



Characterization of alcohol-containing dairy emulsions: Pseudo-ternary phase diagrams of sodium caseinate solution-oil-ethanol systems



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ARTICLE INFO

Article history:

Received 17 November 2012

Accepted 9 March 2013

Keywords:

Emulsions

Alcohol

Cream liqueurs

Phase diagram

Depletion flocculation

ABSTRACT

The physical properties and the stability of alcohol containing emulsions made with sodium caseinate using two types of oil (canola and coconut) were investigated. The region of emulsion stability was presented on ternary phase diagrams. This region was limited to emulsion compositions in the range of sodium caseinate solutions between 32–68 wt.%, oil contents between 10 and 53 wt.% and ethanol concentrations from 8 to 32 wt.%. The type of oil had a minor effect on emulsion stability, but stability was sensitive to ethanol content and casein/oil ratio. Emulsions within the region of emulsion stability behaved as Newtonian fluids with high ethanol content (>22 wt.%) emulsions being low viscosity and those of low ethanol (<22 wt.%) being of high viscosity. Ethanol affected the average droplet size. By establishing the boundaries of emulsion stability for the full phase space in cream liqueurs, formulation strategies for specific product properties can be planned.

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1. Introduction

Dairy emulsions containing ethanol are interesting experimental materials due to their technological application in understanding the properties of cream liqueurs. Stability and shelf life extension has been the focus of a number of studies since the development of those products during the 1980s. Cream formation, serum separation at the bottom of the bottle, and formation of aggregates are the principal instability behaviors that have been noted (Banks, Muir, & Wilson, 1981; Dickinson, Narhan, & Stainsby, 1989; Lynch & Mulvihill, 1997). Improvements in stability have been achieved by modification of the production process and cream liqueur formulation. For example, high pressure homogenization has been used to reduce droplet size (and hence retard creaming rates), while reduction of fat content (i.e., by use of anhydrous milk fat instead of cream) has reduced density differences between dispersed and continuous phases (Dickinson et al., 1989; Lynch & Mulvihill, 1997; Muir & Banks, 1986).

Studies focused on the influence of ethanol on destabilization behavior have been mainly conducted over a narrow range of casein/oil ratios (Agboola & Dagleish, 1996; Dickinson & Golding, 1998; Radford, Dickinson, & Golding, 2004). In addition, despite similar emulsion preparation methodologies, the details often differ, e.g., ethanol added into the emulsion in some studies before homogenization (Dickinson & Golding, 1998) or after (Radford et al., 2004), or initial emulsions were prepared and then diluted with ethanol water mixtures (Agboola &

Dagleish, 1996). Accordingly, it is difficult to draw unambiguous universal rules from the different studies on the phase behavior of dairy emulsions containing ethanol.

Nevertheless, all authors concur that emulsion stability is directly dependent on the ethanol concentration in the continuous phase. Dickinson and Golding (1998) reported that above 30–40 wt.% ethanol content, protein stability is challenged because ethanol alters the polarity of the aqueous phase; the ensuing effects on the steric stabilization of the casein micelles leads to protein aggregation. In contrast, at concentrations less than 20 wt.%, ethanol enhances emulsion stability because the reduced interfacial tension between the oil and the aqueous phase reduces the sizes of the droplets attained during homogenization, and smaller droplet sizes retard creaming rates, as indicated by Stokes' equation (Dickinson & Golding, 1998; McClements, 2007). Ostwald ripening is another factor in the stability of emulsions containing ethanol because ethanol enhances the solubility of the oil in the continuous phase (Radford et al., 2004).

Because of the complex variety of interactions that can occur in the dairy emulsion systems it can be difficult to discern the influence of one component at different concentrations (e.g., ethanol) on the behavior of a mixture of the other components (i.e., sodium caseinate, water and oil). Phase diagrams are useful tools to systematically evaluate the effect of composition on system properties (Predel, Hoch, & Monte, 2004). For this reason, a ternary phase diagram was selected to map out the complete phase diagrams for the pseudo-ternary systems: sodium caseinate solution-ethanol-canola oil, and sodium caseinate solution-ethanol-coconut oil. A secondary objective of the research was to quantify the properties of the emulsions residing in the region of emulsion stability.

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2. Theoretical concepts

Previous studies have shown that two factors in the destabilization of protein stabilized emulsions are insufficient casein molecules for adequate coverage of the oil droplets and an entropically driven depletion flocculation process (Dickinson, Golding, & Povey, 1997; Radford et al., 2004). In the former case, a sufficient concentration of protein must be available for adsorption at the oil droplet interfaces (C_{ad}). This concentration in the emulsion depends on the volume fraction of oil droplets (ϕ_{oil}), the droplet size and the extent of surface coverage of the droplets by the casein molecules (Γ):

$$C_{ad} = \frac{6\Gamma\phi_{oil}}{d_{32}} \quad (1)$$

where d_{32} is the Sauter mean diameter of the droplets. Because the conformation of casein molecules is affected by ethanol content (Horne & Davidson, 1986; Radford et al., 2004), the surface coverage is not a constant (Radford et al., 2004).

The oil volume fraction in Eq. (1) can be described in terms of the densities of the dispersed and continuous phases (McClements, 2004):

$$\phi_{oil} = \frac{\Omega_{oil}\rho_c}{(1-\Omega_{oil})\rho_{oil} + \Omega_{oil}\rho_c} \quad (2)$$

where Ω_{oil} is the mass oil fraction, ρ_c and ρ_{oil} are densities of the continuous and oil phase, respectively.

