Physicochemical Parameters for Biological and Synthetic Surfactants Used as Detergents

Patrícia C. Bernardes, Emiliane A. Araújo, Marcia C. T. R. Vidigal, Nélío J. Andrade, Luis A. Minim and Valéria P. R. Minim

Department of Food Technology, Viçosa Federal University, Viçosa 36570-000, Minas Gerais, Brazil

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Abstract: Biological and synthetic surfactants were compared in terms of their ability to reduce interfacial tension, change the thermodynamic characteristics of a pre-conditioned surface, and to modify the rheological properties of their respective formulations at two different temperatures. Both classes of surfactants were able to reduce the interfacial tension of their formulations to a similar level. However, the biosurfactants were more effective than the synthetics surfactants. Biosurfactants also altered the surface properties of stainless steel, rendering it hydrophilic. Microbial adhesion to stainless steel conditioned with biosurfactants was found to be thermodynamically unfavorable for all microbial strains tested. A linear relationship between shear stress and shear rate was obtained across a range of experimental conditions for all surfactant mixtures, indicating that all formulations behaved as Newtonian fluids.

Key words: Surfactants, biosurfactants, interfacial tension, microbial adhesion, stainless steel.

1. Introduction

The contamination of surfaces by spoilage and pathogenic microorganisms is a concern in the food industry. The development of biofilms in food processing environments results in product spoilage and possible risks to public health, in addition to create a number of serious problems for industrial fluid processing operations [1-3]. The presence of organisms such as *Salmonella* spp., *Listeria monocytogenes* and *Escherichia coli* in food processing environments can be a persistent source of contamination [4].

To reduce or eliminate microorganisms found on food contact surfaces, cleaning and disinfection procedures using physical and chemical methods have been extensively used over the years [5]. An interesting strategy is the pre-treatment of surfaces using surface-active compounds, also known as surfactants.

Surfactants can be classified into two main groups: synthetic surfactants and biosurfactants. Synthetic

surfactants are produced by organic chemical reactions, whereas biosurfactants are produced by biological processes, being excreted extracellularly by microorganisms such as bacteria, fungi, and yeast [6]. Biosurfactants are produced using relatively cheap hydrophilic and hydrophobic substrates such as carbohydrates, vegetable oils, or even waste from the food industry [7]. When compared to synthetic surfactants, biosurfactants have several advantages, including high biodegradability, low toxicity, low irritancy, and compatibility with human skin [8, 9]. Because of these superior properties, biosurfactants have many potential uses in the food, pharmaceutical, and cosmetic industries [10].

Some of the most extensively studied biosurfactants are the rhamnolipids, primarily produced by *Pseudomonas aeruginosa* [11]. The surfactant properties of a rhamnolipid mixture depend on its composition. This factor, in turn, varies according to the bacterial strain, culture conditions, and medium composition used for rhamnolipid production [12].

Corresponding author: Nélío J. Andrade, D.S., researcher, research field: food hygiene. E-mail: nandrade@ufv.br.

Nitschke et al. [13] investigated the effect of the biosurfactant surfactin on the adhesion of the food pathogens *Listeria monocytogenes*, *Enterobacter sakazakii* and *Salmonella* Enteritidis to stainless steel and polypropylene surfaces. The pre-conditioning of stainless steel surfaces with surfactin caused a reduction in the number of adhered cells of *Enterobacter sakazakii* and *Listeria monocytogenes*. The most significant result was obtained with *L. monocytogenes*, where the number of adhered cells was reduced by 10^2 CFU/cm². On polypropylene surfaces, surfactin significantly decreased the adhesion of all strains.

In the literature, there are no references that describe the thermodynamic properties of surfaces that have been pre-conditioned with surfactants. This work aimed to compare biological and synthetic surfactants in terms of their ability to reduce interfacial tension, change the hydrophobicity of pre-conditioned surface and alter the rheological properties of their respective formulations at two different temperatures.

2. Materials and Methods

2.1 Materials

A rhamnolipid biosurfactant, consisting of a mixture of mono- and di-rhamnolipids from the glycolipid group produced by *Pseudomonas aeruginosa* was obtained from Jeneil Biosurfactant Co. (Saukville, Winconsin, USA) [14]. The molecular formulas for mono- and di-rhamnolipids are C₂₆H₄₈O₉ and C₃₂H₅₈O₁₃, respectively (Fig. 1). The critical micelle concentration (CMC) was found to be 0.035 g/L by conductivity measurements performed at various dilutions [15].

