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STABILITY AND RHEOLOGICAL PROPERTIES OF ICE CREAMS PRODUCED WITH DAIRY BY-PRODUCTS

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ABSTRACT

The majority of dairy industries (cheese, butter, ricotta, etc.) discard their by-products in the environment causing intense pollution due to the high concentration of organic matter in these products. An interesting solution would be the reuse of these by-products in foods, such as ice cream. However, unpleasant changes in this emulsion may occur, such as undesirable phase separation. In this context, the aim of this work was to observe the effects of the application of dairy wheys on ice cream's rheological properties and stability. Ice cream formulations differed by flavor (cream and chocolate), by type (milk, cheese whey, ricotta whey and butter whey), and by proportions of wheys (0, 25, 50, 75 and 100%). A commercial sample was also evaluated as a comparison. The evaluated parameters were zeta potential (ZP), particle size (PS), rheological behavior, desorption, and concentration of Ca+Mg. The results showed that the addition of whey, regardless of flavor and origin, reduced the viscosity and increased PS and desorption, but did not compromise the ZP of most of the samples (78.57%). This behavior was concentration-dependent. The Ca+Mg content of the wheys and the flavorings had no influence on the desorption index. Thus, the analyses revealed that different dairy by-products in ice creams could be used without significantly compromising important quality parameters and, at the same time, help to preserve the environment. However, further experiments should be conducted (e.g. sensory analysis) in order to better understand the technological potential of dairy by-products application in ice creams.

1.Introduction

Dairy producers are one of the food industry's examples that produce large quantities of effluent with high organic load, i.e. high Chemical (COD) and Biochemical Oxygen Demands (BOD). These by-products can impose serious challenges in local sewage treatment systems, representing a significant environmental impact when discarded without proper treatment (Janes et al., 2008; Silva, 2011). Among the alternatives that minimize environmental aggression, the partial or total replacement of powdered milk, eggs, fats, sugar, and even protein in the formulations of several other processed food has high added value, considering the nutritional e technological potential of these dairy effluents. In addition, these by-products are inexpensive and could help the economy of many companies while reducing raw material costs, and therefore lowering the cost of production (Singh et al., 2012; Božanić et al., 2014).

One of the most popular desserts in the world is the ice cream and its consumption has been constantly increasing over the years, mainly due to its sweet taste and soft texture. It is a product appreciated by people of all ages and at any time of the year, being considered a healthy and nutritious food, not only because of its high energy value, but also because of its high digestibility (Aboulfazli et al., 2015; Kumar et al., 2016, Makares et al., 2014, Vadiveloo et al., 2014).

The macromolecules present in ice creams (fats, proteins and complex carbohydrates) significantly contribute to the perception of texture and taste (Akesowan, 2009). Among the ice cream quality parameters, two of the most important are the viscosity and stability of its visual characteristics, which should not show any phase separation during and right after the melting (Tharp et al., 1998).

The formation and stability of dispersed colloidal systems as ice cream, depend on many factors such as protein content, salt concentration and ionic strength (Corredig et al., 2011, Tharp et al., 1998, Bodyfelt et al., 1988). Little is known regarding phase separation of ice cream blends, considering that investigations on their stability behavior focus mainly on the physicochemical characteristics and sensory qualities when new ingredients are added, thus leaving a gap in terms of understanding this mechanism (BahramParvar et al., 2008; Cheng et al., 2015).

Taking into consideration the pollutant potential of dairy by-products, the reuse of these wastes in human foods, as well as the possible modifications that they can cause in the composition and structure of food (desirably or not), the aim of this study was to evaluate the behavior of the addition of ricotta whey, cheese whey, and butter whey in rheological properties and ice cream stability.

2. Materials and methods

All procedures were carried out in three experimental replicates.

2.1. Formulation and processing of ice creams

The residues were obtained from the draining step of the production of rennet cheese, butter, and ricotta as liquid whey and then immediately cooled/frozen in cold chamber at -18±2°C. They were kindly provided from an agro-industry located at Federal Institute of Alagoas (IFAL), Campus Satuba, being transported frozen to the Laboratory of Biochemical Engineering of the School of Chemistry at Federal University of Rio de Janeiro (UFRJ) in a time not exceeding 12 hours.

Cream and Chocolate flavors were used in the production of ice creams with different ingredient proportions (% w/w) (Table 1), where the ingredients were purchased in a local market of Rio de Janeiro-RJ. Milk was replaced by different proportions of liquid/thawed residues and a control sample (0% of whey/100% of milk) was also made. A sample of a commercial brand with a high market share was acquired for comparison purposes with the developed ice cream.

The procedure to obtain the ice creams was done using a specific equipment to make the samples (Cuisinart® ice cream model, Ice 100 model), in which the basic unit operations of its processing were provided: homogenization of the ingredients (less emulsifier), pasteurization of the mixture, maturation, beating/freezing (emulsifier addition). The ice creams were transferred to plastic polypropylene recipients with a capacity of 250 mL, then stored in a freezer with the temperature set at -18±2ºC.

Table 1. Ice cream formulations with different whey percentages (% w/w).

Ingredients (%)	Cream flavor						Chocolate flavor				
	0%	25%	50%	75%	100%		0%	25%	50%	75%	100%
Whole Milk	66.86	16.72	33.43	50.14	---		58.14	43.61	29.07	14.53	---
Ricotta whey or Cheese whey or Butter whey	---	50.14	33.43	16.72	66.86		---	14.53	29.07	43.61	58.14
Refined sugar	17.44	17.44	17.44	17.44	17.44		17.44	17.44	17.44	17.44	17.44
Cream milk	11.63	11.63	11.63	11.63	11.63		11.63	11.63	11.63	11.63	11.63
Thickener and Stabilizer	0.58	0.58	0.58	0.58	0.58		0.58	0.58	0.58	0.58	0.58
Emulsifier	0.58	0.58	0.58	0.58	0.58		0.58	0.58	0.58	0.58	0.58
100% cocoa powder	---	---	---	---	---		11.63	11.63	11.63	11.63	11.63
Cream flavoring	2.91	2.91	2.91	2.91	2.91		---	---	---	---	---

2.2. Particle size and Zeta Potential

The mean particle size (PS) and zeta potential (ZP) of the ice cream mixes samples were determined using the Malvern Zetasizer Nano Series (Malvern Instruments, UK) at a constant temperature of 25 °C. Measurements were performed with an approximately 1:10.000 sample dilution in deionized water (Aboulfazli et al., 2014; Aboulfazli et al., 2015).

