

Impact of Weighting Agents and Sucrose on Gravitational Separation of Beverage Emulsions

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The influence of weighting agents and sucrose on gravitational separation in 1 wt % oil-in-water emulsions was studied by measuring changes in the intensity of backscattered light from the emulsions with height. Emulsions with different droplet densities were prepared by mixing weighting agents [brominated vegetable oil (BVO), ester gum (EG), damar gum (DG), or sucrose acetate isobutyrate (SAIB)] with soybean oil prior to homogenization. Sedimentation or creaming occurred when the droplet density was greater than or lower than the aqueous phase density, respectively. The weighting agent concentrations required to match the oil and aqueous phase densities were 25 wt % BVO, 55 wt % EG, 55 wt % DG, and 45 wt % SAIB. The efficiency of droplet reduction during homogenization also depended on weighting agent type (BVO > SAIB > DG, EG) due to differences in oil phase viscosity. The influence of sucrose (0–13 wt %) on the creaming stability of 1 wt % soybean oil-in-water emulsions was also examined. Sucrose increased the aqueous phase viscosity (retarding creaming) and increased the density contrast between droplets and aqueous phase (accelerating creaming). These two effects largely canceled one another so that the creaming stability was relatively insensitive to sucrose concentration.

Keywords: *Creaming; sedimentation; emulsions; beverages; weighting agents*

INTRODUCTION

The term “beverage emulsion” is used to describe a group of products that have similar compositions, preparation procedures, and physicochemical properties, for example, fruit drinks, cordials, punches, and sodas (Tan, 1997). Beverage emulsions are oil-in-water emulsions that are prepared in a concentrated form that is diluted prior to consumption either by the manufacturer or by the consumer. The oil phase consists of some combination of vegetable oil, flavor oil, weighting agent, and antioxidants, whereas the aqueous phase consists of water, emulsifier, sweetener, salts, acids, and preservatives. The low concentration of droplets in diluted beverage emulsions (<0.3 wt %) accounts for their slightly turbid or “cloudy” appearance and the fact that their viscosities are similar to that of the aqueous solution that surrounds the droplets (Trubiano, 1995; McClements, 1999).

Beverage emulsions are thermodynamically unstable systems that tend to break down during storage. The most common manifestations of beverage emulsion deterioration are “ringing” and “oiling-off” (Trubiano, 1995; Tan, 1997, 1998). Ringing is the formation of a whitish “ring” around the neck of the container, whereas oiling-off is the formation of a shiny oil slick on top of the product. Ringing and oiling-off are the result of a variety of physicochemical mechanisms that occur within the beverage emulsion, including gravitational separation, flocculation, and coalescence (Dickinson and Stainsby, 1982; Dickinson, 1992; McClements, 1999). A better understanding of the origin and nature of these instability mechanisms would enable beverage manufactur-

ers to develop products with enhanced shelf lives. Previous researchers have examined the influence of emulsifier characteristics (Dickinson et al., 1989; Ray et al., 1995; Kim et al., 1996; McNamee et al., 1998; Garti, 1999), oil composition (Freeburg et al., 1994), weighting agents (Trubiano, 1995; Tan, 1997, 1998), temperature (Tse and Reineccius, 1995), and pH and ionic strength (Jayme et al., 1999) on the stability of beverage emulsions. In this study, we examine the influence of weighting agents and sucrose on gravitational separation in beverage emulsions.

