Thermal Condensation of Fatty Acids and Amines with Proteins

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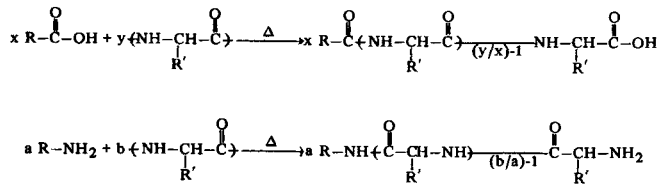
ABSTRACT

Useful, potentially low cost, polypeptide surfactants were prepared directly from the thermal condensation (ca. 240 C, ca. 1 hr) of proteins (wool, vegetable protein, gelatin, and chicken feather) with long chain fatty acids (undecylenic, lauric, and stearic) or fatty amines (dodecylamine and N-[γ-aminopropyl] dodecylamine). Dilute aqueous solutions of these surfactants, at appropriate pHs, exhibit good foaming characteristics and low surface tensions. The condensation reaction is envisioned as a transamidification in which terminal anionic groups (carboxylic acid from fatty acids) or cationic groups (primary amino from fatty amines) are produced according to the following reactions:



INTRODUCTION

The dissolution of human hair in boiling benzyl alcohol via esterification of the peptide bond (1) suggested that N-acylpolypeptides and terminal N-alkylamides of polypeptides might be prepared by direct transamidification of proteins with fatty acids or fatty amines. Current commercial N-acylpolypeptides usually are prepared by the reaction of fatty acid chlorides with protein hydrolysates (2). Several patents describe the reactions of proteins with amines in water followed by heating (3), the reaction of polyamines with proteins to yield polyamines substituted with amino acid residues (4), or the reaction of proteins with alkanolamines followed by acylation with fatty acids (5).

A consideration of the possible mechanism of the benzyl alcohol-wool reaction (1) suggested that fatty acids or fatty amines could react in a one step reaction with proteins at elevated temperatures under equilibrium conditions to undergo transamidifications yielding either carboxy or amino terminated polypeptides, the other terminal group being the fatty group. Indeed, by adjustment of the ratio of equivalents of amino acid residues to either fatty acid or fatty amine, N-acylpolypeptides or terminal N-alkylamides of polypeptides of controlled mol wt can be prepared. This communication describes the results of work demonstrating that these reactions readily occur to yield useful, low cost, anionic or cationic surfactants.

EXPERIMENTAL PROCEDURES

Materials

The protein sources employed in this study were: white chicken feathers (washed in anionic detergent, rinsed in distilled water, then air dried); wool (test fabric 503A, Test Fabrics, Middlesex, N.J., used as received); high gel strength edible gelatin (Darling and Co., Chicago, Ill., used as received); and vegetable protein (Gunthers Products, Chicago, Ill., used as received). Lauric acid (Neo-Fat 12-43, Armak Chemicals, McCook, Ill.); stearic acid (Neo-Fat 18, Armak Chemicals); and undecylenic acid (Baker Castor Oil Co., Bayonne, N.J.) were used as received, as were the amines employed: dodecylamine (Armeen 12D, Armak Chemicals) and N-(γ-aminopropyl)dodecylamine (Duomeen L-11, Armak Chemicals).

Synthetic Procedures

The transamidification reactions (Table I) were run by preheating the fatty acid or fatty amine to 180-190 C. A nitrogen blanket helped to minimize dark color formation. The protein was added slowly with stirring as the temperature was raised to ca. 230 C. The transamidification occurs between 225-250 C, as evidenced by dissolution of the solid protein into a continuous liquid phase with the fatty acid or amine. When addition of the protein was complete, the product was heated at 230 C and stirred an additional one-half hr to ensure complete reaction. The reaction mixture then was cooled, and the solid, dark brown, waxy mass was broken up. The products were completely soluble in acetone, chloroform, and ethanol at the 2% level and were soluble in water at acid or alkaline pH as noted in Table I.

A variety of polypeptide surfactants was synthesized by using different equivalent ratios of protein to fatty acid or amine (Table I). An equivalent wt of 125 for the protein amino acid moiety was used based upon the data of Ward, et al. (6). In this manner, the length of the polypeptide chain attached to the fatty group and, therefore, the average mol wt of the surfactant could be controlled.

Analytical Procedures

Thin layer chromatography (TLC), gas chromatography, and pyrolysis gas chromatography were used to assess the purity of the surfactants. Acetone or ethanol-water solutions of the fatty acid-protein and fatty amine-protein condensates and the corresponding free fatty acid or amine were deposited on a silica gel coated plate and then eluted with the above solvents. After spot development by charring with sulfuric acid, the TLC indicated the absence of free fatty acid or amine from both polypeptide surfactants. The samples were silylated (7) and subjected to gas chromatographic analysis (F & M 5750 detector, silicone column) and pyrolysis gas chromatographic analysis (F & M scientific 80 pyrolysis unit) at 600 C. No free fatty acids were detected. A sample of a 2:1 equivalent gelatin-lauric acid condensate was hydrolyzed, and the free lauric acid content was found to be 41% (theoretical value for bound lauric acid is 42%). The IR spectra (Perkin Elmer 621 IR recording spectrophotometer) of gelatin-dodecylamine (2:1), gelatin-lauric acid (2:1), and wool-lauric acid (5:4) condensates were very similar with prominent absorption bands at 3300 cm^{-1} (polypeptide NH stretching) and 1640 and 1550 cm^{-1} (amide I and II bands) (1). The surfactants were, therefore, assumed to be acylated polypeptides only.