2.3. Rheological behavior

Rheological tests were carried out in melted ice cream samples (Aboulfazli et al., 2014; Aboulfazli et al., 2015) with a rotational viscometer OFITE 900 (OFI Testing Equipment, EUA) equipped with a Couette coaxial cylinder geometry. The viscometer was coupled to a Julabo F25 (GmbH, Germany) refrigerated circulator and all measurements were performed at a constant temperature of 4.0°C ± 0.1°C. Apparent viscosity and shear stress were assessed by linearly increasing the shear rate from 1.7 to 1,021 s^{-1}. Thus, the representative viscosity value of 50 s^{-1} (i.e., the shear rate equivalent to that performed by the mouth during chewing according to Bourne, 2002) was captured and compared to values found in the literature.

Rheological data were used to calculate the consistency index (K) and flow behavior index (n) through power-law model, represented by Eq. 1 (Rossa et al., 2012). Viscosity curves were also obtained and discussed throughout the text.

$$\sigma = K(\gamma)^n \qquad \cdots \text{ Eq. 1}$$

σ = shear stress (mPa);
K = consistency index (mPa s^n);
γ = shear rate (s^{-1});
n = flow behavior index.

2.4. Stability Analysis

Stability analysis of ice creams was carried out according to their desorption as described by the methodology of Cheng et al. (2015) with some modifications. The melted samples were poured into 100 mL glass beakers, slightly sealed and resting for one week. In each day, it was observed the presence of phase separation and the volume of the serum fraction formed in each sample was registered. The desorption index (DI) was determined by plotting the volumes recorded versus time, and the percentage of desorption was determined by the following equation:

$$\%\ DI = (H_{serum\ fraction}/H_{ice\ cream}) * 100$$

Where:
$H_{serum\ fraction}$ = height of the whey layer formed (mL);
$H_{ice\ cream}$ = total height of the ice cream (mL).

2.5. Determination of Calcium (Ca) and Magnesium (Mg)

The determination of Calcium (Ca) and Magnesium (Mg) in the main ingredients, both liquid and solid, was performed by titration with EDTA (ethylenediamine tetraacetic acid) solution as described in the methodology by Bird et al. (1961).

2.6. Statistical analysis

All parameters were performed in triplicate and the results of zeta potential, particle size, rheological behavior, desorption, and Ca + Mg concentration were expressed as the mean value ± standard deviation (SD). One-way ANOVA with post hoc was used to compare data obtained from the application of different dairy wheys and their proportions in the ice creams. The Tukey's HSD test was used when the difference was detected with 95% confidence ($p < 0.05$). Statistical analyses were performed using Statistica 7.0 software (StatSoft - USA).

3.Results and discussions

3.1. Particle size and Zeta Potential

The zeta potential of emulsions determines whether the particles tend to coalesce or not, that is, it evaluates constant stability thereof. Along with particle size, zeta potential measurements can be used to predict the stability of ice cream emulsions. According to Achouri et al. (2012)

and Malvern (2004), a zeta potential with a value (in magnitude) of more than 30 mV indicates the impedance of the droplet aggregation of an emulsion, which in turn, provides the increase of its stability by electrostatic repulsion.

According to table 2, it is observed that the zeta potential increased (it becomes less negative) along with the particle size in a concentration-dependent manner as wheys were added. This behavior indicates that the dairy by-products do not help to prevent the aggregation of droplets present in the ice cream mixes, meaning that the ice creams mixes containing the smallest quantity of residues were more stable, even though only 21.43% (6) of the total samples (28) are considered unstable since the threshold between stable and unstable suspensions is usually at ± 30mV (particles with zeta potential greater than + 30mV or less than -30mV are normally considered stable) (Malvern, 2004; et al., 2006; Tangsuphoom et al., 2009). In this way, chocolate flavor samples, except for the ice cream mix with 100% butter whey, were considered to be stable and those with cream flavor formulation of up to 75% of ricotta whey, 25% of cheese whey, and 75% of butter whey, also presented values of zeta potential below -30mV.

The zeta potential of ice creams mixes developed with 100% milk (without any residues) was similar to the vanilla-flavored ice cream mix also developed with 100% milk by Aboulfazli et al. (2014) (-36.56 mV) and Aboulfazli et al. (2015) (-36.56 and -35.10 mV). Regarding other formulations, the same study by Aboulfazli et al. (2014) when evaluating the effect of vegetable milks on the physical and rheological properties of ice cream, found that the formulation with coconut milk was more unstable (-30.70 mV) than soy milk (-35.50 mV) and the majority of samples developed in the present study (66.67% of samples). The zeta potential variation between the samples was also found in the research by Cheng et al. (2015) (-25 to -50 mV) when analyzing the effects of milk protein-polysaccharides interactions on the stability of ice cream mix model systems.

Compared to the cow's milk and vegetable milk-based ice creams mixes by Aboulfazli et al. (2014) (810-2541 nm) and Aboulfazli et al. (2015) (810-8.628 nm), the particle size values of ice cream mixes of the present study were lower (308-755 nm). Furthermore, Whelan et al. (2008) when studying the physicochemical and sensorial optimization of a low glycemic index in ice cream made with cow's milk, also presented high values (≈ 4,850 nm). For the particle sizes found by Cheng et al. (2015) (610-990 nm) in coconut oil and cow's milk ice creams mixes, only three samples presented sizes greater than 610 nm (100% cream flavored cheese whey, and 100% cream and chocolate-flavored ricotta whey).

The digestive process is affected by a wide variety of factors, including particle size, which is usually related to the surface area available for enzymatic action (Al-Rabadi et al., 2009). Based on this, Blasel et al. (2006) found that the starch access by α-amylase significantly decreases for every 100 μm increase in grain particle size of milled corn. Regarding the ingestion of breads, de la Hera et al. (2014) when evaluating the effects of flour particle size on gluten-free bread at an in vitro digestibility model, found difficulties in the digestibility of the starch as particle size increased, since the larger the particle size is, the larger is the quantity of low digestible starch and resistant starch.

