Effect of Organic Hydrocolloids on Quality of Seabuckthorn Beverages and Cosmetic Emulsions

Gerald Muschiolik* and Rüdiger Schrödter**

*Food Innovation Consultant, Potsdam
**Aroma and Sensory Research, Werder

Abstract

Conditions are shown in which interactions between biopolymers are useful for the development of seabuckthorn oil-enriched beverages and emulsion products.

The study demonstrates the possibility of influencing the phase stability of seabuckthorn beverages (juices, cloudy beverages with seabuckthorn fruit oil) and of tailoring the viscosity and texture of seabuckthorn cosmetics through the use of special combinations of biopolymers (proteins with ionic polysaccharides).

The combination of proteins with ionic polysaccharides can be used to stabilise dispersed systems via zeta potential and to realize a tailored viscosity and texture of emulsions via linkages between the polymers. Examples are given for the zeta potential of protein-polysaccharide solutions, for the application of seabuckthorn oil emulsions in seabuckthorn pulp, juice, cloudy light beverages and cosmetics.

Cloudy light beverages with emulsions containing seabuckthorn oil can be stabilised through selected protein-polysaccharide mixtures. The same protein-polysaccharide combinations are suitable for use in cosmetics and can be used to help gain a creamy consistency and customized texture.

Introduction

There has been growing interest in the utilisation of oils of the superfruit seabuckthorn (pulp oil and seed oil) to increase the additional value and the health-promoting benefits of foods and cosmetics. Therefore, the aim of present paper is to report on a suitable emulsion for such oil enrichment and to test the influence of seabuckthorn emulsions on juices, beverages and cosmetics.

For the phase stability of dispersed systems as juices with both fruit pulp and emulsions, different parameters are of importance. These are: (i) the difference in density (between the dispersed and continuous phase), (ii) the viscosity of continuous phase, (iii) particle size and (vi) the pH-value and the content of electrolytes (Table 1). Depending on the origin of the fruit, the particle size can also be influenced by the technological process.

The phase separation or flocculation in cloudy juices is additionally influenced by the particle charge. The electrical charge of particles can be influenced by charged biopolymers or by emulsions, stabilized by ionic biopolymers (Muschiolik et al, 2006). Such background could be of advantage to enrich juices with seabuckthorn oil emulsions.

In this study, we examine the preparation of biopolymer stabilized emulsions with seabuckthorn oil and the possibility of influencing the phase stability parameters of liquid dispersed systems by using seabuckthorn oil emulsions containing charged biopolymers (proteins and polysaccharides). Electrically-charged biopolymers were applied to the emulsion preparation with the aim of influencing the electrical charge of oil droplets (prevention of droplet aggregation by electrostatic repulsion) and to increase biopolymer water binding through higher electrical charge and biopolymer unfolding.

Consequently, it is of interest to test the influence of such seabuckthorn oil emulsions on the technofunctional properties of juices, beverages and cosmetics.

Table 1: Main parameters influencing the phase stability of dispersed systems as juices with fruit pulp and emulsion droplets

a) Size of particles
b) Difference in density between continuous and dispersed phase
c) Viscosity
d) Content of ionic biopolymers
d) pH value
e) Content of electrolytes
f) Electrical charge of particles and biopolymers

The main parameters for the phase stability are, according to Stokes' law, a) particle size, b) difference in density and c) viscosity (Table 1). Juices containing very small particles (lower than 1 µm) and emulsion droplets (juices enriched with seabuckthorn oil) can be negatively influenced by droplet aggregation (aggregated droplets induce a high creaming rate). Therefore, it is of importance to prevent such droplet aggregation in oil enriched juices. On the other, Stokes' law cannot be adopted to predict the creaming rate if, in hydrocolloid- and oil-enriched juices, a weak or strong particle network takes place (e.g. more highly concentrated systems such as lotions containing seabuckthorn oil).

The phase stability of seabuckthorn fruit oil in pulp can be very different. As such, it is important to emulsify the separated fruit oil, in order to attain better phase stability. This emulsion should be re-added to the pulp or to oil enrichment (Fig. 1).