The rate at which an isolated rigid spherical particle moves in a Newtonian liquid is given by Stoke's law (Hunter, 1986)

$$U_{\text{Stokes}} = -\frac{2gr^2(\rho_2 - \rho_1)}{9\eta_1} \quad (1)$$

where U is the creaming velocity, η is the shear viscosity, r is the particle radius, g is the acceleration due to gravity, ρ is the density, and the subscripts 1 and 2 refer to the continuous and dispersed phases, respectively. The sign of U determines whether the particle moves upward (+) or downward (-). Stoke's law gives a good description of the creaming velocity of isolated *fluid* spherical droplets, provided that there is little movement of the liquid within the droplets (McClements, 1999). This condition is met when the viscosity of the disperse phase is significantly greater than that of the continuous phase (i.e., $\eta_2/\eta_1 > 5$) or when the droplets are surrounded by an emulsifier membrane that resists deformation (McClements, 1999). Equation 1 is therefore applicable to beverage emulsions because the oil phase has a much higher viscosity than the aqueous phase ($\eta_2/\eta_1 > 5$) and the droplets are

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normally surrounded by highly viscoelastic biopolymer membranes (Dickinson et al., 1989). In addition, the droplet concentration in diluted beverage emulsions is low (<0.3 wt %) and the aqueous phase is normally Newtonian, which are also assumptions used to derive the Stoke's equation.

A number of ways to retard gravitational separation in beverage emulsions can be identified by examining Stoke's equation: minimize the density contrast between the droplets and the aqueous phase, reduce the droplet size, or increase the aqueous phase viscosity (Dickinson, 1992; Trubiano, 1995; Tan, 1997, 1998; McClements, 1999). In this study, we focused on the influence of density contrast on gravitational separation in model beverage emulsions. Different types and concentrations of weighting agents were used to adjust the density of the oil phase, and different concentrations of sucrose were used to adjust the density of the aqueous phase. The weighting agents used in this study were brominated vegetable oil (BVO), ester gum (EG), damar gum (DG), and sucrose acetate isobutyrate (SAIB). BVO is made by bromination of vegetable oil (Tan, 1997). Ester gum is made by esterification of wood rosin with glycerol. (Anonymous, 1999). Damar gum is a natural exudate obtained from the shrubs of the Caesalpinaceae and Dipterocarpaceae families (Tan, 1997). SAIB is made by the esterification of sucrose with acetic and isobutyric anhydrides (Anonymous, 1998).

EXPERIMENTAL PROCEDURES

Materials. Soybean oil was purchased from a local retailer and used without further purification. Polyoxyethylene sorbitan monolaurate (Tween 20), a nonionic surfactant, and hexadecane were purchased from the Sigma Chemical Co. (St. Louis, MO). Damar gum was obtained from Colloides Naturels Inc. (Bridgewater, NJ). Ester gum was obtained from Hercules Inc. (Wilmington, DE). Sucrose acetate isobutyrate (SAIB) was obtained from Eastman Chemical Co. (Kingsport, TN). Brominated vegetable oil was obtained from Dominion Products Inc. (Brooklyn, NY). Distilled and deionized water was used in the preparation of all solutions.

Emulsion Preparation. An aqueous surfactant solution was prepared by dispersing 2.5 wt % Tween 20 in water. A 7 wt % soybean oil-in-water emulsion was prepared by weighing 14 g of soybean oil and 186 g of surfactant solution into a 400 cm³ glass beaker and blending with a high-speed homogenizer for 2 min (Bio Homogenizer, Biospec Products Inc., Bartlesville, OK). This coarse emulsion was then sonicated using a Braun-Sonic 2000U ultrasonic generator (Braun Biotec, Allentown, PA) to reduce the size of the emulsion droplets. The influence of droplet density on creaming stability was studied by preparing a series of 1 wt % oil-in-water emulsions from an oil phase that contained different amounts of soybean oil (or hexadecane) and weighting agent. The influence of aqueous phase density on creaming stability was studied by preparing a series of 1 wt % oil-in-water emulsions containing different amounts of sucrose in the aqueous phase. Unless stated otherwise, the final mean droplet radius of the emulsions was ~0.5 μm .

