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Flavour retention in sodium caseinate – Carboxymethylcellulose complex coavervates as a function of storage conditions

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ABSTRACT

Flavour retention in freeze-dried complex coacervates prepared with sodium caseinate and carboxymethylcellulose was followed over storage for 20 days at two relative humidities (0 and 54%) and temperatures (25 and 45 °C). *Beta*-pinene was used as a model volatile compound. Avrami's equation mathematical model was equipped to describe the correlation between release rate and storage time. In general, volatile's retention in the dried powder was considerably affected by the storage conditions along with the wall material characteristics (e.g. protein/polysaccharide ratio, presence of reticulating agents, i.e. glycerol and tannic acid) as a greater rate of release was observed at high relative humidity (RH) and temperature values and low biopolymer addition levels. Moreover, the Arrhenius activation energy E_a was reduced by increasing RH from 0 to 54% while it got either positive or negative values indicating that the release of β-pinene was either related or not to temperature. Rehydration of dried powders in high humidity air conditions and the induced reduction of their effective surface area may account for the decrease of β-pinene retention. Glycerol addition resulted in higher retention of the volatile compound in the powder stored at low RH and temperature (0% RH, 25 °C) as compared to other storage conditions, which was further confirmed by the remarkable increase of half-life release $t_{1/2}$ from 29 to 9303 days, as this was calculated from the Avrami's equation mathematical model.

1. Introduction

Flavour encapsulation is a common way to satisfy the demand for improved flavour performance and shelf-life stability in many food systems. In general, encapsulation provides protection for a flavour by reducing losses in flavour intensity and quality through prevention of degradation (due to exposure to light or oxygen) or retardation of its evaporation. Additionally, encapsulation provides a means for controlled release, as well as conversion of a liquid flavour into a solid powder.

Various techniques (e.g. spray-drying, spray-chilling, melt injection, etc.) have been developed to perform encapsulation of a flavour. Between them complex coacervation is considered particularly suitable for the entrapment of sensitive flavour materials within a protective matrix. This process commonly occurs between biopolymers with opposite electrical charges (i.e. proteins and polysaccharides). It is accomplished by phase separation (biopolymer-rich phase vs. phase depleted in both biopolymers) and the successive deposition of the newly formed coacervate phase around the so-called "core material" (Gouin, 2004) by inducing media modifications (i.e. pH adjustment and/or protein/polysaccharide ratio) (Paraskevopoulou & Kiosseoglou, 2013).

Various combinations of proteins with polysaccharides have been employed for flavour encapsulation by complex coacervation including gelatin/gum arabic for mustard seed essential oil, lavender oil, peppermint oil, turmeric oleoresin, (Dong et al., 2008; Peng et al., 2014; Xiao, Liu, Zhu, Zhou, & Niu, 2013; Zuanon, Malacrida, & Telis, 2010), soy protein isolate – gum arabic for sweet orange oil, (Jun-xia, Hai-yan, & Jian, 2011), whey protein concentrate with gum arabic or mesquite gum for chia essential oil, orange oil flavour or lemon juice flavour (Rodea-González et al., 2012; Weinbreck, Minor, & de Kruif, 2004). Additionally, milk proteins (i.e. sodium caseinate (CN) and whey protein isolate (WPI)) and carboxymethylcellulose (CMC) have been successfully used in a previous study to stimulate the encapsulation of β-pinene by complex coacervation (Koupantsis, Pavlidou, & Paraskevopoulou, 2014). The addition of reticulating agent, i.e. glycerol and tannic acid, led to the preparation of microcapsules with either enhanced (in the case of glycerol) or unaffected (in the case of tannic acid) encapsulation

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loading and efficiency (Koupantsis, Pavlidou, & Paraskevopoulou, 2016).

Apart from providing high volatiles retention during the encapsulation process, enhanced flavour performance during processing or storage is also required. As a consequence, the flavour release characteristics of microcapsules are considered important enough for evaluating their ability to minimize undesired losses and predicting most favourable storage conditions for greatest stability in addition to designating the more sustainable food applications. According to Soottitantawat et al. (2004), the degree of flavour protection is mainly dependent on the maintenance of encapsulates' structural coherence as well as the control of molecular diffusion phenomena through carrier material. Normally, flavour release depends on factors such as the wall material used to form the microcapsules, volatile compounds' characteristics, and the encapsulation method applied (Reineccius, 1995; Whorton, 1995). The main mechanisms of release involve solvent release (i.e. wall solubilisation, usually with water, followed by release of the core material) and diffusion associated with the rate at which flavour molecules pass through the wall's pores. Relative humidity and temperature are considered as the key factors that govern flavour release. Previous studies have reported an increase in flavour release upon humidity's increase attributed to destruction of capsule structure because of excess water uptake (Rosenberg, Kopelman, & Talmon, 1990; Whorton & Reineccius, 1995). More recently, other researchers, who investigated the effect of relative humidity on the release characteristics of encapsulated flavour compounds, found that the release rate was also closely related to the composition of wall materials and more specifically their glass transition temperature (Shiga et al., 2001; Soottitantawat et al., 2004; Yoshii et al., 2001). Flavour release kinetics has been usually followed by applying mathematical models, such as Avrami's equation. This equation, originally developed to describe crystallization process, has been found to very well correlate retention with the release time upon storage of various flavour encapsulates, i.e. freeze/spray dried ethyl butyrate, eugenol, terpinen-4-ol, limonene, ethyl hexanoate -containing powders (Seo, Min, & Choi, 2010; Shiga et al., 2001; Soottitantawat et al., 2004; Yang, Xiao, & Ji, 2015; Yoshii et al., 2001). By taking into account the residual amount of flavour in the powder as well as the initial mass of the flavour, parameters such as the flavour retention in the powder, the release rate constant and the activation energy can be derived (Walzel & Furuta, 2011).