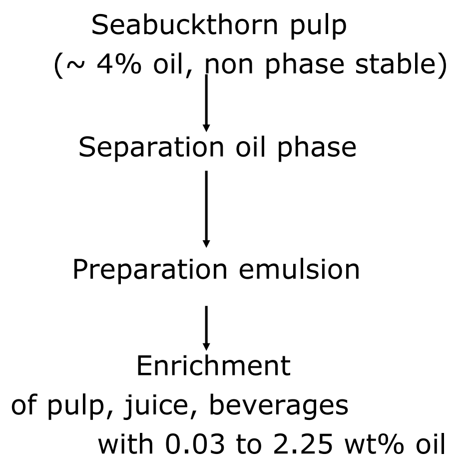

Fig. 1: Isolation and application of Seabuckthorn pulp oil

This paper reports on the preparation of emulsions with seabuckthorn oil, using charged natural biopolymers (e.g. proteins) as emulsifiers. The application of protein-stabilised emulsions in acidic juices mostly provokes droplet aggregation if plant proteins or denatured whey protein are used as emulsifier. The electrical charge of the proteins at the droplet surfaces and the content of electrolytes are the main influencing variables for the strength of droplet flocculation and phase sedimentation (pH range between three and five is normally the range of the isoelectric point of proteins).

Consequently, the experiments to apply seabuckthorn oil emulsions stabilised by proteins were concentrated on changing the electrical potential of the biopolymer by mixing proteins with ionic polysaccharides (pectin and Na-CMC).

The following experiments were completed, based on previous research on improving the creaminess and stability of juices through applied emulsions containing proteins and polysaccharides (Muschiolik et al., 2006, Muschiolik et al., 2008, Muschiolik and Paulus, 2009). Emulsions with seabuckthorn oil were prepared and tested to enrich seabuckthorn pulp, juice with seabuckthorn pulp and the application of such emulsion was tested for cloudy light beverages, liqueur and cosmetics.

Materials and Methods

Materials

Seabuckthorn pulp oil and seabuckhorn pulp was supplied by Sanddorn GbR (Hohenseefeld, Germany). Juice with 25% seabuckthorn pulp (SANDOKAN Sanddorn-Nektar) was purchased from local store. Whey protein isolate (DSE 5669 Lactoglobulin Isolat, 93 % protein) was supplied by Fonterra (Europe) GmbH (Hamburg, Germany). High methoxyl citrus pectin (Classic CU 201) was supplied by Herbstreith & Fox (Neuenbürg, Germany). Sodium carboxymethylcellulose (WALOCEL CRT 1000 GA) was supplied by Dow Europe GmbH (Bomlitz, Germany). Sucrose and ethanol (70 vol%) were purchased from a local store.

Emulsion preparation

An aqueous emulsifier solution was prepared under practical conditions by separately dispersing whey protein isolate powder and polysaccharide powder (pectin or NaCMC) into tap water (~120 mg Ca/ l) and then stirring (protein at room temperature, polysaccharide at 60° C) for at least 2 hours to ensure complete dispersion (the final result was a clear solution).

An oil-in-water emulsion was prepared by blending 15 g of seabuckthorn pulp oil and 85 ml mixed protein-polysaccharide solution (polymer content at least 2 wt%) for one minute using a stirrer with a tooth wheel at 1500 rpm (RW 16, IKA) and then circulating them one time through a one-stage labhomogenizer (HH 20, Muschiolik et al, 1995) at eight MPa (Fig. 2). The texture of the stable and orange-coloured emulsion was characterized as highly viscous (non-flowing).