Particle Size Determination. The particle size distribution of the emulsions was measured using a laser light scattering instrument (Horiba LA-900, Irvine, CA). This instrument measures the angular dependence of the intensity of light scattered from a dilute emulsion. It then finds the particle size distribution that gives the best fit between the experimental measurements and predictions made using light scattering theory. A refractive index ratio of 1.08 was used by the instrument to calculate the particle size distributions. Measurements are reported either as the full particle size distribution or as the volume-surface mean radius: $r_{32} = \sum n_i r_i^3 / \sum n_i r_i^2$, where n_i is the number of droplets of radius r_i .

To prevent multiple scattering effects, the emulsions were diluted with distilled water prior to analysis so that the droplet concentration was <~0.02 wt %. Each sample was analyzed three times, and the data are presented as the average. The droplet size distribution did not change during the course of the experiments, which indicated that emulsions were stable to coalescence and Ostwald ripening.

Rheology Measurements. The viscosity of the oil phases was measured using a dynamic shear rheometer with a concentric cylinder measurement cell (Constant Stress Rheometer, CS-10, Bohlin Instruments, Cranbury, NJ). The diameter of the inner cylinder was 25 mm, and the diameter of the outer cylinder was 27.5 mm. Samples were placed in the temperature-controlled measurement vessel and allowed to equilibrate to the required temperature (25 °C) for 5 min prior to making the measurements. The apparent viscosity of the oil phases was largely independent of shear stress from 1 to 10 Pa, and so the apparent viscosity was reported only at a shear stress of 1 Pa.

Creaming Measurements. The creaming stability of emulsions was determined using an optical scanning instrument (Quickscan, Coulter Corp., Miami, FL). Emulsions were placed into flat-bottom cylindrical glass tubes (100 mm height, 16 mm internal diameter) and stored at room temperature. The backscattering of monochromatic light ($\lambda = 850 \text{ nm}$) from the emulsions was measured as a function of their height. The extent of creaming was assessed by determining the height of the interface between the opaque droplet-rich layer and the transparent droplet-depleted layer as a function of time. Creaming results are reported either as creaming profiles (backscattering versus emulsion height) or as creaming velocities = dH/dt , where H is the thickness of the droplet-depleted layer and t is the time. When the droplets were less dense than the aqueous phase, the transparent layer appeared at the bottom of the emulsions. On the other hand, when the droplets were denser than the aqueous phase, the transparent layer appeared at the top of the emulsions.

Density Measurements. The density of the oil phases was measured using a specific gravity bottle designed for viscous fluids. The oil phase density was determined by weighing the mass of oil (M_o) and then the mass of water (M_w) required to fill the specific gravity bottle at 25.0 °C. The density of the oil (ρ_o) was then calculated from $\rho_o = \rho_w M_o / M_w$, where ρ_w is the density of distilled water at the measurement temperature. The aqueous phase density was determined using an oscillating U-tube density meter (DE 50, Mettler-Toledo, Inc., Worthington, OH) at 25.0 °C. The data are reported as the mean of two measurements.

RESULTS AND DISCUSSIONS

Influence of Droplet Density on Creaming Stability. Soybean oil and BVO were mixed in different ratios to create oil phases with a range of densities. These oil phases were then homogenized with aqueous phase to produce a series of 1 wt % oil-in-water emulsions ($r_{32} \sim 0.5 \mu\text{m}$) with different droplet densities. The backscattering of light from these emulsions was measured as a function of their height over time (Figure 1). Gravitational separation in the emulsions depended on the density contrast between the oil and aqueous phases. Droplets containing 100% soybean oil had a lower density than the aqueous phase and therefore moved upward (Figure 1a). Initially, the backscattering was fairly constant across the entire height of the emulsion because there was an even distribution of droplets throughout the system. As the droplets moved upward there was a decrease in backscattering at the bottom of the emulsion (because the droplet concentration decreased) and an increase at the top (because the droplet concentration increased). As creaming proceeded a clear interface formed between the droplet-depleted

