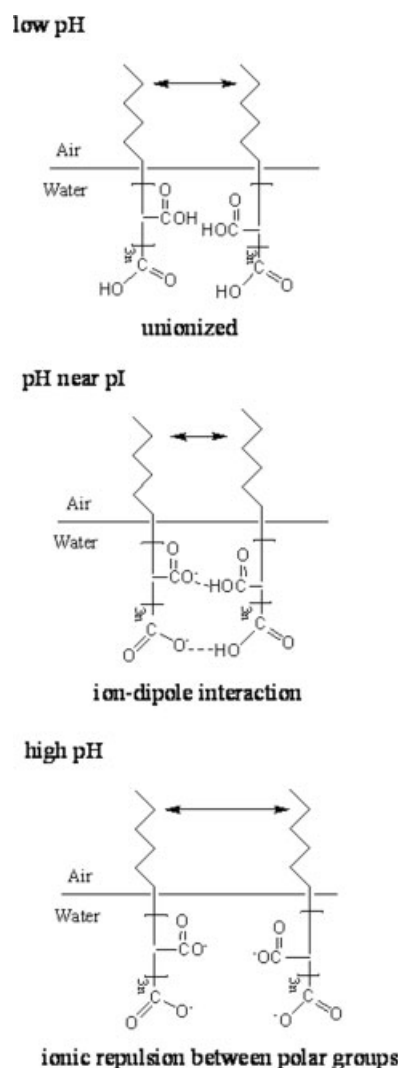


Figure 7 At a pH near the isoelectric point (pI), the gelatin-derived surfactant decreases the intermolecular distance at the air/water interface.

decreasing pH. Furthermore, the derivative surfactants exhibited greater surface activity near their pI, since at this pH the electrostatic repulsion between identically charged adsorbed molecules is minimized.

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