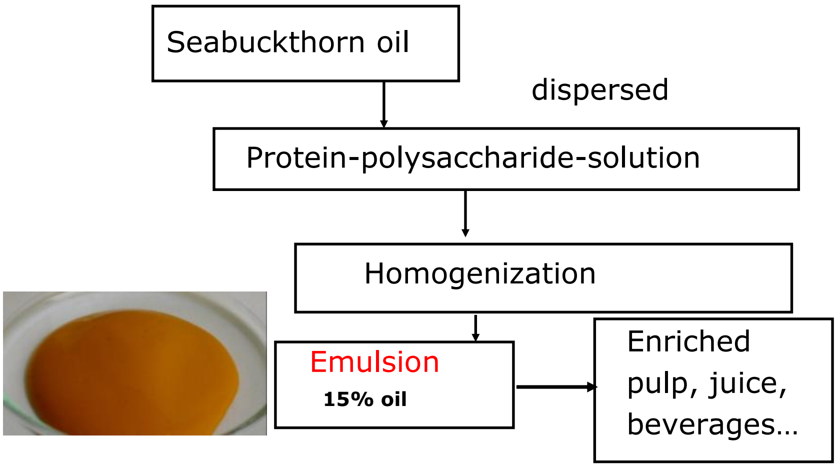

Fig. 2: Preparation emulsions with Seabuckthorn oil

Application of emulsions in seabuckthorn products

Pulp was enriched with 15 wt% emulsion (2.25% seabuckthorn juice oil). Juice with pulp was enriched with 10 wt% emulsion (1.5% seabuckthorn oil). Carbonated, acidified cloudy beverages were prepared with different emulsion contents of 0.2 or 0.4 wt% (0.03 wt% or 0.06 wt% fruit oil), artificial sweetener (aspartame and acesulfame potassium) or 5 wt% sucrose. Two stable liqueurs were prepared with 3 and 15% emulsions (0.45 or 2.25 wt% oil), 5 and 15% sucrose and 17% ethanol.

Furthermore, the texture and sensory characteristics of the emulsion were evaluated for use as cosmetics (e.g. lotion).

Determination of the zeta potential

The electrophoretic mobility of aqueous protein-polysaccharide solutions was measured using a Zetasizer Nano ZS (Malvern Instruments Ltd., UK). The protein-and-polysaccharide solution and the mixed polymer solution were diluted with deionised water to a biopolymer concentration of 1 g/ l. The pH value of solutions was adjusted by lactic acid solution (10 g/ 100 g solution).

Emulsions with 15 wt% of oil, juice and juice enriched with emulsion were diluted to a concentration of approximately 0.01 wt% using deionised water.

Results and discussion

Zeta potential.

The zeta potential of protein-polysaccharide solutions is shown in Figures 3 and 4.

The possibility to change the zeta potential by mixing whey protein with ionic polysaccharides is demonstrated in Figures 3 und 4. Different zeta potentials can be realised in protein polysaccharide mixtures depending on the pH value and the protein-polysaccharide relation (Muschiolik et al., 2008).

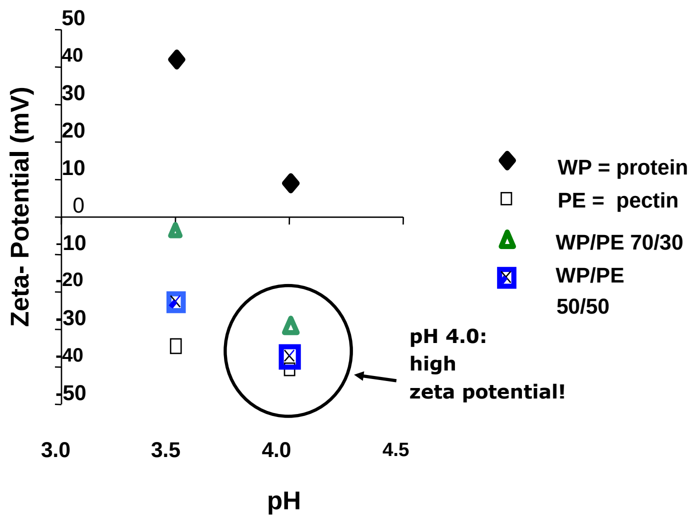

Fig. 3: Zeta potential of biopolymers (WP, whey-protein; PE, high methoxyl pectin) and biopolymer mixtures (WP/PE, 50/50 or 70/30) of) at different pH values

These results for mixtures with a high zeta potential at the acidic pH-range were the basis of preparing stabile emulsions with different oil content. The regulation of the pH value takes place after homogenization and is done by adding citric acid solution or by mixing emulsions with fruit juices.

