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Retention of esters by gellan and pectin solutions or their mixtures

Vasiliki Evageliou*, Konstantina Papastamopoulou, Despoina Frantzeskaki, Christalli – Christina Christodoulidou

Department of Food Science and Human Nutrition, Agricultural University of Athens, 75 Iera Odos, 11855, Athens, Greece

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ABSTRACT

The retention of three esters (ethyl butyrate, isobutyl acetate and butyl acetate) by gellan and pectin solutions was studied. Mixtures of gellan and pectin were also investigated. Both the type and concentration of the biopolymer were important for aroma retention. The retention of ethyl butyrate was greater for pectin concentrations of 0.25–0.75%wt and gellan concentrations of 0.25 and 2.0%wt. As the concentration of the mixtures increased, its release increased. Regarding isobutyl acetate, its release decreased with increased mixture concentration as well as at the three higher gellan concentrations. Not a clear trend could be detected in the case of pectin matrices. Butyl acetate showed decreased partition coefficient values over concentration in all types and matrices. Overall, for all studied matrices isobutyl acetate showed the greatest partition coefficient values, followed by butyl acetate. The percentage of retention was also calculated and both positive and negative values were determined.

1. Introduction

Biopolymers are added to food products in order either to modify it or to impart a new property. Furthermore, their addition can lead to new product formulations in order to satisfy the consumers' specific needs. Biopolymers can be in both the solution and gel state. In the case of solutions, the critical parameter is concentration as dilute and concentrated solutions exhibit different behaviour.

Aroma compounds are volatile organic substances that can be found in various food products, wines, spices, essential oils etc. The nature and the quantity of aroma compounds present in a food are responsible for its aroma which is an important factor in determining food quality and acceptability by the consumers (Evageliou, Mavragani, & Komaitis, 2012).

In order for the aroma of a food product to be perceived, the aroma compounds must be released from the food (matrix) to the gas phase via the interface and carried to the olfactory and gustatory receptors (Juteau, Cayot, Chabanet, Doublier, & Guichard, 2004; Tromelin, Merabtine, Andriot, Lubbers, & Guichard, 2010). Aroma release depends on the type and concentration of the principal components of the food matrix and on the physicochemical properties of the aromatic compound (e.g. hydrophobicity, pressure, solubility, structure) (Guichard, 2002; Secouard, Malhiac, Grisel, & Decroix, 2003).

When carbohydrates are used as a matrix, two mechanisms are proposed to explain their effect on the release of the aromatic compounds (Terta, Blekas, & Paraskevopoulou, 2006). The first mechanism involves the interactions between the biopolymer and the volatile compound due to adsorption, entrapment in microregions, complexation, encapsulation and hydrogen bonding (Godshall, 1997; Kinsella, 1989). The diffusion decrease is the second mechanism. Due to their observed increased viscosity, polysaccharides hinder the transport of the volatiles from the interior of the sample to the surface (Baines & Morris, 1987). Moreover, the mass transfer as a result of adding a thickener to a system disturbs the balance of the released flavour profile (Roberts, Tephen-Elmore, Langley, & Bakker, 1996).

The volatiles present in the air phase are measured by gas chromatography (GC), and especially headspace analysis (HS). Dynamic headspace analysis offers information on the temporal release of the volatiles which is determined by both thermodynamic and kinetic factors (Voilley & Souchon, 2006). The interactions of the aroma compound with the matrix along with its partitioning in the different phases define the thermodynamic aspects of the release. The kinetic ones are connected to the resistance to its mass transfer from the matrix to the vapour phase (Martuscelli, Savary, Pittia, & Cayot, 2008).

* Corresponding author. Tel./fax: +30 210 5294691.
E-mail address: evageliou@aua.gr (V. Evageliou).

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On the other hand, static headspace analysis determines the partition coefficient of the compounds in a sealed system at equilibrium. When biopolymers are used as matrices, the (air/biopolymer) partition coefficient ($K_{a/biopol}$) is determined by dividing the concentration of the aroma compound in the air phase (C^f_{air}) to the corresponding concentration in the biopolymer matrix phase (C^f_{biopol}) according to the following equation:

$$K_{a/biopol} = \frac{C^f_{air}}{C^f_{biopol}} \quad (1)$$

where C^f_{air} is the concentration of the aroma compound in the air phase and C^f_{biopol} the corresponding concentration in the biopolymer gel phase.

Moreover the percentage of retention (R%) can also be calculated:

$$R\% = \frac{K_{a/water} - K_{a/biopol}}{K_{a/biopol}} \times 100(\%) \quad (2)$$

$K_{a/water}$ is the partition coefficient for samples containing only water. A positive percentage value shows that the aroma compound is retained by the biopolymer matrix whereas a negative one, that it is released by the matrix (Seuvre, Philippe, Rochard, & Voilley, 2006).