In view of the above and as part of a general study on milk proteins – CMC complex coacervation, the aim of the present work was to investigate the release characteristics of the encapsulated β-pinene from selected CN/CMC complex coacervates during storage at specific relative humidity (0 and 54%) – temperature (25 and 45 °C) conditions. To the best of our knowledge, the flavour release behaviour from the CMC-CN microcapsules has not been resolved before. The effect of glycerol and tannic acid on the retention of β-pinene was also evaluated. Furthermore, the rate of release of the volatile compound was fitted to Avrami's equation.

2. Materials and methods

2.1. Materials

Sodium caseinate (from bovine milk) was obtained from Sigma Chemical Co. (Germany). Sodium carboxymethylcellulose (low viscosity: 90–200 mPa at 25 °C) and β-pinene (>95%, CAS No.127-91-3) were products of Fluka (Switzerland). Tannic acid and glycerol were purchased from Merck (Germany) and Mellinckrodt (USA), respectively. Analytical grade *n*-hexane was obtained from Merck (Germany). For pH adjustment, solutions of hydrochloric acid and sodium hydroxide from Aldrich (Germany) were used. Magnesium nitrate (Merck, Germany) and silica gel (Merck, Germany) were used for the preparation of relative humidity (RH) environments. Sodium azide from Aldrich (Germany) was used as microbial growth preservative of the protein and polysaccharide solutions (final concentration of 0.01% w/v). Deionised water was used for the preparation of all solutions and emulsions.

2.2. Microcapsules preparation

Microcapsules were prepared as described by Koupantsis et al. (2014; 2016). At first, protein and CMC aqueous solutions were prepared individually by mechanical stirring for more than 5 h at room temperature. The dispersions were kept overnight at 4 °C to warrant complete dispersion and, after mixed together, β-pinene was added. Oil-in-water emulsions were prepared with the aid of a mechanical stirrer at 600 rpm (IKA, Malaysia) by adding the volatile compound dropwise, followed by homogenisation at $50 \cdot 10^6$ Pa (4 passes) using an APV-2000 pressure homogenizer (APV Systems, Denmark) and the pH was adjusted to 2.8 with the aid of hydrochloric acid solution (1 mol/L). Afterwards, an appropriate volume of either 18% (w/w) aqueous solution of glycerol or 12% (w/w) aqueous solution of tannic acid or deionised water was added and the pH was readjusted to 2.8. During the coacervation process the temperature was kept at around 23 °C and the suspension was kept at ~4 °C overnight to allow the coacervation process to be completed (~20 h). The coacervates were first washed by decanting with deionised water and then collected by centrifugation (4000 rpm, 10 min), frozen and lyophilised for 5–6 h by using a laboratory scale freeze dryer (Alpha 1–2, Christ, Germany). The protein/polysaccharide and pinene/wall materials ratios as well as the concentrations of glycerol or tannic acid were selected within the best (in terms of encapsulation efficiency) range of ratios presented in a previous study (Koupantsis et al., 2016). The codes and formulations of the resulting coacervates are given in Table 1.

2.3. Retention of β-pinene in the microcapsules during storage

The stability of encapsulated β-pinene during storage was investigated in view of its retention characteristics at constant temperature and humidity. The experimental setup used was based on that described previously by other scientists in the literature

Table 1
Coacervate formulations and the respective codes.

Code	CN/CMC ratio[a]	β-pinene (g)	Glycerol or tannic acid (%) w/w	Core/Wall ratio[b]	Total biopolymer (%) w/w
CN1	1.20	1.20	0.00	1.09	0.55
CN1-g	1.20	1.20	3.00	1.09	0.55
CN2	0.20	3.60	0.00	6.00	0.30
CN2-g	0.20	3.60	3.00	6.00	0.30
CN2-t	0.20	3.60	2.00	6.00	0.30

[a] Protein/polysaccharide mass ratio.
[b] β-pinene/wall material mass ratio.