Synthesis and Emulsion Properties of a Novel Nonionic Surfactant, Dialkyl Glucosylglutamate

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For the purpose of providing an available surfactant to the field of food processing, a novel nonionic surfactant was synthesized from δ-gluconolactone, glutamic acid, and five alkyl alcohols. The series of synthesized surfactants was designated dialkyl glucosylglutamate (DGG). The introduction of glutamic acid made it simple to synthesize the surfactant which has two alkyl side chains in one molecule. Using DGG, the o/w emulsion was prepared under the model system with buffer and paraffin. The emulsion stability of DGG was compared with that of sucrose laurate, one of the major emulsifiers for foodstuffs, under various conditions of pH and salt concentration. The results revealed that the molecular structure of the surfactant affects the emulsion stability. The emulsion stability of DGG suggested that DGG would be an essential emulsifier in the food industry.

INTRODUCTION

The role of surfactant is important in food processing in terms of its flavor and texture. Especially, surfactants are often used as emulsifiers in many foods that contain lipids. Among these emulsifiers, acyl glyceride is consumed most largely to make the water-in-oil (w/o) type emulsion. On the other hand, sucrose esters of fatty acid are utilized as emulsifiers for oil-in-water (o/w) type emulsion.

For the purpose of providing an emulsifier to the food industry, a nonionic surfactant was synthesized from δ-gluconolactone, glutamic acid, and five alkyl alcohols. The surfactant, designated dialkyl glucosyl glutamate (DGG), is characterized with respect to its unique molecular structure, i.e., the existence of two dialkyl side chains in one molecule and the introduction of amino acid. The emulsion properties of DGG were investigated and compared to that of sucrose laurate. Using a series of surfactants with various lengths of dialkyl side chains, the relation between the emulsion stability and the molecular structure of these surfactants was discussed.

MATERIALS AND METHODS

Reagents. Glutamic acid, δ-gluconolactone, and five alkyl alcohols, which are the materials of the nonionic surfactant, were purchased from Wako Pure Chemical Co. (Osaka, Japan). p-Toluenesulfonic acid monohydrate, triethylamine, toluene, chloroform, and methanol, which were chemicals for synthesis of the surfactant, were purchased from Wako Pure Chemical Co. or Kanto Chemical Co. (Tokyo, Japan) and used without further purification. A commercially available sucrose laurate (SE L-590, monoester, diester, triester, and tetraester are included that 28%, 37%, 25% and 10%, respectively) was obtained from Nihon Yushi Co. Ltd. (Tokyo, Japan).

Synthesis of Surfactant. Nonionic surfactant was synthesized according to the method of Okahata et al. (1988) as follows: 0.22 mol of alcohol, 0.088 mol of glutamic acid, and 0.1 mol of p-toluenesulfonic acid monohydrate were suspended in 400 mL of toluene. The solution was refluxed with a Dean-Stark trap. The period of refluxing was from 1.5 to 4 h depending on the alkyl alcohol. The esterification of alkyl alcohol with long side chains progressed slowly. After filtration, the solvent was

evaporated to dryness under reduced pressure. The residue was washed with acetone at several times and dialkyl glutamate–p-toluene sulfone was precipitated. Its purity was checked by thin-layer chromatography (TLC) [silica gel 60 F_{254} (Merck)]. The sample was developed with the mixture solvent of butanol, acetic acid, and water (5:4:1). The detection was done both with ninhydrin and with a UV lamp. Dialkyl glutamate–p-toluene sulfone (0.015 mol) and 0.023 mol of triethylamine were dissolved with 100 mL of chloroform and 100 mL of water to eliminate triethylamine–p-toluene sulfone. After the chloroform phase was dried by anhydrous sodium sulfate, the solvent was evaporated under reduced pressure and the white-yellow residue of dialkyl glutamate was obtained. The residue and 0.016 mol of δ-gluconolactone were dissolved with 150 mL of methanol and refluxed. The refluxing period was from 2 to 10 h. The esterification of dialkyl glutamate with long side chains progressed slowly. After refluxing, the solvent was evaporated to dryness under reduced pressure. n-Hexane was added to the residue and heated to 50 °C. After filtration, the solvent was chilled to 0 °C with ice and the white precipitate was obtained. The progress of the reaction was traced with TLC. The developing solvent of TLC was the mixture of chloroform and methanol (5:1). The detection was done by sulfate. When cetyl alcohol was used, the synthesized dicetyl glucosylglutamate is contaminated by small amounts of impurities. It was purified with the TLC (Empore 3M, Analytical International Co. Ltd.). The molecular structure and the purity of the DGG synthesized in these procedures were checked using NMR, IR, and melting point.