Therefore, since the smaller the particle size the better the digestibility of a food, the ice creams mixes of the present study were shown to be more digestible, although the particle size increased with the addition of different wheys (those made with ricotta whey had higher sizes than the cheese whey and butter whey ice creams, respectively).

Table 2. Data of zeta potential, particle size, and desorption index (DI) of ice cream samples.

Sample	Zeta potential (mV)		Particles size (nm)		Desorption Index (DI) (%)	
	Cream flavor	Chocolate flavor	Cream flavor	Chocolate flavor	Cream flavor	Chocolate flavor
Ricotta whey						
Commercial	-40.70 ± 1.01^{a}	-42.20 ± 1.47^{a}	334.57 ± 3.5^{c}	307.90 ± 10.69^{e}	15.00 ± 1.00^{d}	3.00 ± 1.00^{ab}
0%	-35.57 ± 2.05^{b}	-38.53 ± 1.96^{ab}	343.27 ± 10.92^{c}	308.97 ± 7.05^{e}	10.00 ± 2.00^{e}	2.00 ± 1.00^{ab}
25%	-33.28 ± 1.33^{bc}	-36.15 ± 2.00^{bc}	346.23 ± 2.82^{c}	353.37 ± 4.04^{d}	15.00 ± 1.00^{d}	1.00 ± 1.00^{b}
50%	-31.00 ± 0.60^{cd}	-33.77 ± 2.22^{c}	349.20 ± 7.45^{c}	397.77 ± 5.90^{c}	20.00 ± 0.00^{c}	1.00 ± 0.00^{b}
75%	-30.22 ± 0.90^{cd}	-33.35 ± 0.76^{c}	551.88 ± 15.09^{b}	541.10 ± 10.99^{b}	30.00 ± 1.00^{b}	3.00 ± 1.00^{ab}
100%	-29.43 ± 1.33^{d}	-32.93 ± 0.81^{c}	754.57 ± 29.05^{a}	684.43 ± 16.65^{a}	39.00 ± 3.00^{a}	4.00 ± 1.00^{a}
Cheese whey						
Commercial	-40.70 ± 1.01^{a}	-42.20 ± 1.47^{a}	334.57 ± 3.65^{d}	307.90 ± 10.69^{d}	15.00 ± 1.00^{c}	3.00 ± 1.00^{a}
0%	-35.57 ± 2.05^{b}	-38.53 ± 1.96^{b}	343.27 ± 10.92^{d}	308.97 ± 7.05^{d}	10.00 ± 2.00^{d}	2.00 ± 1.00^{a}
25%	-32.73 ± 1.11^{bc}	-34.58 ± 0.98^{c}	376.02 ± 9.91^{cd}	340.05 ± 8.74^{cd}	13.00 ± 1.00^{c}	2.00 ± 0.00^{a}
50%	-29.90 ± 1.64^{c}	-30.63 ± 0.67^{d}	408.77 ± 9.00^{c}	371.13 ± 12.60^{c}	15.00 ± 3.00^{c}	1.00 ± 0.00^{a}
75%	-25.97 ± 0.78^{d}	-30.38 ± 0.40^{d}	566.83 ± 23.81^{b}	447.12 ± 13.97^{b}	20.00 ± 2.00^{b}	1.00 ± 1.00^{a}
100%	-22.03 ± 0.49^{e}	-30.13 ± 0.45^{d}	724.90 ± 39.01^{a}	523.10 ± 18.42^{a}	25.00 ± 2.00^{a}	1.00 ± 0.00^{a}
Butter whey						
Commercial	-40.70 ± 1.01^{a}	-42.20 ± 1.47^{a}	334.57 ± 3.65^{e}	307.90 ± 10.69^{c}	15.00 ± 1.00^{a}	3.00 ± 1.00^{a}
0%	-35.57 ± 2.05^{b}	-38.53 ± 1.96^{b}	343.27 ± 10.92^{e}	308.97 ± 7.05^{c}	10.00 ± 2.00^{b}	2.00 ± 1.00^{ab}
25%	-34.52 ± 1.26^{b}	-35.15 ± 0.95^{c}	384.08 ± 8.76^{d}	375.05 ± 11.39^{b}	1.00 ± 1.00^{d}	1.00 ± 0.00^{ab}
50%	-33.47 ± 0.55^{b}	-31.77 ± 0.25^{d}	424.90 ± 9.26^{c}	441.13 ± 26.17^{a}	2.00 ± 0.00^{cd}	0.00 ± 0.00^{b}
75%	-30.05 ± 0.45^{c}	-30.73 ± 0.20^{d}	491.53 ± 0.96^{b}	463.90 ± 19.75^{a}	3.00 ± 0.00^{cd}	0.00 ± 0.00^{b}
100%	-29.82 ± 0.46^{c}	-29.70 ± 0.53^{d}	558.17 ± 11.10^{a}	453.39 ± 19.48^{a}	4.00 ± 1.00^{c}	0.00 ± 0.00^{b}

Data are presented as mean values ± Standard deviation (SD). Mean values followed by the same lowercase letter in the column do not differ between themselves by ANOVA with post hoc Tukey test and 95% of confidence ($p < 0.05$).

Table 3. Rheological parameters of the ice cream obtained by Power Law model (or Ostwald de Waale model).