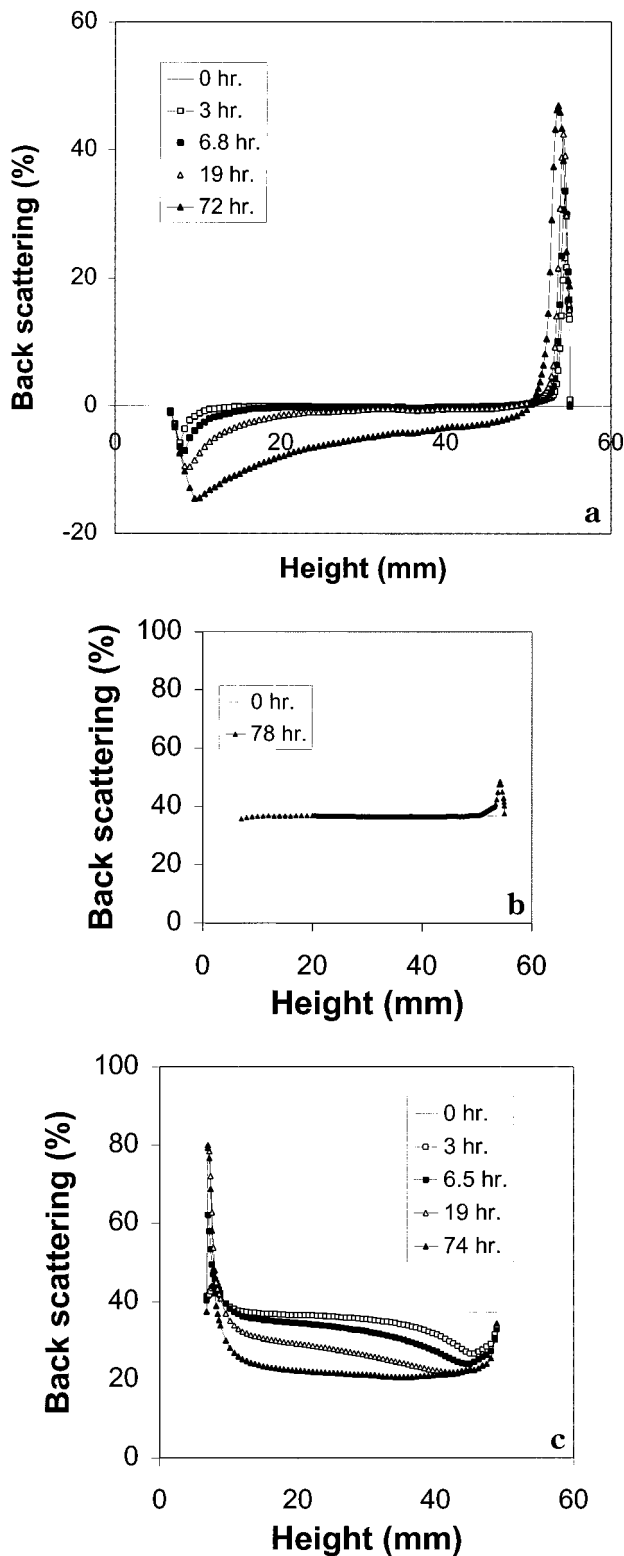


Figure 1. Creaming profiles of 1 wt % soybean oil-in-water emulsions stabilized by 2.5 wt % Tween 20: oil phase made from (a) 100% soybean oil, (b) 75 wt % soybean oil and 25 wt % BVO, and (c) 100% BVO.

layer at the bottom and the droplet-rich layer at the top. Droplets containing 100% BVO had a higher density than the surrounding aqueous phase and therefore moved downward (Figure 1c). Again, the initial backscattering was fairly constant across the entire height of the emulsion because there was an even distribution of droplets throughout the system. As sedimentation proceeded, there was a decrease in backscattering at the

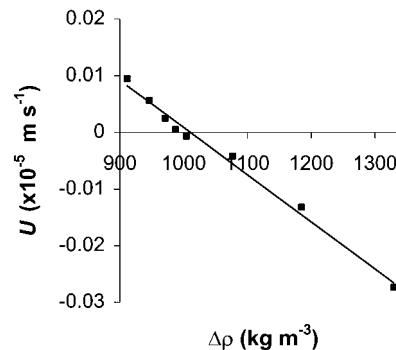


Figure 2. Creaming velocity of 1 wt % oil-in-water emulsions with different soybean/BVO ratios. When the oil and aqueous phase densities were equal, the creaming velocity was zero.