Measurement of Emulsion Stability. The emulsion stability of the surfactant was examined according to the method of Pearce and Kinsella (1978). A definite amount of paraffin oil containing the surfactant and buffer (Britton–Robinson buffer, 0.04 M, pH 7.0) were homogenized with a Polytron PT10-35 (Kinematica, Switzerland) for 10 min at 10 000 rpm. The emulsions were prepared under low temperature around 0 °C. The bottle containing the solvents was surrounded with ice and water through the homogenization step. The emulsion stability was evaluated by the change of the turbidity at 500 nm with a Shimadzu UV-2200 spectrometer. The turbidity of the emulsion decreased remarkably for 10 min just after the preparation. Except for the initial 10 min, the turbidity changed by degree. The gradient of the turbidity from 20 min to 2 h was adopted as experimental data.

RESULTS

Comparison of the HLB Value and Emulsion Stability of Surfactant in the Model System. The stick model of molecular structure and the abbreviations

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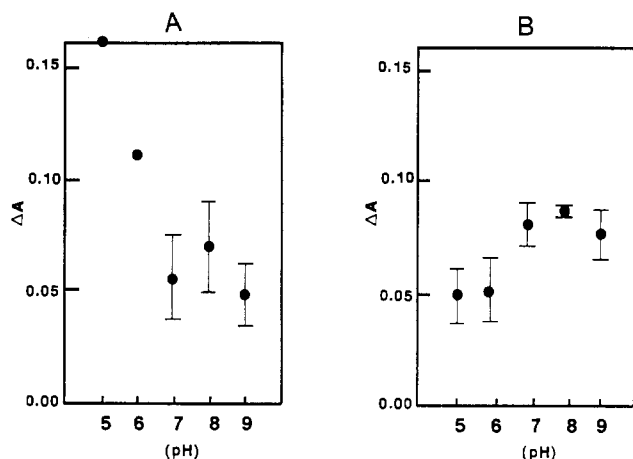‡ Tohoku Social Welfare University.

A

$$CH_2-CH-CH-CH-CH-O-CH-NH-CH-O-CO-(CH_2)n-CH_3$$

with OH OH OH OH OH below, and

$$CH_2$$
$$CH_2-O-CO-(CH_2)n-CH_3$$

B

R = H, or $\overset{O}{\overset{\|}{C}}-CH_2(CH_2)_9-CH_3$

Figure 1. Molecular structures of the surfactants used in this experiment: (A) dialkyl glucosylglutamate, $n = 6$; dioctyl glucosylglutamate (C_8), $n = 8$; didecyl glucosylglutamate (C_{10}), $n = 10$; didodecyl glucosylglutamate (C_{12}), $n = 12$; ditetradecyl glucosylglutamate (C_{14}), $n = 14$; dihexadecyl glucosylglutamate (C_{16}); (B) sucrose laurate (SE L-590).

Table I. HLB Values of the Surfactants Used in the Experiment

surfactant	HLB value[a]
dioctyl glucosylglutamate (C_8)	13.6
didecyl glucosylglutamate (C_{10})	11.7
didodecyl glucosylglutamate (C_{12})	9.8
ditetradecyl glucosylglutamate (C_{14})	7.9
dihexadecyl glucosylglutamate (C_{16})	6.0
sucrose laurate (SE L-590)	11.1

[a] HLB value of each surfactant was calculated according to the method of Davies (1957).

of the surfactant used in this work are shown in Figure 1. The value of hydrophobic–lipophilic balance (HLB) of each surfactant was calculated by the method of Davies (1957). Though the HLB value does not sufficiently predict the functionality of the surfactant, it is able to characterize its usage as an emulsifier. Since the HLB value has been employed as a criterion for the selection of the surfactant, the HLB values of the synthesized surfactants are shown in Table I. The HLB values of the synthesized surfactants depended on the length of the dialkyl side chains in the range 6.0–13.6. The HLB value of commercially available sucrose laurate (SE L-590) was evaluated to be 11.1 depending on the degree of esterification. The value of SE L-590 is close to that of C_{10}.

