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Formation of Fouling Deposit from Several Soft Drinks on Stainless Steel Surfaces

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Fouling of stainless steel surfaces from coffee drinks, oolong tea and apple juice was studied under various conditions by the continuous-flow stirred-tank method using SUS316L particles. Among the soft drinks tested, coffee drinks containing milk protein caused the highest amount of deposit. The amount of deposit formed from the coffee drink increased almost linearly with time and depended on temperature. Furthermore, it was suggested that tannin contained in the coffee drinks is largely responsible for the severe fouling of the stainless steel particles.

Keywords: fouling, stainless steel, soft drink, protein, tannin, β-lactoglobulin

Fouling of processing equipment such as heat exchangers is a severe problem in food industries. Therefore, cleaning operations are carried out at least once per day. Large amounts of cleaning agent, water, energy and time required for the cleaning operation result in a high manufacturing cost and ecological problems. To optimize the cleaning operation, it is necessary to study the formation of fouling deposits on the surface of the equipment and the desorption behavior of the deposit from the surface during the cleaning operation.

Fouling from milk-based liquid foods has been studied (Hallstrom *et al*., 1981; Lund *et al*., 1985; Lalande & Rene, 1988; Kessler & Lund, 1989), and the composition of the deposits has been analyzed. For example, deposits formed at temperatures below 110°C contain approximately 50–60% protein and 30–35% minerals (Burton, 1968), and half of the protein in the deposits is β-lactoglobulin (Lalande *et al*., 1985). The adsorption behavior of β-lactoglobulin has also been studied under various conditions for several kinds of solid surfaces (Skudder *et al*., 1981; Arnebrant & Nylander, 1986; Arnebrant *et al*., 1987; Luey *et al*., 1991; Wahlgren & Arnebrant, 1990; Itoh *et al*., 1995). It has been shown that the amount of β-lactoglobulin adsorbed on chromium surfaces (Arnebrandt *et al*., 1987) and stainless steel surfaces (Itoh *et al*., 1995) increases when the adsorption temperature exceeds 65–75°C. On the other hand, thermal denaturation of β-lactoglobulin has been shown in calorimetric studies to begin at 65–70°C (Park & Lund, 1984; De Witt & Swinkels, 1980). Thus, the thermal denaturation of β-lactoglobulin seems to be closely related to the fouling (Skudder *et al*., 1981). Our previous study (Itoh *et al*., 1995) showed that the thermal aggregation of β-lactoglobulin through intermolecular disulfide linkages occurring on the surface was responsible for the increase in the amount of β-lactoglobulin adsorbed at temperatures above 65°C.

Similarly to milk and milk-based fluids, soft drinks such as coffee drinks usually cause substantial deposits on the surface of heat exchangers. Despite the extensive research on the fouling from milk and milk-based fluids, little work has been done on the fouling from soft drinks. Various kinds of packed soft drinks are produced in Japan, therefore, it is important to study the deposit formation from soft drinks on the surface of the equipment for the optimization of cleaning conditions.

In this report, the fouling of stainless steel surfaces from several soft drinks was studied under various conditions. To study the fouling occurring during continuous processing in practical plants, a continuous-flow stirred-tank method, using fine stainless steel particles, was applied to measure the amount of the fouling deposit.

Materials and Methods

Stainless steel particles Stainless steel particles of SUS316L (average diameter of about 180 μm) were obtained from Fukuda Metal Foil & Powder Co., Ltd. (Kyoto). They were washed with 1 N NaOH solution, and thoroughly rinsed with reagent grade R.O. pure water (MILLI-Q SP, Millipore Japan Co., Tokyo). After being washed with methanol, the particles were dried at 105°C. The specific surface area of the particles was estimated to be 0.06 m^2/g from N_2 adsorption experiments.

Soft drinks and model solutions Three kinds of coffee drinks (coffee drinks A, B and C), oolong tea and apple juice were used for the soft drink samples. All of these samples were the same as commercially available products, except that the samples were not pasteurized or sterilized. Coffee drinks A, B, and C were composed of coffee extract, sugar, pasteurized milk and dried milk powder. The apple juice contained 10% apple extract. The main composition of each sample is listed in Table 1.

As a model of a proteineous soil substance contained in the coffee drinks, β-lactoglobulin from bovine milk (3 times crystallized, Sigma Chemical Co., St Louis, MO, USA) was used. β-Lactoglobulin was dissolved in 35 mM phosphate buffer, pH 6.85, containing 100 mM NaCl, at a concentration of 0.15% (w/v). Denatured β-lactoglobulin solution was prepared by heating the β-lactoglobulin solution at 80°C for 120 min. In some experiments, tannic acid (Nacalai Tesque,

Table 1. Composition of soft drink samples used in this study.

