Available online at www.sciencedirect.com
ScienceDirect
Food Hydrocolloids 21 (2007) 862–869
FOOD HYDROCOLLOIDS
www.elsevier.com/locate/foodhyd

Influence of pH and biopolymer ratio on sodium caseinate—guar gum interactions in aqueous solutions and in O/W emulsions

N. Neirynck[a], K. Van lent[a], K. Dewettinck[b], P. Van der Meeren[a,*]

[a]*Particle and Interfacial Technology Group, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium*
[b]*Laboratory of Food Technology and Engineering, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium*

Received 22 June 2006; accepted 6 October 2006

Abstract

Many colloidal food systems contain both proteins and polysaccharides. In the present study, the phase behaviour of mixed sodium caseinate—guar gum aqueous solutions was investigated: segregative phase separation was observed in solutions containing at least 0.04% of guar gum and 1.6% of sodium caseinate, thus indicating the limited compatibility of the polysaccharide and the protein.

In addition, the functionality of guar gum as gravitational stabilizer in sodium caseinate stabilized 25% O/W emulsions was checked. At pH conditions significantly larger than the iso-electric point (IEP) of sodium caseinate, addition of small amounts of guar gum (0.1–0.2%) gave raise to fast serum separation, which was thought to be due to depletion flocculation. Increasing the polysaccharide concentration and/or the oil volume fraction limited the degree of phase separation, since depletion flocculation induced a sufficiently strong three-dimensional network to withstand gravity effects.

Considering different guar gum concentrations at pH 5.0, 5.5, 6.0 and 6.5, it became obvious that the phase separation behaviour in the absence of guar gum was largely affected by the pH, whereas in the presence of at least 0.1% of guar gum it became mainly affected by the guar gum concentration. Hereby, higher guar gum concentrations introduced a longer delay time before separation could effectively be detected. As laser diffraction particle size analysis results were not significantly affected by guar gum addition, it was concluded that the guar gum-induced flocculation was weak in nature and largely reversible.

Combining all results, it was concluded that guar gum could effectively be used to prevent phase separation problems that could occur due to flocculation around the protein's IEP, provided that at least 1.0% of guar gum is added to ensure depletion stabilization by formation of a sufficiently strong three-dimensional network to overcome separation effects. Increasing the ionic strength through addition of salt further reinforces the network in order to prevent its collapse due to gravity.

Keywords: Sodium caseinate; Guar gum; Emulsion stability; Protein–polysaccharide interactions; Depletion flocculation

1. Introduction

Many food products contain both polysaccharides and proteins. In particular, mixtures of proteins and polysaccharides can be found among the ingredients of a wide range of colloidal food systems ranging from mayonnaise to ice cream. Proteins are present primarily as emulsion forming and stabilizing agents, whereas polysaccharides are mainly used as thickening and water-holding agents. In addition, both kinds of biopolymers may contribute to the structural and textural characteristics of food products through their aggregation and gelling behaviour.

The overall stability and texture of colloidal food systems depends not only on the functional properties of the individual ingredients, but also on the nature and strength of the protein–polysaccharide interactions (Dickinson, 1995). Thus, anionic polysaccharides, such as pectin, can give rise to emulsion droplet aggregation due to charge neutralization and bridging. On the other hand, several studies have indicated the beneficial emulsion stabilizing properties of covalent complexes of proteins and polysaccharides, which may be prepared by mild dry heat treatment of a mixture of these biopolymers

*Corresponding author. Tel.: +32 9 264 60 03; fax: +32 9 264 62 42.
E-mail address: Paul.VanderMeeren@UGent.be (P. Van der Meeren).

0268-005X/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodhyd.2006.10.003

(Neirynck, Van der Meeren, Bayarri Gorbe, Dierckx, & Dewettinck, 2004).