The type of emulsion, i.e., o/w or w/o, is one of the important properties of the surfactant, as are particle size, particle size distribution, viscosity, and so on. The type of emulsion was investigated under various conditions. Total amount of the solution for making the emulsion was set at 6 g. The amount of paraffin was changed from 0.5 to 5.5 g in 0.25-g increments. The surfactant (24 mg) was dissolved in the paraffin fraction. The mixture with various proportions of buffer and paraffin was homogenized, and the type of prepared emulsion was examined. The increase of the ratio of paraffin was correlated with the formation of the w/o emulsion in the case of every surfactant. The maximum amount of paraffin, with which the o/w emulsion could be prepared, is shown in Table II. If more paraffin than that shown in the table was used, a w/o emulsion was formed instead of an o/w emulsion. Among a series of DGG, the maximum amount of paraffin for making o/w emulsions depended on the length of the dialkyl chains. In the case of SE L-590, the maximum amount of paraffin for preparing o/w emulsions was approximated to that of C_{14}, although the HLB value of SE L-590 was close to that of C_{10}. When the solution was

Table II. Maximum Amount of Paraffin with Which the O/W Emulsion Could Be Prepared

surfactant	paraffin[a] (g)	surfactant	paraffin[a] (g)
C_8	2.00	C_{14}	3.00
C_{10}	2.25	SE L-590	3.00
C_{12}	2.50		

[a] Total amount of the solvent (paraffin and buffer) was set at 6 g. More paraffin than the value shown in this table induced the formation of w/o emulsion.

Figure 2. Emulsifying stability of the surfactant. The emulsion was prepared with 1.5 g of paraffin (24 mg of surfactant) and 4.5 g of buffer. The stability was expressed as the change in the absorbance induced in a unit time. The larger values of [A] indicate the more unstable emulsion. The experiments were repeated five times (except C_{16}), and the average and the standard deviation of the measurement are shown.

composed of 1.5 g of paraffin and 4.5 g of buffer, o/w emulsions could be prepared with every surfactant used in this experiment. This solvent composition was regarded as the model system for the study of o/w emulsion stability.

Comparison of Emulsion Stability. The effect of the length of the dialkyl chain of the surfactant on the emulsion stability was investigated. The emulsion stability was determined by measuring the turbidity detected at 500 nm. Changes in the absorbance induced in a unit time were converted into the emulsion stability, and the smaller change in the turbidity corresponded to a more stable emulsion. Minor differences were observed in the turbidity of the o/w emulsion made with these surfactants, thus suggesting these surfactants have similar emulsion activities. On the other hand, the length of the dialkyl chain of the synthetic surfactant affected the emulsion stability as shown in Figure 2. Among the synthetic surfactants, the emulsion made with C_{12} was found to be most stable. The emulsion stability of SE L-590 was good in accordance with that of C_{14}.

Effect of pH on Emulsion Stability. The effect of the pH of the buffer on the emulsion stability was investigated using C_{12} and SE L-590 (Figure 3). The o/w emulsion of SE L-590 was more stable in acidic condition than in alkaline condition. In the case of C_{12}, the emulsion was considerably unstable and the phase inversion sometimes occurred in the acidic range. In alkaline condition, the emulsion of C_{12} was more stable than that of SE L-590. These findings suggest that the effect of pH on the emulsion stability depends on the molecular structure of the nonionic surfactant.

Effect of Salt on Emulsion Stability. The emulsion stabilities of SE L-590 and C_{12} were compared under conditions at various salt concentrations (Figure 4). The stabilities of the emulsions prepared using both the

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Figure 3. Effect of pH of buffer on the emulsion stability. The emulsion was prepared with C_{12} (A) or SE L-590 (B). The emulsion prepared with low-pH buffer (pH 5) was very unstable. Sometimes it changed the phase to w/o emulsion. The point at pH 5 was measured only when the o/w emulsion could be prepared.
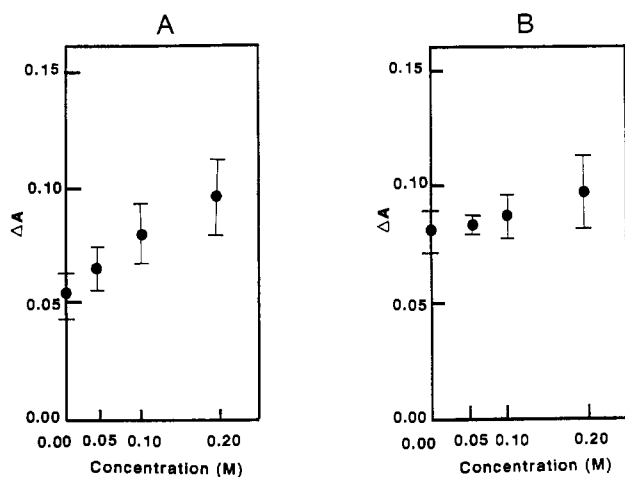