	Coffee drink A	Coffee drink B	Coffee drink C	Oolong tea	Apple juice
Composition (w/w, %)					
Carbohydrate	7.7	8.2	8.8	0.1	1
Lipid	0.3	1.5	0.9	0	—[a]
Protein	0.4	0.6	0.9	0	0.01
Dehydrated caffeine	0.08	0.05	0.05	0.02	—[a]
Tannin	0.2	0.14	0.13	0.07	0.01
Ratio of tannin/protein	0.5	0.23	0.14	—	—

[a] Not measured.

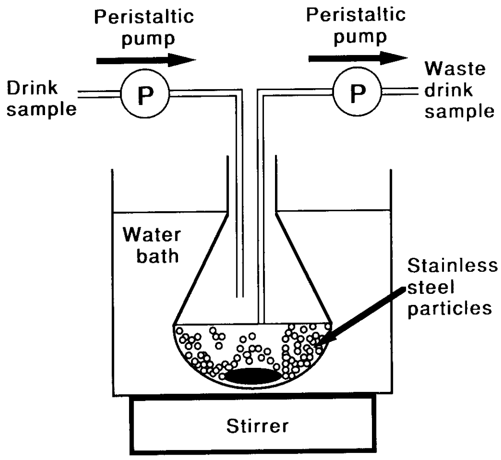

Fig. 1. Schematic diagram of the apparatus for fouling experiments.

Inc., Kyoto), one of the major components of coffee extract, was added to the native or denatured β-lactoglobulin solution at a concentration of 0.0075% (w/v).

Fouling experiment The experimental apparatus used in this study is shown in Fig. 1. Fifteen grams of stainless steel particles were suspended in 50 ml of a sample drink in a 300 ml eggplant-type flask. The mixture was then incubated at a constant temperature with stirring (about 900 rpm). The sample drink was continuously fed into the flask with a peristaltic pump at a flow rate of 2.6 ml/min. Simultaneously, liquid was withdrawn from the flask continuously at the same flow rate with another peristaltic pump. The incubation temperature was varied from 50°C to 75°C for coffee drinks and was 95°C for both oolong tea and apple juice.

In some experiments, the model β-lactoglobulin (native and denatured) solutions with and without tannic acid prepared as described previously were used instead of the sample drink. The model solutions were continuously fed into the flask incubated at 45°C or 75°C at a flow rate of 1.7 ml/min.

Analysis of deposit on stainless steel particles After the fouling experiment, stainless steel particles were washed repeatedly with 30 ml of reagent grade pure water until the total nitrogen concentration in the waste water was less than 100 ppb (for coffee drinks) or the total organic carbon concentration was less than 200 ppb (for oolong tea and apple juice). The total nitrogen and organic carbon concentrations were measured with a total nitrogen analyzer TN-05 (Mitsubishi Chemical Co., Tokyo) and with a total organic carbon analyzer TOC-5000 (Shimadzu Co., Kyoto), respectively. The stainless steel particles were then dried at 105°C for 3 h. The amounts of nitrogen and carbon components deposited on the stainless steel particles were determined by the Pregl-Dumas method with a CHN-Corder MT-05 (Yanaco Analytical Instrument Co., Kyoto), equipped with TCD detectors for CO_2, N_2 and H_2O gases generated quantitatively by combustion of the organic substances (Miki, 1990). In the case of model β-lactoglobulin solutions with and without tannic acid, the amount of protein deposited was calculated from the amount of nitrogen. Taking into consideration the amino acid composition of β-lactoglobulin (Green *et al.*, 1979), 1 g of nitrogen corresponds to 7.5 g of β-lactoglobulin. The deposit from coffee drinks on the stainless steel particles was also analyzed with FT-IR 710 (Nicolet Instrument Co., Madison, WI, USA) by diffuse reflectance spectrometry.

Results

Figure 2 shows the amounts of carbon and nitrogen components of the deposits formed during 18 h treatment of the stainless steel particles with coffee drinks, oolong tea or apple juice. Although the fouling temperature for coffee drinks (75°C) was lower than that for the other samples (95°C), the amount of deposit formed increased in the following order: apple juice<oolong tea<coffee drink C<coffee drink B<coffee drink A. The deposits from oolong tea and apple juice contained carbon but no nitrogen, while those from coffee drinks contained both carbon and nitrogen.

Figure 3 shows an FT-IR spectrum of the deposit formed on stainless steel particles from coffee drink A. Two characteristic absorption bands for the amido bond were detected in the wave number region of 1500 cm^{-1} to 1700 cm^{-1}, indicating that the main constituent of the deposit from the coffee drink A was protein.