Sodium caseinate is obtained from fresh and/or pasteurized skim milk by acid coagulation of the casein, neutralization with sodium hydroxide, and spray drying. This milk-derived ingredient is quite often used in industry, especially for products that require high emulsification and rapid dispersion, such as whipped toppings, coffee creamers, bakery goods, emulsified meats and nutritional beverages. One drawback of using sodium caseinate is its limited applicability for use in acidic (food) products. In the present study, the effect of guar gum, a non-ionic polysaccharide which is commonly used as a cold swelling viscosifier, on the preparation and stability of sodium caseinate stabilized oil-in-water emulsions has been investigated. According to our knowledge, few studies have been carried out on the interactions between these biopolymers in emulsion systems. Perissutti, Bresolin, and Ganter (2002) investigated the rheological properties of mixtures of the galactomannan from Mimosa scabrella and milk and its derived proteins such as sodium caseinate and purified casein fractions, from which they concluded that the galactomannan–sodium caseinate system showed a synergistic effect. Bourriot, Garnier, and Doublier (1999a, 1999b), as well as Tuinier, ten Grotenhuis, and de Kruif (2000) studied the influence of guar gum on skim milk and/or casein micellar dispersions. They observed that these mixtures tended to phase separate, which, according to the authors, was probably due to depletion flocculation mechanisms, yielding a continuous network mostly composed of the aggregated micellar casein. Ye and Singh (2006) investigated the influence of guar gum on the heat stability of emulsions formed with whey protein isolate or extensively hydrolysed whey protein. In the latter case, heating at 121 °C during 16 min gave rise to coalescence, which was enhanced considerably with increasing concentration of guar gum up to 0.2%. At higher levels, the extent of coalescence decreased gradually.

In studying the effect of guar gum on sodium caseinate stabilized emulsions, the pH was varied from 5.0 (i.e. close to the protein's IEP) to 6.5, in order to enable rather unstable as well as charge-stabilized emulsions to be studied. In addition, the influence of added salt was determined at pH 5.5. Emulsion stability was evaluated from both visual creaming observations and particle size analysis, whereas rheological experiments were performed in order to quantify the microstructure of the emulsions.

2. Materials and methods

2.1. Composition of raw materials

Sodium caseinate was obtained from Armor Protéines (Saint Brice en Cogles, France). When calculating the amount of sodium caseinate powder to be added, a correction for the protein content of the powder was taken into account. Guar gum (Viscogum HV3000A) was kindly provided by Degussa Texturant Systems Benelux B.V. (Ghent, Belgium). When calculating the amount of guar gum powder to be added, a correction for the water content of the powder was applied.

Table 1
Composition of sodium caseinate and guar gum powder (in % w/w)

Sample	Dry matter	Protein	K^+	Na^+	Ca^{2+}	Mg^{2+}
Sodium caseinate	94.1	89.2	0.01	0.98	0.05	0.00
Viscogum HV3000A	89.3	4.6	0.22	0.01	0.06	0.04

The moisture content of the protein and polysaccharide powder was determined by drying at 105 °C to constant weight. The protein content was determined by the Kjeldahl method using a conversion factor of 6.38 for caseinate and 6.25 for the guar gum powder. Cations were quantified by flame atomic emission spectrometry (K^+ and Na^+) and flame emission absorption spectrometry (Ca^{2+} and Mg^{2+}). The results of these analyses are summarized in Table 1.

Refined soybean oil was obtained from Vandemoortele N.V. (Izegem, Belgium). All other reagents were of analytical grade. The different buffer solutions were made with double deionized water in the presence of 0.02% Na-azide as an antimicrobial agent.

2.2. Preparation and characterization of caseinate-guar gum solutions

Sodium caseinate and guar gum were dissolved in a 50 mmole L^{-1} Na-phosphate buffer solution at pH 6.0 or 6.5 or in a 50 mmole L^{-1} Na-acetate buffer solution at pH 5.5 or 5.0 while stirring with a magnetic bar. The solutions were stored in the refrigerator overnight to fully hydrate these hydrocolloids. The phase diagram was obtained after intensive stirring of the protein–polysaccharide mixtures for 1 h, and subsequent centrifugation at 3500*g* for 15 min.

2.3. Preparation and characterization of emulsions

The aqueous phase of each emulsion contained 0.3% w/w caseinate. After addition of 25% w/w soybean oil to the protein–polysaccharide solutions, the resulting mixture was premixed with a kitchen mixer during 30 s. The pre-emulsions were subsequently homogenized in two steps (200 + 50 bar) with a lab scale two-stage high-pressure homogenizer (APV-2000, APV, Belgium) at room temperature. Immediately after preparation, 13 mL of each emulsion was poured into a glass tube of 15 mm diameter. The phase separation kinetics were followed during 13 days by means of visual observation. An additional observation was performed at least 1 month after preparation, i.e. when a steady state was reached.

Laser light scattering experiments were carried within the first 24 h after emulsion preparation using a Mastersizer S long bench (Malvern Ltd., UK) with a 300 mm Reverse