Figure 4. Effect of salt concentration on emulsion stability. The emulsion was prepared with C_{12} (A) or SE L-590 (B).

surfactants decreased with the increase in the salt concentration. However, the effect of salt on the emulsion stability of C_{12} was less than that on SE L-590.

DISCUSSION

The molecular structure of DGG is characterized by the presence of glutamic acid and two alkyl side chains. The introduction of glutamic acid to the surfactant resulted in several advantages described as follows. This surfactant may become the resource of supplying glutamic acid. Glutamic acid is important in relation to the transamination reaction of other amino acids, although it is not an essential amino acid. In further work, other amino acids may possibly be introduced as components of the surfactant instead of glutamic acid. Furthermore, glutamic acid in the novel surfactant made it simple to synthesize the surfactant which possesses two alkyl side chains. In the case of conventional surfactants, such as sucrose ester, a purification step is required to separate the specific surfactant with two alkyl side chains from others. The introduction of glutamic acid to the surfactant alleviates this shortcoming.

In the past, the effect of the length of the alkyl side chain of the surfactant on the emulsion properties has been studied in detail (Puschel, 1967; Govin and Leeder, 1974; Lin and Leeder, 1974). However, little information is available on the surfactant with two alkyl side chains. In this work, it is demonstrated that the emulsion stability depends on the length of the two alkyl side chains, using a series of DGG. The findings obtained from this study will be useful for the elucidation of the relation between the molecular structure of the surfactant and its emulsion properties.

One of the interests in this study was the stability of emulsions prepared with a unique surfactant and comparison with that of sucrose laurate. There was a noble difference in the molecular structures of both surfactants in terms of hydrophilic group, junction region, and the position bound to the hydrophobic group. These differences might induce a difference in emulsion stability. The influence of pH and salt on the emulsion stability might be ascribed to the differences in the molecular structure. Previously, the relation between the molecular structure and the emulsion properties has been studied by some investigators (Rosen, 1974; Yamada et al., 1980; Rydhag and Wilton, 1981; Ogawa et al., 1986).

Among the emulsifiers for food, sucrose ester has been known as one of the important surfactants in making o/w emulsions. However, the emulsion containing ionic surfactant is generally more stable than the nonionic one, such as sucrose ester. In the present work, it was revealed that the emulsion stability of DGG was different from that of sucrose ester with respect to the resistance to salt and to the pH conditions. This suggests that the disadvantages of sucrose ester could be removed by the introduction of DGG.

In this work, paraffin oil was used as an oil in the model system. One emphasis of our study was placed on the investigation of the relationship between the molecular structure of the unique surfactant and its emulsion stability. The behavior of the emulsion should be observed in a model system in the initial step. For the purpose of application to the food industry, studies using an edible oil, i.e., soybean oil, are in progress in our laboratory.

DGG is synthesized from edible materials, and it could be hydrolyzed by a digestive enzyme such as esterase. The novel surfactant would be an effective emulsifier, after its use as a foodstuff is approved.

LITERATURE CITED

Davies, J. T. Proc. 2nd Congr. Surface Act. 1957, 1, 426.

Govin, R.; Leeder, J. G. J. Food Sci. 1974, 38, 108.

Lin, P.-M.; Leeder, J. G. J. Food Sci. 1974, 39, 108.

Ogawa, K.; Terada, T.; Muranaka, Y.; Fujii, S. Chem. Pharm. Bull. 1986, 34, 1118.

Okahata, Y.; Ijiro, K. J. Chem. Soc., Chem. Commun. 1988, 1392.

Pearce, K. N.; Kinsella, J. E. J. Agric. Food Chem. 1978, 26, 716.

Puschel, F. Tenside 1967, 4, 320.

Rosen, M. J. J. Am. Oil Chem. Soc. 1974, 51, 461.

Rydhag, L.; Wilton, I. J. Am. Oil Chem. Soc. 1981, 58, 830.

Yamada, T.; Kawase, N.; Ogimoto, K. Yukagaku 1980, 29, 21.