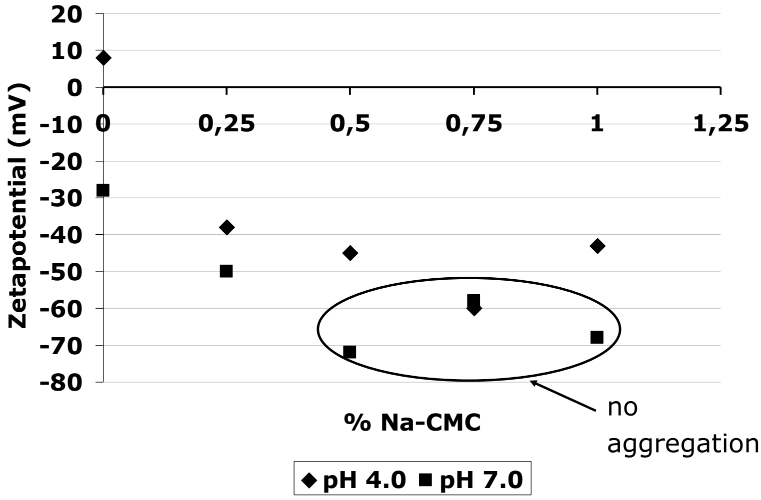

Fig. 4: Zeta potential of solutions with 0.5 wt% whey protein mixed with NaCMC at pHs 4.0 and 7.0

zeta potential measurements of emulsions has shown that, depending on the protein-polysaccharide relation and concentration, the results are different when compared with higher diluted emulsions (not shown). The measured zeta potential of emulsions (diluted 1:100) with 10% MCT oil (medium-chain triglycerides), stabilised by protein-pectin mixtures (1:1, pH 5.4) amounts -30 mV, stabilized with protein-NaCMC mixtures (1:1, pH 6.8) amounts -44 mV. The area of interest for such protein-polysaccharide combinations is the polymer relation of about 1:1 to 1:1.5.

Emulsion application

Seabuckthorn pulp with 15 wt% emulsion (2.25% oil, pH 2.75) was changed in rheological behaviour (better fluidity) and reduced phase separation. The separated phase could be re-dispersed with lower energy input compared to the control, with a strong separated and creamed phase (see Figure 5, zeta potential was not estimated).

The electrical potential of juice with 25% seabuckthorn pulp (pH 2.82) has been increased by adding 10 wt% of emulsion (15% seabuckthorn oil, stabilised by a protein-pectin mixture) from -12.8 mV to -19.3 mV (pH 3.0). Such enriched juice with 1.5 % seabuckthorn oil was improved in phase stability and characterised by a pleasant mouthfeel (better texture and more viscous, Fig. 6).

Carbonated cloudy light drinks (0.15 wt% citric acid) with a sweetener or with sucrose were similar in phase stability (reduced creaming rate without adding a weighting agent, Fig. 7). Such cloudy light drinks without a weighting agent are not characterized by long-term stability to creaming. In addition, it is possible to prepare such drinks as organic food through the use of organic sucrose. By adding pectin to the oil phase (Muschiolik, 2007) or by mixing the seabuckthrorn oil phase with a weighting oil (Muschiolik and Schilling, 2007), it is also possible to reduce the creaming rate.

The electrical charge of highly dispersed seabuckthorn oil emulsions, stabilised by whey protein plus pectin is high enough (zeta potential > -30 mV) to prevent a strong droplet flocculation. After a longer storage time, the creamed oil phase can be suspended by a low energy input (short shaking).

Fig. 5: Pulp with 15 wt% emulsion (left: Na-CMC; right: pectin)

Fig. 6: Juice with 25% pulp and 10% emulsion (left: control; right: emulsion with pectin)

Alcoholic drinks with 17 vol% ethanol are stable over the long term, with a sucrose content lower than 16 wt%. The difference in creaminess and viscosity can be regulated by emulsion and sucrose content. Fig. 9 demonstrates a microscopy image of such dispersed emulsion without droplet aggregation.