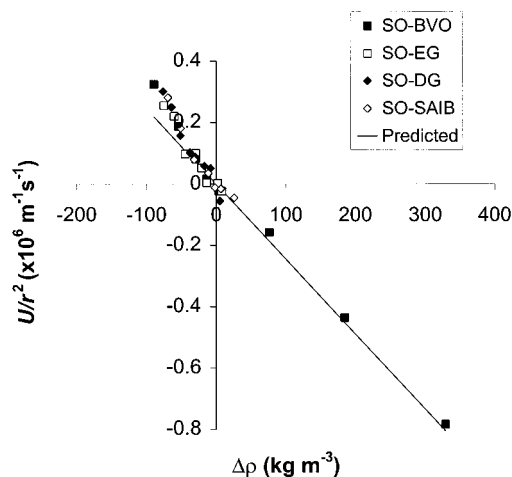


Figure 3. Dependence of normalized creaming velocity (U/r^2) on density contrast ($\Delta\rho$) for 1 wt % oil-in-water emulsions containing droplets with different types and concentrations of weighting agents.

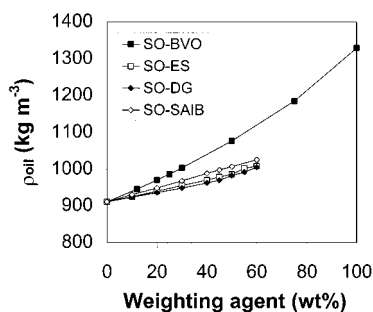
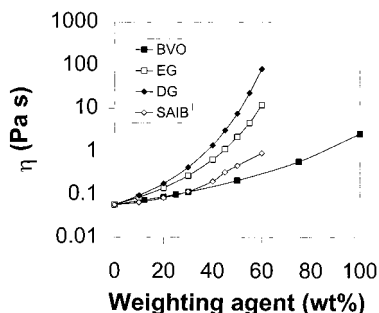
top of the emulsions and an increase at the bottom. Droplets containing 75% soybean oil and 25 wt % BVO had the smallest density contrast with the surrounding aqueous phase, and therefore there was the least change in the creaming profile of these emulsions over time (Figure 1b).

The creaming rate should be proportional to the density contrast ($\Delta\rho = \rho_2 - \rho_1$) between the oil and aqueous phases (eq 1). The creaming velocity (dH/dt) of emulsions containing different ratios of soybean oil and BVO in the oil phase was therefore plotted against the density (Figure 2). As expected from Stoke's law, the relationship between the creaming velocity and density was approximately a straight line that passed through the x -axis at the point where the densities of the aqueous and oil phases were equal. Nevertheless, some of the variations in the creaming velocities of the emulsions were due to slight differences in their mean droplet diameters. These variations were minimized by plotting the creaming velocity divided by the mean droplet radius squared (U/r^2) against the density contrast ($\Delta\rho$) (Figure 3). Stoke's law indicates that a plot of U/r^2 against $\Delta\rho$ should be a straight line that passes through the origin with a slope of $-2g/9\eta_1$ ($= -2447 \text{ m}^2 \text{ s}^{-1} \text{ kg}^{-1}$). There was a high correlation ($r^2 = 0.967$) between the measured normalized creaming velocities (U/r^2) and those predicted by Stoke's law (Figure 3). The normalized creaming velocities of emulsions containing different types of weighting agent fell on the same line (Figure 3), which indicated that the creaming

Table 1. Properties of Different Types of Weighting Agent Used To Achieve Density Matching in Soybean Oil-in-Water Emulsions