Pectin is a natural polysaccharide that has a wide range of applications (e.g. as dietary fibre, for drug delivery, in medical preparations due to its pharmaceutical activities like antidiarrhea, for the formation of biodegradable edible film etc) (Lin & Yeh, 2010; Pérez Espitia, Du, de Jesús Avena-Bustillos, de Fátima Ferreira Soares, & McHugh, 2014; Stasse-Wolthuis et al., 1980; Thibault & Ralet, 2001; Voragen, Pilnik, Thibault, Axelos, & Renard, 1995). However, its major application is in the food industry, as gelling, stabilising and thickening agent (Akhtar, Dickinson, Mazoyer, & Langendorff, 2002).

Gellan is a water soluble polysaccharide that also finds many applications in the food industry. Some of them include confectionery, jams and jellies, water-based gels and dairy products. It forms hard and brittle gels in the presence of cations with the concentration and valency of cations being of great importance (Grasdalen & Smisdrof, 1987; Moritaka, Fukuba, Kumeno, Nakahama, & Nishinari, 1991). In addition, for a given polymer concentration, the gel strength increases with cation concentration up to a certain value above which the strength is decreasing (Sanderson, 1990).

Regarding volatiles, they include a variety of organic compound classes like aldehydes, ketones, esters, alcohols etc. Esters are the most volatiles among the systematic series. They are responsible for the aroma of many fruits and they are highly exploited by the Food Industry as artificial flavouring agents.

The present work focuses on the retention of three isomer esters (ethyl butyrate, butyl acetate, isobutyl acetate) by biopolymer solutions made of gellan, pectin or mixtures of both. The isomer volatiles share the same hydrophobicity but differ on their carbon number of the alcohol chain, their structure and topological characteristics. The effect of biopolymer concentration present in the matrix was also investigated.

2. Materials and methods

2.1. Materials

The deacylated gellan gum was provided by Sigma (Phytagel, P8169). Pectin from citrus peel was obtained from Fluka (76280). Butyl acetate, isobutyl acetate and ethyl butyrate were from Fluka (45860, 45920 and 19230, respectively). Their physicochemical properties are shown in Table 1 (www.sigmaaldrich.com; Seuvre, Philippe, Rochard, & Voilley, 2007). Distilled water was used throughout the experiments.

2.2. Preparation of samples

Gellan and pectin solutions were prepared by dissolution in distilled water at 90 °C under gentle agitation. Their concentration varied from 0.25 to 2.0%wt (0.25, 0.50, 0.75, 1.0 and 2.0% wt). Moreover, 1:1 (wt:wt) mixtures of gellan and pectin at a total concentration of 0.5, 1.0 and 2.0%wt were also prepared. Heating time at 90 °C increased with concentration and varied (~) from 5 to 20 min. All preparations were cooled to ~50 °C and the aroma compound at a concentration of 200 ppm was added. In order to ensure its complete dissolution, additional stirring for 2 min was applied. Then, 10 g of each sample was transferred to a 22 mL screw-capped glass vial with a mininert valve (Sigma–Aldrich, Athens, Greece) which was capped immediately and left to equilibrate at 37 °C for 24 h prior to analysis.

2.3. Static headspace analysis

The headspace of each vial was analysed by gas chromatography. 500 μL of the headspace of the vials were sampled with a gas-tight syringe. The chromatograph (Fisons Instruments, GC 8000 series, Model 8060) was equipped with an FID detector and using an Equity 5 capillary column (30 m × 0.25 mm, film thickness 0.25 μm, Supelco). Helium was used as carrier gas, at a flow rate of 1.0 mL/min. Oven temperature was increased from 40 °C to 250 °C at a rate of 4 °C/min and maintained at 250 °C for 5 min. The injector and the detector temperature were 230 °C and 270 °C, respectively. The analysis was carried out five times for each different sample.

The concentration of each aroma compound in the air phase was determined by means of a calibration curve, which was constructed by the analysis of five aroma concentrations (three different vials per concentration), under the same experimental conditions.

2.4. Flow curves

Steady flow curves were obtained using a Discovery HR3 Hybrid Rheometer (TA Instruments, New Castle, DE, USA) equipped with concentric cylinder geometry (30 mm cup diameter, 28 mm bob diameter) at shear rates from 1 to 20 s^{-1}. Temperature was set to 37 °C via a Peltier system. Samples prior to analysis were left at 37 °C for 30 min.

2.5. Viscosity measurements

Pectin and gellan solutions were characterised with intrinsic viscosity measurements [η] on the basis of the Huggins and Kraemer derivations. Viscosity measurements were made on a falling ball viscometer (Hoppler, HAAKE, Germany) using a Boron silica glass ball with 2.22 g/cm density and 15.81 mm diameter. The viscometer was calibrated using distilled water to find the constant of the viscometer. Each sample was placed in the inner cylinder of the viscometer, while water at 37 °C was circulated in the outer cylinder of the viscometer for 15 min before measuring the viscosity so that the temperature of the sample was constant at 37 °C during measurement. Four measurements of the viscosity for each sample were made.