The synthetic surfactant used was dodecylbenzene sodium sulfonate, and its CMC is 0.4 g/L.

2.2 Bacterial Strains

Staphylococcus aureus ATCC 6538, *Escherichia coli* ATCC 11229 *Listeria innocua* ATCC 33090, *Pseudomonas aeruginosa* ATCC 15442 and *Bacillus cereus*, isolated from pasteurized milk and identified as Ribo 1 222 173 S1 [16], were used throughout this work.

Fig. 1 Chemical structures of mono- and di-rhamnolipids.

2.3 Detergent Formulations

The detergent formulations used in the following experiments are shown in Table 1. The sodium carbonate concentration was selected to match the concentration typically used in the food industry for cleaning procedures. The concentrations chosen for other surfactants were above their respective CMCs to ensure the formation of micelles.

2.4 Interfacial Tension Measurements of the Detergent Formulations

The interfacial tension of each detergent formulation was measured by the pendant drop method using a goniometer (DSA 100, Kruss®, Germany). The surface tension measurement was carried out at 25 ± 1 °C. To calibrate the instrument, the surface tension of pure distilled Milli-Q water (Millipore, Illinois, USA) was measured before each set of experiments.

Table 1 Different formulations for the treatment of stainless steel coupons.

Formulations	Composition
A	Sodium carbonate (0.5%)
B	Sodium carbonate (0.5%) and dodecyl benzene sodium sulfonate (0.2%)
C	Sodium carbonate (0.5%) and rhamnolipid (0.004%)
D	Sodium carbonate (0.5%) and rhamnolipid (0.02%)
Control	Distilled water

2.5 Stainless Steel Conditioning with Detergent Formulations and Surface Hydrophobicity Measurements

Coupons (10 mm × 10 mm × 0.05 mm) of stainless steel #4 were first cleaned by washing with a neutral liquid detergent and water, followed by rinsing with distilled water. Subsequently, they were put in a muffle furnace for 2 h at 200 °C to remove organic materials. After that, the coupons were immersed in detergent formulations (Table 1) for 24 h at 20–25 °C. Control coupons without treatment were maintained in distilled water under the same conditions.

Surface hydrophobicity was determined based on contact angle measurements of the stainless steel with water, formamide and α -bromonaphthalene using a goniometer. The total Gibbs free energy of interaction ($\Delta G_{\text{sws}}^{\text{TOT}}$) and the total free energy of adhesion between stainless steel and different bacteria ($\Delta G_{\text{adhesion}}$) were determined by appropriate formulas [17].

2.6 Hydrophobicity of the Bacterial Strains

One milliliter of each bacterial culture was stored at -80 °C in a nutrient broth (Merck, São Paulo, Brazil) containing glycerol (80:20). A working culture of each strain, containing approximately 10^7 CFU/mL, was prepared by inoculating 10 mL of Brain Heart Infusion (BHI, Merck, São Paulo, Brazil) with 100 μ L of frozen culture, followed by incubation at 32 °C for 24 h. The culture was sub-cultured three times before use. The number of microorganisms in each suspension was obtained by total count using Plate Count Agar (PCA, Merck, São Paulo, Brazil) at 32 °C for 24 h.

Contact angles for microorganism surfaces were determined on a layer of vegetative cells using the drop method [18]. First, the strains were activated twice in BHI broth (Merck, São Paulo, Brazil), creating suspensions with approximately 10^7 CFU/mL. The suspensions were centrifuged at 12,000 g for 10 min and washed three times in 0.1 M phosphate buffered saline (PBS). The cell pellet was suspended in the same buffer, and the suspension was filtered using a cellulose acetate membrane (0.45 μ m pore size, 27 mm in diameter, Millipore, Brazil) with negative pressure. During the filtration, 30 mL of pure water (Milli-Q) was added. The membranes were transferred to Petri plates containing 1% (v/v) of agar and 10% (v/v) of glycerol. The membranes were cut into three parts for contact angle measurements.