Surface Tension Measurements

The Cenco-Du Noüy interfacial tensiometer was used to determine the surface tension of dilute solutions of the ammonium salt of the fatty acid condensate and the hydrochloride salt of the fatty amine condensate. Solutions were

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TABLE I

Polypeptide Surfactants Derived from Thermal Condensation of Proteins with Fatty Acids and Fatty Amines

Protein	Fatty derivative	Equivalent ratio protein/fatty derivative	Percent 2 g sample soluble in 100 ml 0.01 M NH_4OH	Percent 2 g sample soluble in 100 ml 0.01 M HCl	Surface tension dynes/cm (percent concentration)	Foaming (ml)
Chicken feather	Lauric acid	2:1	75		33 (0.1)	2.3
					39 (1.2)	8.0
Chicken feather	Lauric acid	5:1	86		34 (0.9)	3.0
Chicken feather	Undecylenic acid	5:1	92		39 (0.3)	3.0
Vegetable	Lauric acid	2:1	83		29 (0.05)	2.3
Gelatin	Lauric acid	2:1	84		32 (0.3)	4.2
Gelatin	Lauric acid	3:1	70		31 (0.2)	3.0
Gelatin	Lauric acid	5:1	81		31 (0.2)	3.0
Gelatin	Lauric acid	9:1	95		31 (0.9)	4.3
Gelatin	Stearic acid	2:1	22		46 (0.1)	0
Wool	Lauric acid	2:1	90		29 (0.1)	3.0
Gelatin	Dodecylamine	2:1		78	29 (0.4)	1.3
Gelatin	Dodecylamine	5:1		87	31 (0.3)	1.3
Gelatin	N-aminopropyldodecylamine	2:1		100	33 (0.7)	2.2
----------	Sodium lauryl sulfate	----------	----------	----------	39 (0.3)	5.0
----------	Maypon 4C	----------	----------	----------	28 (0.3)	5.0

prepared by dissolving the fatty acid condensate in either 0.01 M HCl or 0.01 M NH_4OH in a Waring blender and then filtering off the small amount of insoluble residue.

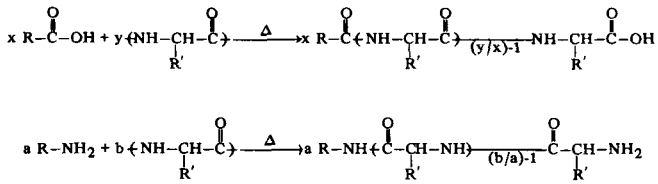
Foaming

Foaming was determined by measuring the volume of stable foam above the liquid layer which forms when 5.0 ml surfactant was shaken in a 10 ml graduate cylinder.

RESULTS AND DISCUSSION

The surface tension, foaming characteristics, and solubility data for the polypeptide surfactants are found in Table I. For comparison, the foaming characteristics and surface tensions of two commercial surfactants also are included in Table I.

The results of the IR, gas chromatographic, and TLC analyses and the solubility experiments suggest that surfactants are formed in the thermal condensation reaction in which terminal anionic carboxylic acid groups are formed from fatty acids and cationic primary amino groups are formed from fatty amines. These transamidification reactions are envisioned as:



with a statistical distribution of mol wt based upon equilibrium reaction conditions.

The two condensation reactions proceeded similarly; however, the proteins tended to dissolve more quickly in the hot amines than in the hot fatty acids. No attempt was made in these initial studies to prevent oxidative decomposition; the surfactants were a brown-black color, a problem which partly is overcome by running the reaction in a nitrogen atmosphere.

The transamidification reactions were carried out using several different equivalent ratios of protein to fatty acid or amine. By using specific ratios, the length of the polypeptide chain attached to the fatty group and, therefore, the average mol wt can be controlled yielding polypeptide surfactants of different physicochemical properties.

As expected, the nature of the fatty chain also influences the properties of the surfactants; for example, the lauric acid derived product displayed better foaming characteristics than did the stearic acid derived product.

The low surface tensions of solutions of the polypeptide surfactants suggest their utility as surfactants. All solutions of the lauric acid-protein or dodecylamine-protein condensates exhibit surface tensions of ca. 30 dynes/cm, comparable to the 28 and 40 dynes/cm obtained for dilute solutions of two commercial detergents, Maypon-4C (collagen tripeptide acylated with coconut fatty acid, Stepan Chemical Co., Northfield, Ill.) and sodium lauryl sulfate, respectively.

Foaming of dilute polypeptide surfactant solutions was somewhat less than that of the two commericial detergent solutions but was increased by use of higher concentrations of polypeptide surfactant.

By choice of raw material sources, such as protein wastes, e.g. animal hide trimmings, and low cost fatty acids, e.g. tall oil fatty acids, a variety of useful, low cost, polypeptide detergents can be made available.

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REFERENCES

1. Smith, I.T., and P.E. Whitney, Tex. Res. J. 39:392 (1969).
2. Stevens, C.E., in "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. 19, Interscience Publishers, New York, N.Y., 1969, p. 515.
3. Krajewski, J.J., U.S. Pat. 3,168,510 (1965).
4. Young, H.H., and K.H. Spitzmueller, U.S. Pat. 3,230,210 (1966).
5. Young, H.H., and K.H. Spitzmueller, U.S. Pat. 3,138,581 (1964).
6. Ward, W.H., in "Analytical Methods of Protein Chemistry," Vol. 4, Edited by P. Alexander and H.P. Lundgren, Pergamon Press, New York, N.Y., 1966, p. 154.
7. Fales, H.M., and J.J. Pisano, "Biomedical Applications of Gas Chromatography," Edited by H.A. Szymanski, Plenum Press, New York, N.Y., 1964, pp. 77-79.

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