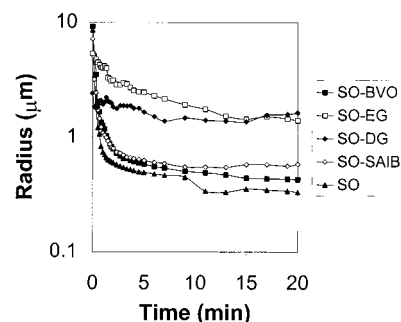
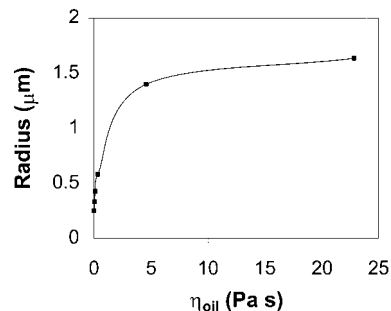
weighting agent type	density matching concentration (wt %)	viscosity of density matching oil phase (Pa·s)	$d\rho/dc$ ($\text{kg m}^{-3}/\text{wt %}$)	$d\eta/dc$ (Pa·s/ wt %)	radius of droplets ^a (μm)
BVO	25	0.100	0.0037	0.0017	0.43
SAIB	45	0.329	0.0019	0.0019	0.58
ester gum	55	4.58	0.0016	0.0042	1.40
damar gum	55	22.8	0.0015	0.0061	1.64

^a Droplet radius after homogenization for 20 min at 240 V using a sonicator.

**Figure 4.** Dependence of density on the ratio of soybean oil and weighting agent in the oil phase.**Figure 5.** Dependence of apparent viscosity on the ratio of soybean oil and weighting agent in the oil phase.

rate depended only on density contrast and not on weighting agent type. The amounts of weighting agent required to match the density of the oil and aqueous phases are given in Table 1.

Influence of Weighting Agent Type on Oil Phase Density and Viscosity. The densities of oil phases containing different types and concentrations of weighting agent were measured (Figure 4). The density of the oil phases increased as the concentration of weighting agent (c) increased. The slope of the increase ($d\rho/dc$) depended on the density of the weighting agent, with $\text{BVO} > \text{SAIB} > \text{ester gum} > \text{damar gum}$ (Table 1). Lower concentrations of BVO than of any of the other weighting agents could therefore be used to increase the droplet density by a given amount. The viscosity of oil phases containing different types and concentrations of weighting agent was also measured (Figure 5). The viscosity of the oil phases increased with increasing weighting agent concentration. The slope of the increase ($d\eta/dc$) depended on the weighting agent, with $\text{damar gum} > \text{ester gum} > \text{SAIB} > \text{BVO}$. The efficiency of droplet disruption during homogenization depends on the viscosities of both the dispersed (η_D) and continuous (η_C) phases (Walstra, 1996). Droplets become increasingly difficult to disrupt when the viscosity ratio (η_D/η_C) increases above ~ 5 . The effect of weighting agent

**Figure 6.** Effect of sonication time on droplet radius for 10 wt % oil-in-water emulsions containing different types and concentrations of weighting agent. All of the emulsions contained oil and aqueous phases with the same density.**Figure 7.** Dependence of the final droplet radius of 10 wt % oil-in-water emulsions produced by sonication on the oil phase viscosity.