Each surface was classified as hydrophobic or hydrophilic according to the determination of the total free energy of interaction ($\Delta G_{\text{sws}}^{\text{TOT}}$). The total free energy of interaction among molecules of a surface (s) immersed in water (w) was determined by the sum of the apolar and polar free energies of interaction, $\Delta G_{\text{sws}}^{\text{LW}}$ and $\Delta G_{\text{sws}}^{\text{AB}}$, respectively:

$$\Delta G_{\text{sws}}^{\text{TOT}} = \Delta G_{\text{sws}}^{\text{LW}} + \Delta G_{\text{sws}}^{\text{AB}} \quad (1)$$

$$\Delta G_{\text{sws}}^{\text{LW}} = -2\sqrt{\gamma_s^{\text{LW}} - \gamma_w^{\text{LW}}} \quad (2)$$

$$\Delta G_{\text{sws}}^{\text{AB}} = -4\left(\sqrt{\gamma_s^+ \gamma_s^-} + \sqrt{\gamma_w^+ \gamma_w^-} - \sqrt{\gamma_s^+ \gamma_w^-} - \sqrt{\gamma_w^+ \gamma_s^-}\right) \quad (3)$$

Here, γ^{LW} is the interfacial tension arising from Lifshitz-van der Waals forces; γ^+ is the interfacial tension arising from the electron acceptor component of the acid-base interaction; γ^- is the interfacial tension of the electron donor component of the acid-base interaction; and s and w indicate surface and water, respectively [17].

When $\Delta G_{\text{sws}}^{\text{TOT}} > 0$, the surface is considered hydrophilic; conversely, if $\Delta G_{\text{sws}}^{\text{TOT}} < 0$, then the surface is considered hydrophobic.

Bacteria were used to determine the total Gibbs free energy of adhesion ($\Delta G_{\text{adhesion}}$) between conditioned stainless steel and each strain.

2.7. Determination of the Total Gibbs Free Energy of Adhesion ($\Delta G_{adhesion}$)

From the values of the individual interfacial tension components, it is possible to determine the $\Delta G_{adhesion}$ between two surfaces: microbial cells (b) and food processing surfaces (s):

$$\gamma_{bs} = \gamma_{bs}^{LW} + \gamma_{bs}^{AB} \quad (4)$$

$$\gamma_{bs}^{LW} = \gamma_b^{LW} + \gamma_s^{LW} - 2\sqrt{\gamma_b^{LW} \gamma_s^{LW}} \quad (5)$$

$$\gamma_{bs}^{AB} = 2\left(\sqrt{\gamma_b^+ \gamma_b^-} + \sqrt{\gamma_s^+ \gamma_s^-} - \sqrt{\gamma_b^+ \gamma_s^-} - \sqrt{\gamma_b^- \gamma_s^+}\right) \quad (6)$$

Because the free energy is related to the interfacial tension, $\Delta G_{adhesion}$ can be represented by the following:

$$\Delta G_{adhesion} = \Delta G_{bls}^{LW} + \Delta G_{bls}^{AB} \quad (7)$$

$$\Delta G_{bls}^{LW} = \gamma_{bs}^{LW} - \gamma_{bl}^{LW} - \gamma_{sl}^{LW} \quad (8)$$

$$\Delta G_{bls}^{AB} = \gamma_{bs}^{AB} - \gamma_{bl}^{AB} - \gamma_{sl}^{AB} \quad (9)$$

Here, γ_{bs} is the interfacial tension between the bacterial surfaces and the adhesion surface; γ_{bl} is the interfacial tension between the bacterial surfaces and the liquid; and γ_{sl} is the interfacial tension between the adhesion surfaces and the liquid.

The $\Delta G_{adhesion}$ values allow for an evaluation of the thermodynamics of the adhesion process: if $\Delta G_{adhesion} < 0$, then the process is favorable; if $\Delta G_{adhesion} > 0$, then the process is unfavorable.

All measurements were performed in duplicate with three repetitions.

2.8 Rheological Measurements of the Detergent Formulations

Rheological measurements were performed using a Modular Advanced Rheometer System (HAAKE MARS, Thermo Electron Corp., Germany). The experiments were carried out at 25 °C and 70 °C for the different surfactant formulations, which correspond to manual cleaning temperatures and cleaning-in-place temperatures, respectively.

Steady rheological measurements were performed with double gap cylinder system (DG41) geometry, using a gap size set to 0.8 mm. Flow curves were

evaluated by measuring the shear rates from 0 to 1,200 s⁻¹. New samples were used for measurements at each experimental temperature. Rheological parameter models were calculated from data using ThermoHaake RheoWin Pro 297 Software by the least squares method.