In the depletion flocculation process, unadsorbed protein molecules are excluded from the interstitial region formed when two adjacent droplets approach each other, thus increasing the concentration of unadsorbed casein micelles in the surrounding region. The difference in protein concentration between the two regions generates an osmotic pressure gradient, drawing solvent out of the interstitial region, and pushing the droplets into contact to induce floc formation. From calculations of the concentration of casein in the continuous phase and in the interfacial layer an estimate of the critical amount of unadsorbed casein that generates osmotic pressure sufficient to induce flocculation for a given casein-oil ratio can be obtained (Berli, 2008; Berli, Quemada, & Parker, 2002; Dickinson & Golding, 1997; Radford & Dickinson, 2004).

The osmotic pressure induced by the presence of casein in the continuous phase of an emulsion as a function of protein concentration can be expressed as (Dickinson & Golding, 1997; Radford & Dickinson, 2004):

$$P_{osm} = nK_bT \left(1 + 2 \frac{C_c}{\rho_{sm}} \right) \quad (3)$$

where C_c is the concentration of casein in the continuous phase, n is the number density of casein molecules, K_b is Boltzmann's constant, T is absolute temperature and ρ_{sm} is the density of casein. The number density (n) of casein molecules is expressed as:

$$n = \frac{C_c N_A}{M} \quad (4)$$

where N_A is Avogadro's number and M is the molecular weight of the casein. The concentration of casein in the aqueous phase, C_c , can be obtained from a balance between the total concentration (C) of protein and the protein adsorbed at the oil droplet interfaces (C_{ad}):

$$C_c = \frac{(C - C_{ad})}{(1 - \phi_{oil})} \quad (5)$$

Eqs. (1)–(5) can be therefore used to estimate the deficit in casein needed for complete droplet coverage to stabilize an emulsion of given composition, or the amount of unadsorbed casein that is available to

generate an osmotic pressure sufficient to destabilize the emulsion by depletion flocculation.

3. Materials and methods

3.1. Materials

The materials used in preparation of the emulsions' aqueous phase were: spray dried sodium caseinate (>87% protein, <6% moisture, <4.5% ash, <0.2% lactose) supplied by Canada Compound Corporation, food grade ethanol (95% AlcVol) supplied by Commercial Alcohols Inc, distilled water and sodium azide (Sigma-Aldrich, analytical grade). Commercial grade canola and coconut oils were obtained from a local store.

The ratio of sodium caseinate and water was fixed based on the amount of water needed to achieve a complete hydration of the sodium caseinate powder. This ratio was determined from the following considerations: (i) casein micelles have an effective hydrodynamic volume of $4.4 \text{ cm}^3 \text{ g}^{-1}$ (De Kruif, 1998); (ii) the moisture content of sodium caseinate powder was 6%; (iii) dry casein has a specific volume of $0.618 \text{ cm}^3 \text{ g}^{-1}$ (Berlin & Pallansch, 1968), so that 3.78 cm^3 of water per gram of casein is required ($4.4 \text{ cm}^3 \text{ g}^{-1} - 0.618 \text{ cm}^3 \text{ g}^{-1}$); (iv) hydrated casein micelles are assumed to pack randomly with a volume fraction of 0.64, so that $5.91 \text{ cm}^3 \text{ g}^{-1}$ represents the amount of water required for minimal hydration of the dry casein. Since the moisture content of the sodium casein was 6%, the ratio of water per gram of sodium caseinate was chosen as 5.5 cm^3 of water per gram of wet protein. Hence, 1 kg of 100% sodium caseinate solution denoted in the phase diagram represents a solution of 153.85 g of "as is" wet sodium caseinate and 846.15 g of water.

3.2. Emulsion preparation

Appropriate amounts of sodium caseinate, water, oil, and ethanol were weighed such that the weights of the sodium caseinate solution, oil and ethanol added up to 100% at every point of the phase diagram. The amount of sodium caseinate was set in order to keep the ratio of water per gram of sodium caseinate constant. On the phase diagram the percentage of sodium caseinate represents the percent of a sodium caseinate solution, varying from 0 to 15.4% sodium caseinate (0 to 100%). The emulsion was prepared based on the procedure of Lynch and Mulvihill (1997). Sodium caseinate was dissolved in hot water (55 °C) with continuous mixing using an Omni mixer type OM for at least 20 min. Sodium azide (0.01%) was added as an antimicrobial agent. The appropriate amount of oil (preheated to 55 °C) was then added and the emulsion stirred for a further 20 min. The required amount of ethanol (95%v/v) was slowly incorporated into the emulsion. This final product was then homogenized in a two stage homogenizer (APV Model 15MR-8TA) by a single pass at a feed temperature of 55 °C under a pressure of 17.5 MPa (first stage) and 4 MPa (second stage). To evaluate phase stability under accelerated shelf-life conditions, emulsions were stored in a water bath at 26 °C. Two replicate emulsions were prepared for each composition.

3.3. Determination of the region of emulsion stability

The analysis was conducted based on adaptation of the procedure of Elysée-Collen and Lencki (1996). Emulsions at different concentration of sodium caseinate solution, ethanol and oil were prepared. A first series of emulsions, with weight increments of 20% from 0 to 100% for each ingredient determined the general phase regions of emulsion stability. The respective increments in sodium caseinate solution, oil and ethanol concentrations were calculated moving horizontally on the phase diagram. In order to refine the phase regions determined from this first series, a second series of emulsions was prepared with 2–5% of weight increments at compositions close to phase boundaries.

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