Sample	Apparent Viscosity (mPa.s) 50 s^{-1}		Consistency Index K ($mPa.s^n$)		Flow Behavior Index (n)		R^2	
	Cream	Chocolate	Cream	Chocolate	Cream	Chocolate	Cream	Chocolate
Ricotta whey								
Commercial	122.20 ± 0.91^{c}	289.40 ± 1.54^{c}	364.99 ± 2.11^{c}	913.66 ± 1.23^{e}	0.76 ± 0.007^{a}	0.72 ± 0.012^{a}	0.909 ± 0.003^{a}	0.981 ± 0.002^{a}
0%	480.20 ± 1.05^{a}	462.70 ± 0.87^{a}	1757.80 ± 3.32^{a}	2305.60 ± 2.21^{a}	0.63 ± 0.005^{a}	0.60 ± 0.009^{a}	0.972 ± 0.002^{a}	0.996 ± 0.001^{a}
25%	274.65 ± 1.03^{b}	455.85 ± 1.20^{a}	957.30 ± 1.02^{b}	2117.30 ± 1.01^{ab}	0.65 ± 0.003^{a}	0.60 ± 0.007^{a}	0.983 ± 0.003^{a}	0.996 ± 0.003^{a}
50%	49.10 ± 0.80^{d}	349.00 ± 1.01^{b}	175.65 ± 2.02^{d}	1926.50 ± 1.14^{bc}	0.74 ± 0.009^{a}	0.60 ± 0.007^{a}	0.912 ± 0.003^{a}	0.989 ± 0.007^{a}
75%	43.10 ± 1.01^{d}	289.00 ± 1.33^{c}	160.65 ± 2.42^{d}	1656.30 ± 3.01^{cd}	0.73 ± 0.005^{a}	0.61 ± 0.003^{a}	0.898 ± 0.005^{a}	0.991 ± 0.003^{a}
100%	37.10 ± 0.93^{d}	229.00 ± 1.87^{d}	144.84 ± 3.07^{d}	1389.30 ± 1.20^{d}	0.73 ± 0.010^{a}	0.63 ± 0.002^{a}	0.862 ± 0.001^{a}	0.979 ± 0.005^{a}
Cheese whey								
Commercial	122.20 ± 0.91^{c}	289.40 ± 1.54^{cd}	364.99 ± 2.11^{c}	913.66 ± 1.23^{b}	0.76 ± 0.007^{a}	0.72 ± 0.012^{a}	0.909 ± 0.003^{a}	0.981 ± 0.002^{a}
0%	480.20 ± 1.05^{a}	462.70 ± 0.87^{a}	1757.80 ± 3.32^{a}	2305.60 ± 2.21^{a}	0.63 ± 0.005^{a}	0.60 ± 0.009^{a}	0.972 ± 0.002^{a}	0.996 ± 0.001^{a}
25%	267.75 ± 0.86^{b}	398.10 ± 1.01^{b}	973.31 ± 1.27^{b}	2120.30 ± 0.92^{a}	0.65 ± 0.006^{a}	0.61 ± 0.005^{a}	0.988 ± 0.001^{a}	0.993 ± 0.004^{a}
50%	55.30 ± 0.97^{d}	393.50 ± 1.32^{b}	204.77 ± 1.01^{d}	1950.70 ± 1.34^{a}	0.73 ± 0.002^{a}	0.61 ± 0.008^{a}	0.840 ± 0.002^{a}	0.987 ± 0.003^{a}
75%	53.55 ± 1.23^{d}	324.55 ± 0.98^{c}	183.63 ± 2.33^{d}	1908.00 ± 1.09^{a}	0.75 ± 0.003^{a}	0.60 ± 0.004^{a}	0.847 ± 0.003^{a}	0.986 ± 0.002^{a}
100%	51.80 ± 0.79^{d}	305.60 ± 0.89^{cd}	162.29 ± 2.02^{d}	1882.40 ± 1.11^{a}	0.77 ± 0.009^{a}	0.60 ± 0.005^{a}	0.855 ± 0.002^{a}	0.987 ± 0.003^{a}
Butter whey								
Commercial	122.20 ± 0.91^{c}	289.40 ± 1.54^{e}	364.99 ± 2.11^{c}	913.66 ± 1.23^{c}	0.76 ± 0.007^{a}	0.72 ± 0.012^{a}	0.909 ± 0.003^{a}	0.981 ± 0.002^{a}
0%	480.20 ± 1.05^{a}	462.70 ± 0.87^{a}	1757.80 ± 3.32^{a}	2305.60 ± 2.21^{a}	0.63 ± 0.005^{a}	0.60 ± 0.009^{a}	0.972 ± 0.002^{a}	0.996 ± 0.001^{a}
25%	272.30 ± 0.97^{b}	433.55 ± 0.91^{b}	1008.80 ± 3.03^{b}	2267.00 ± 2.12^{ab}	0.65 ± 0.009^{a}	0.60 ± 0.002^{a}	0.992 ± 0.004^{a}	0.994 ± 0.006^{a}
50%	74.40 ± 0.85^{d}	404.40 ± 1.27^{c}	275.95 ± 2.01^{cd}	2228.20 ± 1.01^{b}	0.72 ± 0.007^{a}	0.60 ± 0.007^{a}	0.819 ± 0.007^{a}	0.990 ± 0.003^{a}
75%	69.30 ± 1.17^{d}	386.65 ± 1.85^{cd}	239.43 ± 2.01^{d}	2131.00 ± 1.23^{b}	0.74 ± 0.004^{a}	0.60 ± 0.005^{a}	0.837 ± 0.001^{a}	0.989 ± 0.003^{a}
100%	64.20 ± 1.69^{d}	368.90 ± 1.03^{d}	201.83 ± 3.23^{d}	2029.10 ± 2.01^{b}	0.76 ± 0.010^{a}	0.60 ± 0.009^{a}	0.862 ± 0.005^{a}	0.985 ± 0.001^{a}

Data are presented as mean values ± standard deviation (SD). Mean values followed by the same lowercase letter in the column do not differ between themselves by ANOVA with post hoc Tukey test and 95% confidence ($p < 0.05$).

3.2. Rheological behavior

The effect of melted ice cream type (chocolate or cream) and the concentration of dairy whey products (ricotta whey, cheese whey, and butter whey) in the viscosity is shown in Table 3 and Figures 1, 2, and 3. As one can observe, all samples demonstrated pseudoplastic behavior, meaning that apparent viscosity is a function of the imposed shear rate and it decreases as the shear rate increases. The viscosity reduction may be attributed to structural changes occurring during the shearing process: the emulsified particles tend to decrease in size and to orient themselves towards the flow, which has an impact on the viscosity values (Rossa *et al*., 2012).

By the information exposed in Table 3, there is a reduction on apparent viscosity as the whey content increases. This fact is attributed to the lower stability for melted ice creams with high whey content, which reflects in the increase of desorption index (Table 4 and Figure 4) and the reduction of zeta potential (Chiewchan *et al*., 2006).