3. Results and Discussion

3.1 Interfacial Tension of Detergent Formulations

We observed that all surfactant formulations had interfacial tensions that were reduced relative to the control. However, formulations B, C and D produced greater reductions in interfacial tension than formulation A (Table 2). Although there is not a significant difference ($P > 0.05$) among the interfacial tensions of formulations B, C and D, biosurfactants are clearly advantageous as they are effective at low concentrations. It is important to emphasize that formulations C and D employed biosurfactant concentrations 50-fold and 10-fold lower, respectively, than the synthetic surfactant concentration in formulation B. Normally, sodium carbonate is used in the food industry to clean surfaces. In this work, we verified that the addition of a biosurfactant to a sodium carbonate formulation reduced its interfacial tension, thereby making the hygiene procedure easier and more efficient.

The results of this experiment were similar to the findings of Pornsunthorntawe et al. [6]. These researchers found that, in the case of the crude biosurfactant produced by *Pseudomonas aeruginosa*, the surface tension rapidly decreased as the concentration of biosurfactants increased. Furthermore,

Table 2 Interfacial tensions (mN/m) of different detergent formulations.

Formulations	Interfacial tension (mN/m)
A	61.07
B	28.22
C	28.44
D	28.09
E	72.10

they found that a minimum surface tension of 29.0 mN/m was obtained at an initial surfactant concentration greater than 0.02%. In our experiment formulation D with a rhamnolipid concentration of 0.02% (Table 2) decreased the interfacial tension to 28.09 mN/m (46%) when compared with formulation A.

3.2 Hydrophobicity of Conditioned Stainless Steel Surfaces

The conditioning of stainless steel changed its hydrophobicity. The coupons of stainless steel that were immersed in water (control formulation) were classified as hydrophobic because the $\Delta G_{\text{sws}}^{\text{TOT}}$ value was negative, whereas coupons of stainless steel conditioned with the detergent formulations were considered hydrophilic ($\Delta G_{\text{sws}}^{\text{TOT}} > 0$). In particular, treatment with a 0.004% formulation of rhamnolipid (Formulation C) resulted in a more hydrophilic surface (42.48 MJ/m²) (Table 3).

According to thermodynamic principles, when $\Delta G_{\text{sws}}^{\text{TOT}}$ is negative, there is a net cohesive attraction between the molecules of a surface when immersed in water. Thus, for a hydrophobic material, $\Delta G_{\text{sws}}^{\text{TOT}}$ has a negative sign. In other words, molecules of a hydrophobic surface, when immersed in water, prefer to interact with each other rather than form an interface with water, whereas a positive value of $\Delta G_{\text{sws}}^{\text{TOT}}$ shows that the molecules of a surface prefer to interact with adjacent water molecules rather than with themselves. Such a surface is hydrophilic [19].

The contact angle measurements are interpreted directly in terms of the surface energy of the adsorbed layer and provide access to equilibrium or steady-state adsorption because angle measurements do not perturb adsorption dynamics. The treatment of stainless steel with biosurfactants causes its surface properties to change [13]. The addition of a synthetic or biological surfactant alters the wettability of solids because of its adsorption at the solid/liquid interface.

Table 3 Values of the interfacial tension components (γ^{LW} , γ^+ and γ^-) and the total Gibbs free energy of interaction ($\Delta G_{\text{sws}}^{\text{TOT}}$) for stainless steel surfaces conditioned with different detergent formulations.

Formulations	γ^{LW}	γ^+	γ^-	$\Delta G_{\text{sws}}^{\text{TOT}}$ (MJ/m ²)
A	28.53	1.39	51.25	31.75
B	27.16	4.93	37.20	11.30
C	28.73	1.15	60.68	42.48
D	28.36	3.01	59.80	34.60
Control	28.73	4.76	16.67	-12.04

Adsorption profiles suggest that the hydrocarbon chains of biosurfactants attach to hydrophobic surfaces and that their polar groups project toward aqueous solutions. This combination of events makes a surface more hydrophilic. The orientation of surfactant molecules at the solid/liquid interface determines the ability of the surfactant to improve the wetting ability of the liquid. A phenomenon involving a change in orientation of the adsorbed molecules could also be important in the kinetics of the wetting process [20].