Figures 4a and 4b show the courses of deposition of the carbon and nitrogen components from coffee drink A, respectively. The amounts of both elements deposited increased linearly with treatment time at each temperature. From the slope of the lines shown in Figs. 4a and 4b, the deposition rates of the two elements were calculated and are

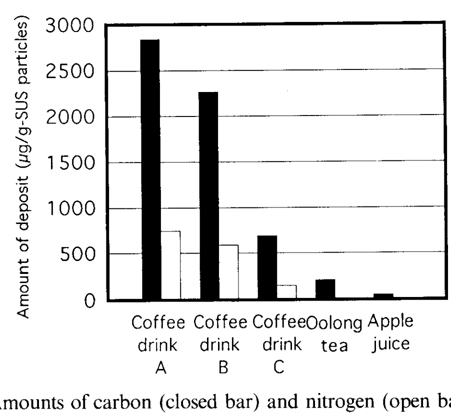

Fig. 2. Amounts of carbon (closed bar) and nitrogen (open bar) deposited after 18 h treatment of stainless steel particles with several soft drinks. Temperature was 75°C for coffee drinks and 95°C for oolong tea and apple juice, respectively.

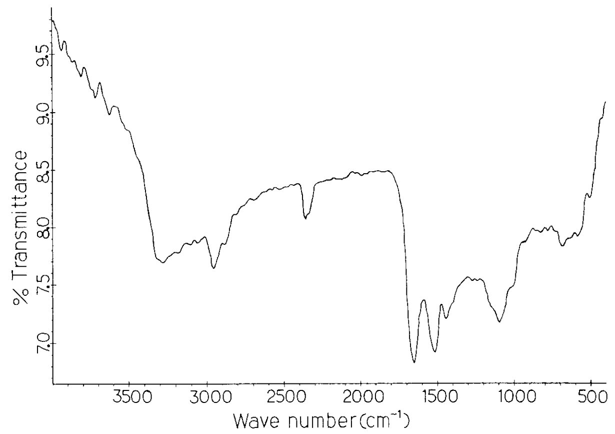

Fig. 3. FT-IR spectrum of the deposit formed on stainless steel particles from coffee drink A. The stainless steel particles were treated at 75°C for 18 h.

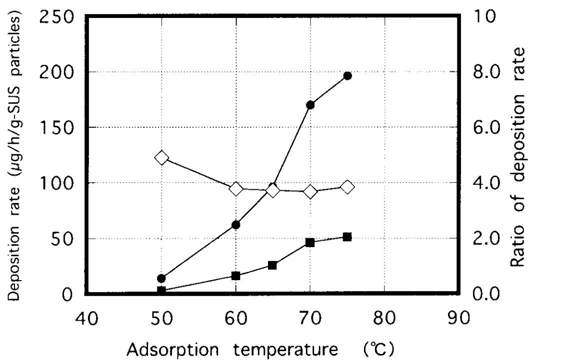

Fig. 5. Effect of temperature on the deposition rate from coffee drink A. Symbols: ● carbon deposit, ■ nitrogen deposit, ◇ ratio of deposition rate of C to that of N.

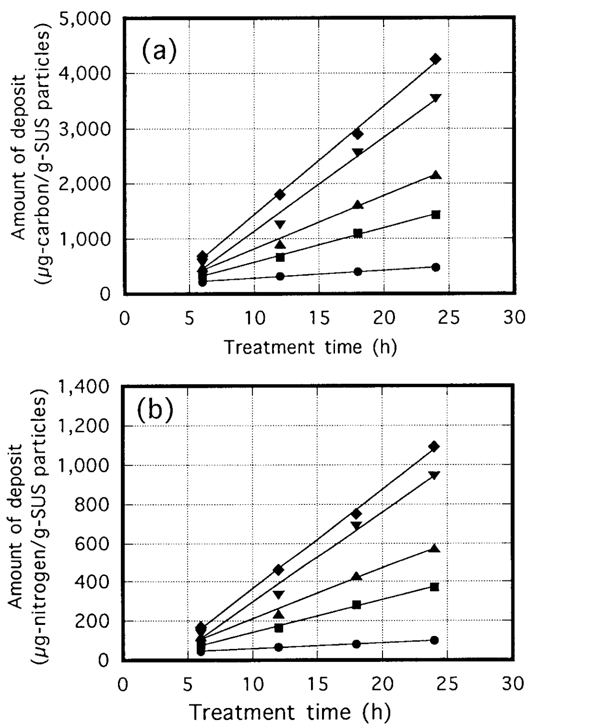

Fig. 4. Courses of deposition of carbon (a) and nitrogen (b) components from coffee drink A. Temperature: ● 50°C, ■ 60°C, ▲ 65°C, ▼ 70°C, ◆ 75°C.