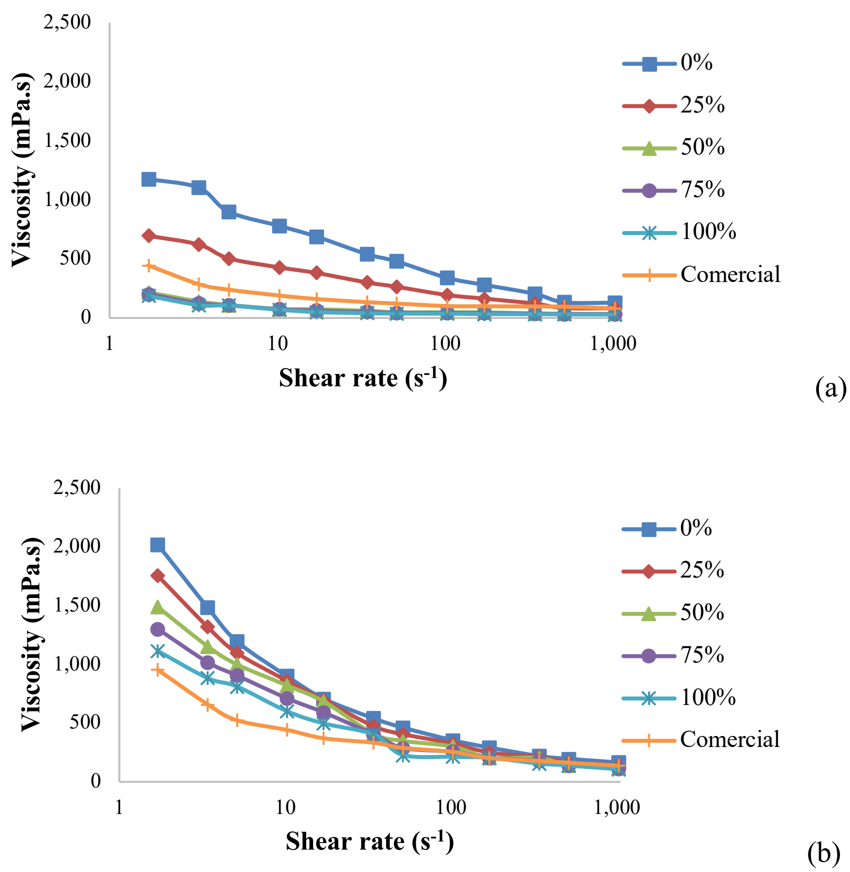


Figure 1. Effect of shear rate on apparent viscosity of cream (a) and chocolate (b) ice creams made with ricotta whey.

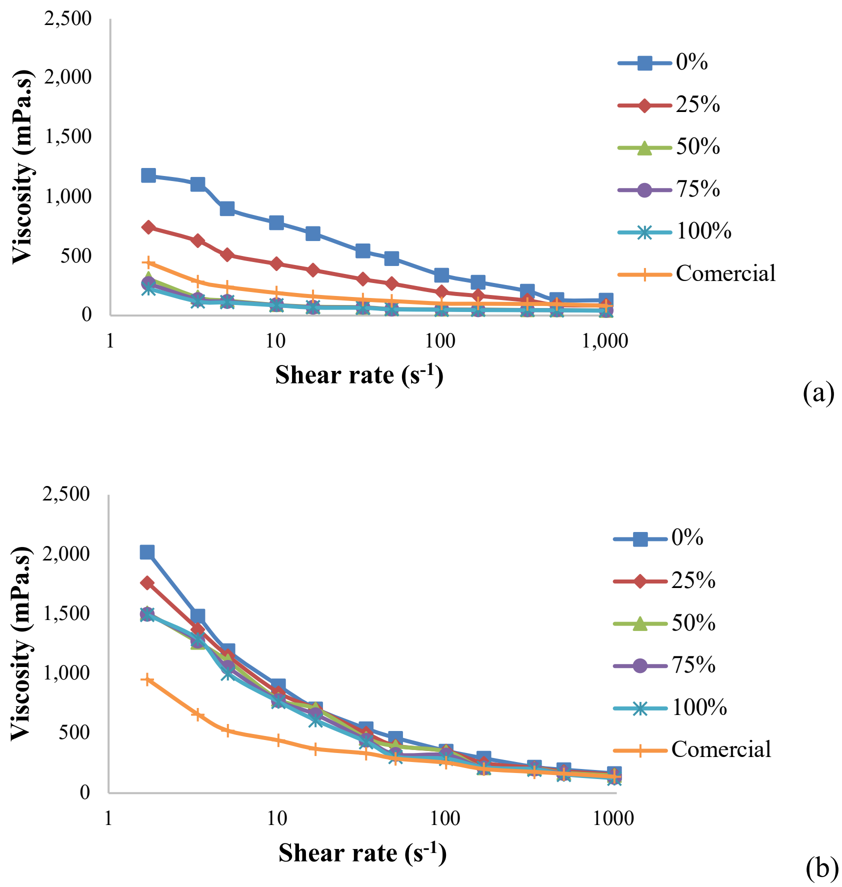
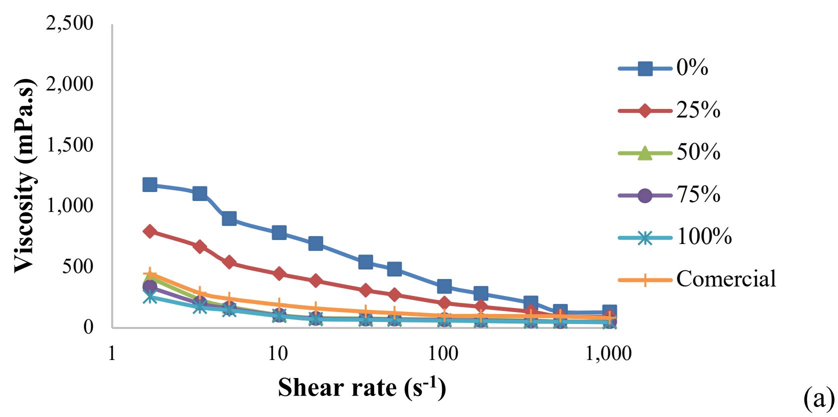
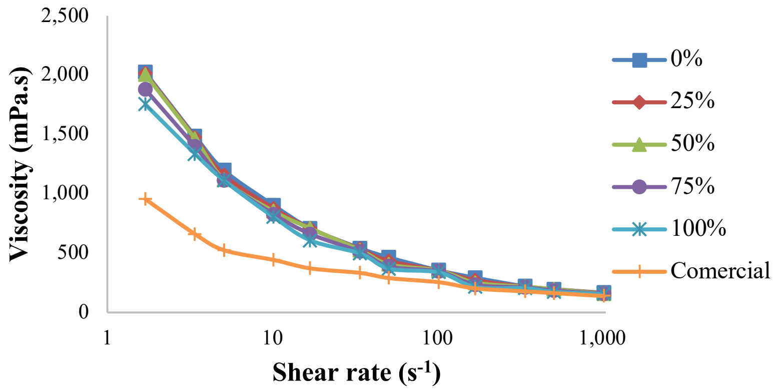


Figure 2. Effect of shear rate on apparent viscosity of cream (a) and chocolate (b) ice creams made with cheese whey.