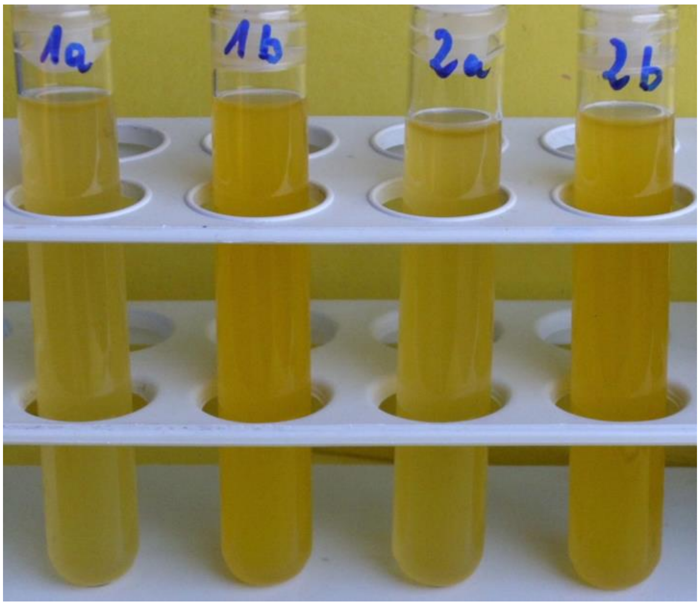

Fig. 7: Stability of cloudy beverages with seabuckthorn emulsion after 7 days
1, with sweetener; 2, with sucrose
a, 0.03% oil; b, 0.06% oil

Bottle with sample 2b (Fig. 7)

The type of o/w-emulsion systems presented here contain whey-protein-pectin-mixtures as an emulsifier/stabiliser. They are suitable to change rheological behaviour by changing the protein-pectin content and relation. Emulsions with 15 wt% seabuckthorn oil can be changed from fluidity to pasty, to be slippery and non-sticky and their handling properties can changed depending on if they are used as a cosmetic cream with higher viscosity or as a dispenser lotion with lower viscosity and with good dropping properties. The advantages of such emulsions with protein-polysaccharide mixtures (relation of 1:1) containing seabuckthorn oil are summarized in Table 2 (different phase volume is possible, e.g. 10 to 40 %).

Fig. 8a: Liqueur
0.45% oil
5% sucrose

Fig 8b: Liqueur
2.25% oil
15% sucrose

Fig. 9: Microscopy image of liqueur oil droplets < 1.1 µm

Table 2: Advantages of o/w emulsions containing protein-polysaccharide-mixtures

- Cosmetics (creams, lotions) can be prepared with a few ingredients (minimum 4 components)
  - Water, oil, protein, polysaccharide, and preservative
- Emulsions containing ionic biopolymers can be tailored in consistency by
  - changing the biopolymer content or
  - the oil content
- Droplet aggregation and flocculation can be prevented by increasing the particle charge
- The emulsion basis is applicable for cosmetics and foods and can be organic

The additional value to the nutritional and healthy value of such emulsions in foods and cosmetics is the improvement in the sensory and rheological behaviour (Table 3).

Table 3: Additional properties of seabuckthorn oil emulsions containing protein-polysaccharide combinations in food and cosmetics

Pulp	Juices, beverages	Cosmetics (cream, lotion)
e.g. - reduction of phase separation - improved consistency - reduced acidity	*e.g.* - reduction phase separation - improved colour - improved texture and taste	*e.g.* - pleasant creaminess - no stickiness - absorbing easily into the skin - organic ingredients are available

Effect of biopolymers

The techno-functional effects of emulsions described here are based on the positive effects of proteins with ionic polysaccharides before emulsion preparation. When ionic polysaccharides are added to emulsions (see Fig. 10, A), the difference of free charged groups is changed.