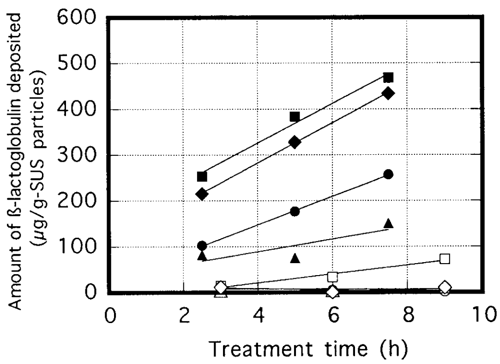

Fig. 6. Courses of deposition from solutions of β-lactoglobulin with and without tannic acid. Stainless steel particles were treated either with a solution of native β-lactoglobulin at 45°C (○, ●) or 75°C (□, ■) or a solution of denatured β-lactoglobulin at 45°C (△, ▲) or 75°C (◇, ◆). Closed symbols represent the cases in the presence of tannic acid.

shown in Fig. 5. The deposition rate of each element increased as the temperature rose. The increase in the deposition rate was slightly steeper in the temperature range from 65°C to 70°C than in the lower temperature region. However, the ratio of the deposition rate of carbon to that of nitrogen was almost constant at all the temperatures tested, suggesting that the composition of the coffee deposit did not change with temperature.

As shown in Fig. 2, coffee drink A gave the highest amount of deposit on the stainless steel particles among the three coffee drinks tested. Compositions of the three coffee drinks were different as shown in Table 1. However, the contents of carbohydrate, lipid and protein had no positive correlation with the amount of deposit formed. The differences in the content of tannin and the ratio of tannin content to protein content seems to be responsible for the difference in the amount of deposit formed (Table 1). Therefore, the effect of tannic acid, a kind of tannin, on the deposit formation was studied in the presence of β-lactoglobulin as a model protein.

Figure 6 shows the courses of deposit formation when native or denatured β-lactoglobulin solution with and without tannic acid was continuously fed at 45°C or 75°C. When native β-lactoglobulin solution was fed in the absence of tannic acid, the amount of deposit formed at 45°C was much less than that at 75°C. From denatured β-lactoglobulin solution in the absence of tannic acid, a deposit was hardly formed at both temperatures. These results coincided with the data reported previously (Itoh, 1995). The presence of tannic acid increased the deposition rates considerably for both native and denatured β-lactoglobulin solutions, though the state of the protein (native or denatured) and the treatment temperature affected the deposition rate.

Discussion

Using a laboratory-scale apparatus for fouling experiments, we found that the amounts of deposits from coffee drinks containing milk proteins were markedly higher than those from oolong tea and apple juice and that the amount of deposits from coffee drinks increased with temperature above 50°C. These findings agree with the qualitative observation of a practical process. Thus, the experimental method used in this study may be efficient for studying the deposit formation from soft drinks in practical processes.

In the case of milk and milk-based fluids, the amount of the deposit is known to increase above 70°C (Lalande *et al.*, 1984). The increase in the amount of deposit is ascribed to the thermal denaturation and aggregation of β-lactoglobulin. This study showed that the rate of deposit formation from coffee drink A increased with temperature above 50°C. Thus, the temperature dependence of deposit formation from coffee drink A was similar to that from milk and milk-based fluids. However, judging from the data shown in Table 1 and Fig. 1, there was no positive correlation between the amount of deposit from coffee drinks and their protein content. Moreover, coffee drinks used in this study contained pasteurized milk and dried milk powder. Therefore, most of the milk proteins contained in the coffee drinks were considered to be denatured. As shown in Fig. 6, a deposit was hardly formed on the stainless steel surface from the solution of denatured β-lactoglobulin in the absence of tannic acid even at 75°C. Thus, the increase in the amount of deposit from coffee drinks with rising temperature could not be ascribed to the denaturation and aggregation of milk proteins. The mechanism for deposit formation from coffee drinks is probably different from that for milk and milk-based fluids.

Coffee extract contains tannin, a kind of polyphenol, which is well known to be bound to protein molecules (Haslam, 1974). Because the amount of deposit from coffee drinks increased with the increase in the tannin content or the ratio of tannin to protein, complexes of protein and tannin might be the major constituents of the deposit from coffee drinks. As shown in Fig. 6, the presence of tannic acid increased the amount of deposit from the β-lactoglobulin solution at 75°C by about 10 times. Even at 45°C, the presence of tannic acid increased the amount of deposit by about 5 times. The presence of tannic acid also significantly increased the amount of deposit from the denatured β-lactoglobulin solution.

In this study, deposit formation on stainless steel surfaces from soft drinks, especially from coffee drinks, was studied. In particular, we found that the rate of deposit formation from coffee drinks strongly depended on temperature. Coffee drinks usually cause substantial deposits on the surface of heat exchangers in practical processes. If coffee drinks could be thermally processed at a temperature as low as possible but sufficient for pasteurization, the amount of deposit formed on the equipment, and hence the time required for cleaning of the fouled equipment, would be reduced.

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