(b)

Figure 3. Effect of shear rate on apparent viscosity of cream (a) and chocolate (b) ice creams made with butter whey.

The highest apparent viscosity values were obtained from butter whey, followed by cheese whey and ricotta whey, irrespective to the melted ice cream type. The qualitative behavior between the commercial melted ice cream brand assessed (which has great acceptance in the Brazilian market) and the formulated melted ice creams is evident as whey products are added to the samples.

For the same whey product, chocolate samples exhibited higher apparent viscosity values compared to the cream samples, which is reflected by the higher parameter *K* (consistency index, Table 3). This constant was calculated through viscosity data fit from power-law model (also known as Ostwald de Waale model). Besides, the pseudoplastic behavior is more pronounced for chocolate melted ice creams, reflected in the low values of parameter *n* (flow behavior index) when compared to the cream flavor. It is likely that this result was influenced by the presence of cocoa powder that is obtained from the cocoa paste prepared with seeds that underwent fermentation, drying, roasting, grinding and pressing for the separation of cocoa butter (Medeiros *et al*., 2009). Precisely because it is devoid of cocoa butter (which according to Gao *et al*., 2015 causes viscosity reduction), cocoa powder can cause the inverse effect.

At 20 s^{-1} all samples (except 0 and 25% ricotta whey) presented lower apparent viscosity than those developed with cow's milk (294 mPa.s), coconut milk (287 mPa.s), and soy milk (1,012 mPa.s) as seen in the study of Aboulfazli *et al.* (2015). In the present investigation, the values varied in a relatively large range for both flavors: chocolate (371.4 mPa.s, commercial sample to 708.8 mPa.s, 100% milk) and cream (50.2 mPa.s, 100% ricotta whey to 690.1 mPa.s, 100% milk).

Choi *et al.* (2014) obtained apparent viscosity values at 340.5 s-1 for the vanilla melted ice cream investigated, ranging from 26.3 to 198.9 mPa.s. In this study, this property ranged from 155.4 mPa.s (100% ricotta whey) to 219.7 mPa.s (100% milk) for chocolate melted ice cream and 32.2 mPa.s (100% ricotta whey) to 135.2 mPa.s (100% milk) for the cream melted ice cream. At 50 s^{-1}, Li *et al.* (2015) had samples varying from 100 to 430 mPa.s. At this same shear rate our results ranged from 289.4 mPa.s (commercial sample) to 462.7 mPa.s (100% milk) for chocolate type and 37.1 mPa.s (100% ricotta whey) to 480.2 mPa.s (100% milk) for the cream type.

The average apparent viscosity for the melted ice creams assessed by Whelan *et al.* (2008) at 30 s^{-1} was 51.5 mPa.s. On the other hand, in this investigation the apparent viscosity of chocolate melted ice cream ranged from 333.2 mPa.s (commercial sample) to 540.8 mPa.s (100% milk), whereas the cream samples ranged from 40.5 mPa.s (100% ricotta whey) to 540.9 mPa.s, i.e., a much broader range.

In Figures 1, 2 and 3, it is clear the viscosity convergence of all samples to relatively low values (~ 100 mPa.s) as the shear rate is increased to ~ 1,000 s^{-1}. This fact is likely to be connected to the structural breakage of the melted ice cream proteins network due to shear imposed, as emphasized by Rossa *et al*. (2012).

Considering the high values for the linear correlation coefficient (R^2) presented in Table 3, it is possible to attest that power-law model provided good adjustment parameters, since 72% of the samples exhibited $R^2 > 0.90$. Thus, the rheological behavior of the samples can be satisfactorily described by this model.

3.3. Stability analysis

Besides a palatable taste, it is expected from a good ice cream to have moderate melt resistance in the form of uniform homogeneous liquid and the appearance of the original blend (without phase separation), exhibiting a natural color and particles regularly distributed as long as a certain consistency is also maintained when the ice crystals melt. The heterogeneity can be identified by the presence of clots, slag, large, varied size air bubbles, and/or phase separation (Bodyfelt et al., 1988, Marshall, 2003).

Due to the fact that emulsions are thermodynamically unstable, they are susceptible to coalescing interactions immediately after production or during storage. For this reason, this effect was investigated in the present study by measuring the total whey content (Table 2) at different time intervals, from one to seven days after preparation (Figures 4, 5 and 6).

Generally, the samples with ricotta whey desorbed more than the samples with cheese whey and butter whey, respectively.