3.3 Total Gibbs Free Energy of Adhesion

The adhesion process was thermodynamically favorable ($\Delta G_{\text{adhesion}} < 0$) for all tested strains on stainless steel surfaces conditioned with formulation B or a control formulation (Table 4). In contrast, the adhesion process was unfavorable ($\Delta G_{\text{adhesion}} > 0$) on stainless steel surfaces conditioned with formulations C or D. According to thermodynamic theory, adhesion is favorable only if the process results in a decrease in total free energy. Therefore, the rhamnolipid biosurfactant may potentially be incorporated into detergent formulations to reduce or avoid microbial adhesion and subsequent biofilm formation.

3.4 Rheological Characteristics of the Detergent Formulations

A linear relationship between shear stress and shear rate was obtained across a range of experimental conditions for all surfactant mixtures, indicating that all formulations behaved as Newtonian fluids (Figs. 2 and 3). Penott-Chang et al. [21] observed similar

Table 4 Values of the total Gibbs free energy of adhesion ($\Delta G_{\text{adhesion}}$) between different bacteria and conditioned stainless steel surfaces.

Bacterial strain	Total Gibbs free energy of adhesion (MJ/m ²)				
	A	B	C	D	Control
<i>S. aureus</i>	12.17	-0.86	15.45	8.13	-5.84
<i>E. coli</i>	9.46	-1.37	11.82	5.08	-3.50
<i>L. innocua</i>	4.20	-6.05	6.51	0.15	-8.40
<i>P. aeruginosa</i>	5.58	-5.11	8.00	1.44	-7.73
<i>B. cereus</i>	10.60	-1.94	13.74	6.64	-6.60

Newtonian behavior while studying the rheology of aqueous solutions containing hydrophobically modified polyacrylamides and sodium dodecyl sulfate.

At a temperature of 25 °C, surfactant formulations containing dodecyl benzene sodium sulfonate or diluted rhamnolipid (0.004%) showed a reduction in viscosity compared to a solution containing only sodium carbonate. Table 5 shows the viscosity of all tested formulations at two temperatures (25 °C and 70 °C). The surfactant systems presented a low viscosity, i.e., comparable to the viscosity of water. According to Penott-Chang et al. [21], the presence of ionic groups in diluted solutions such as B and C promotes a reduction in viscosity. However, surfactant

formulation D exhibited an increase in viscosity relative to the sodium carbonate control. The high concentration of rhamnolipid in this formulation (0.02%) may have contributed to the formation of micelles, resulting in an increased viscosity for this solution.

As expected, an increase in temperature decreased the viscosity of all tested solutions. In an industrial context, a decreased viscosity can lead to more efficient cleaning procedures. More specifically, by decreasing the absolute viscosity (μ) at elevated temperatures, solvent flow across cleaning surfaces may be increased, thereby reducing pump power consumption and therefore energy costs.

4. Conclusions

Surfactant formulations containing low concentrations of rhamnolipids achieved reductions in interfacial tension comparable to a formulation containing a higher concentration of a synthetic surfactant. The pre-conditioning with biosurfactant converted microbial adhesion to stainless steel into a thermodynamically unfavorable process. Moreover, at

Fig. 2 Flow curves for different surfactant formulations at a temperature of 25 °C (♦ Formulation A, ■ Formulation B, ▲ Formulation C and ● Formulation D).

Fig. 3 Flow curves for different surfactant formulations at a temperature of 70 °C (◆ Formulation A, ■ Formulation B, ▲ Formulation C and ● Formulation D).

Table 5 Rheological parameters of a Newtonian fluid model fitted to data from different surfactants at temperatures of 25 and 70 °C.

Temperature (°C)	Formulations	μ (MPa s)	R^2
25	A	1.146	0.999
	B	1.068	0.999
	C	1.055	0.999
	D	1.210	0.999
70	A	0.536	0.999
	B	0.577	0.958
	C	0.567	0.999
	D	0.614	0.973

room temperature, a detergent formulation containing a low rhamnolipid concentration exhibited a reduced viscosity relative to a control. This formulation potentially offers a great advantage for cleaning procedures within the food industry. Therefore, a biosurfactant can be superior to a synthetic surfactant for preventing or delaying microbial colonization of food contact surfaces.

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