type on homogenization efficiency was examined by preparing a series of 10 wt % oil-in-water emulsions in which the densities of the oil and aqueous phases were matched. This was achieved by mixing the appropriate concentration of each type of weighting agent with soybean oil (Table 1). In addition, oil phases consisting of 100% soybean oil, 100% hexadecane, and 55% BVO/45% hexadecane were also used. The oil and aqueous phases were then homogenized using a sonicator at a constant power level (240 V and 0.4 MHz), and the mean droplet size was measured over time (Figure 6). For all of the emulsions there was a rapid decrease in droplet size during the first few minutes followed by a plateau region where the droplet size remained fairly constant. As the viscosity of the oil phase increased, the final droplet size achieved increased (Figure 7), indicating that droplet disruption became more difficult as the oil phase viscosity increased. It is therefore important to consider the effect of weighting agents on the efficiency of droplet disruption, as well as on droplet density. Our study suggests that BVO would be the best weighting agent because a lower concentration is needed to match the oil and aqueous phase densities and because smaller droplets can be produced using the same homogenization conditions. Nevertheless, there are other factors that also need to be considered when a weighting agent for use in beverage emulsions is chosen, such as legal limits, cost, and consumer acceptability.

The droplets used in this study ($r_{32} \sim 0.5 \mu\text{m}$) were fairly large compared to those in commercial beverage emulsions. The amount of weighting agent required to match the density of a droplet to that of the aqueous phase has been shown to decrease as the droplet size decreases (Trubiano, 1995; Tan, 1997, 1998). This is because the emulsifiers used in beverage emulsions form relatively thick and dense interfacial layers around

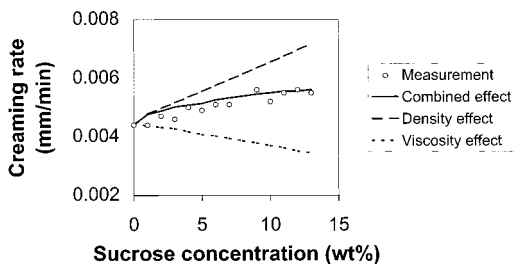


Figure 8. Comparison of theoretical predictions (Stoke's law) and measured creaming velocities of 1 wt % soybean oil-in-water emulsions containing different sucrose concentrations in the aqueous phase.

the oil droplets, which substantially increases the overall density of small droplets.

Influence of Aqueous Phase Density and Viscosity on Creaming Rate. The creaming velocities of 1 wt % soybean oil-in-water emulsions ($r_{32} = 0.51 \mu\text{m}$) containing different sucrose concentrations in the aqueous phase were measured (Figure 8). Sucrose increased the viscosity of the aqueous phase (which should retard creaming) and increased the density contrast between the droplets and the aqueous phase (which should accelerate creaming). The impact of changes in the density and viscosity of the aqueous phase caused by sucrose on the creaming stability of beverage emulsions was therefore examined. Equation 1 was used to predict the creaming velocity for three situations: (i) density effect [varying $\Delta\rho (= \rho_o - \rho_s)$, constant $\eta_1 (= \eta_w)$]; (ii) viscosity effect [constant $\Delta\rho (= \rho_o - \rho_w)$, varying $\eta_1 (= \eta_s)$]; (iii) combined effect [varying $\Delta\rho (= \rho_o - \rho_s)$, varying $\eta_1 (= \eta_s)$]. The subscripts S, O, and W refer to sucrose solutions, pure soybean oil, and pure water, respectively. The increase in creaming velocity caused by the increase in density contrast is largely compensated for by the decrease in creaming velocity caused by the increased viscosity. Overall, the addition of sugar to the aqueous phase of beverage emulsions therefore has little impact on their creaming stability. There was good agreement between the experimentally measured creaming velocity and that predicted by Stoke's law (Figure 8).

Conclusions. The gravitational separation of soybean oil-in-water emulsions was strongly influenced by the density contrast between the oil and aqueous phases. Adding weighting agent to the oil phase to match its density to that of the aqueous phase largely eliminated gravitational separation. The amount of weighting agent required to achieve density matching and the ease of droplet disruption during homogenization depended on weighting agent type. BVO was the most effective weighting agent because a lower concentration could be used to achieve density matching and because smaller droplets could be produced using the same homogenization conditions. There are government regulations on the amounts of weighting agents that can be incorporated into beverage emulsions, which means that it is not always possible to achieve complete density matching. This problem can be partly alleviated by using combinations of weighting agents, for example, BVO and ester gum.

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