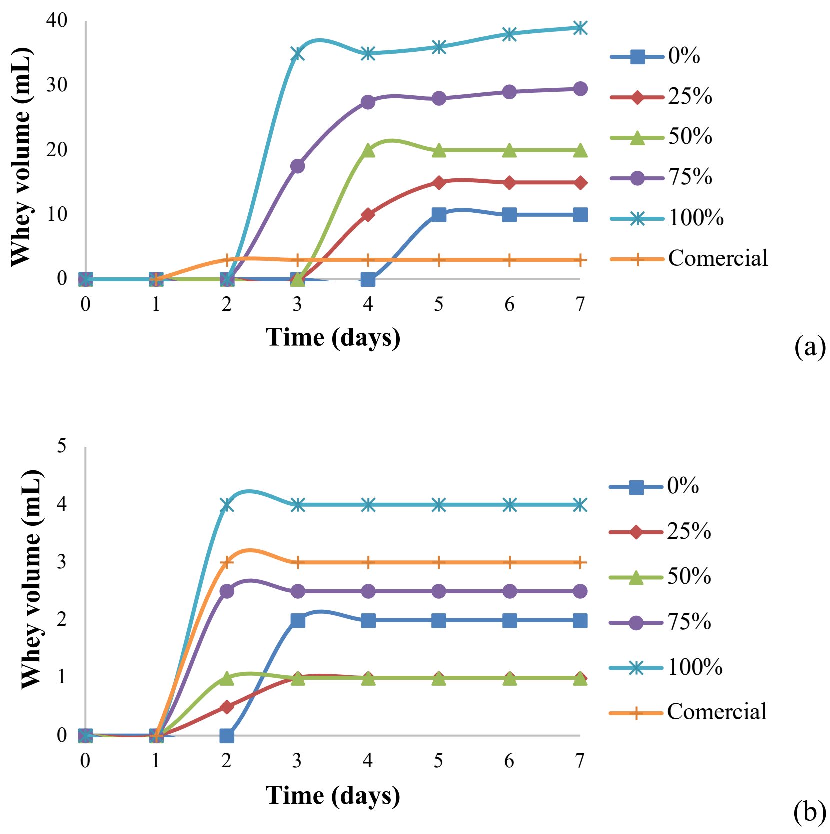
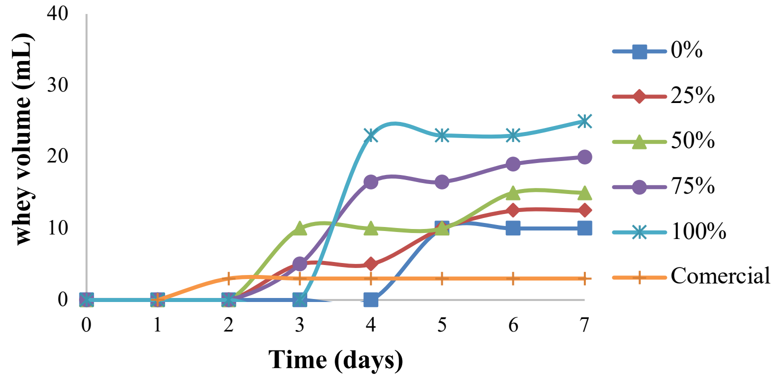
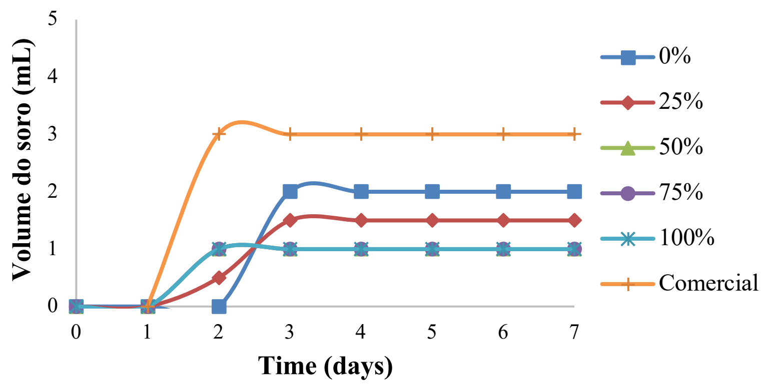


Figure 4. Effect of ricotta whey concentration in the desorption of cream (a) and chocolate (b) flavor ice cream.

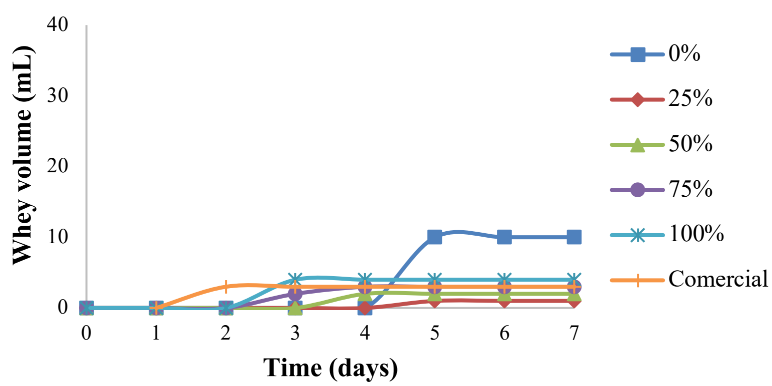


(a)

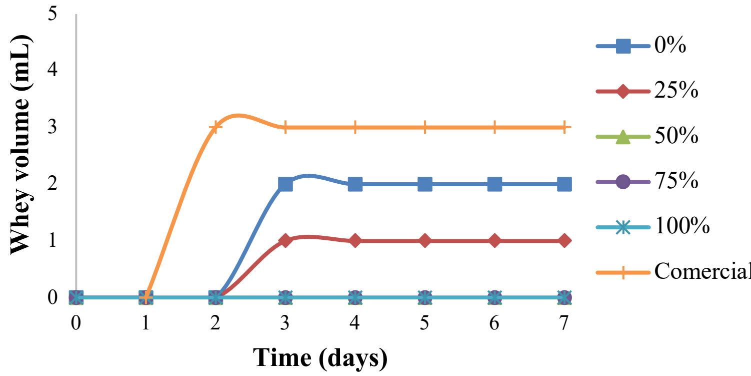


(b)

Figure 5. Effect of cheese whey concentration in the desorption of cream (a) and chocolate (b) flavor ice cream.



(a)



(b)

Figure 6. Effect of butter whey concentration in the desorption of cream (a) and chocolate (b) flavor ice cream.

Taking into consideration the chocolate flavored ice creams, only the 100% ricotta whey sample desorbed more than the 0% commercial samples. Besides the type and amount of flavorings, the greater presence of liquid ingredients in the cream flavored ice cream formulations (66.86% versus 55.14% in the chocolate flavor - Table 1) promoted a different behavior, which was the large whey formation right in the early days for most of these ice creams. Samples with butter whey had the lowest D and only the samples with 25% ricotta whey, and 25 and 50% cheese whey behaved similarly to the 0% commercial samples.

Thus, according to the results above, chocolate ice creams show a remarkably superior macroscopic stability than the cream flavor ice cream, regardless of the type of whey added.

3.4. Determination of Calcium (Ca) and Magnesium (Mg)

According to Chen et al. (2011), there are three factors that regulate the stability of an emulsion: particle size, particle flocculation and particle distribution between the different phases. In this context, calcium and magnesium ions can destabilize an emulsion, causing precipitation and compromising foaming (Ramkumar et al., 2000).