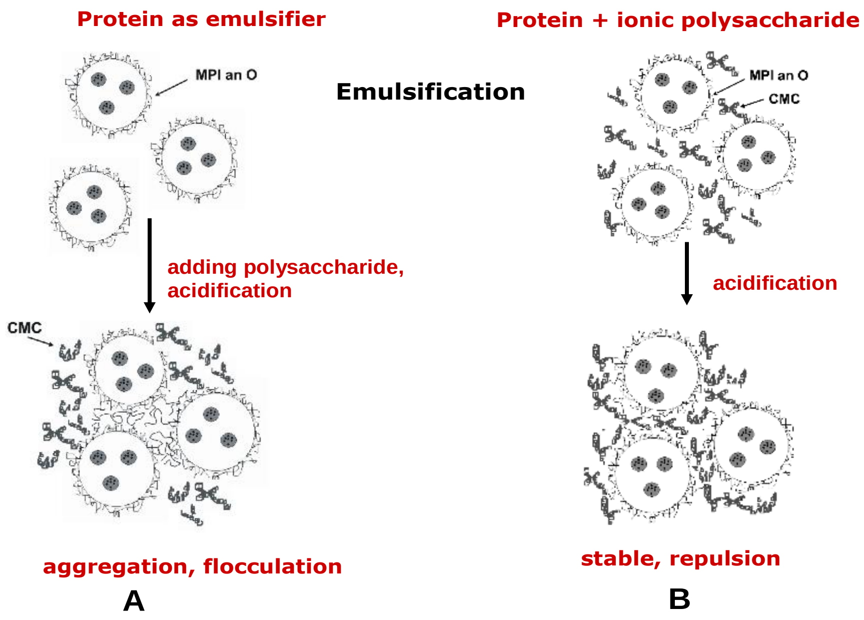

Fig. 10: Influence of the order adding the components for emulsion properties

The electrical charge of proteins in solutions and proteins at droplet interfaces and the changed free volume in continuous phase after dispersing the oil phase influences the aggregation behaviour of droplets after acidification. Protein stabilized emulsions aggregates mainly by adding ionic polysaccharides (NaCMC, pectin) followed by additional acidification. The droplet stability to aggregation has been realized here by using protein-polysaccharide solutions as an emulsifier (see Fig. 10, B; Muschiolik et al., 2006 and Muschiolik and Paulus, 2009).

Discussion

The interactions between positive and negative ionic groups in adsorbed polymers depend on the content of free charged groups. Therefore, the potential measured is not the same in emulsions and mixtures for the same molecular protein-polysaccharide relation, biopolymer content and pH value. Nevertheless the zeta potential results from liquid polymer mixtures give valuable information with regard to possible biopolymer combinations as emulsifier-stabilizer compounds for diluted emulsion application.

The zeta potential is of importance in higher diluted systems to prevent a droplet aggregation by electrostatic repulsion. Highly viscous emulsions systems should be characterised by a high water binding (to prevent water separation). A higher zeta potential gives information on more free ionic groups. These realize a phase stability and a higher unfolding and overlapping of the present biopolymers.

The main parameters for tailoring the rheological properties of emulsions with the same ionic composition are the degree of unfolding and overlapping of biopolymers, the oil phase volume and the oil particle size.

Conclusion

It can be concluded that highly valuable oil phases as seabuckthorn oils applied in emulsions and stabilized by protein-polysaccharide combinations create new possibilities for enriching beverages, providing food and cosmetics with health-promoting benefits and tailoring the rheological and texture properties of such products.

References

1. Muschiolik G, Roeder R, Lengfeld K: DE 195 30 247 A1, 1995.
2. Muschiolik G, Knoth A, Kobow K, Scherze I, Härtel D, Kämmerling H, Schrödter R, Kramer M, Schilling B: DE 10 2006 019 241 B4, 2006.
3. Muschiolik G: DE 10 2007 057 258 B4, 2007.
4. Muschiolik G, Schilling B: DE 10 2007 026 090 A1, 2007.
5. Muschiolik G, Kramer M. Härtel D: Nutzung der Wechselwirkungen zwischen Proteinen und ionischen Polysacchariden, Tagungsband GDL-Symposium „Hydrokolloide VI“, 2008.
6. Muschiolik G, Paulus K O: EP 2010/002654, 2009.