Figure 7 shows the Ca + Mg concentration in the main liquid and solid ingredients used in the formulations. Among the liquid ingredients, milk had the highest concentration of Ca and Mg, followed by butter whey, cheese whey and ricotta whey, respectively. In contrast, presenting an unexpected behavior, the samples developed with butter whey desorbed less, showed smaller particle sizes and were more stable (Table 2) compared to the samples with cheese whey and ricotta whey. In addition, even the milk-based sample with higher zeta potential and smaller particle size, presented low DI among the samples. This demonstrates the great complexity of the characterization of these materials in terms of their stability, because the parameters are often conflicting between different samples (either favoring or disfavoring the stability).

Regarding the solid ingredients, powdered cocoa was 14.28 times higher in Ca + Mg content when compared to the cream flavoring powder, however, it did not negatively influence the stability of the ice creams since they were more stable (higher zeta potential, lower particle size, and lower desorption). This fact may be associated with the small percentage of these flavorings in the ice cream formulations (2.91% cream flavor versus 11.63% cocoa powder - Table 1) when compared to the liquid ingredients (66.86% for cream flavor versus 55.14% for the chocolate flavor - Table 1).

Other authors found similar results with that of the present study for Ca + Mg in cow's milk: Visentin et al. (2018) (150.52 mg / 100 mL), Franzoi et al. (2018) (123.35 mg / 100 mL), Martino et al. (2011) (102.00 mg / 100 mL), and Yildiz et al. (2005) (116.05 mg / 100 mL). Taking into consideration the different influences on food composition, Jensen et al. (2012) when analyzing the composition of cow's milk from different breeds, showed that Ca + Mg content varied between Jersey (158.59 mg / 100 mL) and Holstein-Friesian breed (122.55 mg / 100 mL). Haug et al. (2007) pointed out that the milk composition of cows varies in different regions of Norway: north (137.00 mg / 100 ml), south (133.90 mg / 100 ml), east (131.90 mg / 100 ml), and west 132.70 mg / 100 mL).

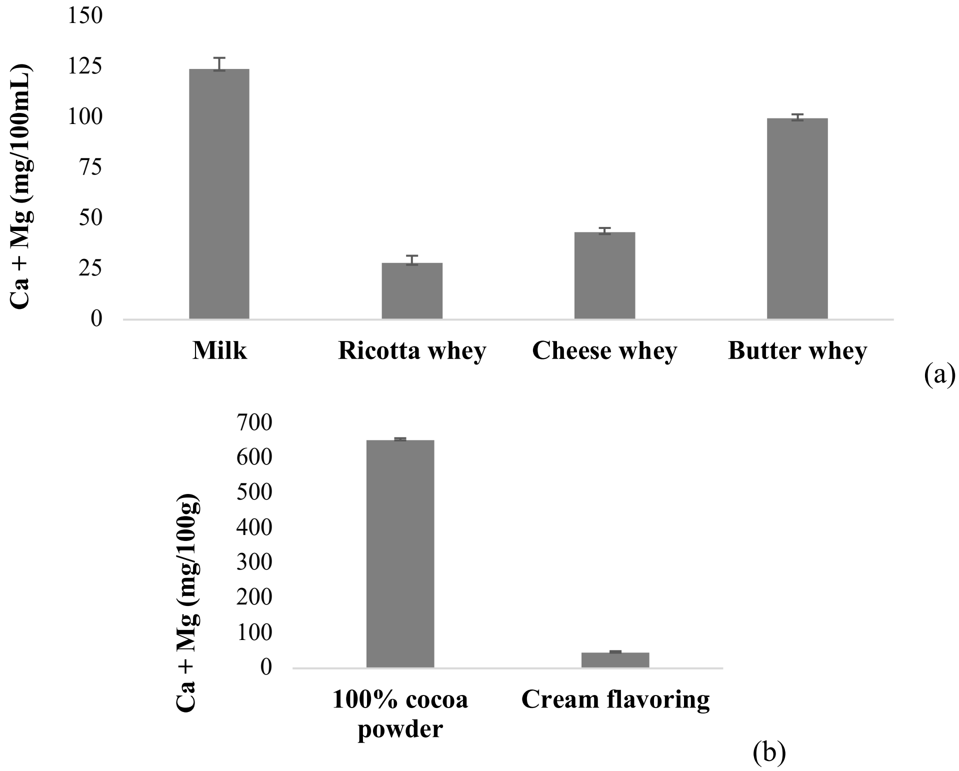


Figure 7. Content of Calcium and Magnesium in the main liquid (a) and solid (b) ingredients of ice cream. Data are presented as mean values ± standard deviation.

The content of Ca + Mg for cheese whey of the present research was lower, but similar to the one found by Martino et al. (54.80 mg / 100 mL), despite Franzoi et al. (2018) founding a lower content (28.87 mg / 100 mL). It should be noted that this variation occurs naturally and is mainly associated with the type of cheese from which the whey originates (Kandarakis, 1986).

4. Conclusions

The results showed that the high contents of ricotta whey (100% cream flavor), cheese whey (50% cream flavor), and butter whey (100% cream and chocolate flavor) had zeta potential values between +30 and -30mV, which compromises the stability of ice creams.

Regarding the rheological behavior, all samples showed predominant pseudoplastic character, with prevalence of the samples of chocolate over those of cream flavor. However, under high shear rates (~ 1000 s^{-1}), the apparent viscosity values converge to a Newtonian plateau of approximately 100 mPa.s

In the chocolate ice creams, practically no phase separation was observed, except in those developed with 75 and 100% of ricotta whey, that is, significant amounts of whey. In contrast, cream flavor samples, as indicated by their zeta potential values, were more unstable and the phase separation occurred more quickly and intensely, evidencing the influence of the type of ice cream flavor on its stability, particle size, rheology, and desorption.

Ca + Mg content of the main ingredients used was not a strong and decisive factor in the destabilization of the samples. Although the wheys had lower concentrations of these minerals in comparison to milk, as well as the flavoring of cream in relation to the cocoa powder, they did not prevent or delay the phases separation of the ice cream for up to a week.

Thus, ricotta whey (up to 25%), cheese whey (up to 50%) and butter whey (up to 75%) were promising candidates for the production of ice cream. In addition, taking into consideration the difficulty of analyzing the stability and performance factors evaluated here, the present study indicates the importance thereof and suggests that other quality parameters should be also analyzed in order to clarify the influence of these wheys on the characteristics of ice cream.

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